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PROCEEDINGS OF THE

DEPARTMENT OF DEFENSE ENVIRONMENTAL TECHNOLOGY WORKSHOP

"Environmental Quality Technology: Advancing the Pillars Toward the 21st Century."

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Proceedings of the
DEPARTMENT OF DEFENSE ENVIRONMENTAL TECHNOLOGY WORKSHOP
Convened at Hershey Lodge and Convention Center, Hershey, PA
22–24 May 1995

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"ENVIRONMENTAL QUALITY TECHNOLOGY: ADVANCING THE PILLARS TOWARD THE 21ST CENTURY"

THE U.S. ARMY PERSPECTIVE

by COL DANIEL F. UYESUGI

DRIVERS PUSHING ENVIRONMENTAL TECHNOLOGY

- ***Readiness***

The driving military catch phrase for the end of the 20th century is "readiness". But, it is also a way to look to the future as we enter the 21st century. To the soldier, readiness means being prepared and capable of going into battle, today. To the civilian, readiness often means looking ahead to the next budget cycle or to the next weapon system, the future.

But, how does this drive the need for environmental technology?

Well, the environment is here today and directly related to the soldier's ability to be ready. The military must train and they must have places to train. Over the years land has been bought and set aside specifically for the military to use to train. Also, over the years we have found that these lands contain threatened and endangered species, that by constant use the land has eroded and vegetation has receded, and finally that the land has become contaminated with hazardous and/or toxic substances. All of which limit the military's use of these lands and therefore affect readiness.

Also, the environment will be here in the future. The military and civilian communities need to plan on how we are going to work in concert with the environment so that training can continue.

So, what has this got to do with environmental technology? Everything!

Environmental technologies have allowed us to track and protect threatened and endangered species while the soldier is training. Environmental technologies have lessened erosion and reinstated vegetation which provides the soldier with a type of training land structure that is more realistic. Environmental technologies have cleaned up contaminated lands so that the health of the soldier is not compromised while they are trained.

But, what has been done is not enough!

And what about the materiel side of the Army. In the last 50 years there has been three major production periods for the military, World War II, The Korean Conflict, and the Vietnam Conflict. Most of the facilities that provide materiel to the Army were built during World War II. Most have had few equipment upgrades during the intervening periods because what they had was good enough to produce what was needed. Most recently, during the Gulf War, we saw what a full mobilization really meant to the entire military. Old facilities were called on to increase their production rates, or brought out of mothballs entirely. We also saw how much waste these systems could produce. How these systems while capable of producing the materiel needed did not always also comply with the environmental regulations that have appeared since the last time they were really called upon to produce.

So again environmental technology is needed and is needed to ensure production of required war fighting supplies. But, environmental technology is also needed, to ensure that those families and communities left behind don't have to be endangered by the waste products that are also produced.

- *Goals*

There are also environmental goals that drive the need for environmental technology.

For the clean up pillar there are the goals to implement all clean up actions by the year 2000, to increase community involvement and acceptance of remedial actions, and implement the best demonstrated available technology.

Our compliance with environmental regulations includes a 15% reduction in open enforcement actions, the upgrade of facilities to comply with the Clean Water and Clean Air Acts, and develop and adopt more cost effective approaches to environmental compliance.

Under the stewardship aspects of military installations the Army will manage installation natural resources to sustain the military mission, optimize land management, and improve aesthetic values and ecological relationships. Also, use historic buildings, structures, and places in a manner consistent with the mission that does not destroy the historic integrity of the property; protect the research integrity of archeological sites; and honor places and traditions of value to the military and others.

The pollution prevention goals are to integrate pollution prevention into weapon systems acquisition, reduce toxic releases by 50% from 1994 to 1999, have a recycling program at every installation, and use alternative fuels for 25% of vehicles by 1997.

- ***Quality of Life***

The quality of life on our military installations is also a major driver to environmental technology. A military installation is very much like a small city in that people work, live, and recreate on the land. They also conduct commercial business, education, and operate municipal type utilities. Therefore, not only the soldier needs to be protected from environmental dangers but, also the soldier's family. So, housing needs to be free of lead based paint, schools need to be free of asbestos, playgrounds and parks need to be free of hazardous wastes, and drinking water supplies need to be in compliance with drinking water standards.

- ***User Needs***

So, the Army needs environmental technology. We know it and have begun to really focus on those needs. The Army conducted a study to determine the greatest environmental needs and their priority. This study showed that in clean up the highest priority need was for technologies for unexploded ordnance detection and removal, remediation of soil contaminated with explosives, and groundwater contaminated with explosives and solvents. In compliance the generation of hazardous waste, solid waste, and noise, and how to manage them are the greatest need. Threatened and endangered species, forest management, land rehabilitation, and archeological preservation are the highest needs in the conservation program. And, in pollution prevention ozone depleting substances, heavy metals, solvents, and petroleum, oil, and lubricants are in need of the most minimization.

So, now we know that we need environmental technology but what can it do for us. New technology can be; better, cheaper, faster, safer, and/or more acceptable. Let us look at some examples.

PILLAR TECHNOLOGY

- ***Existing Technology***

There are many technologies in use today that we are trying to get rid of but, these same technologies were considered state-of-the-art only a few years ago. The state-of-the-art for the clean up of explosives in soil is incineration. It is a proven technology, it's permanent, and fast. But, it is expensive, between $500 and $800 per ton, it can be a dangerous process, as unfortunately we have found out, and it is not very acceptable to most local populations.

Heavy metals is another major problem not only for clean up but also for compliance in wastewater sludges and National Pollutant Discharge Elimination System permit outfalls. Again, the state-of-the-art is stabilization with a cementatious mixture or to just haul it to a hazardous waste landfill. These processes are also expensive, no longer considered permanent, and unless the landfill already exists not readily acceptable by the local population.

Let's look at plating. The purpose of plating a part is to make it stronger and more resistant to stress. So, we have found new methods to plate parts. We have done a marvelous job of extending the life of parts. But, chrome and cadmium are very toxic and just as hard to get out of the environment as the hardness it gives to the part it protects.

Conservation activities are mostly carried out by people who walk the land. They manually characterize the condition of the land, flora, and fauna. This is usually a very exhausting and long process. While this process is looked at as being the most acceptable way to do a good characterization it could be done faster so that trends could be monitored better.

- ***PROJECT RELIANCE***

So, existing technologies, processes, and procedures need to change as the times change. The Army is doing this, as are the other services, and we are going about it in a much more systematic way than in previous years. The systematic way is called Project Reliance. Each service has some unique environmental problems or just has more of a particular problem than the others. So, the responsibility to develop and prove technologies has been divided among the services. The Army's responsibility is for technologies dealing with explosives and heavy metals.

- ***FUTURE TECHNOLOGIES***

Therefore, with all of the drivers pushing the need for new technology and existing technology becoming obsolete and through Project Reliance there is on the horizon other technologies that should offer even greater benefits than those we already have. Technologies such as enhanced biodegredation of explosive contaminated soil, the use of wetlands to degrade explosives in groundwater and maybe process water. Better field detection capabilities for environmental contaminants and UXO. Heavy metal removal/stabilization with soil washing/leaching, vitrification, membrane separation, micro encapsulation. Satellite imagery tied to geographic information systems to track land changes. Increased acceptability and use of alternate solvents, strippers, and plating processes.

TECHNOLOGY TRANSFER ACTIVITIES

- ***Partnering***

To make environmental technology work you first must have a viable technology and then you have to transfer that technology to the users. The Army has instituted many methods to transfer these technologies. This workshop is one such method as is partnering with other services and departments. We presently have joint projects with the other services that will allow all to reap the benefits of the technology. We are also talking to the Department of Energy to work out how technologies developed by one can be demonstrated and transferred to the other. Also, there is the Department of Agriculture, who is represented here today and you may hear more about later.

- ***Environmental Technology Implementation Program***

Another method for technology transfer is what we call the Environmental Technology Implementation Program (ETIP). The concept of ETIP is to form a workgroup consisting of the users and the technology implementers and focus everyone on the best available technologies and get it or them out into the field where they can actually do some good. The ETIP program is presently focusing on clean up technologies since they have the greatest potential for cost savings. The first workgroup is focusing on the problem of explosives in soil. In the next year the Army Environmental Center will demonstrate clean up technologies for this problem on at least three installations. One of the tenants of the ETIP program is the use of multiple site demonstrations to show a broader perspective for the applicability of the technology and to gain a wider acceptance of the technology by the regulatory community. This is not unique to the ETIP program. Multiple demonstrations actually was an Air Force concept that has worked out very well. Other ETIP workgroups will be established in the next year to look at many other of the Army's problems. This program also helps get the word out to local populations, Corps of Engineers Districts, Federal and state regulators, contractors, and installations on what new technology is available and ready for use.

- ***Successes***

The Army Environmental Center has demonstrated many emerging technologies and transferred these technologies to the users over the last 20 years. Some of these technologies have been developed by Federal laboratories and some are the product of the private sector. Some of the more noteworthy examples are:

◊ Pollution Prevention

* ALUMINUM ION VAPOR DEPOSITION
AVID plating does not generate hazardous waste streams. The aluminum is deposited directly on the part without using chemical solutions. Therefore, it is safer to work with. Aluminum plating has shown to provide superior corrosion resistance to cadmium plating. In use or planned by many of the operating Army depots.

* PLATING BATH FILTRATION
The life of plating baths can be extended by simply providing a filter in the system to remove much of the grit and other contaminants that lessen the effectiveness of the plating solution. In use at many installations were plating is conducted.

◊ Compliance

* X-RAY FLUORESCENCE
X-ray Fluorescence has quickly grown into one of the best field detection methods available for heavy metals, especially lead. Millions of dollars have been saved by field screening soil and paint samples to determine which samples actually should be shipped to the laboratory for confirmatory analysis. In use by most contractors in the environmental field.

◊ Conservation

- REMOTE SENSING
  Remote sensing by use of satellite imagery or fly over techniques allows a land manager to get to the big picture of what is happening on the installation faster than other methods. In use at many Army installations.

◊ Clean Up

- COMPOSTING EXPLOSIVE SOIL
  Composting has been proven to biologically degrade explosive contaminated soil at a significantly lower cost than incineration and with greater local acceptability. The final material is fertile and can be put back in place. In use as the record of decision remedial action at Umatilla Army Depot.

- ADVANCED OXIDATION
  The use of advanced oxidation, by oxidation catalyst either with or without ultraviolet light is available for groundwater clean up of solvents and explosives. This system provides a more effective destruction technology that is permanent. In use at Milan Army Ammunition Plant.

NEEDS TO ADVANCE ENVIRONMENTAL TECHNOLOGY

So far I have talked about technology drivers, technologies themselves, and technology transfer but, all of these have to do with yesterday and today. Let me finish with what is needed in the future.

- ***OCONUS Policy***

An OCONUS environmental technology policy is needed. This needs to cover such issues as joint government development of technology, use of technology OCONUS, use of foreign government technology on U.S. installations either OCONUS or CONUS.

- ***Timely Availability***

Environmental technologies that are better, cheaper, faster, safer, or more acceptable are needed now not ten years from now. Good ideas that languish in the laboratory will be the death of themselves. With environmental funding going down and more and more sites entering the actual clean up phase if technologies are not available in the next two to maybe three years they will not be used or useful.

- ***Reliable Funding***

Second, because there are available technologies that need to get into the field from either Federal labs or the private sector there needs to be a reliable and dedicated source of demonstration funding. The Army has not made available any research and development (6.4) money for the demonstration of environmental technologies. Some talk about SERDP (the Strategic Environmental Research and Development Program) and ESTCP (Environmental Security Technology Certification Program) as being the funding sources. But, this is not the case. SERDP is for basic and applied research not demonstration and is down to about 25% of what it once was. ESTCP while actually for the demonstration of environmental technologies may not exist next year with all of the budget cutbacks. Also, with the number of congressional earmarks the amount of funding available for demonstrations that the services actually need is small. Compounded by the fact that a small amount of funding has to be spread among the services and the length of time it takes to get the money to the actual executors this program does not begin to cover the need.

ENVIRONMENTAL QUALITY
TECHNOLOGY

THE U.S. ARMY PERSPECTIVE

COL DANIEL F. UYESUGI
COMMANDER
U.S. ARMY ENVIRONMENTAL CENTER

ENVIRONMENTAL QUALITY
TECHNOLOGY

READINESS

LAND REQUIRED FOR TRAINING

THREATENED AND ENDANGERED SPECIES

EROSION

LOSS OF VEGETATION

DEPARTMENT OF THE ARMY • UNITED STATES OF AMERICA

ENVIRONMENTAL QUALITY
TECHNOLOGY

U.S. ARMY ENVIRONMENTAL CENTER

READINESS

PRODUCTION FACILITIES

MOBILIZATION

COMPLIANCE DURING INCREASED OPERATIONS

ENVIRONMENTAL QUALITY TECHNOLOGY

QUALITY OF LIFE

- SOLDIER'S FAMILIES SAFE FROM HARM
- HOUSING FREE OF LEAD BASED PAINT
- SCHOOLS FREE OF ASBESTOS
- PLAYGROUNDS, PARKS, AND DRINKING WATER FREE OF TOXIC WASTE

ENVIRONMENTAL QUALITY TECHNOLOGY

GOALS - CLEAN UP

INITIATE ALL CLEAN UP ACTIONS AT HIGH RELATIVE RISK SITES BY END 2002

INCREASE COMMUNITY INVOLVEMENT AND ACCEPTANCE OF REMEDIAL ACTIONS

IMPLEMENT BEST DEMONSTRATED AVAILABLE TECHNOLOGY

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ENVIRONMENTAL QUALITY TECHNOLOGY

U.S. ARMY ENVIRONMENTAL CENTER

GOALS - COMPLIANCE

15% REDUCTION IN OPEN ENFORCEMENT ACTIONS

UPGRADE FACILITIES TO COMPLY WITH CLEAN WATER AND AIR ACTS

DEVELOP AND ADOPT COST EFFECTIVE APPROACHES TO COMPLIANCE

ENVIRONMENTAL QUALITY TECHNOLOGY

GOALS - CONSERVATION

MANAGE NATURAL RESOURCES TO SUSTAIN THE MISSION

OPTIMIZE LAND MANAGEMENT, IMPROVE AESTHETIC VALUES AND ECOLOGICAL RELATIONSHIPS

USE, PROTECT, AND HONOR PLACES OF HISTORIC SIGNIFICANCE

ENVIRONMENTAL QUALITY TECHNOLOGY

GOALS - POLLUTION PREVENTION

INTEGRATE POLLUTION PREVENTION INTO WEAPON SYSTEM ACQUISITION

REDUCE TOXIC RELEASES BY 50% FROM 1994 TO 1999

RECYCLING PROGRAM AT EVERY INSTALLATION

ENVIRONMENTAL QUALITY TECHNOLOGY

USER NEEDS - CLEAN UP

UNEXPLODED ORDNANCE DETECTION AND REMOVAL

CLEAN UP OF EXPLOSIVE CONTAMINATED SOIL

CLEAN UP OF EXPLOSIVE AND SOLVENT CONTAMINATED GROUNDWATER

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ENVIRONMENTAL QUALITY TECHNOLOGY

U.S. ARMY ENVIRONMENTAL CENTER

USER NEEDS - COMPLIANCE

IMPROVED HAZARDOUS WASTE MANAGEMENT

IMPROVED SOLID WASTE MANAGEMENT

CONTROL NOISE

ENVIRONMENTAL QUALITY
TECHNOLOGY

USER NEEDS - CONSERVATION

THREATENED AND ENDANGERED SPECIES

FOREST MANAGEMENT

LAND REHABILITATION

ARCHAEOLOGICAL PRESERVATION

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1775

ENVIRONMENTAL QUALITY
TECHNOLOGY

U.S. ARMY ENVIRONMENTAL CENTER

USER NEEDS - POLLUTION PREVENTION

OZONE DEPLETING SUBSTANCES

HEAVY METALS

SOLVENTS

PETROLEUM, OIL, AND LUBRICANTS

EXISTING TECHNOLOGY

INCINERATION

PRODUCT SUBSTITUTION

CONTAINERIZE AND HAUL

MANUAL TRANSECTS

ENVIRONMENTAL QUALITY TECHNOLOGY

PROJECT RELIANCE

EACH SERVICE RESPONSIBLE FOR CERTAIN PROBLEMS

ARMY RESPONSIBLE FOR

- ENERGETICS
- HEAVY METALS
- SITE CHARACTERIZATION

ENVIRONMENTAL QUALITY TECHNOLOGY

FUTURE TECHNOLOGY

BIOSLURRY DEGREDATION OF EXPLOSIVES

ADVANCED SOIL LEACHING OF HEAVY METALS

REMOTE SENSING FOR CONSERVATION IMPACTS

IMPROVED INDUSTRIAL PROCESSES

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ENVIRONMENTAL QUALITY TECHNOLOGY

U.S. ARMY ENVIRONMENTAL CENTER

PARTNERING

- JOINT PROJECTS
- TRI-SERVICE WORKSHOPS
- INTER-AGENCY WORKSHOPS

ENVIRONMENTAL QUALITY
TECHNOLOGY

ENVIRONMENTAL TECHNOLOGY IMPLEMENTATION PROGRAM (ETIP)

JOINT USER/DEMONSTRATOR WORKGROUPS

MULTIPLE SITE DEMONSTRATIONS

WIDER TECHNOLOGY TRANSFER APPLICABILITY

ENVIRONMENTAL QUALITY TECHNOLOGY

SUCCESS STORIES

- ALUMINUM ION VAPOR DEPOSITION
- PLATING BATH FILTRATION
- X-RAY FLUORESCENCE
- REMOTE SENSING
- COMPOSTING EXPLOSIVE SOIL
- ADVANCED OXIDATION

ENVIRONMENTAL QUALITY TECHNOLOGY

ENVIRONMENTAL TECHNOLOGY NEEDS

OCONUS POLICY

TIMELY AVAILABILITY

RELIABLE/DEDICATED FUNDING

ENVIRONMENTAL QUALITY TECHNOLOGY

TECHNOLOGY TRANSFER

PARTNERING

ENVIRONMENTAL TECHNOLOGY IMPLEMENTATION PROGRAM

SUCCESSES

ENVIRONMENTAL QUALITY TECHNOLOGY

TECHNOLOGY DRIVERS

READINESS

GOALS

QUALITY OF LIFE

USER NEEDS

Air Force Center for Environmental Excellence

Presented by

Col Samuel E. Garcia

Director, Environmental Restoration

Air Force Center for Environmental Excellence

AF/CC

AF/CE

AFCEE

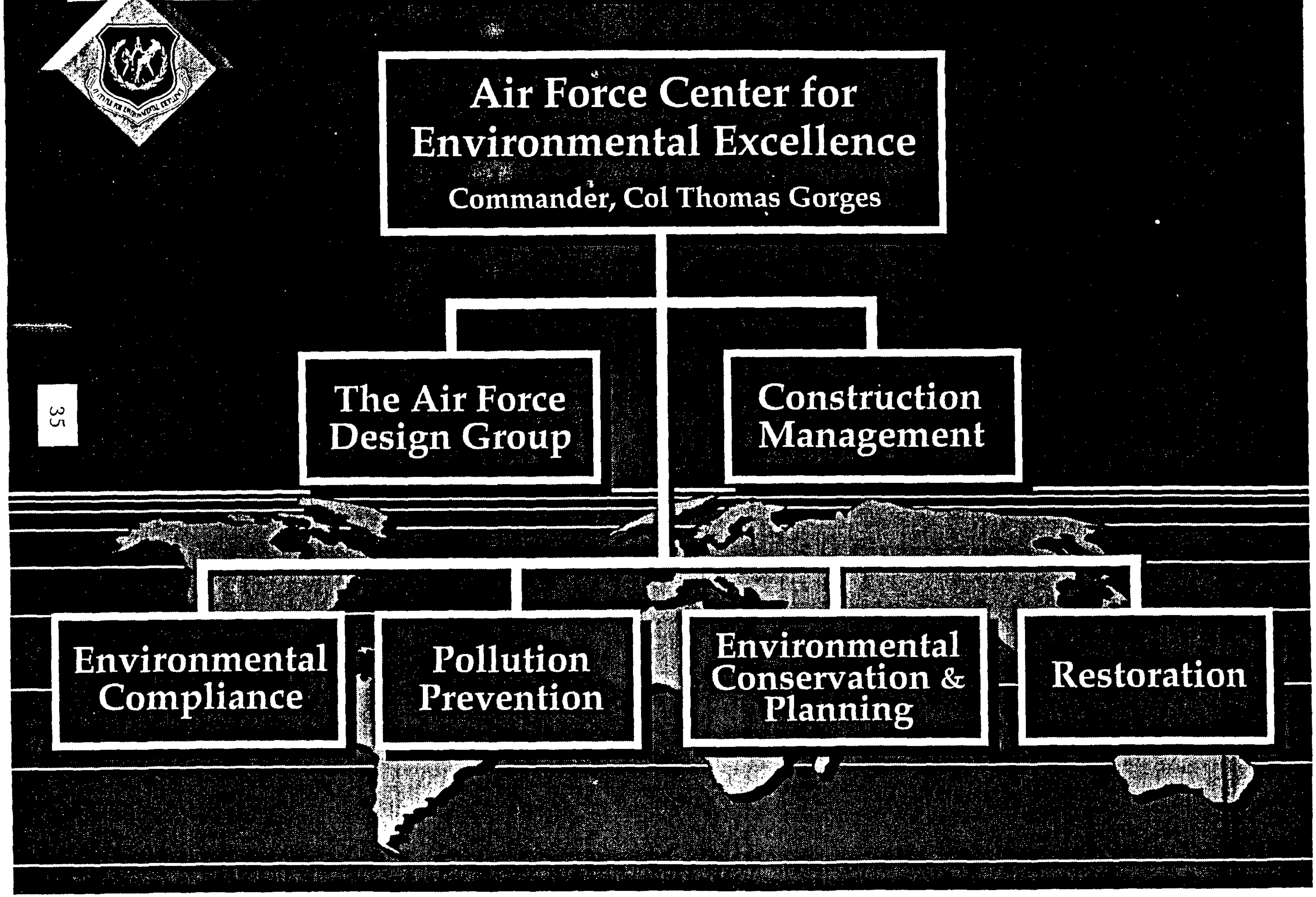
Air Force Center for Environmental Excellence

Mission Statement

The Air Force Center for Environmental Excellence aggregates in a single organization at Brooks AFB a capability to provide a full range of technical services to Air Force commanders in areas related to Environmental Compliance, Pollution Prevention, Hazardous Waste Cleanup (IRP), Environmental Planning and Impact Assessments, and Design and Construction Management.

Authority: AF PAD 91-22

Air Force Center for Environmental Excellence



Air Force Center for Environmental Excellence
Commander, Col Thomas Gorges

The Air Force Design Group

Construction Management

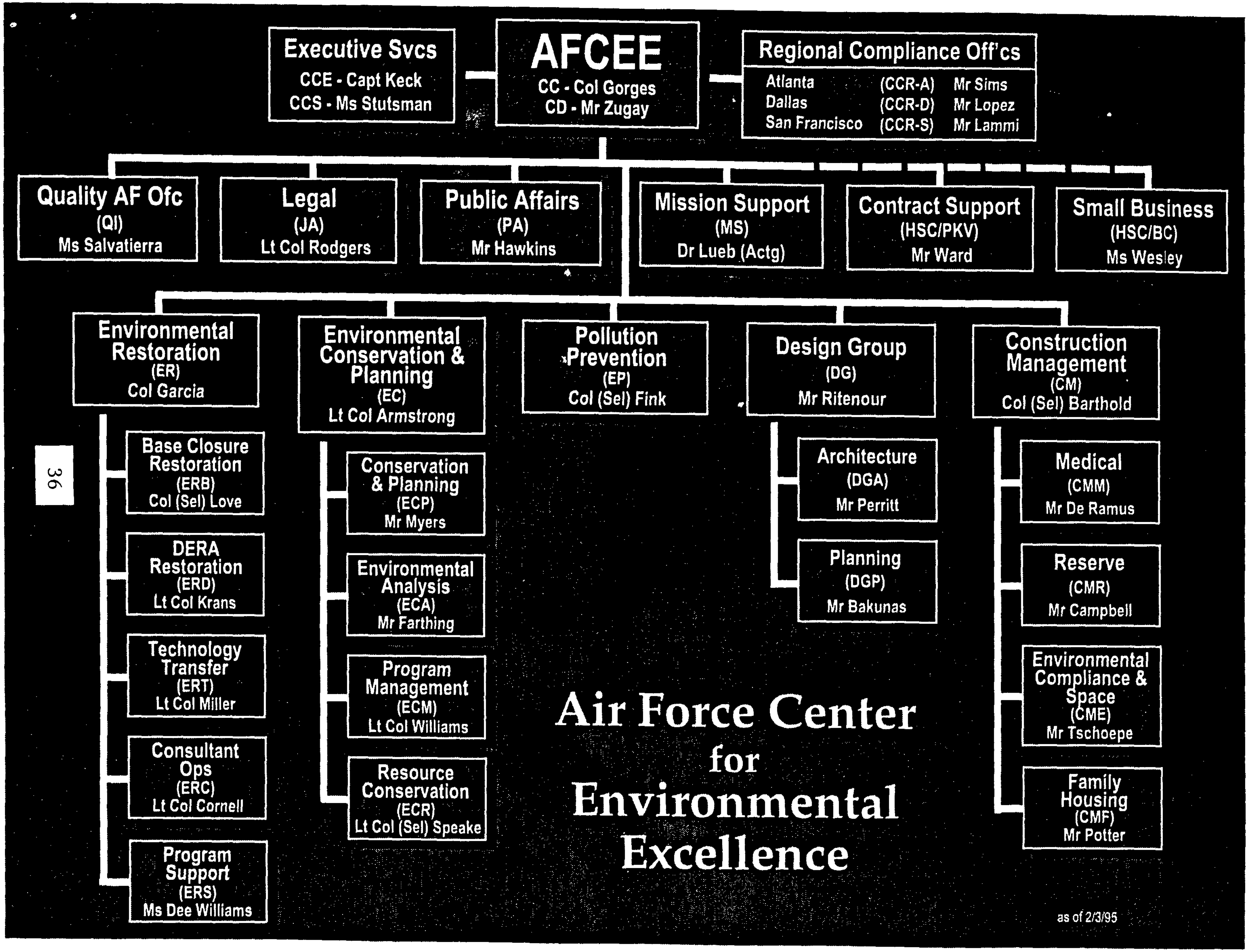
Environmental Compliance

Pollution Prevention

Environmental Conservation & Planning

Restoration

Air Force Center for Environmental Excellence



AFCEE
CC - Col Gorges
CD - Mr Zugay

Executive Svcs
CCE - Capt Keck
CCS - Ms Stutsman

Regional Compliance Off'cs

Atlanta	(CCR-A)	Mr Sims
Dallas	(CCR-D)	Mr Lopez
San Francisco	(CCR-S)	Mr Lammi

Quality AF Ofc
(QI)
Ms Salvatierra

Legal
(JA)
Lt Col Rodgers

Public Affairs
(PA)
Mr Hawkins

Mission Support
(MS)
Dr Lueb (Actg)

Contract Support
(HSC/PKV)
Mr Ward

Small Business
(HSC/BC)
Ms Wesley

Environmental Restoration
(ER)
Col Garcia

- Base Closure Restoration (ERB) Col (Sel) Love
- DERA Restoration (ERD) Lt Col Krans
- Technology Transfer (ERT) Lt Col Miller
- Consultant Ops (ERC) Lt Col Cornell
- Program Support (ERS) Ms Dee Williams

Environmental Conservation & Planning
(EC)
Lt Col Armstrong

- Conservation & Planning (ECP) Mr Myers
- Environmental Analysis (ECA) Mr Farthing
- Program Management (ECM) Lt Col Williams
- Resource Conservation (ECR) Lt Col (Sel) Speake

Pollution Prevention
(EP)
Col (Sel) Fink

Design Group
(DG)
Mr Ritenour

- Architecture (DGA) Mr Perritt
- Planning (DGP) Mr Bakunas

Construction Management
(CM)
Col (Sel) Barthold

- Medical (CMM) Mr De Ramus
- Reserve (CMR) Mr Campbell
- Environmental Compliance & Space (CME) Mr Tschoepe
- Family Housing (CMF) Mr Potter

as of 2/3/95

Environmental Restoration

- Restoration Project Management
  - Cradle-to-grave
    - ◆ Preliminary assessment thru remedial action
  - Requirement definition
    - ◆ Program development assistance
    - ◆ Scoping
    - ◆ SOW development
    - ◆ Technology validation
    - ◆ Cost Estimating
  - Oversight of field activities
    - ◆ Cost and schedule compliance
    - ◆ Quality assurance
    - ◆ Contracting Officer's Representative
  - Management Action Plan / BRAC Cleanup Plan update assistance

Environmental Restoration

- Regulatory / community interface
  - Technical review committee / Restoration Advisory Boards
  - Media (fact sheets)
- Acquisition of contract services
  - Development of contract strategy
  - Contractor selection
  - Technical evaluation of proposal
  - Technical support for negotiations

Existing Restoration Contracts

• 5 Remedial Design Contracts	$115M
• 8 Remedial Action Contracts	$200M
• 10 Remedial Studies & Design	$500M
• 5 Small Business Studies & Design	$125M

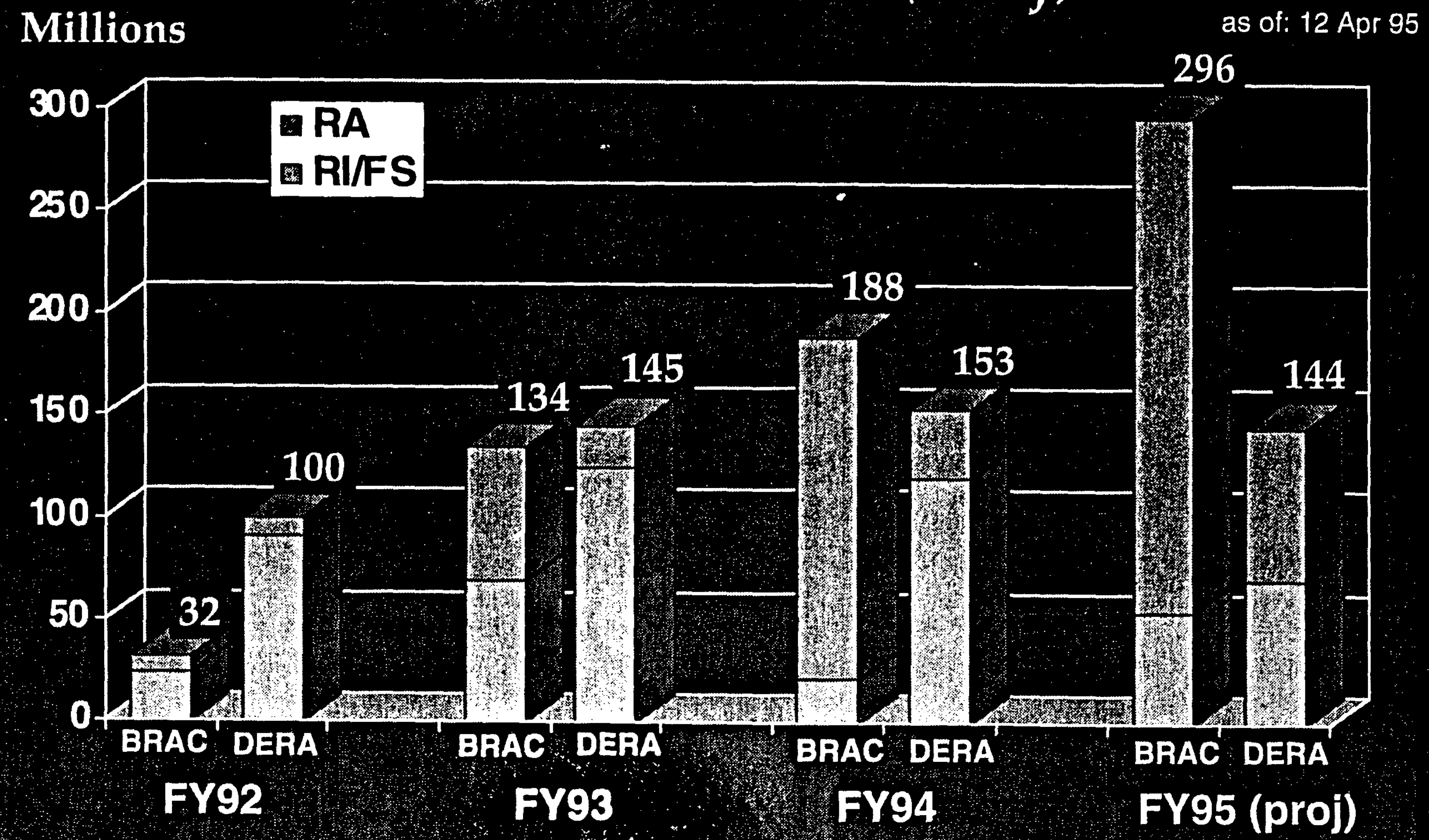
Existing Restoration Contracts *(cont)*

- Full Service Remedial Action (Summer 94) **$1,390M**
  - 2 Nationwide
  - 17 Base Specific (2 Small Business)
- UST/AST Remedial Action (2nd/3rd Qtr FY94) **$260M**
  - Multiple Regional Contracts
  - 12 Total Contracts (All Small Business)

Air Force Center for Environmental Excellence

BRAC / DERA Program

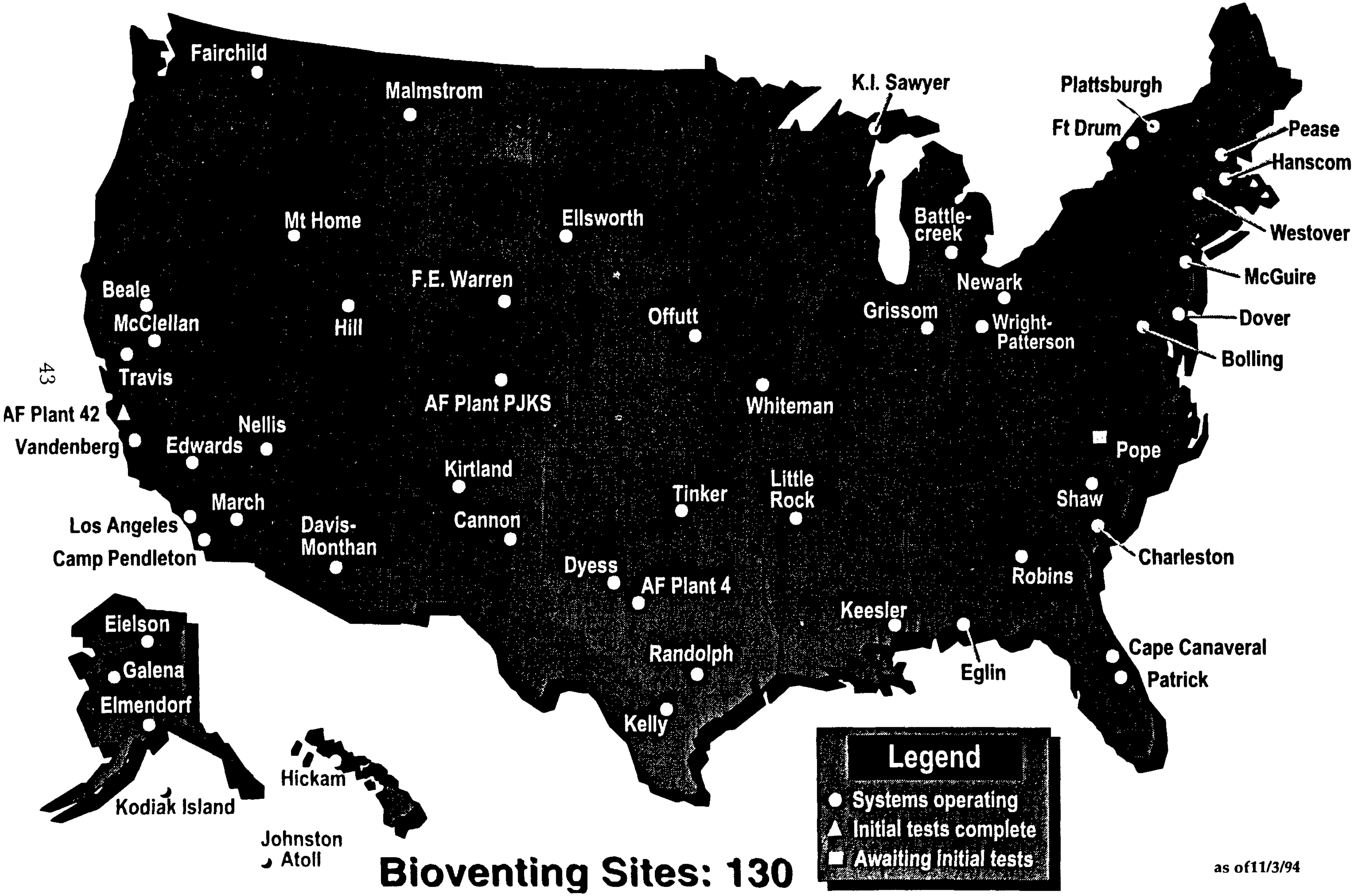
FY92/93/94 /95 (Proj)



Restoration Technology Initiatives

- Ongoing
  - Bioventing
  - Natural Attenuation
  - Cone Penetrometer
  - Solvent Remediation
  - Cost-effective Vapor Phase Treatment
  - BTEX - Risk-based Cleanup Standard for soil
  - TCE - Risk-based Cleanup Standard for groundwater
  - Streamlined Site Characterization
    - USAF/ Environmental Protection Agency / Los Alamos National Lab Demonstrations
- Broad Agency Announcement for Technology Demonstrations

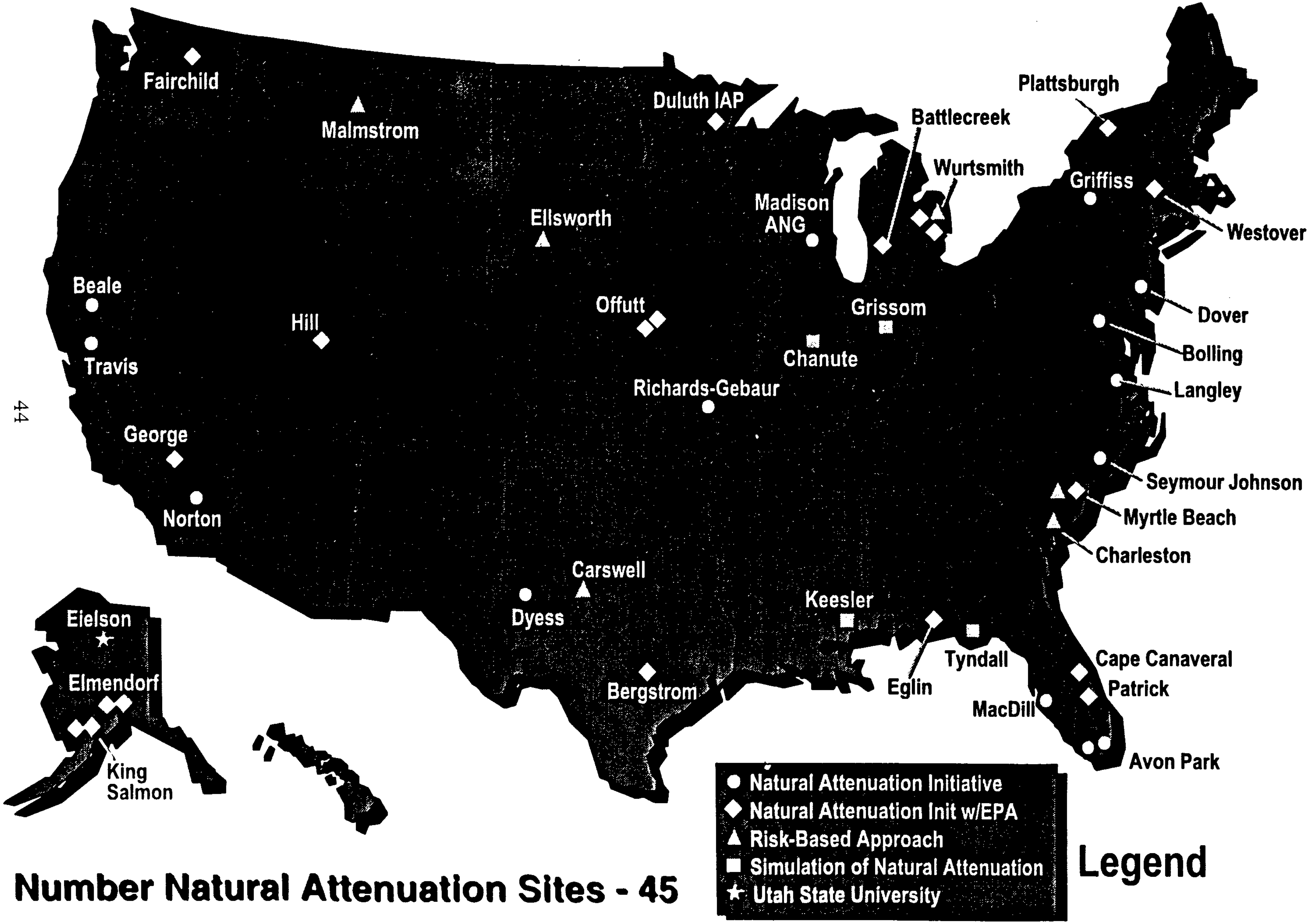
AFCEE Bioventing Initiative Sites



Bioventing Sites: 130

as of11/3/94

AFCEE Natural Attenuation Sites



Number Natural Attenuation Sites - 45

AFCEE Bioslurper Sites

Legend
- ● Pilot test sites
- ▲ Extended testing sites
- ★ Expanded testing sites

Bioslurper Sites: 35

as of 10/12/94

Broad Agency Announcment

- Purpose
  - Field application of emerging technologies
    - Environmental restoration
    - Pollution prevention
  - Incorporate results into AFCEE guidelines and protocols
  - Provide more remediation and pollution prevention options at reduced overall cost

Program Trends

- Less fuel-related - more solvent-related
- Technology maturity
  - Fuel-related - more mature
  - Solvent-related - less mature
  - Fewer nationwide applications - more single site applications
- Application/design and cost and performance guides
  - Completing fuels risk-based approach
  - Initiating solvents
- Regulatory acceptance
  - Fuels - nearer term: joint AF/EPA publications
  - Solvents - future

Environmental Conservation & Planning

- Directorate is structured to produce Environmental Impact Statements and related special studies
  - Environmental Impact Statements
  - Socioeconomic Impact Studies
  - Environmental Assessments
  - Wetlands delineations; biological assessments; historical/ archeological field surveys; other special studies
- Multidisciplinary team of scientists, economists, planners and engineers -- teamed with the best contractors and AFCEE Environmental Law staff

Pollution Prevention

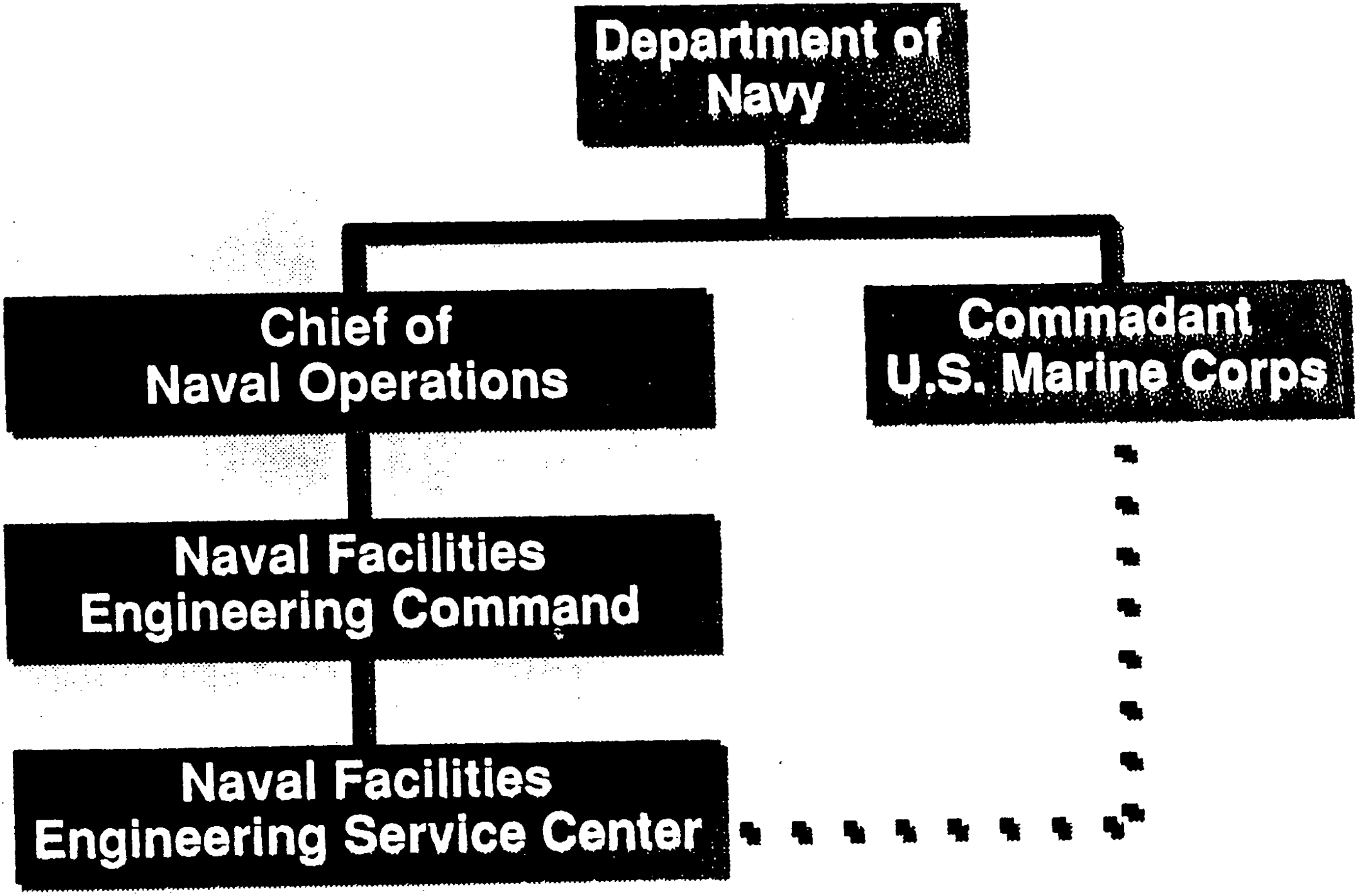
- Training and awareness
  - Environmental Compliance, Assessment and Management Program
  - Base level outreach and awareness training
  - Opportunity Assessment training
  - Emergency Planning Community Right-to-Know Act training
- Crossfeed
  - PRO-ACT information clearinghouse
  - Defense Environmental Information and Exchange Network
  - “How-to” guides
- Access/export -- new / off-shelf technology
  - Worldwide Pollution Prevention Conference
  - Technology transition/insertion with multiple AFMC organizations

Non-Restoration Environmental Contracts

- Environmental Services Nationwide **$195M**
  - 5 Contracts
  - $39M each

Regional Compliance Offices

- Represent The AF to State and Federal Environmental Authorities
- Provide Environmental Compliance Program Oversight on a Regional Basis
- Facilitate Consistent Application of Environmental Standards
- Assist Major Commands and Bases With Compliance Issues
- Ensure AF leaders at All Levels Are Aware of Environmental Compliance Status, Trends, and Problem Areas
- Protect AF Interests at Third Party Hazardous Waste Sites
- Represent DoD as Executive Agent for DoD Regional Environmental Security Office



Department of Navy

Chief of Naval Operations

Commadant U.S. Marine Corps

Naval Facilities Engineering Command

Naval Facilities Engineering Service Center

1BCIntm.37

Facilities Engineering / Public Works

Activity Level	Regional Public Works Centers	Geographic Engineering Field Divisions (Activities)	Navy Wide
Public Works Departments	Yokosuka San Diego Pearl Harbor Guam etc.	Atlantic Southern Southwest Pacific etc.	Naval Facilities Engineering Service Center

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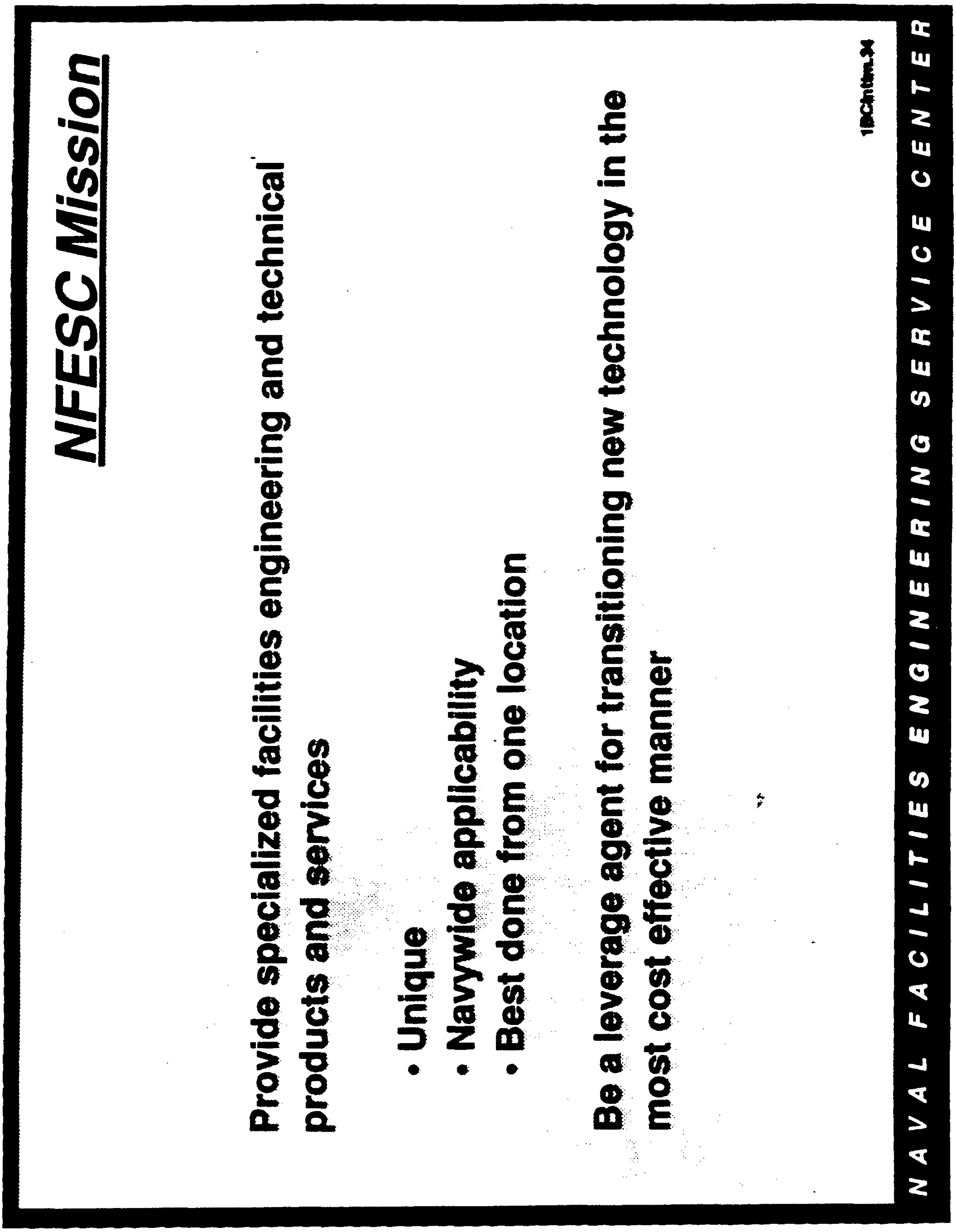


NFESC Mission

Provide specialized facilities engineering and technical products and services

- Unique
- Navywide applicability
- Best done from one location

Be a leverage agent for transitioning new technology in the most cost effective manner

1BCntm.94

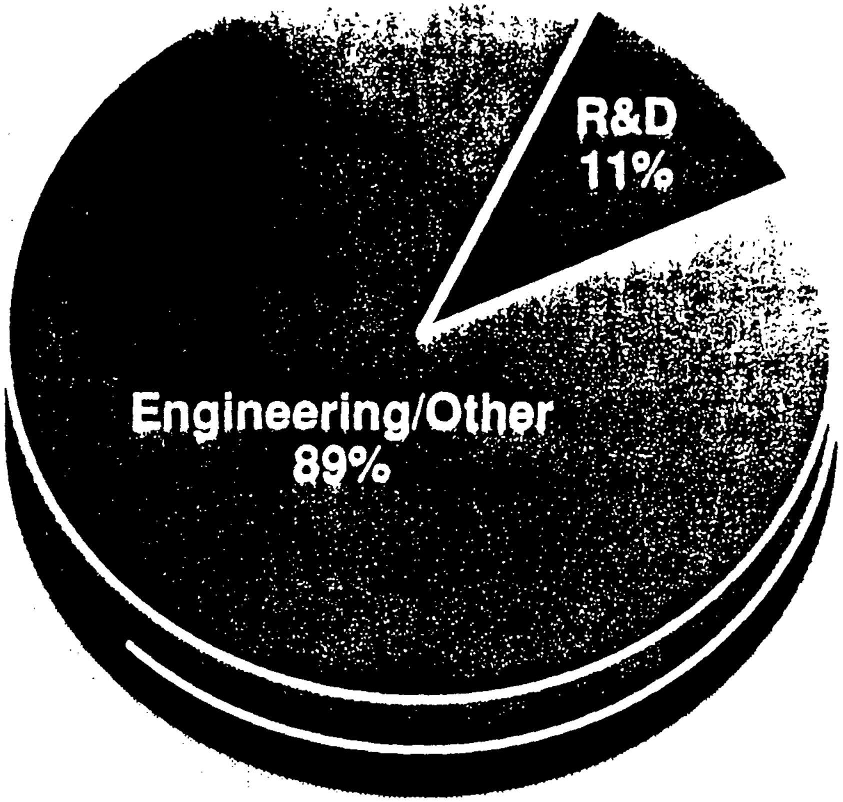
NAVAL FACILITIES ENGINEERING SERVICE CENTER

ESC Staff Breakout

Engineers	324
Scientists	54
Technicians	40
Support/Clerical	152
	570

1RCMactm.30

FY94 Command R&D



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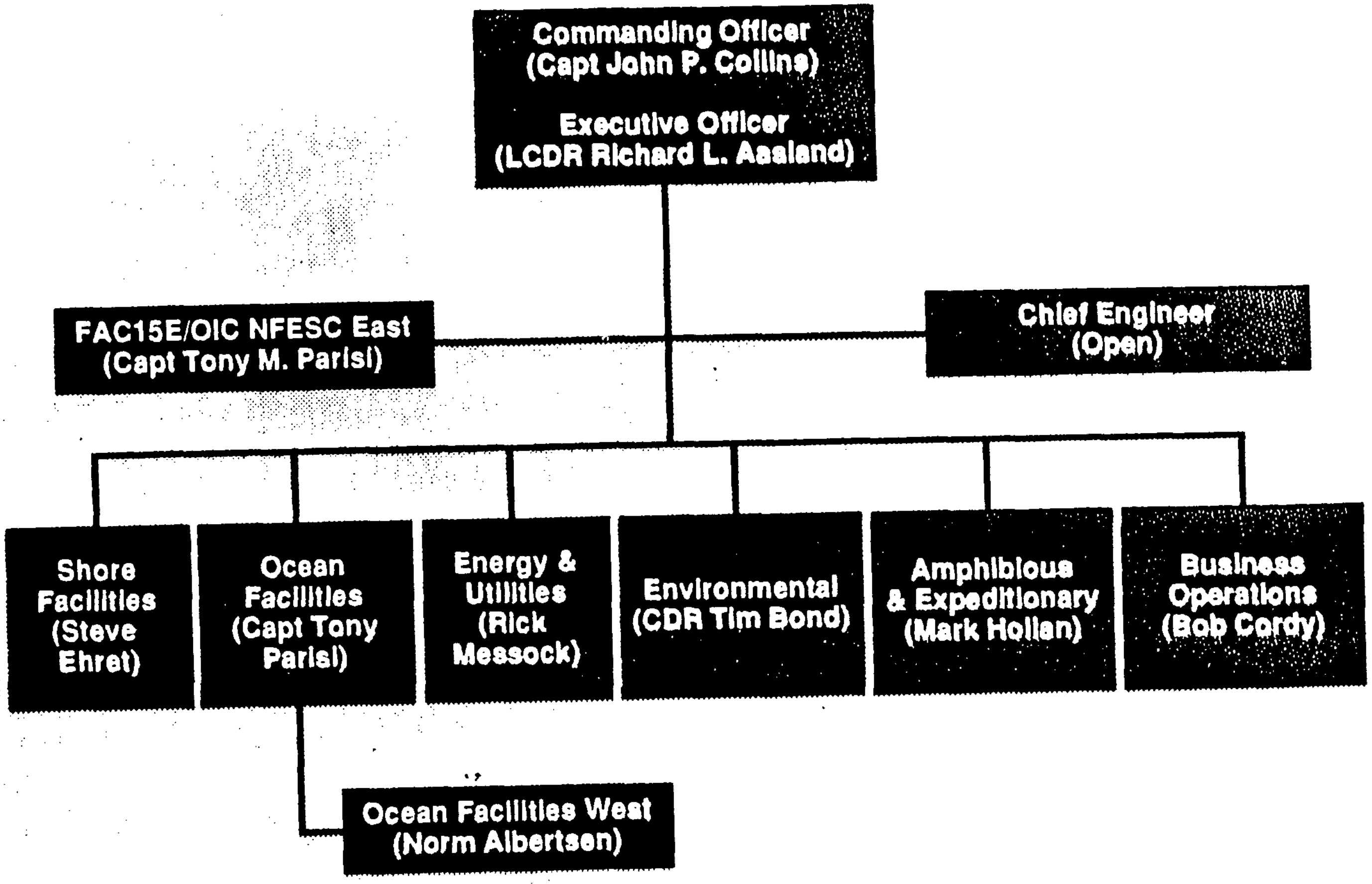
Naval Facilities Engineering Service Center



Commanding Officer
(Capt John P. Collins)

Executive Officer
(LCDR Richard L. Aasland)

FAC15E/OIC NFESC East
(Capt Tony M. Parisi)

Chief Engineer
(Open)

Shore Facilities (Steve Ehret)

Ocean Facilities (Capt Tony Parisi)

Energy & Utilities (Rick Messock)

Environmental (CDR Tim Bond)

Amphibious & Expeditionary (Mark Hollan)

Business Operations (Bob Cordy)

Ocean Facilities West (Norm Albertsen)

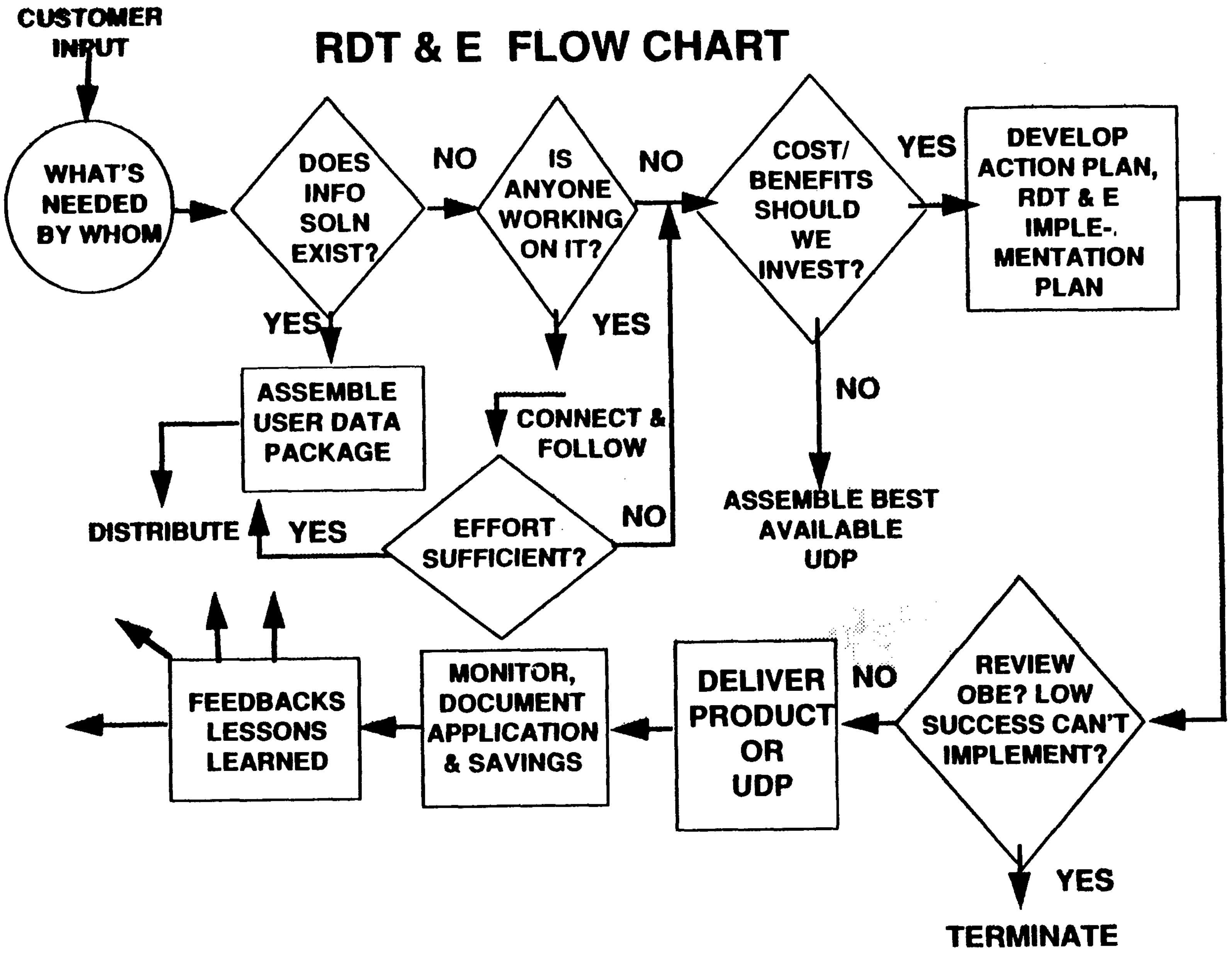
1BCIntrm.17

NAVAL FACILITIES ENGINEERING SERVICE CENTER

Technology Transfer Strategy

- **Transfer Existing Technology**
- **Modify Existing Technology to Meet Unique Requirements**
- **Develop Technology (R&D)**

RDT & E FLOW CHART



NAVAL FACILITIES ENGINEERING SERVICE CENTER

Navy Innovative Remediation Technology Working Group

(NIRTWG)

NAVAL FACILITIES ENGINEERING SERVICE CENTER

Who Is Involved With NIRTWG?

- **Engineering Field Divisions**
- **Engineering Field Activities**
- **Public Works Centers**
- **NAVFAC Headquarters**
- **Other Headquarters Commands**

NFESC Efforts

- **Remedial Action Contract For Innovative Technologies**
- **NELP II Contracting Support**
- **Site Characterization And Analysis Penetrometer System (SCAPS)**
- **Demonstrate Vitrification Facility In Hawaii**
- **Developing Contract To Remediate Sites Using BCDP Process**
- **Established *Technology Application* [illegible] for Key Technologies**
- **Hydrocarbon National Test Site Demonstrations**

NAVAL FACILITIES ENGINEERING SERVICE CENTER

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BCDP	Chuck Schulz	cschulz@nfesc.navy.mil 805/982-5210
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Stabilization/Solidification	Genny Fanning	gfannin[illegible]c.navy.mil 805/982-[illegible]
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General Assistance	Vern Novstrup	vnovstr@nfesc.navy.mil 805/982-1276

NAVAL FACILITIES ENGINEERING SERVICE CENTER

Other NFESC Efforts

- Remedial Project Manager Technology Training
- Review Cost-To-Complete Data to evaluate "Mission Needs"
- Released Remedial Technologies Screening Matrix and Reference Guide in coordination with DOD Environmental Technology Transfer Committee
- Evaluating POL/BTX Sensor that provides continuous monitoring of treatment processes water (Late 95)

New Tasks Being Considered

- **Expand Innovative Technology Training Programs**
- **Develop Team to Install Bioventing Systems**
- **Develop Discussion Groups using Email Capability to Facilitate Communication Between RPMs**
- **Establish Formal Process for Technical Information support to RPMs Using NFESC Technical Information Center. Pilot Test is in progress**
- **Encourage RPM Hands-on involvement With Innovative Technology Projects**

New Tasks Being Considered

- **Development of Generic Remedies Guidance For Common Site Types**
- **Technology Specific Products**
  - **Promotional and Technical Videos**
  - **Implementation Handbooks**
  - **Standard Design Package**
  - **Technical Support Services**
  - **Protocol Documents**
  - **Cost and Performance Reports**
  - **Implementation Contracts**

Meetings

- Meetings 3-4 times per year
- Each meeting 2.5 to 3 days
- Goals of each meeting
  - Discuss methods for removing barriers
  - Share technical information
  - Review and refine NFESC, PWC and NAVFAC Program plans for technology implementation

POLLUTION PREVENTION

TREATMENT OF MIXED WASTE COOLANT

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INTRODUCTION

Coolants are a complex form of multilayered heterogeneous waste. At LLNL, the term "coolant" describes waste that is generated in metal cutting. This waste has been considered difficult to treat to meet either land disposal restrictions, National Pollution Discharge Elimination System (NPDES) discharge limits, or both. Because most of the matrix is water, the logical approach is to treat the entire waste stream in an industrial aqueous waste treatment setting using a variety of industrial treatment techniques.

Although there is some diversity in the constituents, the range of contamination, and the original product makeup among coolants, the treatment techniques used are the same.

WASTE STREAM GENERATION AND MAKEUP

Coolant, as product, is primarily made up of a proprietary emulsion concentrate and water (90% water by volume). The concentrate includes triethanolamine, polyoxyethylene nonionic surface agent, pine oil, dimethyl silicone polymer (antifoam), alkali borate (rust inhibitor), and fungicide and bactericide (phenol derivative). This material is mixed with water to form a 10% solution by volume. An emission spectroscopy performed on the solution yielded the results shown in Table 1.

The coolant is pumped from a reservoir to the metal part that is being machined using a mill or a lathe. The stream of coolant is directed onto the metal part at the tool interface. The coolant's purpose is to sweep away metal turnings as the tool cuts into the part. The coolant also keeps the tool-part interface cool and lubricated. The coolant is recirculated by continually directing the flow of the coolant to the tool interface and allowing the coolant to fall back into the reservoir.

Occasionally, parts are cut using tetrachloroethylene as a coolant such as when parts are made from titanium. Other coolants are used for cutting magnesium, lead, and other metals, because triethanolamine is quite corrosive to these metals.

TABLE 1

Emission Spectroscopy Results for Raw Coolant Solution

Constituent	Concentration
Boron	1%
Sodium	0.2%
Potassium	0.1%
Silicon	500 mg/L
Calcium	300 mg/L
Iron	100 mg/L
Magnesium	25 mg/L
Aluminum	10 mg/L
Copper	40 mg/L

Other contaminants (methyl chloroform and oil) are found in the coolant. These contaminants are from residues on the metal part or from basic operation and maintenance of the machining equipment. The parts are occasionally degreased with methyl chloroform. The methyl chloroform can carry over into the coolant when the part is placed back on the lathe or mill. Operation and maintenance of the mills and lathes allows for oil (tramp oil) to be deposited into the coolant reservoir.

The coolant is no longer used when it contains too much metal, oil, and or chlorosolvent. After a while, the coolant may also get rancid due to bacterial decay. When the coolant is spent, it is vacuumed up with a wet/dry vacuum or sump sucker and transferred from the reservoir(s) into drums. . It is then shipped to the aqueous waste treatment facility for treatment and subsequent disposal.

LLNL composited and sampled approximately 260 drums of spent coolant. The sampling method consisted of using a drum stirrer and mixing the solution for 1 minute to ensure that particulate metals and heavy solvents were representatively mixed into the fluid, then using a long glass tube or a Composite Liquid Waste Sampler (COLIWASA) to collect the material. The samples were analyzed for:

- pH using a pH electrode
- Percent oil by volume using a graduated cylinder and measuring the phases after settling
- Organics using EPA SW-846 Methods: 8010, Halogenated Volatile Organics, and 8020, Aromatic Volatile Organics
- Metals using EPA SW-846 Methods: 6010, Inductively Coupled Plasma Atomic Emission Spectroscopy; 7470, Mercury in Liquid Waste/Manual Cold-Vapor Technique; 7061, Arsenic/Atomic Absorption, Gaseous Hydride; and 7741, Selenium/Atomic Absorption, Gaseous Hydride
- Gross alpha and gross beta using approved preparation and counting methods
- Tritium using distillation and scintillation counting.

The results of these test are given in Table 2.

TABLE 2

Analytical Results for Spent Coolant

Constituent	Concentration	Detection limit
pH*	9.67	N/A
Percent unemulsified oil	1%	N/A
Antimony	<9 mg/L	9 mg/L
Arsenic	0.26 mg/L	0.02 mg/L
Barium	1.4 mg/L	0.02 mg/L
Beryllium	10 mg/L	0.02 mg/L
Cadmium	0.3 mg/L	0.1 mg/L
Chromium	0.51 mg/L	0.04 mg/L
Cobalt	0.2 mg/L	0.2 mg/L
Copper	11 mg/L	<0.03 mg/L
Lead	9.3 mg/L	0.6 mg/L
Manganese	2.1 mg/L	0.04 mg/L
Mercury	<0.06 mg/L	0.06 mg/L
Molybdenum	2.9 mg/L	0.03 mg/L
Nickel	2.1 mg/L	<0.05 mg/L
Selenium	<0.02 mg/L	0.02 mg/L
Silver	0.04 mg/L	0.03 mg/L
Thallium	<0.1 mg/L	0.1 mg/L
Vanadium	0.4 mg/L	0.06 mg/L
Zinc	63 mg/L	0.6 mg/L
Tetrachloroethylene	540 mg/L	10 mg/L
Methyl chloroform	680 mg/L	10 mg/L
Gross alpha	0.107 Bq/L	0.003 Bq/L
Gross beta	0.145 Bq/L	0.005 Bq/L
Tritium	0.052 Bq/L	0.018 Bq/L

* pH by hydronium mass balance

Mixing is needed to obtain a representative sample of the waste and to reach material that may have settled to the bottom of the tank. Although it may cause some release of volatile constituents (e.g., tetrachloroethylene and methyl chloroform), mixing prevents the problem of not being able to collect sediment at the bottom of the tank, which is a major source of the contamination. The escape of volatiles is minimized by the short mixing duration and by the limited space (two small bung holes in the drum) for molecular diffusion and subsequent release into the atmosphere.

PRINCIPLES USED IN TREATING COOLANTS

The methods used for removing radionuclides and metals from industrial waste water treatment are usually described as precipitation, flocculation, and filtration. Table 2 shows that antimony, mercury, selenium, and thallium were not found above detection limits, and arsenic was not significantly high. The gross alpha and beta concentration is most likely from natural and depleted uranium. Although some thorium gets machined, compared to uranium, very little of this material is generated. The tritium is not a concern here because it is below what the discharge criteria is for disposal with the Publicly Owned Treatment Waterworks (POTW) NPDES permit.

Organics are usually treated with carbon canisters in the water phase, but this method does not work well for mixed waste. Carbon canisters are not used for the following reasons:

1. A substantial amount of oil in the waste causes frequent saturation of carbon, resulting in added costs for using more canisters.
2. The carbon canister becomes slightly contaminated with radioactivity and prevents cost-effective measures for commercially recycling the carbon canisters.

Several principles are used to precipitate industrial waste. The most important are based on:

- Optimizing pH on metals that are amphoteric in nature
- Increasing solubility by calculating the ionic strengths and reducing the activity coefficient of the solute
- Calculating the oxidation-reduction potential or net potential difference as a function of pH as in an pE-pH (Pourbiax-diagrams) chart and then adjusting the pH for desired solubility.

Many metals are amphoteric. These metals are weak acids; at low-to-moderate pH, they precipitate out at an optimum pH, and then they become weak bases or form complex hydroxides at an elevated pH. Formation constants and hydroxide solubility product for most common metal hydroxide complexes and precipitates are given in Lange's *Handbook of Chemistry*. Calculations can be performed using these values to determine the optimum pH (i.e., the pH at which the metal is least soluble). These optimum pH values are given in Table 3 for a few metals.

Other precipitation techniques are available, but most deal with agents that are more toxic and less environmentally sound than hydroxide. Sulfide salt is a great precipitating agent that is very pH insensitive and has extremely low solubility products. The difficulty with using sulfide is that it has a low odor threshold, it creates a toxic gas in acidic conditions, and is difficult to disperse in liquid. Nevertheless, it is used as a polishing treatment. As one can see, lead concentrations are high when standard hydroxide precipitation is used.

TABLE 3

pH of Lowest Solubility

Constituent	pH	Concentration in (mg/L) at Given pH When the Activity Coefficients Are Unity
Beryllium (+2)	9.2	0.0009
Cadmium (+2)	11.6	0.005
Chromium (+3)	8.0	0.004
Copper (+2)	9.0	0.02
Lead (+2)	10.6	16.4
Nickel (+2)	10.8	0.03
Zinc (+2)	9.4	0.005
UO_2 (+2)	6.2	7.1 (88 Bq/L)
PuO_2 (+2)	7.8	0.00004 (91 Bq/L)

Ionic strengths of coolant are often high because of the high concentrations of dissolved salts and the type of chemical that is added to the coolant when precipitating metals. Usually activity coefficients cannot be estimated accurately due to high ionic strengths. The Debye-Hückel expression cannot be used when the ionic strengths exceed about 0.01 mol/L. For solutions with moderate ionic strengths, a modification to the Debye-Hückel expression given by Robinson, Guggenheim and Bates can be used. The modified expression can be found in Lange's *Handbook of Chemistry* and is given below:

$$\text{Log } f = bI - \frac{Az^2\sqrt{I}}{1 + B\text{å}\sqrt{I}}$$

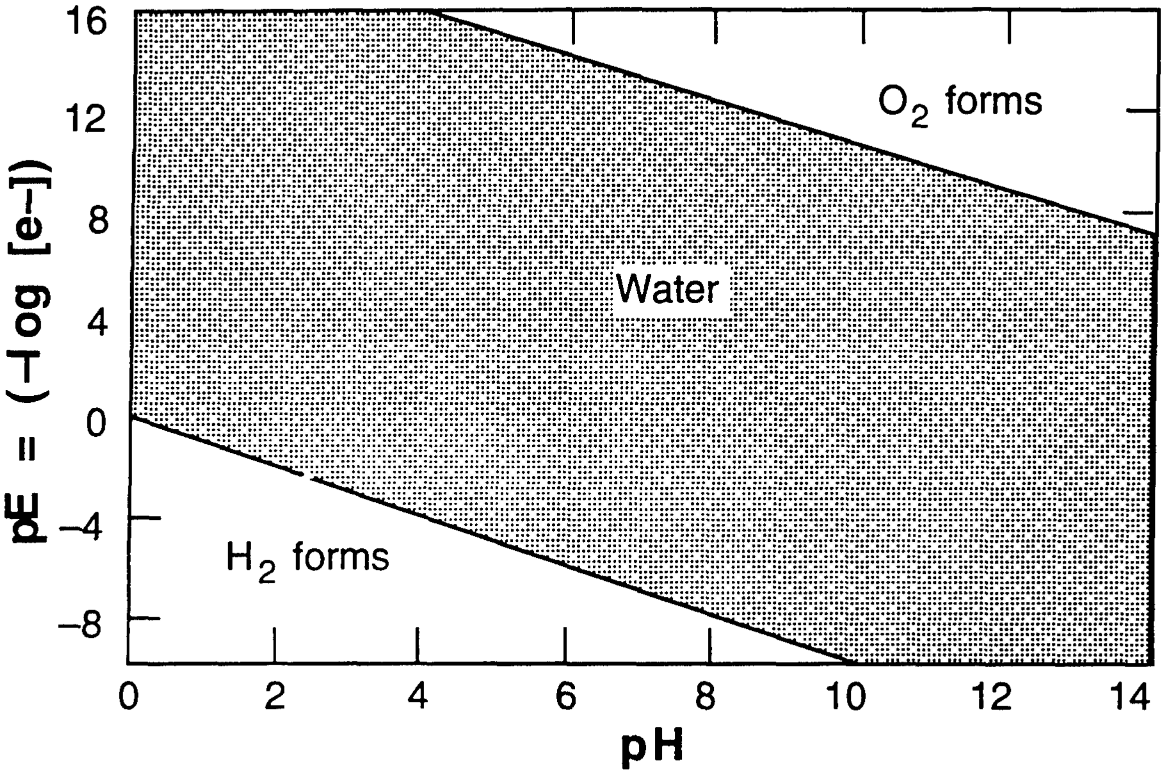
f = Activity coefficient
b = Constant (0.2 for water solvent)
I = Ionic strength
A = Constant (0.5115 for water, 25°C)
Z = Valence of the solute
B = Constant (0.3291 for water, 25°C)
å = Ionic radii of the aqueous solute

The activity coefficient calculated for the waste is approximated using sodium sulfate as the primary solute with an ionic strength of 0.081 mol/L. Using the modified expression, the activity coefficient for the waste is approximately 0.4. The use of sodium sulfate increases the solubility of the solution by 2.5 because actual solubility is estimated by dividing the ideal solubility by the activity coefficient.

The behavior of precipitation is influenced by potential differences residing in the waste water in the form of a pE-pH diagram. This is usually measured in industrial waste water by oxidation-reduction potential. This measurement determines if the environment is an oxidizing environment or a reducing environment, which is important because metals have the lowest solubility at the highest oxidation state. The range of potential in water as a function of pH is valuable to know because it provides an understanding of the environment affected by coolants. Figure 1 shows the stability region for water by plotting electron concentration as a function of pH. The higher the electron concentration, the higher the reduction potential. The lower the electron concentration, the higher the oxidation potential. So, with low electron concentrations, the results yield higher metal oxidation states and lower solubilities.

FIGURE 1

Water Stability Electron Concentration as a Function of pH



Organics can be treated in the same setting as industrial waste water. Figure 1 also sheds light on ways to deal with organics. If the oxidation potential is high, organics can be broken up into smaller molecules by oxidation. This is practiced by adding oxygen to the coolant in the form of hydrogen peroxide and iron salt (Fenton's Reagent). Organics, even halogenated organics, can be broken up into carbon dioxide and halidic acids by the use of this material. Saturated bonds like those in many oil constituents are also destroyed.

Low-grade activated carbon is used and added to coolant to remove the remaining organics. This is simpler in principle than using columns or adding granular activated carbon because the Freundlich Isotherms for this material apply directly. The low-grade activated carbon is also readily available through carbon manufacturers. For each carbon type, there are two parameters given for each adsorbing species.

These parameters are used in an isotherm equation, presented below:

$$Q = KC^{1/n}$$

Q = Concentration of contaminant on carbon (usually mg/g)
K = Freundlich isotherm parameter
C = Concentration of contaminant in coolant (usually mg/L)
n = Freundlich isotherm parameter

An estimate the amount of carbon to add is based on the original constituent concentration and this equation.

SEQUENCE OF TREATMENT

Once a methodology has been developed based on the principles discussed above, treatment of the coolant waste can begin. In the overall treatment sequence, waste coolant is put into the waste water treatment plant. The waste water treatment plant consists of a rotary-drum vacuum-filter (RDVF) unit and several 7000-L (1,850-gal) capacity tanks that are equipped with stirrers.

The coolant is placed into a tank and mixed. The coolant pH is dropped to about 3.0 by adding sulfuric acid. This breaks up coolant emulsion and facilitates the oxidation reaction to follow. Hydrogen peroxide is added to the coolant, which raises the oxidation states of all the metals and breaks up the oil and organic film.

At this point, you can detect oxygen and carbon dioxide gases being emitted from the solution. Foaming occurs at this stage, but it is not substantial and often subsides during filtration. Ferric sulfate is added after hydrogen peroxide. The ferric sulfate serves as a flocculant and destabilizes the charge around the precipitate that will be formed later.

The coolant now has very little oil on its surface. Precipitates form as the orange color caused by the ferric sulfate swirls around the tank. These precipitates are saturated sulfate salts. In many cases, sulfates have low solubility but low not enough to preclude hydroxide precipitation. After mixing the tank for several minutes, sodium hydroxide is added to precipitate the metals. Usually the precipitation will be carried out at a pH of 9.0, but high radioactivity concentrations are reduced more efficiently at higher a pH (usually around 12).

Once the sodium hydroxide has been added to the coolant, the solution is allowed to mix for at least 20 minutes. During this time, valves are lined up to route the tank contents to the RDVF. After performing the valve line up, carbon is added to the coolant solution. The carbon adsorbs the remaining organic constituents and is filtered out along with the precipitates. The filter used in the RDVF system to trap the spent carbon and precipitates is a diatomaceous earth media. The filter cake residue (i.e., diatomaceous earth, spent carbon, and precipitates) is cut off the rotary filtration drum and stored for further stabilization.

The effluent leaves the filter clear and relatively colorless. If metals such as lead, radionuclides, or other contaminants are still present at unacceptable levels, the waste is treated again. If the constituents are low enough in concentration, sulfide will be used as a polishing treatment.

RESULTS

Table 4 shows typical before and after treatment analysis. The analyses were performed using the Environmental Protection Agency's *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (EPA publication SW-846). For these particular samples, organic concentrations were lower than the composite given in Table 2. Organic concentrations before treatment and after one or more treatments are given in Figure 2. Data reported in Figure 2 are for organics that can be extracted by Freon 113.

FIGURE 2

Organic Concentrations Before and After Treatment(s)

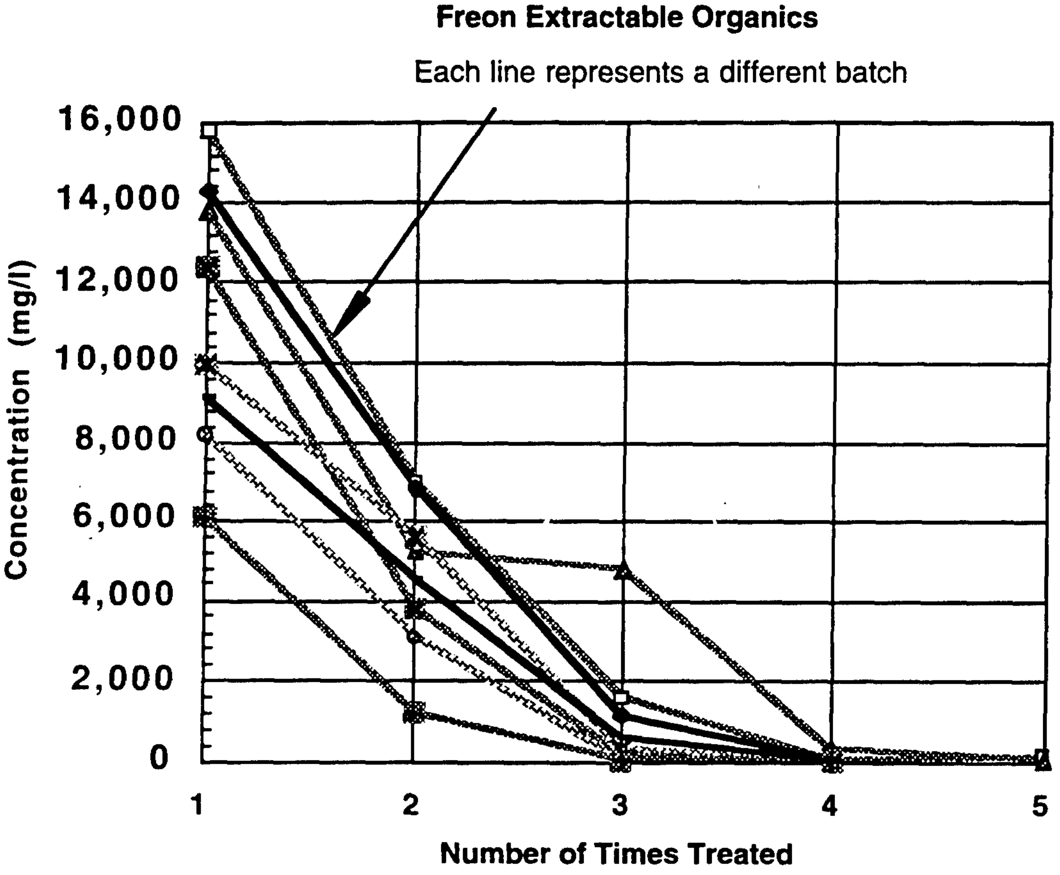


TABLE 4

pH of Lowest Solubility

Type	**Before Treat**	**After Treat**	**Before Treat**	**After Treat**	**Before Treat**	**After Treat**	**Before Treat**	**After Treat**
Batch No.	92-06	92-06	92-07	92-07	92-13	92-13	92-16	92-16
Sample No.	9103001	9200025	9200169	9200165	9200563	9200626	9200662	9200738
Liters	4901	5046	5046	5046	4685	5118	4974	5046
CAM-WET Metals in mg/L (ppm)								
Antimony	<0.6	<0.6	<0.6	<0.6	0.800	<0.9	<0.9	<0.8
Arsenic	0.020	0.050	ND	0.007	0.006	<0.001	0.010	0.005
Barium	4.500	0.520	10.000	0.052	0.120	0.010	0.120	0.006
Beryllium	1.800	0.089	0.190	<0.003	0.066	<0.004	0.020	<0.004
Cadmium	0.100	<0.02	0.040	<0.02	0.760	<0.02	0.360	<0.03
Chromium	17.000	4.200	0.770	0.230	16.000	0.730	5.400	1.000
Cobalt	0.090	0.100	0.070	0.050	0.500	0.040	0.440	<0.03
Copper	36.000	16.000	4.200	0.670	34.000	0.057	24.000	0.096
Lead	9.700	0.500	0.880	<0.04	2.300	<0.05	1.700	0.060
Manganese	6.100	0.490	0.890	<0.006	7.700	<0.006	1.300	0.007
Mercury	2.200	0.410	0.160	<0.005	0.049	<0.003	0.006	<0.003
Molybdenum	0.440	0.630	0.290	0.350	1.900	1.000	3.200	2.000
Nickel	9.600	4.600	1.100	0.500	340.000	0.420	63.000	0.120
Selenium	<0.001	0.006	ND	<0.002	<0.001	0.033	0.003	0.100
Silver	2.500	0.350	0.110	<0.005	2.800	0.010	0.079	<0.006
Thallium	0.030	<0.01	<0.01	<0.02	0.720	<0.01	<0.01	<0.02
Vanadium	0.490	0.440	0.110	0.088	0.910	0.250	0.640	0.040
Zinc	8.200	0.900	20.000	0.300	9.600	<0.07	4.600	0.100
RAD ANALYSIS								
alpha (µCi/ml)	3.70E-04	5.40E-05	1.30E-05	ND	2.10E-06	ND	1.20E-07	ND
beta (µCi/ml)	3.00E-05	2.00E-05	6.80E-06	3.10E-07	2.10E-06	ND	ND	ND
tritium (µCi/ml)	2.00E-04	1.80E-04	2.10E-05	2.70E-05	2.80E-05	2.10E-05	6.30E-06	5.10E-06

CONCLUSION

Radioactive waste coolants can be treated successfully with industrial waste water methods by applying the principles of pH optimization, ionic strength, oxidation-reduction potential, and carbon adsorption principles.

ACKNOWLEDGMENTS

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WASTE MINIMIZATION AT FITZSIMONS ARMY MEDICAL CENTER'S OPTICAL FABRICATION LABORATORY RESULTS IN WASTE ELIMINATION

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INTRODUCTION

The mission of the Optical Fabrication Laboratory (OFL) is to manufacture prescription optical devices for the U.S. armed forces. The laboratory has been located in Building 628 at Fitzsimons Army Medical Center (FAMC) since 1971. The facility now produces an average of 1100 eyeglasses per day. It is one of two large, full capability optical laboratories operated by the U.S. armed forces. The other is the U.S. Navy Ophthalmic Support and Training Activity (NOSTRA) in Yorktown, Virginia. The OFL employs approximately 75 persons, military and civilian, in production and administrative positions.

In 1991, typical average eyeglass production was 30,000 pairs per month, which included 85% glass and 15% plastic lens manufacture. Liquid wastewater is the byproduct of eyeglass manufacturing at the OFL. A quantity of 18,000 pounds per month of lead and cadmium contaminated wastewater with high pH was generated as of mid-1991. From its establishment in 1971 to the late 1980s, the OFL discharged liquid wastes to the post's sanitary sewer. More recently, these wastes were drummed and removed by a certified hazardous waste hauler to an approved RCRA Treatment, Storage, and Disposal Facility (TSDF). A waste minimization and pollution prevention program was undertaken due to regulatory and economic pressures.

The cost of waste disposal combined with recent regulatory incentives for waste minimization and pollution prevention, caused FAMC's Directorate of Public Works (DPW) and OFL management to evaluate alternatives to the waste hauling/TSDF scenario. A Waste Minimization Feasibility Study evaluated alternatives for generation, treatment and disposal of OFL wastes.

The thrust of this program followed the U.S. Army and U.S. Environmental Protection Agency's (EPA) recent emphasis on pollution prevention as its top priority, rather than end-of-pipe treatment. EPA's strategy is influenced by the Pollution Prevention Act of 1990, which is a federal law placing high priority on source reduction and recycling, and elimination of environmental risks rather than control of those risks. Also, a Waste Minimization Program was required by law in the 1984 Hazardous and Solid Wastes Amendments in the Resource Conservation and Recovery Act (RCRA) for hazardous waste generators such as the OFL. This requirement is for a comprehensive, organized and on-going effort to reduce the volume and toxicity of wastes produced as much as economically practical.

Capital and operational economics played an important part in the selection of alternatives. Labor cost for labor intensive substitutes and costs for non-hazardous replacement materials were weighed against hazardous waste disposal costs.

DESCRIPTION OF WASTE GENERATING PROCESSES

During eyeglass manufacturing, the lenses are ground, shaped, and polished to meet a particular prescription and frame style. Historically, several eyeglass manufacturing unit operations at OFL were associated with the generation of hazardous wastes, including:

- Surfacing
  - Pre-Coating
  - Blocking
  - Deblocking
- Edging
  - Blocking
  - Deblocking
- Glass Lens Fining
- Glass Lens Polishing
- Glass Lens Tempering
- Cleaning
  - Tools
  - Lenses
  - Floors

A description of these waste generating operations is as follows.

Surfacing and Edging

Pre-Coating

The blocking operation is a process where a fixture (block) is attached to each lens to hold the lens while it is ground or edged. A lens coating process was used which enhanced the adherence of the block to the lens and also protects the lens from scratching. Historically, a solution called Autocoat Blue (Coburn Industries, Muskegee, OK) which contains a polyvinyl propylene solid fraction and a mixture of methanol, ethanol, and 4-methyl-2-pentanone as the volatile fraction was used. In the application of Autocoat Blue, a technician placed a quantity of lenses on a ventilated hood drying rack, and the Autocoat was sprayed onto the lens' surface. The Autocoat was allowed to dry on the rack for approximately one-half hour. The majority of the volatile fraction of the Autocoat Blue was contained in the ventilation hood and discharged to the atmosphere through a vent duct in the roof. However, a fraction of the fumes were released to the work area, and were a respiratory and skin exposure hazard to optical technicians. The sprayer technician used a paper dust mask and a box fan for personal health protection. The sprayer was periodically cleaned using acetone, and the fumes from cleaning were discharged through the vent hood to the atmosphere.

Lens Blocking

During blocking, the attaching material has historically been a low melting point alloy (LMPA) containing the heavy metals lead and cadmium. The alloy was attached to the Autocoat Blue-coated lens in a blocking machine which injects a molten alloy between the lens and the iron block. As the alloy cools and solidifies, it adheres to the iron block and the coated lens, providing a "handle" for the lens during the surfacing or edging procedures. A small amount of alloy slag, consisting of alloy contaminated during blocking with dirt or foreign particles, is produced and disposed of as hazardous waste.

Lens Deblocking

The deblocking operation involves removal of the blocking fixture after the lens is ground or edged. Historically, this was accomplished using a commercial dishwasher with a high temperature water wash/rinse cycle and a high pH detergent (LC-100 Optical Detergent, Ecolab, Inc., St. Paul MN), creating a highly alkaline wastewater contaminated with lead and cadmium. The LMPA melted at this high temperature and drained to a sump in the dishwasher. Most of the LMPA was subsequently removed from the sump and recovered for reuse in a reclaim tank.

Glass Unique Waste Generators

Glass Lens Fining and Polishing

Historically with glass lens production, the fining process required the use of zinc pads and aluminum oxide slurry. Aluminum oxide was mixed with water to form this abrasive slurry. The zinc fining pads aided the fining process by distributing the aluminum oxide slurry between the tool (lap) and the lens. The spent fining slurry contained particulate contaminants which were collected at the end of each day. This slurry was run through a centrifuge which allowed the liquid waste to be pumped to the sanitary sewer, and the solid waste to be hauled to a landfill. Both aluminum oxide and zinc were a concern for future environmental regulation. Cerium oxide polishing powder (containing thorium dioxide) was mixed with water into a slurry form and used for final polishing of glass lenses.

This slurry was contaminated and disposed of in the sanitary sewer when spent. Thorium dioxide is a documented releaser of alpha radiation. The softer plastic lens materials do not require such a vigorous process or harsh abrasive pads and polishes.

Glass Lens Chemical Tempering

To reduce the risk of the lens shattering into sharp pieces upon impact, the lenses are heat treated or chemically tempered. Historically, the chemical tempering process was used at OFL. This was accomplished by placing the lenses in a potassium nitrate bath, which was disposed of as hazardous waste when spent. Plastic lenses do not require tempering. Physical properties of plastic lenses are more impact resistant than tempered glass of comparable thickness. If plastic breaks, the fragments are larger and less sharp than glass.

Tool Cleaning

Cleaning of lens grinding tools (laps) used in glass production was another source of air emissions and hazardous waste. A mineral spirits solvent (Stoddard solvent) bath was used to remove zinc fining pads from aluminum laps. The bath created hazardous emissions as the solvent evaporated, which were vented to the atmosphere except for a minor fraction which remained in the work area and was a health concern. The spent solvent was removed by a recycling vendor. To completely remove residual adhesive from the laps, a sandblaster was sometimes used. The aluminum laps were cleaned in a sandblaster using glass beads. Release of silicon dust into the environment during this operation represented a worker respiratory health concern. Such vigorous pad removal and lap cleaning is not required in plastic production.

Acetone Cleaning

Historically, acetone was the solvent of choice and was used in many phases of glass production; to clean manufacturer's marks off lenses, to prepare lens surfaces for blocking, and for general clean-up. Acetone is not used in plastic lens production since it is damaging to the lens material.

Floor Cleaning

Floors were cleaned every day by dry sweeping followed by wet mopping to the floor drains. Floor drains were discharged to the sanitary sewer.

HAZARDOUS WASTE GENERATION AND CHARACTERIZATION

For the lens deblocking wastewater and contaminants (cadmium, lead and high pH), the contaminants of concern (cadmium and lead) originated in the Low Melting Point Alloy used for blocking, and in the caustic detergent used for deblocking and cleaning.

In 1992 after initial waste reduction took place, average deblocking wastewater production was 450 to 900 lbs. per week from surface deblocking, 450 lbs. per month from finish deblocking, and 450 lbs. per month from the plastics lab. An additional 450 lbs. every 4 months was generated from reclaiming contaminated alloy. For the entire OFL, typical deblocking wastewater generation was 4600 lbs. per month in 1992. Peak waste production was estimated at twice the average rate, or 9200 lbs. per month. A summary of constituents of the deblocking waste is presented in Table 1.

TABLE 1
Chemical Characteristics of Deblocking Wastewater

Chemical Constituent	Concentration
pH	12.7 - 13.5
Lead	3.2 - 150 mg/l
Cadmium	14 - 350 mg/l

The LMPA was the source of cadmium and lead contaminants in the deblocking wastewater. The LMPA predominantly used at the OFL was Indalloy 158, which is composed of bismuth, lead, tin, and cadmium. Indalloy 117 was used for plastic lens manufacturing and is composed of bismuth, lead, tin, cadmium, and indium. The lead and cadmium in the LMPA dissolve in the high temperature, high pH deblocking wash water and contribute to the hazardous characteristics of the waste. Any waste containing lead concentration above 5.0 mg/L or cadmium above 1.0 mg/L is a RCRA hazardous waste by virtue of the toxicity characteristic (40 CFR 261.24). Another hazardous characteristic of the deblocking waste was high pH, which is RCRA classified as corrosive if greater than 12.5.

The lens precoating step with Autocoat Blue resulted in air emissions of up to 240 pounds per month of methyl ethyl ketone, methanol and ethanol vapors released to the atmosphere.

Hazardous waste and emissions production from smaller sources was unquantified, including thorium dioxide and cerium oxide from glass polishing, potassium nitrate from chemical tempering, silicon dust from sand blasting, aluminum oxides from lens grinding, and floor drain discharges from floor cleaning.

EVALUATION METHODS

The EPA's *Waste Minimization Opportunity Assessment Manual*[1] presents details and guidance on waste minimization. At the OFL, a Waste Minimization Opportunity Assessment was prepared in September 1990, and was a facility-wide survey of waste minimization opportunities at the OFL. This study identified materials or processes which were candidates for waste minimization, and narrowed the field to those for further evaluation. This assessment followed the procedures presented in EPA's manual, which focuses on waste minimization through source reduction and recycling.

A Waste Minimization Feasibility Study was conducted by Parsons Engineering Science, Inc. to evaluate alternatives for the generation, treatment and disposal of OFL wastes and contaminants. OFL optical technicians, maintenance and environmental personnel, and management contributed to the study in a large way. Several types of waste minimization and treatment alternatives were considered, which included substitution of process materials and unit operations; hazardous materials elimination; replacement of product lines; pre-treatment/discharge; and recycling.

Materials substitution with non-toxic alternatives and hazardous materials elimination through process change were selected for implementation. A process and economic feasibility analysis determined the most feasible alternatives for waste minimization. Several inspections of the OFL were conducted to determine wastewater sources, locations, process theory, and space availability for treatment units. A review of existing records was undertaken including chemical analysis reports, waste quantification estimates, floor plans, sewer plans, and raw material usage. Interviews with technicians shed insight into existing plant operations, acceptable process substitution alternatives, operations, maintenance, safety and production requirements, and source reduction alternatives. Industry surveys were conducted and trade associations were contacted for information.

The study examined the technical feasibility and cost of alternatives for waste minimization and disposal, including source reduction, source elimination, treatment, and discharge.

EVALUATION OF WASTE MINIMIZATION ALTERNATIVES

The Waste Minimization Feasibility Study examined several types of waste minimization alternatives for consideration at the OFL. These are described as follows.

Substitution of Process Solutions

Investigation of process substitution considered alternatives for lens blocking agent, blocking agent adhesive compound, deblocking detergent and deblocking/wash operation. Source reduction and elimination alternatives were pursued by literature search, contact with trade associations, manufacturers, commercial optical fabrication laboratories, and Naval Ophthalmic Support and Training Activity (NOSTRA), Yorktown, Virginia.

Low Melting Point Alloy

The LMPA was the source of cadmium and lead contaminants in the deblocking wastewater. Substitution for the LMPA (Indalloy 158 and Indalloy 117) with non-hazardous alloy was pursued with the alloy manufacturer, Indium Corporation of America, and others. Several alternatives to Indium 158 and 117 are commercially available, including ones with non-hazardous characteristics. The use of Indium 158 and 117 at the OFL was driven by their relatively low cost, compared to non-hazardous alternatives. However, these cost comparisons did not factor in the cost of hazardous waste removal. When this cost was included, non-hazardous LMPAs were cost effective.

Two non-hazardous LMPAs were identified as viable substitutes for use in the glass lens production. These were Indalloy 162 and Indalloy 119, which do not contain lead or cadmium. Indalloy 162 is composed of bismuth and indium, and Indalloy 119 is composed of bismuth, indium, and tin. Bismuth, indium, and tin are not constituents on the lists of the toxicity and extraction procedure toxicity characteristic of hazardous waste (40 CFR 261.24). Bismuth, indium, and tin, and the deblocking process waste are not included in any of the lists of hazardous waste (40 CFR 261 Subpart D). Also, bismuth, indium and tin are not listed as chemical hazards by the National Institute for Occupational Health and Safety (NIOSH) and the U.S. Department of Labor, Occupational Safety and Health Administration[2].

Leap blocking was another non-hazardous alternative to LMPA which can be used for the edging operation. A neoprene adhesive pad called a Leap Pad (3M product distributed by Semi-Tech, Inc.) is utilized to adhere an aluminum block to the glass or plastic lens. Leap blocking works equally well for edging of glass and plastic lenses, and is the universal standard of the industry for the edging operation. The Leap Pad and block are applied one at a time by hand by a technician using an applicator called a Leap Blocker. With leap blocking, no LMPA or precoat is required, and consequently, there are no water pollutants or air emissions. This hand application operation is more time consuming and operator intensive than the alloy blocking method. The lenses are manually deblocked using a Leap Deblocker (Semi-Tech). Leap blocking cannot be used for the surfacing operation due to incompatibility of blocking system to surfacing equipment, and inadequate bonding for this more aggressive production process.

The melting point temperature of Indalloy 162 and Indalloy 119 is so high that they cannot be used for plastic lens manufacture. However, non-hazardous substitutes for blocking agent have been developed for the plastic lens surfacing operation. Featherlite Blocking Compound (Optical Laboratory Supply, Evansville, IN) is a product composed of non-hazardous, biodegradable wax material. For the blocking operation, Featherlite bonds a polycarbonate block to the lens, which has been covered with Surface Saver Tape (Semi-Tech Inc., Garland, TX). A special Featherlite blocking machine is required. Featherlite will not adhere to Autocoat Blue and must be used with Surface Saver Tape. Gerber One Step Blocking System (Gerber Optical, Inc. South Windsor, Connecticut) also utilizes a wax-like blocking medium, with better adhesion to the lens without Surface Saver Tape.

Blocking Adhesive/Protective Lens Coating

Substitution of the Autocoat Blue precoat blocking solution was pursued with the manufacturer and others. The spray coating method and equipment for Autocoat Blue application at the OFL was a mass production technique and not used in low production scenarios.

The dishwasher deblocking technique for Autocoat used at the OFL is a non-standard procedure according to the manufacturer. Manufacturer's data sheets indicate that the Autocoat product may cause pollution when mixed or discharged in water. The modern substitute for the lens adhesive for glass and plastic surfacing operation is Surface Saver Tape, applied by an OptiSpeed Lens Tape Applicator (Semi-Tech). Application of the tape creates no water pollution or air emissions. This material has been adopted as the standard of the industry due to its environmental and operator health advantages over spray precoats. The tape application operation is more time consuming and operator intensive than the Autocoat mass spraying. However, it does have certain time efficiencies over Autocoat, such as no drying time and no equipment cleaning required. With this time factored in, some industry experts suggested that use of Surface Saver Tape can be as time efficient as Autocoat Blue application. The used tape contains small amounts of LMPA which sticks to its surface, and must be disposed of as hazardous waste.

Optical Detergent

The caustic optical detergent (LC-100) was causing a pH 12.7 and upwards in wash water. A waste with pH of 12.5 or greater is considered to be a RCRA waste. Consequently, the optical detergent alone caused the wastewater to be classified as hazardous. Substitute optical detergents are commercially available which have non-hazardous composition. Use of Simple Green Cleaner/Detergent (Sunshine Makers, Huntington Harbor, California) was selected for pilot testing at the OFL.

Substitution of Process Unit Operations - Conversion to Primarily Plastic Lens Fabrication

From the previous description of process operations, it is noted that the glass lens production process produces significantly more hazardous waste than plastic lens production. At the same time the OFL was embarking upon a waste minimization program, the military services were about to make a decision to direct their optical laboratories to substitute plastic for glass lenses. This decision was made for reasons other than waste minimization, including reduced weight, increased impact resistance, and economic advantages resulting from industry trends toward plastic. Since 1993, the large military labs have manufactured primarily plastic lenses, and the OFL has converted to 100% plastic production. The revised Army Regulation (AR) 40-63 is to be fielded in 1995 and will include this change. Coincidentally, a substantial environmental gain has also been achieved with the less damaging plastic lens production.

Deblocking Method Alternatives

Hand Deblocking

Alternatives to the dishwasher deblocking method were considered. Hand deblocking using a deblocking ring impacted on a flat surface is an alternative to dishwasher deblocking. However, this is a slow process which is not acceptable for high production quotas and caused increased lens breakage. Also, the impacting of the tool is jarring, unpleasant, and possibly unhealthy for the opticians.

Series Operation of Deblocking Dishwashers

While permanent measures for waste minimization were being planned, OFL personnel undertook temporary measures to reduce the amount of waste generated and cost of off-site removal. A major step taken in this respect was the conversion of the two dishwashers in the glass deblocking operation from parallel operation to series operation. The primary dishwasher was then operated for several wash cycles without discharging the soap/waste concentration and, thereby reducing the amount of waste generated. As a secondary benefit, this can be considered a process material conservation/reuse measure with regard to the alkaline soap. The second dishwasher was then converted to a rinse-only dishwasher and continued to discharge to the sanitary sewer.

Unfortunately, the recycle of caustic soap in the dishwasher caused weekly maintenance requirements, due to the corrosive nature of the soap and the lack of clean rinse cycles. The dishwashers were not constructed for constant emersion in corrosive liquid. The maintenance outages of the primary dishwasher created other operational difficulties at the plant. Consequently, the dishwasher recycling program was only a temporary measure.

Substitution of Dry Alloy Melting

A dry alloy melting process was identified which uses a drying oven to remove the alloy from the blocks. This process avoids the hazardous waste producing wet method. Many optical labs use this deblocking method and review of their experience was positive. However, this method requires hand deblocking prior to the alloy melting oven, with the disadvantages discussed previously. Additionally, in a high production facility such as OFL, the labor expense, manpower availability, and power consumption expense for the ovens make this alternative infeasible and uneconomical.

Pretreatment of Wastewater and Discharge to Sewer

Alternatives for pretreatment of the OFL deblocking waste were considered, but had an overriding disadvantage. The deblocking wastewater contained elevated levels of lead and cadmium metals and high pH, which are characteristics that classify the waste as hazardous. In order to treat a waste which is classified as a RCRA hazardous waste, the treatment unit would be classified as a RCRA hazardous TSDF. TSDF are subject to extremely stringent RCRA regulations with regard to waste management, handling, treatment and record keeping. The level, cost and complexity of environmental controls, EPA permits and record keeping is increased tremendously for TSDF, over that of waste generators. The cost and regulatory burden of a RCRA TSDF permit make this very unattractive.

Treatment of Wastewater for Reuse in Process

A fundamental process operation of the existing lens fabrication system at the OFL was the reclamation of LMPA from the deblocking washers. Reclamation of the LMPA was good engineering practice from both an environmental and economic standpoint. Waste reuse was evaluated to reduce the total volume of waste generated, and to reduce the quantity and cost of raw materials required.

Treatment and reuse of deblocking wastewater was considered for the dishwashers. Because of the high pH and metals concentration in the reuse water, recurring maintenance outages in the dishwashers are expected. Also, increased spill potential and reduced redundancy are associated with these maintenance outages. This is an untried concept which has uncertainties with regard to negative effects on the deblocking/washing process and on subsequent lens fabrication operations. The concern is that the buildup of dissolved material in the wash water due to the concentrating effect of recycling will create incomplete lens washing. For this reason, treatment and recycle of the wash water was not an acceptable alternative at the OFL.

PILOT TESTING

Bench scale and full scale testing of non-toxic blocking materials at the OFL was necessary to determine their effectiveness. Pilot testing on the glass lens production line was undertaken to determine the effectiveness of Indalloy 162 and Indalloy 119 for glass lens blocking. These alloys were tested and found to be a viable substitute for glass lens production (not plastic lenses).

For the plastic lens surfacing operation, a biodegradable, non-hazardous substitute blocking adhesive called Featherlite Blocking Compound (F.B. Optical Manufacturing, Inc., Saint Cloud, Minnesota) material was tested, with generally negative results. The material was relatively unstable, resulting in unwanted prism and spontaneous deblocking during processing. The material itself was difficult to work with, contaminated easily, and required a manually operated deblocking unit. Part of the problem results from an inadequate amount of blocking material between the lens blank and the block. Recent improvements by Featherlite have been reported, but the failure rate of the new formulation are unknown at this time.

The Advanced Blocking System (ABS) utilizes a disposable, single-use adhesive pad to adhere the lens to the grinding fixture. This new optical technology is unproven in a large volume production facility at this time. Pilot testing at the OFL, performed by the U.S. Army Medical Equipment and Optical School (USAMEOS), showed unfavorable preliminary results.

The Gerber One Step Blocking System (Gerber Optical, Inc, St. Windsor, CT) is a computerized unit compatible with existing surfacing writeup/layout programs. The material is stable, workable, and recyclable. In initial testing, the lens blanks adhered throughout the surfacing process, producing a finished lens superior to any of the other substitute materials and processes.

Use of the Simple Green Cleaner/Detergent was tested at the OFL, and found to be acceptable for production. Use of this detergent removed the caustic hazardous component from the deblocking waste.

RESULTS

Substitution of process solutions with non-hazardous materials was a viable waste minimization approach. Non-hazardous substitutes were identified and successfully tested for LMPA and

Autocoat Blue lens adhesive, for both glass and plastic surfacing and edging operations.

Revision of the fundamental mission at the OFL, from glass lens to plastic lens fabrication, significantly contributed to the waste minimization success. The mission at the OFL has traditionally been primarily for production of glass lens eyeglasses due to requirements of AR 40-63. However, the military's preference for lightweight, safe and comfortable plastic lenses, coinciding with industry trends, helped promote a modification in AR 40-63 to allow plastic lenses.

Waste minimization and conversion to plastic lens production required significant overhaul of the OFL processes and building. Building renovation, equipment replacement and upgrades, retooling, product trials, recalibrations, and personnel training were implemented.

A summary of the hazardous materials which were eliminated and replaced with non-toxic substitutes, contributing to the waste minimization effort, is presented in Table 2.

A non-hazardous substitute for the lens adhesive for glass and plastic surfacing operation is Surface Saver Tape, which was substituted for Autocoat Blue spray adhesive. Non-hazardous Simple Green optical detergent was substituted for the use of hazardous LC-100. Leap blocking is a non-hazardous alternative to LMPA which was substituted in both the glass and plastic edging operations.

Floor drains to the sanitary sewer were plugged to prohibit LMPA Indalloy 158 and 117 from entering the sewer. For floor cleaning, dry cleanup methods followed by wet methods with liquid capture and disposal (as required) were substituted.

TABLE 2
Summary of Non-hazardous Material Substitutes

Process	Hazardous Material	Non-Hazardous Substitute
Lens edging/ blocking	Lead/cadmium alloy	Leap blocking
Lens surfacing/ blocking	Autocoat Blue	Surface Saver tape
Cleaning/ deblocking	Potassium hydroxide optical detergent	Simple Green detergent
Glass fining	Aluminum oxide	Water
Glass polishing	Cerium oxide, Thorium dioxide	Polishing compound
Chemical tempering	Potassium Nitrate	Eliminated
Tool/lens cleaning	Acetone	Eliminated
Tool cleaning	Silicon dust	Eliminated
Tool cleaning	Stoddard solvent	Eliminated
Floor cleaning	Lead/cadmium alloy/silicon dust	Dry cleanup, Floor drains plugged

Results of this program are admirable to date. The 18,000 pounds of hazardous waste per month generated in mid-1991 has been reduced to 1,500 pounds per month as of January 1995, with associated cost reduction from $11,340 per month in disposal cost in 1991 to $1,263 per month in 1995. A phased approach to the waste minimization program was implemented with the following results:

Time period	Hazardous Waste Generated	Disposal Cost
Mid-1991	18,000 lbs./mo.	$11,340/mo.
Mid-1992	6,300 lbs./mo.	$3,969/mo.
Jan. 1993	3,600 lbs./mo.	$2,268/mo.
Jan. 1994	2,700 lbs./mo.	$1,701/mo.
Jan. 1995	1,500 lbs./mo.	$1,263/mo.
Feasible in Future	0 lbs./mo.	$0/mo.

The cost for waste removal can be expected to increase greatly in the future, further magnifying the advantages of this waste minimization program.

Another effect of the waste minimization program, was the elimination of hazardous air emissions from the OFL. The lens precoating step for blocking resulted in air emissions of up to 240 pounds per month of methyl ethyl ketone, methanol and ethanol vapors released to the atmosphere. These emissions were eliminated by the waste minimization program.

Worker health benefits have been derived from the program in terms of fewer visits to the Occupational Health Nurse. The result has been higher productivity by the work force. Also, the program has lessened the potential for compensatory health claims in the future.

The Waste Minimization and Pollution Prevention program when fully implemented can result in complete elimination of hazardous waste generation at the OFL. To date, the United States Army Environmental Center (USAEC) has provided approximately $690,000 in funds for the hazardous waste minimization project. The result is a 92 percent reduction in hazardous waste generation, at a cost savings of $121,000 per year.

CONCLUSIONS

Numerous advantages were derived from this program including tangible and intangible benefits, such as:

- Reduced waste treatment and disposal costs, and operating costs
- Compliance with regulatory waste minimization requirements
- Protection of worker health and safety and public health
- Protection of the environment.

In addition to cost savings and other advantages, waste minimization reduced liability (environmental, economic, and health and safety) for the OFL associated with long term waste hauling and disposal. This is an unquantifiable item which is a significant advantage for the OFL over the long term.

The OFL is at the leading edge of the waste minimization program for large-scale optical fabrication facilities. The OFL, in coordination with optical equipment manufacturers, conducts ongoing testing of non-toxic alternative materials and processes. Those compatible with its high volume production are integrated into the system. Most commercial large-scale optical laboratories to our knowledge are not as advanced in incorporating these more environmentally sound technologies into their laboratories, but rather are awaiting successful test results before joining the waste minimization trend.

The OFL has exhibited a commitment to this waste minimization program which is extraordinary. Their efforts continue to identify and implement change with the objective of total hazardous waste elimination. Testing for the final step towards complete elimination of hazardous waste is now completed. New equipment (the Gerber One Step Blocking System) has been requested, pending funding under the Capital Expense Equipment Program (CEEP). Non-hazardous substitute materials for lead/cadmium alloy used in the lens grinding process will be used once the Gerber system is installed. Complete elimination of toxic materials is feasible during 1995.

REFERENCES

1. *Waste Minimization Opportunity Assessment Manual*, EPA Technology Transfer Manual, (EPA/625/7-88/003), July 1988.
2. *NIOSH/OSHA Pocket Guide to Chemical Hazards*, U.S. Department of Health, Education and Welfare, and U.S. Department of Labor, September 1978.

ALTERNATIVE PAINT STRIPPER TRIALS FOR DIFFICULT PAINT SYSTEMS

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INTRODUCTION

Solvent paint strippers historically used by the United States Army Depot System Command (U.S. Army) contain 60 to 80% methylene chloride (dichloromethane), which is considered to be a potential occupational carcinogen by the National Institute for Occupational Safety and Health (NIOSH), and a suspected carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH). U.S. Army sought to eliminate methylene chloride use because of potential health hazards.

In addition, stripper emissions and aqueous rinses are sources of methylene chloride release to the environment. These releases represent both regulatory compliance issues and pollution prevention opportunities. Methylene chloride is considered a hazardous air pollutant (HAP) by the Environmental Protection Agency (EPA) and is subject to Toxic Chemical Inventory Release reporting requirements under Section 313 of the Emergency Planning and Community Right-to-Know Act, also known as Title III of the Superfund Amendments and Reauthorization Act (SARA).

Methylene-chloride-based paint strippers are widely used throughout the Department of Defense (DOD) and in industries such as aerospace. In recent years, alternative paint stripping techniques have been extensively studied and applied, including:

- More durable blasting media, advanced techniques for dust emission control, and media recirculation and recycling to minimize waste.
- For more sensitive metals and structures, blasting with alternative media, such as plastic beads, nut shells or wheat starch. These processes also extensively control emissions and recover and reuse the blast media.

- High-pressure water/bicarbonate blasting has been applied for paint stripping from military airplane surfaces.
- Robotically controlled very-high-pressure water blasting has been extensively tested by the U.S. Air Force (USAF) for airplane surfaces.
- A robotically controlled xenon lamp/carbon dioxide pellet paint removal system has been tested for paint removal from airplane surfaces.
- Alternative chemical paint strippers.

The Army uses mechanical depainting to remove paint from most large- and medium-size items. For certain parts, however, paint cannot be removed by abrasive blasting due to equipment size, shape, sensitive areas (e.g., threads), and recessed surfaces. An example of such a part is a gasoline tank with both exterior and interior paint and threaded openings. For these parts, chemical immersion paint removal is necessary.

Whenever possible, the Army uses strong caustic solutions for chemical depainting. Environmental and safety risk for caustic solutions are lower and more manageable than solvent solutions. These solutions are filtered and chemically adjusted to improve their service life. Caustic paint strippers are not as effective, particularly for Chemical Agent Resistant Coatings (CARCs). The Army's switch to CARCs in the late 1980s has made the search for a nonmethylene-chloride-based stripper more difficult.

Past evaluations of alternative strippers have identified potential substitutes to the present methylene-chloride-based stripper(1,2,3). While the alternative strippers did not perform as well as the methylene-chloride-based stripper, investigations conducted by the U.S. Army suggested that their performance may be improved by employing higher operating temperatures and using more aggressive agitation techniques. However, these prior studies did not utilize test substrates and conditions that represent actual field conditions for the robust paint systems used by the U.S. Army.

This study focused on the two most promising alternative paint strippers from past studies and tested their performance against the current stripper. After initial results indicated insufficient performance, a third promising commercial paint stripper was added to the tests. The study also gauged the effect of temperature, time, and various mechanical assistance techniques (e.g., ultrasonics and vigorous mechanical agitation) on performance.

OBJECTIVES

The goal of this study was to identify an alternative stripper process that eliminated the use of methylene chloride and other hazardous constituents. Letterkenny Army Depot (LEAD), located in Chambersburg, PA, retained Roy F. Weston, Inc. (WESTON®) to complete this alternative paint stripper investigation. The specific objectives of the study were fourfold:

- Identify the most promising alternative strippers with significantly different formulations for bench-scale trials.

- Compare the performance of the selected alternative strippers to the presently used methylene-chloride-based stripper on robust paint systems and substrates indicative of actual field conditions. LEAD selected an epoxy primer and epoxy topcoat military paint system applied to an aluminum substrate for the investigation.

- Determine if agitation techniques and elevated temperatures improved the performance of the selected alternative strippers. Agitation techniques evaluated include ultrasonic agitation and vigorous mechanical agitation. Pressurized spray systems were not evaluated due to potential safety hazards.

- Conduct a comparative environmental, health and safety evaluation for the best-performing alternative stripper to ensure that the substitute chemicals are a true improvement rather than a substitution of listed hazardous chemicals with lesser known unlisted hazardous chemicals.

EXPERIMENTAL METHODS

The alternative paint stripper investigation was conducted at WESTON's Environmental Technology Laboratory in Lionville, PA, from October 1992 through October 1993. The following subsections describe the procedures used to conduct the investigation.

Alternative Stripper Selection

Based on discussions with LEAD personnel and a review of existing DOD and commercial literature on methylene chloride substitutes, the following three alternative strippers were identified for use in the study:

- *Fine Organics® 606 (FO®-606)* — FO-606 is a commercial stripper whose primary active components are n-methylpyrrolidone (NMP) and ethanolamine. A surfactant and wetting agent are also present as minor components. FO-606 is manufactured by Fine Organics Corporation.

- *U.S. Army Construction Engineering Research Laboratory (CERL) Stripper (CERL Strip)* — CERL Strip is a proprietary mixture developed by CERL whose primary active components are heptyl acetate, butyrolactone, and formic acid. A surfactant is also present as a minor component.

- *Turco® 6776 Thin* — Turco 6776 Thin is a commercial stripper whose primary active components are petroleum distillates, formic acid, and two proprietary ingredients. A surfactant is also present as a minor component. Turco 6776 Thin is manufactured by Turco Products, Inc.

The performance of the alternative strippers was compared to a baseline (e.g., control) stripper formulation, *Stripper 9619*, whose primary active components were methylene chloride and formic acid. Stripper 9619 is equivalent to the methylene-chlorine-based strippers used at LEAD, and is manufactured by Ramken®, Inc.

Test Panel Preparation

Red River Army Depot and Sacramento Army Depot both installed NMP mixtures based on lab results from CERL. Neither depot kept the material in service very long because of performance and evaporation problems at the temperatures required to get even modest performance. After experimenting with several panel configurations, LEAD concluded that a very adherent, artificially aged flat coupon can simulate the problems caused by the geometry of the part and thorough aging.

To ensure that the paint system and substrate used in this investigation were representative of the robust paint systems encountered at LEAD, all test panels used in the investigation were prepared and aged at LEAD. Individual test panels were 2 inches wide by 6 inches tall by ⅛ inch thick. All test panels were cut from a single ⅛-inch-thick sheet of 5000 series aluminum. Burrs and sharp edges were removed from with a vibratory finisher, and the surfaces were roughened using glass blast media.

The panel surfaces were chromate conversion coated prior to applying a waterborne epoxy primer (MIL-P-53030) and a high-solids epoxy topcoat (MIL-C-22750). The panels were allowed to dry approximately 1 to 2 days, and aged at 140°F for 7 days. Both primer and topcoat thicknesses were determined at LEAD with an electronic thickness gauge.

Individual panels were randomly selected for use in the investigation and screened against the following acceptable coating thickness ranges (as provided by LEAD):

- Epoxy primer:	1.0 to 2.0 mils
- Epoxy topcoat:	1.0 to 2.7 mils
- Total coating:	2.3 to 4.0 mils

Panels satisfying these criteria were visually inspected for defects. Panels showing paint runs, chips, or unusual coloration were rejected. All panels were weighed prior to testing.

Performance Test Equipment

The bench-scale test equipment used for the alternative paint stripper investigation consisted of an ultrasonic cleaning bath (immersion tank) and agitation apparatus (mechanical stirrers). Figure 1 provides a schematic of the test equipment. The immersion tank was a Bransonic® Ultrasonic Cleaner Model 8200R-4 equipped with a heater. The ultrasonic bath operates at a frequency of 40 kilohertz with 400 watts of power. The stainless steel tank has a 5.5-gallon capacity and is 19.5 inches long, 11 inches wide, and 6 inches high. The immersion tank can be operated with or without the heater or ultrasonics operating. The ultrasonics could not be operated at temperatures above 130°F. As a result, supplemental heating was provided using an immersed heating coil, increasing the maximum operating temperature to 180°F.

Hangers were fabricated to suspend nine test panels in the immersion tank in three rows of three panels each. The hangers were designed to spread the test panels evenly, and to immerse the 6-inch test panels approximately 4 inches into the stripper solution.

Four variable-speed stirrers with dual propellers provided mixing. Under static conditions, the mechanical stirrers were operated at a minimum speed to eliminate phase separation of the stripper solutions and to ensure uniform stripper temperature throughout the tank. Under mechanical agitation conditions, the stirrers were operated at the maximum speed that would not result in splashing.

Baseline Performance Test

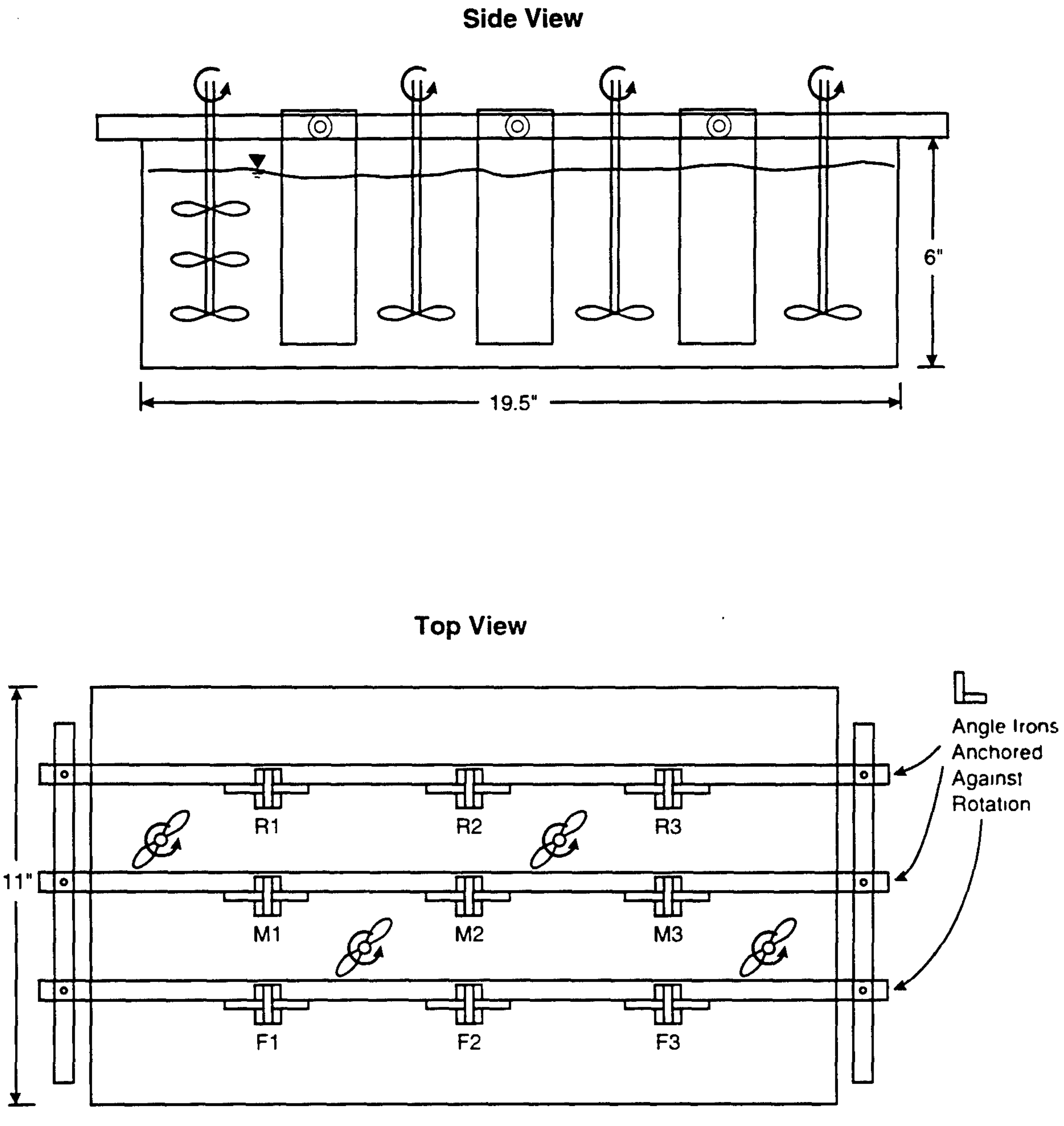
Baseline performance tests were conducted to determine the minimum exposure time required to remove 95 to 100% of the paint from the test panels using Stripper 9619 at ambient temperature. The minimum effective exposure time was evaluated under static conditions and with the assistance of mechanical agitation.

Baseline performance tests were conducted on three sets of triplicate test panels immersed at the same time under the same temperature and method of agitation (static versus mechanical agitation). One set of triplicate test panels was withdrawn from the immersion tank after 20 minutes, another at 30 minutes and the final set at 40 minutes. These immersion times were selected based on past experiences at LEAD using Stripper 9619 with similar paint systems. After removal, the panels were immersed in an ambient temperature water bath for 2 minutes to remove the residual stripper. The panels were then removed from the water bath, the surfaces sprayed with water from a spray bottle to remove loose paint, and the panels allowed to air dry. Once dry, the panels were weighed and the performance results were recorded.

The minimum effective exposure time (i.e., time required to remove 95% or more of the epoxy paint system) for Stripper 9619 was determined to be 40 minutes at ambient temperature both with and without mechanical agitation.

Alternative Stripper Performance Tests

Alternative stripper performance tests were conducted on three sets of triplicate test panels immersed under the same temperature and method of agitation. The



Side View

Top View

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FIGURE 1 SCHEMATIC OF TEST EQUIPMENT

temperatures evaluated for each stripper were based on manufacturers' recommendations and formulation flash points. The immersion times selected for the alternative strippers were one, two, and three times the minimum effective exposure time for Stripper 9619 (i.e., 40, 80, and 120 minutes). Table 1 provides a summary of the temperature and methods of agitation evaluated for each alternative stripper.

For each alternative stripper, one set of triplicate test panels was withdrawn from the immersion tank after 40, 80, and 120 minutes of immersion. After removal, the panels were rinsed, sprayed, dried, and weighed using the same procedures established for the baseline tests. One replicate test run was performed for each alternative stripper at a single immersion time, temperature, and method of agitation.

Performance was evaluated by visually examining the panels to estimate the percentage of paint removed. Individual panels were assigned an overall qualitative rating on a scale of 0 to 10 based on the percentage of paint removed. A rating of 10 corresponded to 100% paint removal, while a rating of 0 corresponded to 0% paint removal. A target rating of 9 or better within 120 minutes was considered necessary for a successful stripping system and to maintain a practical work schedule.

Stripper Volatilization

Stripper volatilization rates were determined based on levels in the immersion tank measured before and after each performance test. Volatilization rates were estimated based on changes in the level. The baseline and alternative stripper performance tests were conducted without a wax or mineral oil seal, and therefore reflect maximum volatilization rates. A wax seal had been used at LEAD and a mineral oil seal is recommended by the respective manufacturers for use with CERL Strip and Turco 6776 Thin.

ALTERNATIVE STRIPPER PERFORMANCE

Tables 2 through 5 provide summaries of the performance test results for the baseline stripper and the three alternative strippers. The average results are reported for each set of triplicate test panels at each test condition. All test results are based on visual estimations of the percentage of paint removed. These results are presented in greater detail in the following subsections, along with a discussion of actual field test results communicated by U.S. Army personnel, whenever applicable.

FO-606 Results

FO-606 was evaluated at temperatures up to the manufacturer's recommended maximum operating temperature of 180°F (30°F below the flash point of 210°F) under both static conditions and with mechanical agitation, and at a temperature of 130°F with ultrasonic agitation. The performance test results indicate that at temperatures up to 180°F, FO-606 failed to adequately strip the epoxy paint system from the panels even after 120 minutes.

TABLE 1
Summary of Performance Test Operating Conditions

Stripper Solution	Mechanical Assistance	Solution Temperature (°F)
Stripper 9619	None (Static)	68
	Mechanical Agitation	68
FO-606	None (Static)	180
	Mechanical Agitation	180
	Ultrasonic	130
CERL Strip	None (Static)	120
	Mechanical Agitation	120
	Ultrasonic	120
Turco 6776 Thin	None (Static)	100
	Ultrasonic	100
	None (Static)	85
	Ultrasonic	85
	Ultrasonic	70

TABLE 2
Baseline Performance Test Results for Paint Stripper 9619

Test Conditions						
Solution Temperature, °F	68					
Mechanical Assistance	None (Static)			Agitation		
Immersion Time, minutes	20	30	40	20	30	40
Performance Results*						
Paint Removed, %	80	92	98	85	95	98
Overall Rating (1 to 10)	8	9	10	9	9	10

TABLE 3
Performance Test Results for Paint Stripper FO-606

Test Conditions								
Solution Temperature, °F	180							
Mechanical Assistance	None (Static)					Agitation		
Immersion Time, minutes	40	80	120	180	240	40	80	120
Performance Results*								
Paint Removed, %	2	1	2	2	6	1	1	3
Overall Rating (1 to 10)	0	0	0	0	0	0	0	0

*Average results of triplicate test panels.

TABLE 4
Performance Test Results for Paint Stripper CERL Strip

Test Conditions											
Solution Temperature, °F	120										
Mechanical Assistance	None (Static)					Agitation			Ultrasonic		
Immersion Time, minutes	40	80	120	210	240	40	80	120	40	80	120
Performance Results*											
Paint Removed, %	2	6	18	17	9	2	10	6	1	6	17
Overall Rating (1 to 10)	0	1	2	2	1	0	1	1	0	1	2

*Average results of triplicate test panels.

TABLE 5
Performance Test Results for Paint Stripper Turco 6776

Test Conditions															
Solution Temperature, °F	70			85						100					
Mechanical Assistance	Ultrasonics			None (Static)			Ultrasonic			None (Static)			Ultrasonic		
Immersion Time, minutes	40	80	120	40	80	120	40	80	120	40	80	120	40	80	120
Performance Results*															
Paint Removed, %	0	18	17	1	45	82	3	18	73	17	68	92	57	93	95
Overall Rating (1 to 10)	0	2	2	0	5	8	0	2	7	2	7	9	6	9	10

*Average results of triplicate test panels.

All FO-606 performance tests conducted at temperatures from 130°F to 180°F resulted in 1 to 3% paint removal with overall performance rating of 0 after 120 minutes of immersion time. Mechanical and ultrasonic agitation did not increase the performance of FO-606 as compared to FO-606's performance under static conditions. Extended immersion times of 180 and 240 minutes under static conditions at a temperature of 180°F showed minor improvement, with 6% paint removal after 240 minutes of immersion time. The 240-minute immersion time also resulted in a softening of the paint system in comparison with the 120-minute immersion time. Forceful scraping of the softened paint system resulted in partial paint removal from the panels; however, this performance is unacceptable for the stripping of complex parts with inaccessible surfaces.

The performance of FO-606 was marginally worse in the alternative paint stripper investigation than in field demonstrations. At the Red River Army Depot (Texarkana, TX), 25% paint removal was reported after 120-minute immersion times and up to 50% paint removal after a 180-minute immersion time for epoxy/epoxy paint systems.

CERL Strip Results

CERL Strip was evaluated at temperatures up to 120°F (30°F below CERL Strip's flash point of 150°F) under both static conditions and with mechanical and ultrasonic agitation. The performance test results indicate that at temperatures up to 120°F, CERL Strip failed to adequately remove the epoxy paint system from the panels even after 120 minutes.

All CERL Strip performance tests conducted at a temperature of 120°F resulted in 6 to 18% paint removal with overall performance ratings of 1 or 2 after 120 minutes of immersion time. Mechanical and ultrasonic agitation did not increase the performance of CERL Strip, as compared to CERL Strip's performance under static conditions. Extended immersion times of 210 and 240 minutes under static conditions at a temperature of 120°F did not increase the performance of CERL Strip, as compared to the 120-minute immersion time results.

No field demonstrations using CERL Strip were known at the time of the study.

Turco 6776 Thin Results

Turco 6776 Thin was evaluated at temperatures up to the manufacturer's recommended maximum operating temperature of 100°F (Turco 6776 Thin's flash-point is over 200°F) under both static conditions and with ultrasonic agitation. The performance test results indicate that at 100°F, Turco 6776 Thin adequately removed the epoxy paint system from the panels after 120 minutes.

The Turco 6776 Thin performance tests conducted at 100°F resulted in 92 to 95% paint removal with overall performance ratings of 9 or 10 after 120 minutes of immersion time. Observations for the 40-minute immersion time indicated cracking and removal of the paint system from the panel edges. Observations for the 80- and 120-minute immersion times indicated removal of the paint system from the panel edges, and bubbling and/or complete removal of the paint system from large areas of the panel surfaces.

With ultrasonic agitation and a temperature of 100°F, adequate paint removal was achieved after an 80-minute immersion time. However, Turco Products did not recommend the use of ultrasonic agitation in full-scale applications because it could emulsify the oil seal into the stripper and potentially impede actual performance. Given the minor improvement in performance using ultrasonic agitation, evaluation of full-scale implementation of ultrasonic agitation is not recommended.

The Turco 6776 Thin performance test was repeated at temperatures of 85°F and 75°F. At 85°F or less, under static conditions or with ultrasonic agitation, Turco 6776 Thin did not adequately remove the epoxy paint system from the panels even after 120 minutes of immersion time. At 85°F under static conditions, an 82% paint removal with an overall performance rating of 8 was achieved after 120 minutes.

Alternative Stripper Performance Comparison

A comparison of the best results achieved for the baseline and alternative strippers is provided in Table 6. The results indicate that Turco 6776 Thin performed significantly better than FO-606 and CERL Strip and was the only alternative stripper that adequately stripped the epoxy paint system with a practical immersion time.

Stripper Volatilization

Table 7 provides a summary of the stripper volatilization rates for the baseline and three alternative strippers in gallons of stripper volatilized per day per square foot of exposed surface (gal/day/ft^2). All tests were conducted without the use of a wax or mineral oil seal, and therefore reflect maximum volatilization rates.

Methylene-chloride-based stripper (Stripper 9619) had the greatest volatilization rate under static conditions. The volatilization rates of the alternative strippers under static conditions were generally lower, even at the higher temperatures tested. Mechanical agitation appeared to significantly increase the volatilization rate of Stripper 9619 and FO-606, while ultrasonic agitation did not appear to increase volatilization rates of the three alternative strippers.

ENVIRONMENTAL, HEALTH AND SAFETY EVALUATION

An environmental, health and safety evaluation was performed on the best-performing alternative stripper (Turco 6776 Thin) for comparison with the methylene-chloride-based stripper. This included a safety and environmental hazard assessment scoring

TABLE 6
Comparison of Maximum Performance Test Results for Stripper 9619 and Alternative Paint Strippers

Stripper Solution	Stripper 9619	FO-606	CERL Strip	Turco 6776	
Test Conditions					
Solution Temperature, °F	68	180	120	100	
Mechanical Assistance	None (Static)	None (Static)	None (Static)	None (Static)	Ultrasonic
Immersion Time, minutes	40	240	120	120	120
Performance Results*					
Paint Removed, %	98	6	18	92	95
Overall Rating (1 to 10)	10	0	2	9	10

*Average results of triplicate test panels.

TABLE 7
Stripper Solution Volatilization Rates (Gallons per Day per Square Foot)

Stripper Solution	Stripper 9619	FO-606		CERL Strip	Turco 6776		
Temperature, °F	68	131-149	180	120	70	85	100
Mechanical Assistance	Volatilization Rates, gallons per day per square foot						
None (Static)	1.1	0.30	0.81	0.40	0.11	0.50	0.55
Agitation	4.2	0.35	1.45	0.49	NT	NT	NT
Ultrasonic	NT	0.33	NT	0.44	0.13	0.50	0.54

NT = Not tested.

using methods previously applied by the CERL for evaluation of alternative chemicals(4). This included the following toxicity, environmental fate, and safety criteria:

- Human toxicity
- Acute environmental toxicity
- Chronic environmental toxicity
- Bioaccumulation
- Persistence
- Transport
- Corrosivity
- Reactivity
- Ignitability

The hazard rating scores were developed for each individual component, where data were available. The resulting weighted sum score for the alternative stripper was 7.04, which was well below the weighted sum score of 16.3 previously derived by CERL for a methylene chloride stripper similar to that used in these tests. These results suggest that a significant reduction in safety and environmental risks can be achieved with the alternative stripper. However, this stripper still contains hazardous chemicals and its use requires an understanding of these hazards. Safety and environmental aspects of using the alternative stripper are summarized in the following subsections.

Air Emissions and Reporting

Based upon manufacturer's material safety data sheets (MSDSs), Stripper 9619 has a vapor pressure of 300 mm Hg at 20°C, while Turco 6776 Thin has a vapor pressure of 17 mm Hg at 20°C, which is largely attributed to the water content of Turco 6776 Thin. As a result, volatile organic compound emissions will decrease by using the alternative stripper. No HAP emissions (methylene chloride is listed as an HAP by EPA) will be associated with the stripping operations using Turco 6776 Thin.

Methylene chloride is subject to toxic chemical release inventory (TCRI) reporting requirements under SARA. Turco 6776 Thin does not contain any hazardous substances subject to TCRI reporting.

Wastewater

The methylene-chloride-based paint stripper used at LEAD is a significant contributor to the overall methylene chloride load at LEAD's wastewater treatment plant (WWTP) due to the dragout of stripper on removal of parts from the immersion bath into the aqueous rinses, which are directed to the WWTP. Turco 6776 Thin contains no toxic organic or National Pollutant Discharge Elimination System (NPDES) priority pollutants or chlorinated hydrocarbons. The compounds present are readily biodegradable and treatable.

Hazardous and Solid Waste

Paint solids accumulate in the immersion bath. In addition, the acidity of the bath declines over time until it is insufficient to achieve the required performance. As a result, the stripping solution is occasionally replaced. At the time of the study, LEAD sent both the spent stripping solution and paint solids off-site as an F002 (spent halogenated solvent) hazardous waste for incineration.

Spent Turco 6776 Thin stripping solution is not a listed hazardous waste under current regulations; however, it may be classified a characteristic waste due to corrosivity or toxicity. The waste should be tested for these characteristics prior to disposal to determine the appropriate waste management requirements. If acid depletion is the primary cause of reduced stripper effectiveness, Turco 6776 Thin (which contains 10% formic acid) may have a shorter life compared to the methylene-chloride-based stripper (which contains 25% formic acid). However, Turco Products provides a procedure for testing and restoring the acidity of the stripper with an acid additive. This may result in an equivalent (or perhaps superior) stripper life.

Safety Hazards

Turco 6776 Thin does not contain methylene chloride or any other known or suspected carcinogens. Turco 6776 Thin does contain formic acid, although in a lower concentration than the existing methylene chloride based stripper, which represents an inhalation hazard due to its acidity and toxicity. Formic acid has an OSHA Permissible Exposure Limit (PEL) of 5 ppm and an Immediately Dangerous to Life and Health (IDLH) concentration of 30 ppm. The elevated temperature of 100°F necessary to achieve more rapid paint removal requires a heated bath, which makes the formic acid more volatile. In addition, the possibility of a failure of temperature control could result in a very high rate of volatilization.

As a result, personnel must still exercise care in the storage, handling, and use of the alternative stripper, and adequate ventilation is still required in the vicinity of the immersion and rinse tanks. Further, special precautions are called for in the design of the bath heating. Care should be taken not to restrict circulation around the heating element. In addition, independent temperature elements with high-temperature shutoffs are suggested.

CONCLUSIONS

Bench-scale trials of three alternative paint strippers (FO-606, CERL Strip, and Turco 6776 Thin) were performed to identify a replacement for the methylene-chloride-based stripper historically used at LEAD. The trial results identified Turco 6776 Thin as the only tested alternative that had the minimum performance characteristics needed to substitute for the methylene-chloride-based stripper. Turco 6776 Thin adequately stripped the epoxy paint system from the test panels after an immersion time of 120 minutes at a temperature of 100°F under static conditions. The 120-minute effective immersion time for Turco 6776 Thin, although three times longer than the 40-minute effective immersion time of the methylene-chloride-based stripper, is considered adequate to maintain a practical production schedule. Ultrasonic agitation reduced the minimum effective exposure time of Turco 6776 Thin to 80 minutes at a temperature of 100°F. The effects of agitation, while helpful, were not found to be sufficient to overcome the shortcomings of the less effective strippers, nor to warrant equipment modification for application of the successful alternative. The mechanism of removal for this coating appears to be penetration and swelling of the coating, which results in its lifting off the substrate.

Substituting Turco 6776 Thin for the present methylene chloride based stripper results in significant environmental, health and safety advantages for LEAD. Specifically, Turco 6776 Thin does not contain methylene chloride or any other halogenated solvents, hazardous air pollutants, or potential carcinogens.

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POLLUTION PREVENTION LESSONS LEARNED

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INTRODUCTION

Beginning in 1990, the U.S. Army Acquisition Pollution Prevention Support Office (AAPPSO) initiated a long term program to eliminate the use of chromate conversion coatings (CCC) at Red River Army Depot (RRAD). The program has been completely successful and chromate conversion coatings have been eliminated from the maintenance process for two major weapon systems. As the elimination effort progressed, however, a number of important lessons surfaced which are worthy of discussion and highlight. These lessons can affect the success or failure of pollution prevention efforts and they will certainly affect AAPPSO's approach to similar programs in the future. This article acquaints readers with the CCC elimination program and the lessons the program has provided.

BACKGROUND

The U.S. Army performs depot level maintenance on the M113, Armored Personnel Carrier, and the M2/M3, Bradley Fighting Vehicle at RRAD. The hulls of these vehicles are constructed of 5000 series armor-grade aluminum alloys having thicknesses of one inch or more. These alloys are inherently corrosion resistant.

The maintenance process for these vehicles includes the application of the Chemical Agent Resistant Coating (CARC) on the vehicle hulls. The CARC painting process is a four-step procedure which includes cleaning the vehicles and application of chemical pretreatments, epoxy primers and polyurethane topcoats. CARC topcoats are produced in camouflage colors and are designed not to absorb toxic chemical agents, and to withstand exposure to DS2, a chemical warfare decontaminating agent.

The CARC coatings applied at RRAD are lead-free and do not contain soluble chromates. The chemical pretreatment of CCC, which is called out in the CARC specification, however, does contain hexavalent chromium. Hexavalent chromium is a known carcinogen, and a hazardous air pollutant as prescribed by the 1990 Clean Air Act Amendments. OSHA also considers the hexavalent chrome in aqueous chromic acid solutions to be extremely hazardous, and is expected to issue a new standard in May 1995.

The application of CCC is the only step in the vehicle maintenance process where chromates are used. In 1989, RRAD personnel initiated an evaluation of environmentally acceptable production processes that might be considered alternatives to the hazardous chromate conversion coating process. RRAD identified a two-stage abrasive blasting process as a viable alternative. Using this environmentally acceptable alternative process as a replacement for CCC, RRAD could avoid $200,000 in annual costs for materials and hazardous waste disposal, and could also avoid $3,000,000 in costs for necessary air emissions control equipment. When RRAD queried the Project Management (PM) staffs for both weapon systems, the depot was told more coating system corrosion control data was needed before they would approve use of the alternative process.

In 1990, AAPPSO initiated a cooperative program with RRAD to generate the data required to obtain PM approval for the alternative process. AAPPSO tasked Ocean City Research Corporation to perform a long-term corrosion control performance assessment. The assessment included a natural marine atmosphere exposure test of armor-grade aluminum specimens, numerous adhesion assessments, and an exposure test using the Army's DS2 decontamination agent as the exposure solution. The performance data collected by Ocean City demonstrated that CCC could be eliminated from the CARC coating process with no degradation in corrosion control or adhesion, if the proper surface roughness and cleanliness were achieved.

As a follow-on to the above assessment, Ocean City examined the production process at RRAD to determine specific production steps requiring change. The goal was to eliminate the CCC application step while still ensuring adequate CARC primer adhesion, and while minimizing disruptions in the RRAD production process. The examination revealed that use of garnet blasting to remove dirt, welding smut and grinding wax was the key to successful coating adhesion. To verify the revised procedures, a vehicle was cleaned and coated with CARC using abrasive garnet blasting and no CCC application. The CARC coating was then evaluated in accordance with MIL-C-53072 and it met or exceeded all specifications.

DISCUSSION

The final phase of AAPPSO's program involved gaining PM approval to implement the environmentally acceptable alternative process, and then putting it in place at RRAD. Gaining PM approval proved to be every bit as challenging as all the previous technical, engineering and analytical work done by RRAD and Ocean City.

Throughout the course of this project, AAPPSO had been communicating with the PM staffs and had kept them appraised of progress and new developments. There were a number of briefings, meetings and discussions, and the PM staff reaction was skeptical at best. There was no great urgency on either PM's part to give immediate approval for a changed CARC painting procedure. In fact, in several of the discussions the PM staffs suggested that further field testing may be necessary before the new procedure was implemented.

In September 1994, AAPPSO began a "full-court press" to get the PMs' approval. Formal presentations were provided that highlighted all the test data and the work performed at RRAD. The presentations pointed out that the cost, schedule and performance risks for the PMs were minimal. The PMs, however, remained cautious and undecided. Finally, AAPPSO learned that Mainz Army Depot in Germany had been applying CARC without using CCC as a matter of practice because the German Government prohibited its use. After making this information available to the PMs, and after inspecting the performance of CARC on vehicles reworked by Mainz, the PMs finally consented to changing the process. PM approval was granted in January 1995, the depot fully implemented the alternative procedure in February 1995, and a brief ceremony was performed in April 1995.

An analysis of this program after-the-fact reveals some interesting and important points. The two primary parties having interest in the program, RRAD and the PMs, had totally different perspectives on all the issues. Their interests, their concerns and their responsibilities were 180° apart. The depot faced the day-to-day challenge of environmental compliance. They met the regulators, stood the audits and inspections, and paid the fines for noncompliance. They also paid the bills for compliance upgrades to facilities, for safety equipment and safety management, and for workman's compensation due to injury or illness. All these costs affected the depot's overhead rates and, thus, jeopardized the depot's capability to be competitive for future work. For RRAD, eliminating CCC was imperative.

The PMs' concerns were completely different. They were responsible for the performance of their vehicles, to include the performance of the CARC coating. If they approved the modified maintenance process and the CARC coatings failed prematurely, or if the hulls corroded prematurely, they were then responsible for the repairs and corrections. Although they were sensitive to environmental issues, their systems' performance was not directly affected by the environmental problems faced by RRAD. Also, both the Bradley and the APC were mature systems that were fielded, that performed satisfactorily, and that had good user acceptance. The PMs felt they would be taking all the risks and would receive little tangible benefit in return.

Finally, in large organizations such as the Army, there is always a great reluctance to change anything that seems to be working well. This age old truth certainly came into play during this program.

CONCLUSIONS

Army pollution prevention projects in the acquisition arena will almost always involve participants having diverse interests and perspectives. At the same time, the supportive and cooperative participation of all involved parties is critical to project success, and the ease at which these projects are accomplished. The most successful pollution prevention project leaders will be those that recognize the various interests and concerns, and then develop their plans to deal with them. There is no cookbook solution or best approach, but there are some common sense things that can be done. First, you can identify all the players early and get them involved in the project as active participants early. Second, you can be sensitive to the varying interests and develop your project strategy to satisfy each player's interests. Finally, you can develop a convincing argument that leaves little room for legitimate challenge. If all the players have been actively participating in the project, then the final argument should be fully supported by all parties.

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NDCEE REDUCES RISK IN TECHNOLOGY TRANSFER

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INTRODUCTION

Executive Order (EO)12856 requires that the Department of Defense (DOD) reduce its release and off-site transfer of toxic chemicals. DOD's commitment to leadership in pollution prevention (P2) is consistent with this executive order in that EO 12856 emphasizes pollution prevention as the preferred alternative to addressing toxic chemical issues. P2 in EO 12856 means "source reduction", as defined in the Pollution Prevention Act of 1990 (PPA). Source reduction includes practices that reduce or eliminate the creation of pollutants through increased efficiency in the use of raw materials, energy, water, or other resources. Under the PPA, the term "source reduction" includes any practice which:

- Reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment prior to treatment, or disposal
- Reduces the hazards to public health and the environment associated with such.

The problem with implementing source reduction is the risk that changes in current operations will not produce the desired result. It is impractical to think we can eliminate all risk when making changes. We can, however, reduce risks by verifying key pieces of information before committing to the change.

Concurrent Technologies Corporation (*CTC*), operates four national centers of excellence with emphasis in technology transfer. The National Defense Center for Environmental Excellence (NDCEE) is one of those centers. *CTC* refers to "technology transfer", as a process of making change. Many people limit their definition of technology transfer to one or two elements of that process. By ignoring other elements of the process, they lose opportunities for reducing risk. The complete technology transfer process starts when the users identify a requirement and continue until the change has met that requirement. There are many actions between identifying and implementing the requirement. These actions include: establishing a baseline on the current process, demonstrating and validating performance factors for the new process, performing life-cycle cost analysis, designing and procuring equipment, training people on process operations, and installing the equipment. With each action there are opportunities to reduce risk.

We can consolidate the risks associated with P2 technology transfer into four categories:

- Technical
- Financial
- Schedule
- Regulatory

TECHNICAL RISK

Technical risk includes uncertainty with the capability of the new technology to meet the technical requirement of the user. The users may not know if the technology will meet their requirements unless they have a baseline to work from, and a test plan to evaluate product performance using real data. In an ideal situation, the test plan is one developed by the user, the tests are conducted in valid operating conditions using real data, and those affected by the change are trained in an environment that accurately portrays the operating conditions. We reduce the risk of change when the baseline assessment, test plan, demonstration, and validation take place before implementing the technology.

There are risks in making comparisons of existing processes to new ones when facility managers do not use comparable operating parameters. It may be that demonstration and validation is done under operating conditions that don't represent the user's true environment. In other cases, the validation is completed by people other than the ultimate users. The NDCEE reduces this risk by making the demonstration and validation conditions as realistic as possible.

The new process may be validated under conditions comparable to those of the ultimate user, and still not be the best technology alternative. People often select a technology without knowing the alternatives. A good choice is not always the best choice. There is a risk that we will not select the best technology without having knowledge of alternatives.

A recent DOD installation of an aqueous cleaning system is a good example of technical risk in the transfer process. The system was installed prior to validating the systems performance on the user's specific applications. The goal of acquiring this technology was to eliminate the use of ozone depleting chemicals when cleaning parts for reuse. The decision to acquire this specific technology was based on vendor data for applications other than those of the DOD depot. When the technology was put into operation at the actual depot site, the depot personnel found that it did not remove certain carbon deposits on parts that it was processing. The problem may be technology related or it may be that the operators were not properly trained. Correcting the problem will now involve additional disruption in production as well as setbacks in the quality of the depot's operations. The end result will require that the depot either live with the quality problem, replace this technology, or invest in additional equipment or training to address problems with the specific carbon deposits.

FINANCIAL RISK

This example also illustrates the financial risk assumed when making a decision that requires an investment. Having financial data related to materials, labor, maintenance, utilities, and disposal costs helps reduce that risk. Being able to quantify this information requires knowledge of resources, and the use of financial criteria such as return on investment, cash flow, and payback period consistent with established business strategy. Reducing financial risk requires that we have accurate data in a form used to determine if investing in a technology change will provide an appropriate return.

A facility that invested in an airless electrostatic spray gun increased its technical and financial risk by not defining its cost and performance criteria before making the investment. The facility recognized that electrostatic spray guns could potentially lower the cost of painting by increasing transfer efficiency. The increased efficiency reduces paint costs, minimizes discharge of pollutants into the air, and decreases the cost of hazardous waste disposal. The facility purchased the system without establishing a baseline for its current operations or quantifying the criteria it considered acceptable for making the investment. During a survey of the operation, those on the survey team found that transfer efficiency for the electrostatic spray guns was about 30 percent, similar to the efficiency of most conventional spray guns. Efficiency for electrostatic guns is normally in the 60 percent range The quality of this facility's paint operations appeared to show improvement, but it could not quantify the improvements to justify the cost of the more advanced technology. With the lower transfer efficiency, this facility is not reducing its material costs or minimizing its toxic wastes. It is spending approximately $210/day more for paint than it might expect with normal electrostatic spray gun transfer efficiency. From a technical perspective, it continues to generate high levels of volatile air emissions, and must account for about 6 gal/day of additional paint that ends up as a hazardous waste. The facility could have benefited both technically and financially from this more environmentally friendly technology by using a more comprehensive approach to technology transfer. In this situation, training the operators should have taken place before implementing the change. The lack of training is probably contributing to their problem and keeping them from realizing immediate cost savings.

SCHEDULE RISK

Schedule risk relates to production requirements following a change, and the ability to meet user timeframes. Investment decisions limited to product quality and cost might not account for the time differences between new and old process production rates. The learning curve of people affected by the change as well as the physical limitations of the processes involved in production will affect schedule risk. The NDCEE can minimize this risk by verifying the production capabilities of a new technology, and by training and qualifying operators to reduce the learning curve in the actual production setting.

The following example illustrates schedule risk. A painting facility invested in a small powder coat booth to reduce its VOC emissions and improve the quality of its products. The powder coat system met all the technical requirements for product quality. This particular powder coat system is very efficient with large production runs using the same color. Frequent color changes, however, made the use of a powder coat booth impractical in normal production. The end result was a $15,000 investment for new technology that is collecting dust on a shop floor.

REGULATORY RISK

Regulatory risk is the risk of making a change that is required to comply with the regulations. Many changes regarding technologies that impact the environment, or the health and safety of our workers, are driven by regulations. If we know what the regulations require, we can reduce this risk of change by comparing the discharges from a process to the regulatory limits. Unless a facility understands the impact of both current and future regulations, it faces the risk that technology changes will not meet its requirements either today or in the future.

A recent DOD acquisition is a successful example of how regulatory risks were reduced. A facility evaluating an ultrahigh-pressure waterjet system to eliminate trichloroethane as a stripping agent, validated cost and performance data on the system before making an investment. In its validation scenario, this facility verified the quality and production criteria it had specified in a test plan for its own parts, using an independent facility. It validated the ability to reduce its RCRA waste stream and eliminate the requirement to use a substance targeted on the EPA toxic chemical list. The facility did so while maintaining levels of quality and reducing overall costs.

NDCEE RISK REDUCTION

CTC operates the NDCEE program which was established to address high priority environmental problems for DOD and to reduce the risk of making technology changes for the DOD and its industrial base. The NDCEE program uses resources of *CTC* that include a Demonstration Factory and an Environmental Information Analysis (EIA) center. The resources supporting the NDCEE, assist DOD-related organizations in meeting the requirements of EO 12856, with minimal risk.

The Demonstration Factory was designed to validate performance and cost data on parts that represent 80 percent of those processed in DOD facilities. This factory includes state-of-the-art "clean" technologies that affect the most commonly performed operations in DOD industrial activities. The factory provides a realistic environment to support all elements of the complete technology transfer process.

The EIA center complements the demonstration factory. The EIA analyzes environmental information obtained from a variety of sources, and organizes and consolidates this information in a usable and understandable form. This information minimizes uncertainty for those making decision on material and process changes.

Through the NDCEE program, the DOD and industrial facilities can take advantage of services that improve their operations on-site. These services include help with performing baseline assessments and address training issues that come into play before and after implementing process changes.

The NDCEE program emphasizes pollution prevention as the most cost-effective means of addressing environmental needs. Its approach recognizes that the ultimate driving forces behind most DOD decisions are quality, cost, productivity, and environmental mandates.

The NDCEE program has several major examples of how it has compared the risks of technology transfer to current practices:

- Stripping Applications -- comparing the ultrahigh-pressure waterjet to acid dip/dry media blast
- Nonhalogenated Cleaning Systems -- comparing a power washer to vapor degreasing
- Painting Systems -- comparing powder coating to conventional painting

In each of these comparisons, the quality, cost, productivity, and environmental data supported the investment in a more advanced technology, given the operating parameters of the individual facilities. For a facility with different operating parameters, the data may support a different conclusion. The NDCEE program provides independent validation tailored to the objectives of a specific user. As an independent non-profit organization, *CTC* does not sell environmental technologies. Through tasks directed by the NDCEE program it informs and assists decision-making organizations in reducing their risks of making operational changes.

CONCLUSIONS

Successful transferring of technology is a complex process that goes beyond identifying and installing equipment. The key to success is reducing risks in all phases of the process prior to investing in a technology. Risk reduction involves:

- Gathering and validating information in an environment that represents the user's operating conditions, with parts and materials that the represent the user's production cost and regulatory requirements

- Including baseline assessment, cost analysis, technology demonstration, equipment design, procurement, installation start-up, and training as part of the transfer process
- Assessing information related to the entire life-cycle rather than some limited stage of operation
- Independently validating information related to the technology to maintain a high level of objectivity.

All phases are important and are considered in most technology transfer scenarios. When considering pollution prevention related technologies in an industrial environment, the technical, financial, schedule and regulatory risks all play an important role in decision making. The facility making the change must decide on the tradeoffs, but has help when working with organizations such as the *CTC* and the NDCEE program.

HAZARDOUS MATERIAL ELIMINATION USING AVAILABLE TECHNOLOGIES

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Introduction

On 11 August 1994, William Perry, Secretary of Defense, issued a policy memorandum regarding Pollution Prevention in the Department of Defense. Executive Order 12856, Pollution Prevention and Right to Know in the Government, is the document providing the impetus for pollution prevention initiatives. Executive Order 12856 challenges the Federal government to publicly lead by example by applying source reduction in the management of its facilities and in its acquisition practices. By preventing pollution, the Federal government conserves scarce resources necessary to maintain readiness. The Executive Order requires each Federal agency to establish a voluntary goal to reduce total releases and off-site transfers of toxic chemicals or toxic pollutants 50% by 1999.

Alternative Technologies

As a result of P2 efforts, depots have introduced alternate processes such as electrodeposition coating (E-coat), aluminum ion vapor deposition (AIVD), ion implantation and zinc-nickel plating. Approvals from appropriate Major Subordinate Commands are in process. Issues such as readiness and personnel safety must be addressed prior to a substitution being implemented.

E-coat has proven to be a superior primer base for structural adhesives, surpassing the performance of standard spray-applied epoxy primers. The E-coat painting method immerses the part to be coated in an aqueous bath containing ionized paint materials. A current is run through the part, causing the paint to be deposited on the surface of the part by electric forces. After being withdrawn from the bath, the part is drained and then cured in a conventional oven. Capital costs are higher with E-coat systems because the equipment is more complex than conventional spray equipment such as HVLP, air-assisted airless guns, and airless guns. Operating costs, however, are lower due to the use of an aqueous solution. Since water is the carrying agent, air emissions are very low thus eliminating many air permitting concerns. Additionally, E-coat processes are highly efficient having a typical transfer efficiency ranging from 95-100%. [1]

AIVD is a technology that may be suitable in some applications as a cadmium electroplating substitute. AIVD is a process in which parts to be coated are placed in a chamber, and the chamber is evacuated and then filled with an inert gas, usually argon. A high negative potential is applied to the part and, subsequently, the surrounding inert gas becomes ionized. Positive ions in the ionized, inert gas are attracted to and bombard the oppositely charged part, thereby cleaning the part. Next, the aluminum source, which is the coating material, is added the chamber, melted and vaporized. The vaporized aluminum is ionized and attracted to the part, forming a protective coating. AIVD offers soft, ductile, adherent coatings that are currently used to coat fuel line fittings. [2]

The Navy has approved AIVD in lieu of cadmium plating on flight safety parts such as aircraft landing gear. Again, this application may be transferred to the other services with little or no research and development costs.

Ion implantation is an environmentally clean process in that no hazardous wastes are generated. Ion implantation provides enhanced performance compared to chrome plated components. Corpus Christi Army Depot has placed the first DoD production ion implantation process on-line. The system is processing metal cutting tools and punch and die sets for several Naval shipyards. Laboratory testing performed by the Army and Navy Research Lab has verified tool life extension. Further applications of the ion implantation process are underway. For example, aircraft components such as the T-53 engine, which are normally chrome plated, have been successfully ion implanted with nitrogen ions on a nickel-aluminum coating. Laboratory testing showed no component degradation. Additionally, aviation bearings implanted with chromium revealed no degradation under laboratory testing. [3,4]

Zinc-nickel plating, as well as other zinc alloy processes may be suitable substitutes for cadmium electroplating as a corrosion protective coating. Additionally, zinc alloy coatings are useful as substitutes for cadmium when specified for enhanced lubricity, solderability, low electrical contact resistance, and ease of disassembly after corrosion has occurred.

Presently, there are numerous zinc alloy processes commercially available including zinc-cobalt, zinc-nickel, zinc-tin, and zinc-iron. Testing sponsored by NAVSEA is underway to evaluate zinc-nickel and zinc-tin plating with respect to properties and performance such as torque, tension, wear and lubricity. The findings may have application in the other services with little or no research and development costs.

Cadmium: A Case Study

Where is cadmium used?

Cadmium and its chemical compounds are incorporated into a wide range of military and civilian products. Cadmium-containing products have historically provided effective and economical levels of in-service performance. The promulgation of new environmental and worker health statutes by the United States and throughout the international community has started to adversely impact the economics of using cadmium. Some members of the international community have actually taken steps to ban cadmium. These bans completely forbid the importation or production of certain items that typically contain cadmium. In the United States, using cadmium will become more expensive because of recently revised worker health regulations. To date, the United States has not "banned" or "outlawed" the use of cadmium. However, in the era of the increasing economic competitiveness, both within the United States and as part of the international community, continued widespread cadmium use may create unacceptable economic burdens.

Cadmium is a lustrous, silver-white metal produced as a by-product of zinc refining. In its bulk form, cadmium is soft enough to be cut with a knife and has one of the lowest melting points of all metals (608° F, 321° C). The most industrially significant current applications for cadmium include rechargeable batteries, metal plating, pigments, plastic additives, and low melting point alloys. [5]

To help identify where cadmium plating is used, Table 1 lists some common cadmium coating specifications.

Cadmium may be used in specialized solders, sprinkler system fusible links, and video tube phosphors. To help identify cadmium bearing solders, Table 2 lists some common cadmium-bearing solder specifications.

There are many more examples of where cadmium is used in Army weapon systems and these are discussed in an AAPPSO report entitled, Strategic Plan for Eliminating Cadmium from U.S. Army Tactical Weapon Systems. The report will be available for staffing review in July 1995.

TABLE 1

Cadmium Coating Specifications

Document Number	Document Title
AIA NAS 672	Plating, High-Strength steels, Cadmium
ASTM B 696-86	Standard Specification for Coatings of Cadmium, Mechanically Deposited
MI-C-8837B	Coating, Cadmium (Vacuum Deposited)
MIL-C-81562B	Coatings, Cadmium, Tin-Cadmium, and Zinc (Mechanically Deposited)
MIL-M-6874	Metal Spray, Process For (Cadmium)
MIL-P-23408B	Plating, Tin-Cadmium (Electrodeposited)
MIL-STD-870	Cadmium Plating, Low Embrittlement, Electrodeposition
MIL-STD-1500	Cadmium-Titanium Plating, Low Embrittlement
SAE AMS 2400S	Cadmium Plating
SAE AMS 2401D	Cadmium Plating, Low Hydrogen Content
SAE AMS 2416	Plating, Nickel-Cadmium, Diffused
QQ-P-416E	Plating, Cadmium (Electrodeposited)

TABLE 2

Cadmium-bearing Solder Alloys

Designation	***Composition (weight percent)***
AWS/ASTM BAg-1	44-46 Ag, 23-25 Cd, 14-16 Cu, 14-18 Zn
AWS/ASTM BAg-2	34-36 Ag, 17-19 Cd, 25-27 Cu, 19-23 Zn
AWS/ASTM BAg-3	49-51 Ag, 15-17 Cd, 14-16 Cu, 13-17 Zn

Why is Cadmium a Problem?

Cadmium is considered a significant problem by the Army because the material can adversely impact the environment as well as worker health. Any cadmium included in Army materiel creates both economic and programmatic problems for facilities during every life cycle phase. The primary economic problem associated with cadmium use is the increasing costs to purchase, handle, and dispose of the material. OSHA estimates that the United States will spend $159 million/year to comply with the worker health regulations related to cadmium use. In addition to these worker health compliance costs are the increasing costs of cadmium-bearing hazardous waste disposal. Given that Army budgets are decreasing, any expenses related to unnecessary cadmium use should be avoided. In addition to direct costs, cadmium use creates numerous programmatic problems for the Army. These programmatic problems range from justifying cadmium use during environmental analyses to the record provisions associated with hazardous waste disposal.

At one activity, several concerns regarding worker exposure to cadmium were surfaced. As a result of the OSHA exposure limitations being lowered, the activity has had to change the manner in which cadmium coated parts are removed from equipment during routine maintenance. Prior to removing a cadmium coated part, the part must be chemically stripped to avoid exceeding cadmium worker exposure limits. This change in procedure has increased processing time thereby increasing manufacturing costs.

A second location voiced similar concerns. At this particular location, two welders who had previously worked with cadmium have developed cancer. Although a definite link between cadmium exposure and the cancer has not been established, the location expects workmans' compensation claims to be filed. The Safety Director noted the average workman's compensation claim costs $800,000.00 based on a forty year old employee with a life expectancy of 75 years for a man, and 78 years for a woman. This cost does not reflect medical expenses. Additionally, the location has also changed its process for removing cadmium coated parts from equipment. Once again, the parts are chemically stripped prior to mechanical removal adding to processing time and manufacturing costs.

Several activities have undertaken projects to upgrade or replace existing metal finishing facilities. One activity reported a $22 million dollar new metal finishing facility scheduled to open in 1997 while a second activity is spending $275,000 to upgrade an existing facility. The impetus for new facilities and upgrades is to reduce worker exposure to cadmium.

There are also additional hidden costs associated with OSHA cadmium compliance.[6] The following issues must be addressed in areas where cadmium usage will exceed the exposure level of 5 mg/m^3, calculated as an eight-hour, time weighted average exposure:

- engineering controls;
- respirator program;
- enhanced hazard communication training;
- written compliance plan;
- work practice controls;
- protective clothing;
- clothing laundering services;
- separate eating, changing, and washing facilities; and
- medical monitoring and surveillance.

From an environmental standpoint, facility upgrades are necessary to meet the cadmium limits set forth in the 1990 Clean Air Act Amendments. Additionally, cadmium wastes must be handled as hazardous wastes. One depot reported an annual cost of $60,000 for disposal of cadmium wastes.

The costs cited above all deflect resources from readiness issues. Greatly reducing cadmium usage will free resources to maintain the Army's readiness objectives.

Army Strategy for Reducing Cadmium Usage

The Army's objective is to eliminate cadmium from weapon systems in a manner that will support mission and readiness. To accomplish this in a timely fashion, an industry survey was conducted to identify commercially available alternate technologies. Many of the available technologies require little or no research and development efforts prior to implementation. To determine the effect of eliminating cadmium on the operations level, several depots were visited to assess the impact of introducing cadmium alternatives. With a unified effort, PMS, depots, and other approving authorities can accomplish the transfer to non-cadmium based technologies and requirements.

Eliminating cadmium makes good business sense from several perspectives. First, cadmium has strict OSHA worker exposure limits associated with its use. The cost of complying with the OSHA regulations is expensive and funding could be more effectively used elsewhere. Secondly, purchase and disposal costs of cadmium is also expensive. Scarce resources are not being wisely spent when committed to cadmium.

CONCLUSIONS

Reducing the Army's dependence on cadmium will free resources otherwise identified for disposal of hazardous waste, process controls, facility modifications and worker protection/training to enhance the Army's ability to maintain its mission and readiness. The cadmium reduction plan will assist the Army in meeting its pollutant reduction goal of 50% by 1999 as set forth in Executive Order 12856. Additionally, liability for worker exposure to cadmium will be significantly reduced as well as the compliance costs for respirator programs, hazard communication training, work practice controls, medical monitoring and surveillance, protective clothing, engineering controls, separate eating, changing and engineering controls, uniform laundering services and written plans.

By reducing cadmium usage in a strategic manner, the Army will be able to achieve its mission without impacting readiness. In addition, pollution prevention initiatives promote the good will and environmental stewardship the Army has always maintained.

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RECONDITIONING CONTAMINATED GRAVEL

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INTRODUCTION

Lawrence Livermore National Laboratory performs experimental testing of explosives at designated remote locations in an area called Site 300. An experimental device is used for the explosive test. The construction of the experimental device varies, but it usually has a metal sheath and often contains depleted uranium, beryllium, copper, and zinc. Experimental devices can also contain lead. The experimental testing at Site 300 is conducted on gravel pads. The gravel on the pad is approximately 1.3 cm (0.5 in.) in diameter, with the smallest particles being 2 mm in diameter. The gravel is used to reduce shock wave propagation during explosive testing.

The experimental device is buried with gravel, which surrounds it and buffers the energy generated from the explosion. During the explosion, the gravel is broken down into smaller particles and mixes with contaminants. Contaminants in the used gravel originate from metal sheathing and other parts comprising the experimental device. These contaminants may consist of radionuclides (primarily depleted uranium) and metals (e.g., beryllium, copper, zinc) that the State of California considers hazardous to dispose of.

After an explosive test, a higher percentage of the gravel material is 2 mm or smaller. These small particles generated during the explosion mix with the gravel and reduce its effectiveness for shock wave reduction. With repeated use of the gravel, a buildup of contaminants and radioactivity is deposited on the gravel. When the contaminants are beryllium, copper, and zinc, the buildup results in the potential generation of low-level radioactive waste with California hazardous metals. When the contaminants are lead and chromium, the buildup results in the potential generation of Resource Conservation and Recovery Act (RCRA) mixed waste. See Table 1 for a listing of the state and federal regulated hazardous metals and their regulatory levels. To avoid the possibility of generating mixed waste after it is used, the gravel must be removed from the pad and either discarded or reconditioned.

TABLE 1
Metal Constituents, Regulatory Levels, and Characteristic Codes

Metals Leached	State Regulatory Levels		Federal Regulatory Levels	Characteristic EPA[1] Code
	STLC (mg/l)	TTLC (mg/kg)	TCLP (mg/l)	
Antimony	15	500	–	–
Arsenic	5.0	500	5.0	D004
Barium	100	10,000[2]	100.0	D005
Beryllium	0.75	75	–	–
Cadmium	1.0	100	1.0	D006
Chromium (VI)	5	500	5.0	D007
Cobalt	80	8,000	–	–
Copper	25	2,500	–	–
Lead	5.0	1,000	5.0	D008
Mercury	0.2	20	0.2	D009
Molybdenum	350	3,500	–	–
Nickel	20	2,000	–	–
Selenium	1.0	100	1.0	D010
Silver	5	500	5.0	D011
Thallium	7.0	700	–	–
Vanadium	24	2,400	–	–
Zinc	250	5,000	–	–

1 EPA = Environmental Protection Agency
2 Excluding barium sulfate

To determine whether or not a waste is hazardous, the State of California requires a leach test and/or a total waste analysis using the California Assessment Manual Wet Extraction Test (CAM-WET) for Soluble Threshold Limit Concentration (STLC) and for Total Threshold Limit Concentration (TTLC). The STLC is a extraction method that measures the amount of extractable substances in the material. The TTLC provides a total analysis of the material by determining which analytes are present and their concentrations. These tests are used instead of the federal Toxicity Characteristic Leaching Procedure (TCLP).

Before we developed the gravel reconditioning method, the gravel was removed from the gravel pad when it no longer reduced shock waves effectively and was placed into disposal containers, sampled, and analyzed. Depending on the analysis, the waste was disposed of as low-level radioactive waste or low-level radioactive waste with California hazardous metals. The contamination had not built-up enough to consider the waste RCRA mixed waste. The amount of gravel removed averaged around 4,536 kg (10,000 lb) per explosive test, and about 4,536 kg (10,000 lb) of clean makeup gravel was added to replenish the pad.

Using our reconditioning method, the small particles (particles less than 2 mm) and some contamination are removed from the gravel. Now, up to 90% of the gravel (4,082 kg or 9,000 lb per test) is reconditioned and placed back into use. About 454 kg (1,000 lb) of clean makeup gravel is needed to replenish the pad after an explosive test.

TREATABILITY STUDIES

We performed small-scale treatability studies to determine if screening would be an effective way of reconditioning gravel. A multitiered bench-top sieve unit (or screener) with an assortment of screen mesh sizes was used in the experiments.

Dry Screening

The first experiment was performed on dry gravel to determine the particle distribution of the gravel so that we could determine the optimal screen size(s) for retaining undersized particles. Six screens were selected with the sieve mesh ranging from 8 to 400 (i.e., sieve openings ranging from 2.8 mm to 0.037 mm). Approximately 1,600 g of dirty gravel was added to the top tray and allowed to shake in the sieve unit for 10 minutes. After shaking, the amount of gravel in each tray and in the bottom of the pan was calculated. See Table 2 for results of the test.

The design for the gravel reconditioning process made use of two screens: one screen for removing coarse fines from the gravel and the other for removing silt and small fines from the coarse material. Table 2 indicates that particles less than 2 mm account for 4.1% of the total gravel. When using a screen with a larger opening (i.e., No. 8 mesh), only a small increase of particles was noted, so we determined that No. 10 mesh screen could adequately remove coarse fines from the gravel. Both the No. 200 mesh and No. 325 mesh screens could adequately remove silt and small fines from the coarse material; however, the No. 325 mesh screen is constructed of fine wires and is very fragile. Because the No. 325 mesh screen tears easily and is expensive ($300 compared to $186) to replace, we decided to use the No. 200 mesh screen.

TABLE 2
Particle Distribution With Various Sieves
(Sample Weight: 1,608.9 g)

Sieve Mesh No.	Sieve Mesh Opening (mm)	Range of Particles (mm)	Weight of Retained Gravel (g)	Weight Fraction (%)
8	2.38	≥ 2.38	1,531.4	95.2
10	2.00	< 2.38 and ≥ 2.00	10.3	0.6
40	0.42	< 2.00 and ≥ 0.42	29.5	1.8
200	0.74	< 0.42 and ≥ 0.74	23.1	1.4
325	0.044	< 0.74 and ≥ 0.044	4.8	0.3
400	0.037	< 0.044 and ≥ 0.037	2.1	0.1
bottom of pan	< 0.037	< 0.037	7.3	0.5

Wet Screening

In the second experiment, we tested wet gravel to determine the effectiveness of spraying the gravel with water while screening and calculated the moisture content of the wet gravel removed from the unit. The sieve unit was adapted with a recirculating water system. The test was scaled down from the assumptions that the gravel will be fed at a rate of 907 kg/h (2,000 lb/h), the water flow rate will be twice the mass flow rate of gravel or 30.3 L/min (8 gal/min), and the screener will have an estimated sieve diameter of 1.2 m (48 in.). The bench scale test was performed with 1.8 kg (4 lb) of gravel, 3.6 L (0.96 gal) of water, using a water recirculation rate of 0.83 L/min (0.22 gal/min), and on the sieve unit that has a 20.3 cm (8 in.) sieve diameter. Only two trays (No. 10 mesh and No. 200 mesh screens) were added to the sieve unit. The dirty gravel was added into the top tray (No. 10 mesh screen) of the sieve unit, the water recirculation system was turned on, and the unit was allowed to shake 4.32 minutes. After shaking, the amount of gravel was calculated in each tray and for the bottom of the pan. See Table 3 for the wet screening results.

Table 3 indicates that particles less than 2 mm account for 9.6% of the total gravel. Compared to dry screening (where particles less than 2 mm account for 4.1% of the total gravel), we determined that wet screening is more effective at removing smaller particles from the gravel. In addition, the amount of water removed from the system when the gravel is discharged is small. The water makeup rate for both the top tray and middle tray of the wet gravel is 3.8%.

TABLE 3
Particle Distribution and Moisture Content of Wet Gravel
(Weight of Dry Gravel Before Testing: 1,814.4 g)

Gravel	Top Tray Gravel (≥ 2 mm)	Middle Tray Gravel Sludge (<2 mm and ≥0.074 mm)	Bottom Pan Gravel Silt and Fines (< 0.074 mm)
Wet gravel	1,735.0 g	148.4 g	63.3 g*
Dry gravel	1,640.5 g	104.6 g	63.3 g*
Amount of water	94.5 g	43.8 g	3,495.7 g*
% by weight solids	90.4	5.8	3.8
% by weight moisture	5.4	29.5	N/A
% by volume water removed	2.6	1.2	N/A

* By mass balance.

Test for Cleaning Ability

We also studied how well wet screening could clean. We performed the wet screening operation described earlier several times using water and twice using a nitric acid solution (pH 2) on contaminated gravel. Samples of the gravel in the top tray, middle tray, and bottom pan were taken and analyzed. The test results for gravel washed with water are shown in Table 4.

The analyses shown in Table 4 are based on the State of California's leach test and total waste analysis. The differences between the Federal (TCLP) and the California State (STLC) leaching tests are subtle. The California State leaching test is more rigorous and, therefore, provides us with more conservative results. The differences in these tests are summarized in Table 5.

The STLC test was performed on the larger pieces of gravel (particles > 2.0 mm) to test the effectiveness for reducing leaching, and the TTLC test was performed on the sludge and silt (particles ≤ 2.0 mm) to determine the type and concentration of material that was removed by the screening process.

Table 4 shows that some beryllium, chromium, copper, lead, and zinc was removed; however, when performing a mass balance on each contaminant, the exact amounts or percentages could not be calculated with the limited number of samples taken. The gravel is heterogeneous, which made it difficult to collect representative samples. Future samples will be taken of the gravel, sludge, silt, and fines. These sampling results may help us determine how well wet screening cleans the gravel.

TABLE 4
Analysis of Gravel Washed with Water

Contaminant	**Unwashed Gravel**		**Gravel Washed with Water**		
	Before Study		**Top Tray Gravel > 2.00 mm**	**Middle Tray Sludge < 2 mm ≥ 0.074 mm**	**Bottom Pan Silt and Fines < 0.074 mm**
Metal Analyzed	**TTLC (mg/kg)**	**STLC (mg/l)**	**STLC (mg/l)**	**TTLC (mg/kg)**	**TTLC (mg/kg)**
Antimony	ND (<10.0)	ND (<0.5)	ND	10.6	ND
Arsenic	ND (<50.0)	ND (<2.5)	ND	ND	ND
Barium	56.6	4.3	9.6	86.6	6.8
Beryllium	ND (<0.70)	0.057	0.085	23.4	0.48
Cadmium	ND (<1.0)	ND (<0.05)	ND	ND	ND
Chromium	10.5	0.12	ND (<0.1)	213	0.83
Cobalt	3.5	0.094	0.12	9.6	0.3
Copper	15.1	0.76	0.41	654	6.7
Lead	ND (<10.0)	ND (<0.5)	ND	43.2	2.5
Mercury	ND (<0.10)	ND (<0.002)	ND	ND	0.022
Molybdenum	ND (<2.0)	ND (<0.1)	ND	3.5	ND
Nickel	10.2	ND (<0.2)	ND	123	0.94
Selenium	ND (<25.0)	ND (<0.3)	ND	ND	ND
Silver	ND (<1.0)	ND (<0.05)	ND	ND	ND
Thallium	ND (<100)	ND (<5.0)	ND	ND	ND
Vanadium	12.9	0.22	ND	58.2	1.4
Zinc	19.1	0.99	1.8	75.7	3
Radioactivity	**pCi/g**		**pCi/g**	**pCi/g**	**pCi/g**
Gross Alpha	7.52		4.07	not measured	4,460
Gross Beta	24.9		17.4	not measured	3,670

ND means not detected.

TABLE 5
Leaching Test Comparison (Federal versus State)

Criterion	TCLP (Federal)	STLC (California)
Extraction Fluid Type	Acetate buffer	Citrate buffer
Approximate Extraction Fluid pH	5	5
Approximate Solids Diameter (Maximum)	0.01 m	0.002 m
Leaching Time	18 h	48 h
Extraction Fluid Weight Ratio	20:1	10:1

DESIGN REQUIREMENTS

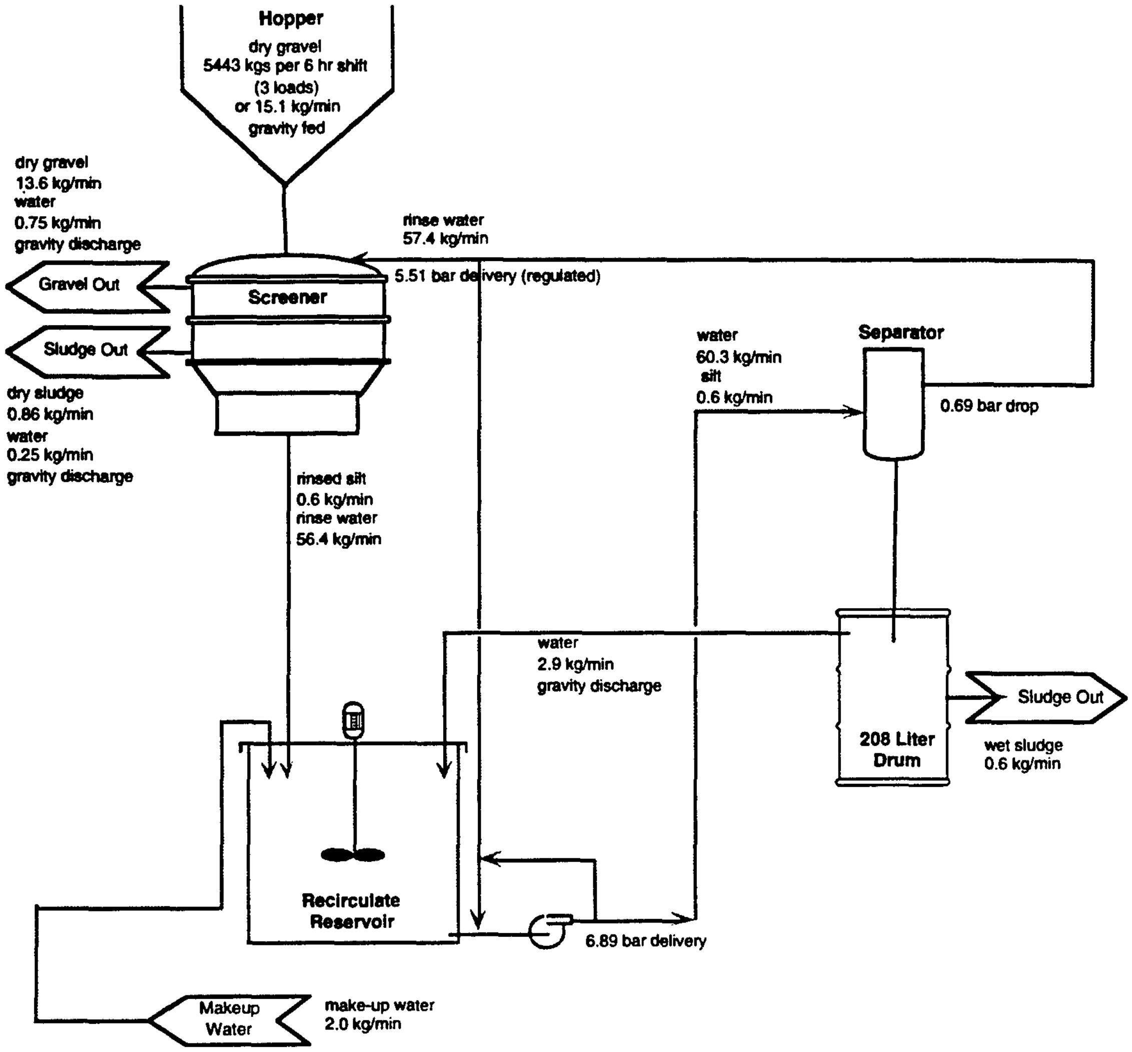
The full-scale Gravel Reconditioning Unit was designed to meet the following criteria:

- A gravel process rate of approximately 5,443 kg (12,000 lb) in a 6-hour day or 907 kg/h (2,000 lb/h)
- Ability to feed gravel to the screener with a front-end loader if conveyors are not used
- Hopper loading minimized to 2–3 times a day [i.e., gravel capacity of between 1.2–1.8 m^3 (42–63 ft^3) if a hopper is used]
- Skid-mounted unit, transportable by a flatbed truck, so that it can be moved from one gravel pad to another
- Ability to withstand an outside environment and outdoor location
- Portable so that it can be operated in the field on the gravel pad at a distance of 30 m (100 ft) from any electrical or water source
- Easy to operate and requiring minimal set-up, operating, and shutdown effort
- No use of an air compressor in its operation
- LLNL seismic criteria at all times
- Design and fabrication cost of less than $100,000 for the unit
- Design, procurement, and fabrication schedule of 7 months

Design Overview

The Gravel Reconditioning Unit is a skid-mounted unit used to recondition gravel at Site 300. The reconditioned gravel is restored to its original size with its original dampening effectiveness and is placed back into use. The Gravel Reconditioning Unit contains a feed delivery system, screen separator unit, water reservoir, water recirculation system, rinsate separation system, and control panel. A schematic layout of the gravel reconditioning process, including the mass balance for the gravel and water, is shown in Figure 1.

FIGURE 1
Gravel Reconditioning Process Schematic



Feed Delivery System

The feed delivery system contains a hopper, slide control valve, and flexible connector. The feed delivery system uses a front-end loader to place the gravel into the hopper. Because a front-end loader is used, the height of the hopper is restricted to less than 2.90 m (9.5 ft). The hopper feeds to the screen separator unit that is mounted on the skid. The screen separator requires a 0.15-m (0.5-ft) clearance above the unit to change out the screens. Given the height of the screen separator and the necessary clearance, the bottom of the hopper must be at least 1.90 m (6.25 ft) off the ground. In addition, for seismic considerations, the hopper needs to be as low to the ground as possible. For these reasons, the hopper was designed to be 2.72 m (8.92 ft) tall × 0.76 m (2.5 ft) deep, with a hopper bottom 1.96 m (6.42 ft) off the ground.

The angle of slide for the gravel was determined using Marks' *Standard Handbook for Mechanical Engineers,* which states that the angle of slide (i.e., the angle at which material will flow on an inclined surface) for stone is about 30° with the finer material being 35–40°. For stone, ore, and coal, it is customary to build chutes on a angle of 45°; however, by using a 45° angle of slide, the height of the hopper would have exceeded the maximum height by 20 cm (8 in.). Therefore, the slide angles for the hopper were determined by experiment. Gravel was piled on one end on a metal sheet. The gravel-end of the metal sheet was raised, and the height at which the gravel slid freely was measured. From the height and the length of the metal sheet, the angle of slide was calculated. This experiment was repeated several times, and the calculated angles ranged from 26° to 27.5°; therefore, we determined that 30° would be an acceptable minimum slide angle for the hopper.

For ease in construction, the hopper was designed as an inverted pyramid with a rectangular opening and base. The hopper was designed with the top opening 2.44 m long and 1.67 m wide (8 ft × 5.5 ft) and is tapered down to a square opening at the bottom 0.30 m long and 0.30 m wide (1 ft × 1 ft). The side angles of the hopper are 41.9°, while the end angles are 30°. The capacity of the hopper is 1.6 m^3 (55 ft^3).

The hopper could be constructed of either aluminum or stainless steel because neither one of these materials deposit contaminants on the gravel. Aluminum is less expensive and lighter in weight (i.e., ideal for seismic considerations since the center of gravity is lower); however, the material is soft and may dent or erode with the addition of gravel. Aluminum is also difficult to weld and, at LLNL, the time and staff to fabricate the hopper out of aluminum is greater than for stainless steel. For these reasons, the hopper was constructed out of 304 stainless steel with all exposed seams welded.

Structural steel is used to support the hopper. Each corner of the hopper is supported by 15.2 cm × 15.2 cm × 0.63 cm (6 in. × 6 in. × 1/4 in.) box tubing. To maintain seismic stability, outriggers, hinged at the corners of the hopper support structure and pinned in place, are used when the hopper is loaded. The overall dimensions of the Gravel Reconditioning Unit, without the extension of the outriggers, is 1.7 m wide × 2.4 m long × 2.7 m high (5.5 ft × 8 ft × 8.9 ft). With the extension of the outriggers, the length and width are both increased by 1.4 m (4.7 ft).

The bottom opening of the hopper is located directly over the inlet to the screen separator unit. The slide control valve is mounted under the hopper and regulates the amount of gravel entering the screen separator unit. The slide control valve is a manually operated slide valve with an aluminum body and a steel slide plate. With a little effort, the manual valve can be shut against a full hopper of gravel.

The flexible connector is mounted at the bottom of the slide valve and is connected to the screen separator unit. The flexible connector is constructed out of neoprene. The connector is flexible so that it can move with the screen separator when it vibrates and can be lifted off easily to change out screens.

Screen Separator Unit

The screen separator for the Gravel Reconditioning Unit is a commercial unit used for wet classification (i.e., solid classification in a liquid medium). The screen separator is cylindrical, has a screen diameter of 0.76 m (30 in.), is 1.06 m (42 in.) tall, and is constructed out of stainless steel. The screen separator has two screens and antiblinding features to dislodge small particles from the screen. The sieve mesh for the screens are No. 10 mesh and No. 200 mesh, but additional sieve mesh sizes are available.

The screen separator has one inlet at the top of the screen separator, three discharge ports, and a spray system. To prevent incoming gravel from damaging the screen, a velocity breaker (strike plate) was installed on the screener lid. The top discharge port is for effluent gravel (particles > 2 mm), the middle discharge port is for effluent sludge (particles ≤ 2 mm and > 0.074 mm), and the bottom discharge port is for the effluent silt, fines, and water. The top and middle discharge ports were extended to 1.02 m (40 in.) to reach past the skid. To prevent gravel or sludge from blocking the outlet, a 20° slant was provided on the extended discharge ports. A spray system was also designed for this unit using six nonclog spray nozzles that wash the gravel as it vibrates on the top screen. The nozzles are designed for a maximum flow rate of 60.5 L/min (16 gpm) and a pressure of 5.515 bars (80 psi).

The screen separator uses a three-dimensional inertial vibratory motion to separate particles by size. The screen separator vibrates horizontally, vertically, and tangentially. The control for gravel flow in the unit is adjustable by increasing and/or decreasing the mass of the top and bottom eccentric weights and the increasing or decreasing the lead angle of the bottom eccentric weight. Increasing the bottom eccentric weight increases the vertical component of motion, increasing the top eccentric weight increases the horizontal throw and cause oversized material to discharge at a faster rate, and increasing the lead angle of the bottom eccentric weight imparts a spiral motion of the particles on the screen. If gravel requires additional cleaning, the lead angle of the bottom eccentric weight is increased to keep the gravel on the screen longer.

The screener separator is mounted on a stand to the skid. The height at which the screener separator was mounted to the skid was critical because it affects the overall height of the hopper. The height of the discharge ports determined how high to raise the screener separator. The height of the top discharge port (gravel spout) was designed to be high enough so that the bucket of the front-end loader can be positioned under the spout to collect clean gravel or to facilitate placement of approximately 1.56 m^3 (55 ft^3) of gravel on the ground. The height of the middle discharge port (sludge spout) is high enough above the ground so that a 208-L (55-gal) drum, 0.89 m (35 in.) tall, can be placed under the spout.

Water Reservoir

The silt, fines, and water out of the bottom discharge flows into a water reservoir that is constructed out of stainless steel, has a total capacity of 566 L (150 gal), and an average operating volume of 330 L (87 gal). Makeup water is also introduced in the water reservoir. The discharge for the silt solution is at the bottom of the water reservoir. A hinged lid is mounted on top of the reservoir for easy cleanout.

A mixer and instrumentation for monitoring pH, conductivity, high water level, low water level, and high-high water level are mounted to the water reservoir. The mixer is located on top of the water reservoir and uses a 1/3 horsepower motor and a 5.1-cm (2-in.) turbine blade to agitate the contents. A pH probe and conductivity probe are mounted inside the water reservoir and monitor the conditions of the solution. High water level, low water level, and high-high water level sensors are mounted in the water reservoir. When the water level is below the low water level, an alarm is activated and indicates that the system is low and makeup water is required. The makeup water continues to fill into the system until the high water level indication is reached. When the water level reaches the high water level, the makeup water is automatically shut off. If the water level reaches the high-high water level, an alarm is activated and indicates that the system is near overflow (85% of total capacity).

Water Recirculation System

The water recirculation system consists of a pump, valves, and piping. The system is designed to process the reservoir water through the rinsate separation system and recirculate it back into the screener separator. The system was designed to the maximum flow rate and pressure requirements of the spray nozzles. The water recirculation system is designed to provide a flow rate of 60.5 L/min (16 gpm) and a pressure of 5.515 bars (80 psi) at the spray nozzles. At the designed pressure and flow rate, there is a 1.4–1.7 bar (20–25 psi) drop across the system due to friction losses. Therefore, the pump is designed to operate at 60.5 L/min (16 gpm) and at a pressure of 6.9–7.3 bars (100–105 psi). The pump is also designed so that it doesn't pulsate because pulsating flows cause interferences with the rinsate separation process. The pump chosen is a multistage centrifugal pump that operates at 60.5 L/min (16 gpm) at 7.0 bars (102 psi).

The valves and piping are designed to meet high system working pressures and constructed out of material that is protected against outdoor environments (ultraviolet radiation). The valves and piping used is chlorinated polyvinyl chloride (CPVC), schedule 80, and designed for a maximum working pressure of 47.6 bars (690 psi) at 23°C (73.4°F).

In addition to the valves that direct and regulate flow, an overpressure relief valve and pump bypass valve was installed to prevent over pressuring the system. A flow meter was also installed on the water recirculation line to monitor the flow rate of the recirculated water.

Rinsate Separation System

The rinsate separation system consists of a hydrocyclone separator, motor-operated ball valve, purge diffuser, and drum decant system. The rinsate separation system is installed in the water recirculation system to remove silt and fines from the recirculated water. The solid-free water is discharged out the top of the hydrocyclone separator and into the screen separator. The solids are discharged out the bottom of the hydrocyclone separator and into a 208-L (55-gal) drum. Liquid from the 208-L (55-gal) drum is decanted off and gravity fed into the water reservoir.

The solution pumped from the water reservoir enters the hydrocyclone separator tangentially, which sets up a circular flow. The solution is then drawn through tangential slots and accelerated into the separation chamber of the hydrocyclone separator. Centrifugal action tosses particles heavier than the water to the perimeter of the separation chamber. The particles drop along the perimeter of the cyclone separator and settle into the collection chamber. The solid-free water is drawn up the separator's vortex, up through the separator's outlet, and into the screen separator.

For particles with a specific gravity of 2.6, the hydrocyclone separator is designed to remove approximately 95% of particle greater than 0.074 mm, 75% of particle between 0.040 mm and 0.074 mm, and 40% of particles between 0.020 mm and 0.040 mm. In recirculated systems, the hydrocyclone separator is designed to remove 98% of particle greater than 0.074 mm, 93% of particle between 0.040 mm and 0.074 mm, and 65% of particles between 0.020 mm and 0.040 mm.

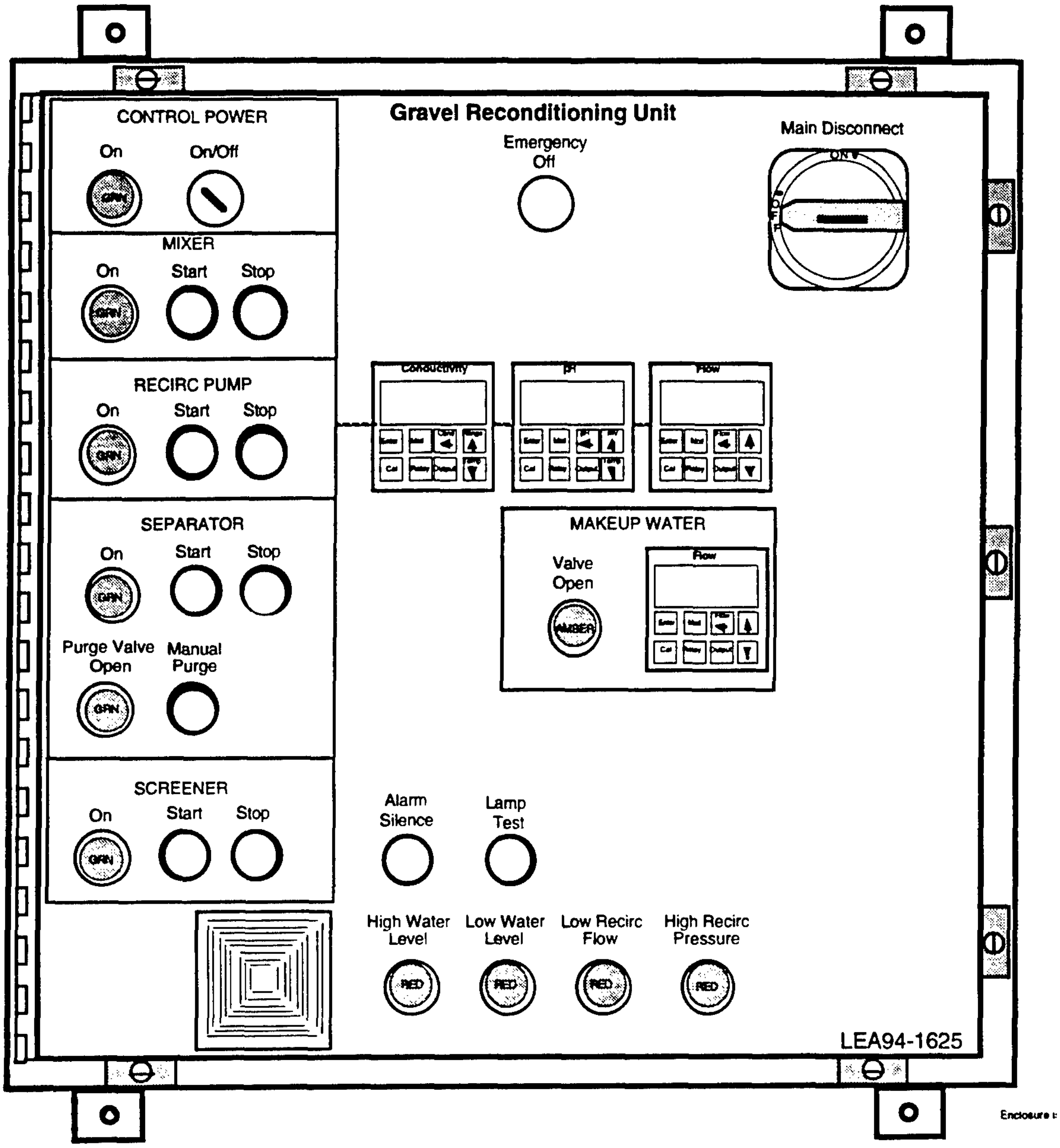
The solids remain in the hydrocyclone separator until approximately 1.2 L (0.3 gal) of solids has been collected. When the collection chamber is full, the motor-operated ball valve opens and the contents discharge into a 208-L (55-gal) drum located underneath the cyclone separator. Due to high system pressures, a purge diffuser was installed on the hydrocyclone separator discharge line to prevent inadvertent spraying of liquid. Approximately 7 parts liquid to 1 part solid is ejected each time the cyclone separator is purged.

The drum decant system, which consists of a drum shroud with baffle plate and a discharge line to the water reservoir, is attached to the 208-L (55-gal) drum. The gasketed drum shroud is clamped to the top of the drum and allows the water level to raise past the height of the drum without leaking out. As the discharged material (solids and water) fill the 208-L (55-gal) drum, the solid material tends to settle to the bottom of the container while the lighter material remains on the top. When the water reaches the discharge port, the water gravity flows into the water reservoir. The drum decant system minimizes the amount of makeup water to be added to the system, minimizes the amount of liquid waste to treat, and maximizes the solid holding capacity in the drum.

Control Panel

All controls for the Gravel Reconditioning Unit are located on a control panel (see Figure 2 for a layout of the control panel). The frequency and duration for purging the hydrocyclone separator are also adjustable from within the panel. The panel is a NEMA 4 enclosure, and all controls are weather resistant and rated for outdoor use. The lights and controls on the control panel are visible from outside the enclosure. A crash button and main disconnect are also mounted on the control panel. A 38.1-m (125-ft) grounded cable with connections to a 208-V, 20-A receptacle provides the power for the screen separator, pump, mixer, and miscellaneous controller. The power cable is routed to the back of the control panel.

FIGURE 2
Layout of the Control Panel



CONCLUSIONS

The Gravel Reconditioning Unit was designed and fabricated in 8 months for less than $100,000. Testing began in January 1995. Preliminary results proved acceptable for clean pea gravel. Further testing will be on the contaminated gravel at Site 300.

During testing, the clean gravel was loaded into the hopper by a front-end loader in less than 5 minutes. No spillage was noted when loading the gravel. With a little effort, the slide control valve under the hopper could be opened and closed against a 0.84-m (33-in.) head of gravel. The flow rate of gravel was regulated by slide control valve. Gravel entered the screener separator easily, and the velocity breaker prevented the gravel from damaging the top screen of the screener separator. Water from the spray nozzles removed a majority of the silt and fines from the gravel. The gravel discharged out of the top tray was considerably silt-free and greater than 2 mm in size.

The particles smaller than 2 mm entered the middle screen. A majority of the larger sludge particles came out the middle discharge port. When the middle screen became clogged, unexpected water came out with the sludge and emptied into the drum. This problem is being corrected by using a screen with larger openings and providing a modified drum decant system on the sludge drum to return excess water to the water reservoir.

The remaining water and silt (particles $< 74\ \mu m$) in the screener separator was discharged into the water reservoir. The mixer adequately kept the silt in solution. The centrifugal pump was able to pump the silt solution up through the hydrocyclone separator and to the screener separator. At the specified frequency and duration, the hydrocyclone separator discharged the silt into the drum decant system. The excess liquid in the drum decant system successfully flowed into the water reservoir.

The handling and treatment of the waste water generated by the reconditioning process is a routine practice for LLNL. The waste water can be treated at the Tank Farm and (when analytical results indicate that it meets acceptance criteria) emptied into the LLNL sewer (ultimately to reach the city water reclamation plant). The silt and sludge waste generated by the reconditioning process can also be treated at LLNL. The silt and sludge will be stabilized in their container.

The Gravel Reconditioning Unit is an inexpensive, easy-to-use, low maintenance, portable, and effective way to recondition gravel. Applying the Gravel Reconditioning technique to the gravel on the gravel pads at Site 300 will reduce the amount of low-level radioactive waste, low-level radioactive waste with California hazardous metals, or RCRA mixed waste generated. In an 8-h period approximately 5,443 kg of gravel will be processed with up to 90% by weight (or 4,899 kg) of the large gravel being recycled. This procedure results in a cost benefit of up to $1,800/day savings in disposal costs and additional savings in costs associated with the procurement and delivery of new gravel.

ACKNOWLEDGMENTS

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1. *Standard Handbook for Mechanical Engineers,* Eighth Edition. Published by McGraw Hill Book Company (1978).

CONSERVATION FOR READINESS

AN ASSESSMENT OF THREATENED AND ENDANGERED SPECIES HABITAT ON THE U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER, PICATINNY ARSENAL

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ABSTRACT: A planning level habitat assessment was conducted on approximately 1751.7 ha of the U.S. Army Armament Research, Engineering, and Development Center, Picatinny Arsenal, from January-August 1994. Installation lands were evaluated to determine their suitability for ten threatened, endangered, or candidate species. Target species included: the bald eagle (*Haliaeetus leucocephalus*), peregrine falcon (*Falco peregrinus anatum*), Indiana bat (*Myotis sodalis*), bog turtle (*Clemmys muhlenbergii*), long-tailed salamander (*Eurycea longicauda longicauda*), timber rattlesnake (*Crotalus horridus horridus*), New England cottontail (*Sylvilagus transitionalis transitionalis*), eastern woodrat (*Neotoma floridana magister*), long-tailed shrew (*Sorex dispar*), and cerulean warbler (*Dendroica cerulea*). A simple, qualitative stand rating system was developed which compared habitat data from individual stands on the arsenal to habitat conditions on areas described in the literature as being suitable or preferred habitat for each target species. Ecological requirements (i.e., cover, food, moisture, soils, forest type, etc.) for each target species were determined using the scientific literature and a scoring system was developed to estimate the relative suitability of each stand to the target species. Stands more closely resembling preferred or suitable conditions scored higher during the assessment than did those with habitat conditions different from preferred conditions (as reported in the literature). Habitat variables used in the assessment were divided into distinct classes for scoring purposes with "preferred" or "optimum" conditions receiving the highest scores and less suitable or lower quality conditions receiving the lowest scores. Stands were classified into high, medium, low, or marginal categories depending on their scores.

Key words: habitat assessment, stand rating system, threatened and endangered species, military installations, New Jersey.

INTRODUCTION

A multi-disciplinary project was initiated in 1993 to provide personnel at the U.S. Army Armament Research, Development, and Engineering Center (ARDEC), Picatinny Arsenal, with baseline natural and cultural resource data for compliance and management related activities. Natural and cultural resource data were obtained from a variety of sources (i.e., field surveys, historical data sets, installation data sets, etc.) and incorporated into a geographic information system (GIS) to determine the distribution and areal coverage of wetlands, floodplains, threatened and endangered species (TES) habitat, geomorphological resources, and cultural resources. The study was conducted by a interdisciplinary team of scientists at the U.S. Army Engineer Waterways Experiment Station (WES).

Objectives

A major component of the Picatinny study was the identification and assessment of TES habitat. Specific objectives included: 1) coordinating with installation, state, and Federal personnel to develop a list of species of interest (target species), 2) reviewing the scientific literature on each of the target species and compiling information necessary to develop species profiles (i.e., taxonomy, regulatory status, taxonomic characteristics, distribution and numbers, reproduction and development, life history and ecology, habitat requirements, cause of current status, and management) for each of the target species, 3) developing a method for identifying and rating target species habitat, 4) identifying critical areas on the arsenal (in terms of target species habitat) that had the potential to support one or more of the target species, and 5) providing installation level management recommendations for target species. This paper will discuss the methodology associated with developing the stand rating system for conducting the single species habitat assessments, and the procedures used to conduct the installation level assessment.

Methodology

Lists of Federally and state protected/sensitive species with the potential to occur on the arsenal were provided to Picatinny personnel by the U.S. Fish and Wildlife Service (USFWS) and the New Jersey Department of Environmental Protection (NJDEP) prior to the WES study. WES researchers used these lists to select ten species that had either: 1) the potential to occur on the installation (i.e., arsenal was within the reported range of the species), 2) were species of special interest to installation, state, or Federal personnel in the area, or 3) were species that had previously been reported as occurring on the arsenal. Selection of individual target species was coordinated with the USFWS, the NJDEP, The Nature Conservancy (TNC), and the Natural Resources Office at Picatinny. Ten target species were selected. These included the eastern woodrat (*Neotoma floridana magister*), the New England cottontail (*Sylvilagus transitionalis transitionalis*), the long-tailed shrew (*Sorex dispar*), the Indiana bat (*Myotis sodalis*), the timber rattlesnake (*Crotalus horridus horridus*), the bog turtle (*Clemmys muhlenbergii*), the long-tailed salamander (*Eurycea longicauda longicauda*), the bald eagle (*Haliaeetus leucocephalus*), the peregrine falcon (*Falco peregrinus anatum*), and the cerulean warbler (*Dendroica cerulea*). The bald eagle, peregrine falcon, and Indiana bat are Federally protected species, and the remaining seven are considered significant, sensitive, threatened, or rare (Table 1).

TABLE 1

Table 1. Species selected for habitat assessment study conducted on the U.S. Army Armament Research Development, and Engineering Center, Picatinny Arsenal, 1993.

Species	Taxonomy	Status[1]
bald eagle	**ACCIPITRIDAE**: *Haliaeetus leucocephalus*	FE
American peregrine falcon	**FALCONIDAE**: *Falco peregrinus anatum*	FE
Indiana bat	**VESPERTILIONIDAE**: *Myotis sodalis*	FE
bog turtle	**EMYDIDAE**: *Clemmys muhlenbergii*	C2
long-tailed salamander	**PLETHODONTIDAE**: *Eurycea longicauda longicauda*	NA
timber rattlesnake	**VIPERIDAE**: *Crotalus horridus horridus*	NA
New England cottontail	**LEPORIDAE**: *Sylvilagus transitionalis transitionalis*	C2
eastern woodrat	**CRICETIDAE**: *Neotoma floridana magister*	C2
long-tailed shrew	**SORICIDAE**: *Sorex dispar*	C2
cerulean warbler	**PARULIDAE**: *Dendroica cerulea*	C2

[1] - U.S. Fish and Wildlife Service Ecological Services Office, Pleasantville, New Jersey 08232.

FE - Federally listed species that is in danger of extinction throughout all or a significant portion of its range.

C - Species that appear to warrant consideration for addition to List of Endangered and Threatened Wildlife and Plants. USFWS encourages Federal agencies and planners to give consideration to these species in their environmental planning.

C2 - Taxa for which information now in the possession of the USFWS indicates that proposing to list the species as threatened or endangered is possibly appropriate, but for which conclusive data are not available to support proposed rules at this time.

An exhaustive literature review was conducted to compile information on the ecology of each target species, and over 1500 pertinent citations were obtained. Information from the literature was used to develop a stand rating system for evaluating the potential of installation lands to support each of the target species. The scoring system compared habitat conditions (i.e., species composition, structural characteristics, areal coverage, land-use, etc.) on the arsenal to areas described in the literature as being suitable or preferred habitat. Variables used in the assessment were divided into distinct classes for scoring purposes. Stands more closely resembling suitable or preferred habitat scored higher in the assessment than did stands with habitat conditions different from those reported in the literature. Each stand on the arsenal was scored, ranked, and placed into one of four categories which represented the stand's potential for providing habitat for the target species. Categories included high, medium, and low, with an additional category (marginal) included in the cerulean warbler and long-tailed shrew assessment. After all of the stands on the arsenal were scored and ranked, stand attribute data were analyzed to determine if the stand rating system was selecting stands with suitable conditions for each of the target species. If it were indicated that the rating system did not function as planned (e.g., incorrectly classifying stands), modifications would have been made until the rating system was refined. Color coded stand rating maps were produced to indicate a stand's potential for supporting each of the target species. High potential stands were coded red (warning), medium potential stands were coded yellow (caution), and low potential stands were coded in green (proceed after inspection).

Single Species Habitat Assessment

The cerulean warbler is a species of interest to installation personnel and will be included here to illustrate the methodology associated with developing the stand rating system. Regional interest in ceruleans is high and the species has been reported on the arsenal several times in the past (per. comm., J. Van DeVenter, Picatinny Arsenal). In addition, cerulean nests have been documented in areas adjacent to the installation (per. comm., J. Van DeVenter, Picatinny Arsenal).

The species is a small, neotropical migrant once common in the mature, floodplain forests of the central United States [1,2,3]. Ceruleans spend the summer months in the hardwood forests of the northeastern United States and winter in the Andean foothills of Peru[3]. Little is known about the species, and the population has declined dramatically over the last 25-30 years (3.4% annually since 1966) [3,4,5]. The cause of the population decline has been widely debated, but it is most often attributed to habitat loss (especially on the wintering grounds) [6].

Our review of the literature indicated that summer habitat selection as well as habitat usage by cerulean warblers were influenced largely by eight habitat variables (Table 2). These included: canopy height, dbh of dominant overstory species, percent oak in the overstory, percent of the ground covered by vegetation <1.0 m tall, percent occurrance of preferred understory species, size of the stand (ha), number of woody understory stems $\leq$5.3 cm/ha, and the suitability of surrounding stands to provide for the species[1,2,3,6,7,8,9]. Each stand on the arsenal was scored individually and placed into one of four qualitative categories depending on its score. Maps delineating each stand's rating were developed using the above information and digitized into the GIS for reference and later use in the planning level assessment.

TABLE 2

Table 2. Habitat variables and scoring criteria used in the assessment of cerulean warbler habitat on the U.S. Army Armament Research, Development, and Engineering Center (ARDEC), Picatinny Arsenal.

VARIABLE	SCORING CLASSES	SCORE	REFERENCES
Canopy Height (m)			
	> 18.3	5	Hamel 1981, Lynch 1981, Robbins et. al. 1992
	16.8-18.0	4	
	15.2-16.4	3	
	13.7-15.0	2	
	< 13.4	1	
DBH (cm)			
	≥ 25.4	5	Hamel 1981, Kahl et. al. 1985
	20.3-25.1	4	
	15.2-20.0	3	
	10.2-15.0	2	
	< 10.1	1	
Overstory Species Composition (% oak)			
	75-100%	4	Lynch 1981 Peck and James 1987 Brewer et. al. 1991
	50-74%	3	
	25-49%	2	
	< 25%	1	
	none	0	
% Ground Covered by Vegetation < 0.9 m High			
	Dense	4	Lynch 1981
	Moderate	3	
	Light	2	
	Sparse	1	
% Occurrence of Preferred Understory Species			
Spicebush, Buckeye, or Paw Paw			
	75-100%	4	Lynch 1981
	50-74%	3	
	25-49%	2	
	< 25%	1	
	none	0	
Size (ha)			
	> 526.1	5	Bond 1957 Hamel 1981 Robbins et. al. 1992
	404.7-526	4	
	283.3-404.3	3	
	161.9-282.9	2	
	< 161.9	1	

TABLE 2

Table 2. (*continued*) Habitat variables and scoring criteria used in the assessment of cerulean warbler habitat on the U.S. Army Armament Research, Development, and Engineering Center (ARDEC), Picatinny Arsenal.

VARIABLE	SCORING CLASSES	SCORE	REFERENCES
Number of stems (≤ 5.1 cm) per acre			
	417-1134	2	Kahl et. al. 1985
	⟩1134	1	
	⟨417	0	
Suitability of Surrounding Land to Ceruleans			
	suitable	1	Robbins et. al. 1992
	non-suitable	0	

Results

One hundred twenty-one stands (953.3 ha) were identified as potential cerulean warbler habitat. Twelve (63.9 ha) were classified as high potential habitat, fifty-one (694.4 ha) were classified as medium potential, and twenty-four (195.3 ha) were classified as low potential. Average diameter and height of overstory species in high potential stands were 23.1 cm and 19.5 m, respectively, and three forest/habitat types (6 northern hardwood, 4 mixed oak, 1 red maple) were represented. Oak in the overstory averaged 14.1%. Average diameter and height of overstory species in medium potential stands were 19.8 cm and 18.9 m, respectively, and five forest/habitat types (34 mixed oak, 12 northern hardwood, 3 hemlock hardwood, 1 aspen, 1 black birch) were represented. Oak in the overstory of medium potential stands averaged 30.1%. Average diameter and height of overstory species in low potential stands were 17.5 cm and 17.5 m, respectively, and four forest/habitat types (17 mixed oak, 5 northern hardwood, 1 aspen, 1 non-specified deciduous hardwood) were represented. Oak in the overstory of these stands averaged 27.0%.

Planning Level Habitat Assessment

The second phase of the study involved the compilation of information from each of the single species habitat assessments into a single database for a multi-species, or planning level, assessment. Our goal in conducting the multi-species, or planning level, assessment was to provide installation planners and biologists access to stand rating information and maps that could be used: 1) for preliminary environmental consultations to determine if proposed activities (i.e., road construction, clearing, building/range construction, firewood removal, power line right-of-way construction, etc.) would impact portions of the installation that are important to any of the target species, 2) to identify areas of the installation where management efforts for the target species could be concentrated, and 3) to provide installation biologists with an indication as to the composition, distribution, importance, and coverage of the various forest/habitat types identified as being important to one or more of the target species. Stand rating maps can also be used to determine the most logical areas to initiate field surveys to satisfy regulatory requirements (i.e., Section 7 consultations, environmental impact statements, biological assessments, etc.).

The database created for the planning level assessment contained information on all stands determined to represent potential habitat for one or more of the target species. Information contained in the database included: stand identification number, habitat type, size, the target species that each stand had the potential to support, and the stand rating (e.g., high, medium, low, or marginal).

Single species stand rating maps were digitized into a GIS and used to identify stands that represented potential habitat for one or more of the target species. Color coded stand maps of the installation were produced which showed the number of target species that each stand could support. Statistical and graphical analysis of stand attribute data identified numerous stands with habitat potential for multiple species (Table 3). Two stands (77.6 ha) have potentially suitable habitat conditions for seven of the target species, and two stands (49.3 ha) have the potential to provide habitat for six of the target species. Eleven stands (116.7 ha) represented potential habitat for five of the target species and twenty-seven stands (311.1) represented potential habitat for four of the target species. Fifty-three stands (480.9 ha) had potential for three of the target species and ninety-four stands (288.3 ha) represented potential habitat for two of the target species. Seventy-seven stands (413.5 ha) had suitable habitat conditions for only a single species.

TABLE 3

Table 3. Areal covereage of stands on the U.S. Army Armament Research, Development, and Engineering Center, Picatinny Arsenal, determined to be important to one or more target species

Number of Target Species	Number of Stands	Size
Seven	2	77.6
Six	2	49.3
Five	11	116.7
Four	27	311.1
Three	53	80.9
Two	95	288.3
One	77	413.5

Seventeen habitat types representing 1643.9 ha were identified as being important to one or more of the target species. Inspection of stand data indicated that the mixed oak (*n*=75; 929.3 ha), red maple, (*n*=61; 308.6 ha), old field (*n*=61; 108.3 ha), and northern hardwood (*n*=35; 165.6 ha) habitat types appear to be extremely important to target species on the installation (Table 4).

TABLE 4

Table 4. Areal coverage of habitat types on the U.S. Army Armament Research, Development, and Engineering Center, Picatinny Arsenal, identified as potential habitat for target species[1].

Habitat Type	Number of Stands	Size
Mixed Oak	75	929.3
Red Maple	61	308.6
Old Field	61	108.3
Northern Hardwoods	35	165.6
Hemlock Hardwoods	8	115.5
Shrub	5	73.2
Aspen	7	11.2
White Pine/Red Pine	5	1.4
Hardwoods	2	3.0
Early Succession	1	6.6
Buttonbush	1	5.4
Deciduous	1	4.3
Black Birch	1	1.7
Alder	1	1.2
Wetland	1	0.9
Total	248	1726.6

---

[1] Included the: bald eagle, peregrine falcon, Indiana bat, bog turtle, long-tailed salamander, long-tailed shrew, timber rattlesnake, eastern woodrat, New England cottontail, and cerulean warbler.

These habitat types represent approximately ninety-two percent (*n*=232 stands; 1511.8 ha) of the total acreage (*n*=248; 1643.9 ha) evaluated as potential target species habitat. Additional stands identified as potential target species habitat included: eight hemlock hardwood stands (115.5 ha), five shrub stands (73.2 ha), seven aspen stands (11.2 ha), and five pine (white, red, and unclassified pine) stands (1.4 ha). Seven additional habitat types (i.e., unclassified hardwood, early succession, buttonbush, deciduous, black birch, alder, and wetland) were also identified as potential habitat but only accounted for one and one-half percent (n=8; 23.1 ha) of all stands evaluated as potential habitat for the target species.

n = the number of stands in each habitat type.

CONCLUSIONS

Installation planners and natural resources personnel have an on-going need for reliable, cost-effective techniques for assessing habitat quality. Compliance related issues as well as d
day management activities require installation personnel to make difficult, an
controversial, decisions concerning the use of resources under th
habitat evaluation techniques often require intensive, seasonal fi
followed by extensive model development and validation. Asses
sensitive species habitat is equally difficult because in the past mo
for species with special regulatory status (i.e., threatened or endan
develop a set of regionally- oriented, single-species habitat assessm
used together for multi-species, assessment. The techniques are str
designed to provide a planning/reconnaissance level evaluation of th
associated with developing these types of evaluation techniques are n
obtained can be an extremely useful management tool for installation
resources personnel.

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Dr. Robert Whalin and the installation was commanded by Colonel Bruce How
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THE QWIKLITE BIOLUMINESCENCE BIOASSAY SYSTEM TO ASSESS TOXIC EFFECTS IN THE BIOSPHERE

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INTRODUCTION

The ongoing accumulation of pollutants in the earth's soils and waters presents an increasingly important need to be able to assess the potential risks to our environment with confidence and ease. Regulations exist today to place limits on chemical concentrations in the air, the ground, and in receiving waters. For this reason, early detection of excessive toxicants could mean the difference between simple prevention and costly cleanup.

Our laboratory has developed a bioassay that is capable of accurately assessing acute, chronic, and sublethal toxicity effects and in terms of labor and equipment, is less expensive than costly standard bioassays using fish or invertebrates. The basis of detection is to measure a light reduction from bioluminescent dinoflagellates, a marine single cell phytoplankton found in all oceans of the world. This light output, often referred to as bioluminescence, is a visible blue-green light (470-490 nm) and is commonly observed in the oceans at all depths at all times of the year. The position of these test organims in the food web makes them a valuable indicator of stress on the environment. Early observations indicated that the presence of some toxicants inhibited the amount of light produced by bioluminescent bacteria [1,2,3]. Traditional phytoplankton bioassays involve labor intensive enumerations of algal cells or measuring extracted chlorophyll via fluorescence for biomass estimates. The QWIKLITE bioassay is suited for assessing a wide variety of toxins and at sites where remediation is necessary, whether it be soil or in an aquatic environment. The QWIKLITE bioassay can quickly assess the progress of reducing contamination effects. The response can be measured within 24 hours of test setup and can be conducted for a standard 4-day acute test or 7-day chronic test [4]. Data collection and calculations require approximately 2-3 hours to produce IC_{50} values (where there is a 50% inhibition of light output) or toxicity units (TU).

MATERIALS AND METHODS

The dinoflagellate, *Gonyaulax polyedra,* has been used in our assays to detect toxicity from metals (copper sulfate, zinc sulfate, tributyltin, and dibutyltin) storm drain effluents, leachates of various materials, and marine sediments. Effluent samples are usually diluted from a 100% solution through a series of half-dilutions to 6.25%. If the sample has a salinity of less than 33 parts-per-thousand (normal sea water), commercial grade salts (Americam Society for Testing and Materials, Lake Products, U.S.A.) are added to increase the salinity. Assays have been conducted for as long as 11 days, however, tests of 4 days duration are more typical.

Instrumentation

Testing of the dinoflagellates is accomplished by placing individual cuvettes containing the test material, media, and cells into a darkened test chamber which is attached to a photomultiplier tube (PMT). We have used our QWIKLITE bioassay system which uses a 2-inch diameter 8575 PMT with an S-20 response used in the photon count mode. The top of the test chamber is removable and houses a small adjustable motor which drives a stainless steel shaft terminating in a plastic propeller. The propeller is seated into the cuvette and as the contents are stirred, bioluminescence is generated and measured by the PMT (Figure 1). At the end of each stir period (30 sec), the accumulated "PMT counts" are displayed on a red LED window. Each test period is completed at 24 hour intervals thereafter until completion of the bioassay. Mean light output (PMT counts) is calculated for each experimental group and control. Light output means are then graphed as light output (percent of control) as a function of time. An IC_{50} is then estimated for all assays.

The control box in the QWIKLITE system has face displays for PMT and stirring motor voltages, PMT count LEDS, preset count time settings, manual and automatic switches to run the system, and backlit start, stop, and reset buttons (Figure 2). Neutral density optical filters (ND-1, ND-2, ND-3) (Oriel, Stratford, CT, U.S.A.) are arranged in front of the PMT and between the darkened test chamber housing the cuvette to prevent PMT saturation from the generated bioluminescence.

The QWIKLITE bioassay system is run in an automatic mode. Following insertion of a cuvette into the darkened test chamber, the start button will activate and stabilize the high voltage of the PMT for 5 sec and the scaler/counter accumulates 2 sec of background data (system noise) before the stir motor is engaged to drive the propeller stirring the cells. While stirring (variable preset time, but usually set at 30 sec) PMT counts are accumulated. At the end of the sequence, the PMT count is displayed by the LED display while the voltage to the stir motor and PMT are automatically turned off. In this mode, an entire day's test period is completed in less than 60 min. Each test period is completed at 24 hour intervals until completion of the bioassay (either 4 or 7 days).

FIGURE 1

Simplified schematic of the QWIKLITE test chamber showing a cuvette containing bioluminescent dinoflagellates seated in front of the light detector within the chamber housing.

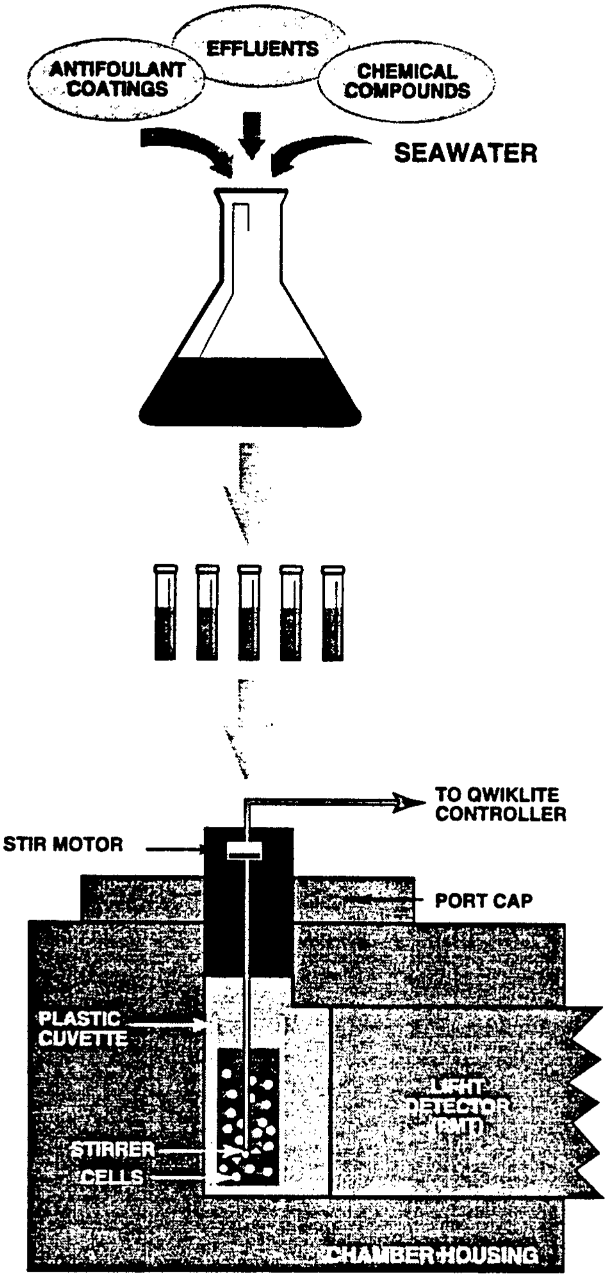
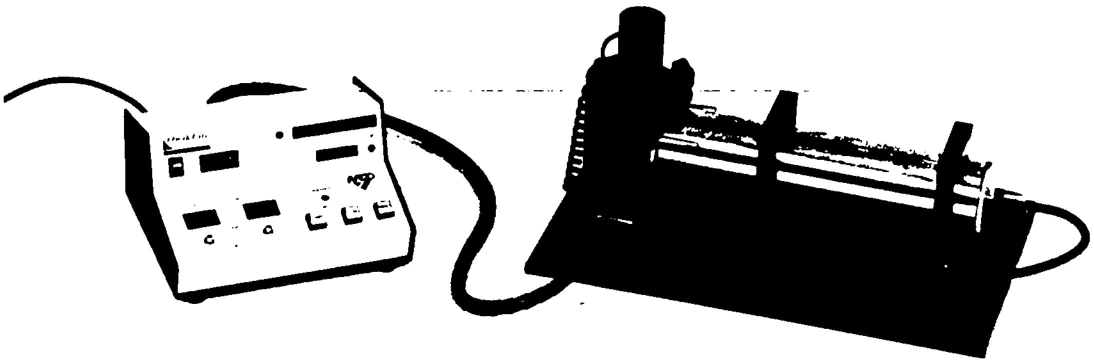


FIGURE 2

Photograph of QWIKLITE bioluminescence system. On the right, the photomultiplier tube (PMT) is attached to the chamber fitted with a removable cap where test samples are inserted. The controller box, on the left, provides power to the PMT, stir motor, displays PMT counts (bioluminescence light output), and PMT and stir motor voltages.



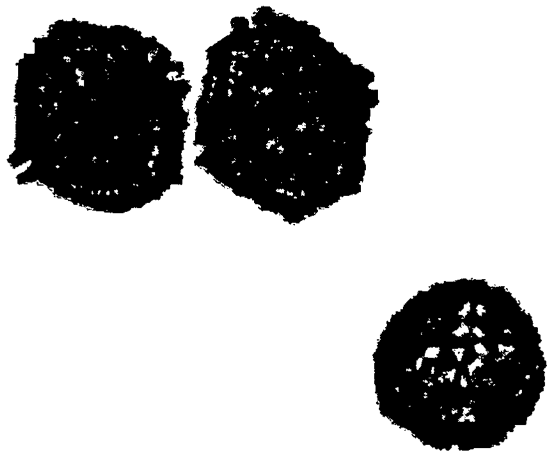
Culture Preparation

The test organism of choice is the photosynthetic species *Gonyaulax polyedra* (Figure 3). It is commonly encountered in coastal waters along most continents of the world. *G. polyedra* was isolated from waters in San Diego Bay. This species can be obtained from several phytoplankton supply houses in North America (North East Pacific Culture Collection, University of British Columbia; Bigelow Marine Laboratory, Boothbay, Maine, U.S.A.). This species is maintained in an enriched seawater medium (ESM)^5. All seawater used for the culture of *G. polyedra* is filtered through membrane filters (0.2 μm) and prepared using ESM. The micronutrient stock solution A, the macronutrient salt stock solution B, and the vitamin stock solution C should be added to the filtered seawater as directed in ASTM Guide E 1218. The ESM filtered seawater is sterilized by microwaving 1

L for 25 min. Seawater may be microwaved in a 1500 mL Pyrex beakers fitted with a watch glass at the top. The salinity of the seawater must be checked and adjusted to 33 parts-per-thousand following microwaving and evaporation of the water. To dilute the hypersaline seawater, deionized water may be added to the heated seawater to a final salinity of 33 parts-per-thousand. Sterilization of ESM seawater is not necessary to conduct the bioassay because of the short test period with respect to potential contamination problems. Cultures are maintained in 2 L Erlenmeyer borosilicate flasks under a light regime of 12:12 h (light:dark) at approximately 400 μEinsteins m^{-2} sec^{-1} (4000 lux) from cool white bulbs. The cells' day-night cycle is reversed to accommodate daytime testing and consequently are in their night phase and most stimulable for light production (bioluminescence).

FIGURE 3

Photomicrograph of the bioluminescent, autotrophic dinoflagellate *Gonyaulax polyedra*. Cell size ~ 60 μm, ventral view. This species is commonly found worldwide along coastal shores and bays.



Cultures of *G. polyedra* are maintained at 19-20°C and are maintained at 3000-4000 cells ml^{-1} of media. Media is normally changed at monthly intervals, however, higher densities may be maintained by changing the media more frequently. For purposes of an assay, a culture 12-20 days old is recommended.

Procedure

The bioluminescent assay is intended to allow calculation of an IC_{50} and usually consists of a control treatment and a geometric series of at least 5 concentrations of the test material. In the dilution water control, dinoflagellates are exposed to dilution water to which no test material has been added. Except for the controls and the highest concentration, each concentration should be at least 50% of the next higher one, unless information concerning the concentration-effect curve indicates that a different dilution factor is more appropriate. At a dilution factor of 0.5, five properly chosen concentrations are a reasonable compromise between cost and the risk of all concentrations being either too high or too low. Effluent samples are usually reduced from a 100% solution through a series of dilutions to 6.25%. A working solution for each concentration is prepared using ESM and adding the dinoflagellates at a concentration of approximately 200 cells ml^{-1}. Three ml aliquots from each working solution are dispensed into 5 replicates for each of the 5 test concentrations and 1 control [4,6]. Trays of the cuvettes are then placed into a constant temperature water bath (19°C) until testing the following day, 3-4 hours into the cells' dark phase.

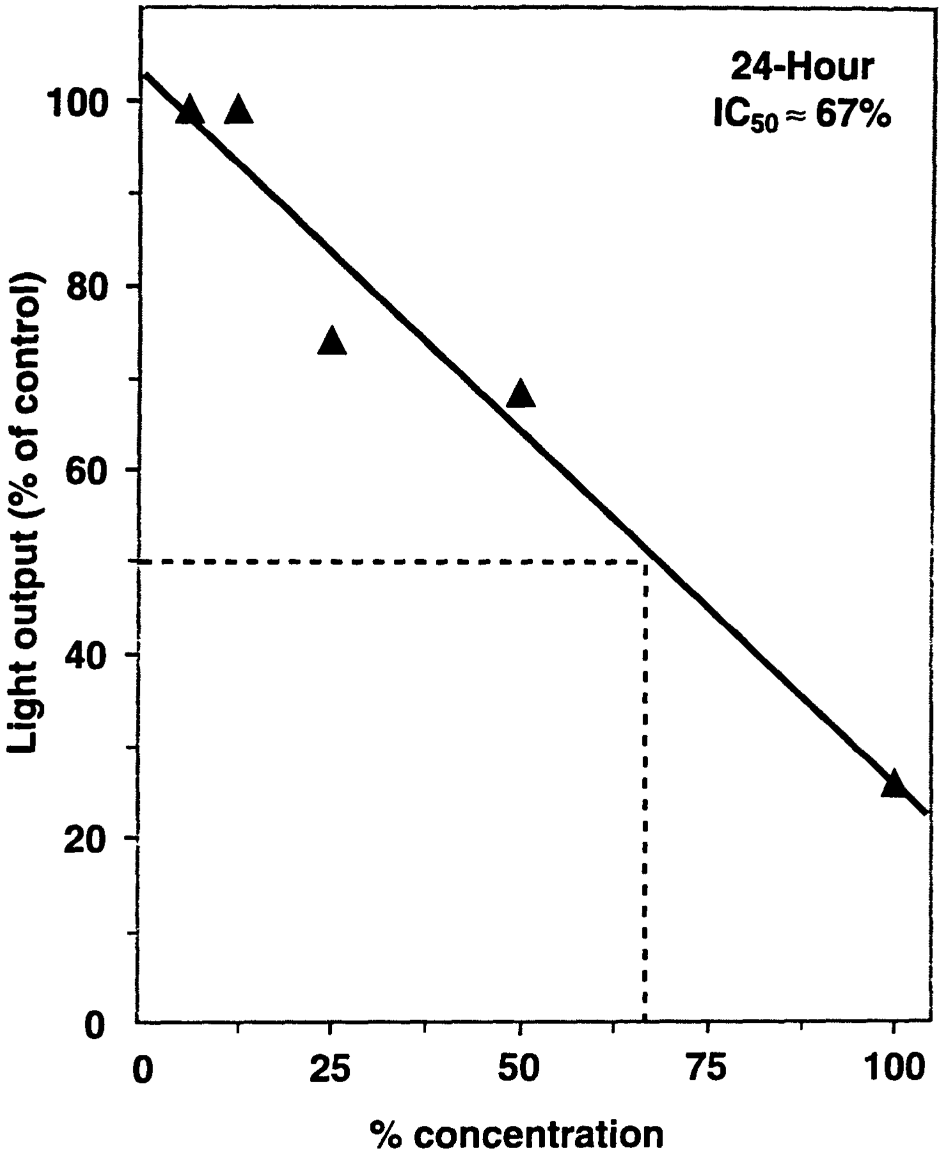
The average bioluminescence detected at a given exposure hour for each test concentration is analyzed as a percent of the control's average. The average of the control measurements, likewise compared as a percent of control, is always equal to 100%. The following formula simplifies:

$$\%\text{ of Control} = \frac{\text{Average of Specific Concentration}}{\text{Average of Control}} \times 100$$

The values for % control for all test concentrations may be plotted against the corresponding concentrations of the test material, and the IC_{50} can be determined by graphical or statistical interpolation to the concentration of the test material at which a 50% reduction from the control's average bioluminescence is exhibited. An example of an IC_{50} (either calculated or estimated concentration which is likely to cause a 50% reduction in light output) is presented (Figure 4).

FIGURE 4

Representative IC_{50} plot for bioluminescence. Cells of *G. polyedra* were exposed to a leachate solution containing dibutyltin (DBT). $IC_{50,s}$ were observed to decrease throughout the entire 96 hour acute test. While the 24 hour IC_{50} was estimated at a 67% leachate solution (shown), the final 96 hour IC_{50} was calculated at a 17% leachate solution which is the equivalent of approximately 34 μg/L DBT.



RESULTS

Copper sulfate effects

In a series of range finding tests (48 hour to 72 hour) to test the sensitivity of *G. polyedra* to a standard reference toxicant, copper sulfate was used at exposures from 10 μg/L to as high as 20 mg/L. The objective of this study was to observe where the IC_{50} occurred. In the intial range finding test (Figure 5), almost total bioluminescence inhibition was observed at all concentrations after 72 hours of exposure. Bioluminescence decreased each day at all exposures. In the next 72 hour range finding acute test, copper sulfate concentrations ranged from 10 μg/L to 2000 μg/L. Almost total light inhibition was observed at concentrations greater than 50 μg/L (Figure 6). No light inhibition was observed at 10 μg/L. A final 48 hour acute test was conducted at copper sulfate concentrations ranging from 10 μg/L to 1000 μg/L. A dose response to copper sulfate was observed from 10 through 30 μg/L. While no reduction in bioluminescence was observed at 10 μg/L, a 45% reduction in bioluminescence was observed with cells exposed to 20 μg/L and a 90% reduction in light output in cells exposed to 30 μg/L copper sulfate (Figure 7). The IC_{50} was observed between 20 and 30 μg/L copper sulfate.

FIGURE 5

Copper sulfate range finding test on bioluminescence inhibition in *G. ployedra*. The left plot presents the day to day effect of copper sulfate concentrations while the right plot displays the end point inhibition following 72 hours of exposure. Range of copper sulfate concentrations used: 0.1 mg/L - 20 mg/L.

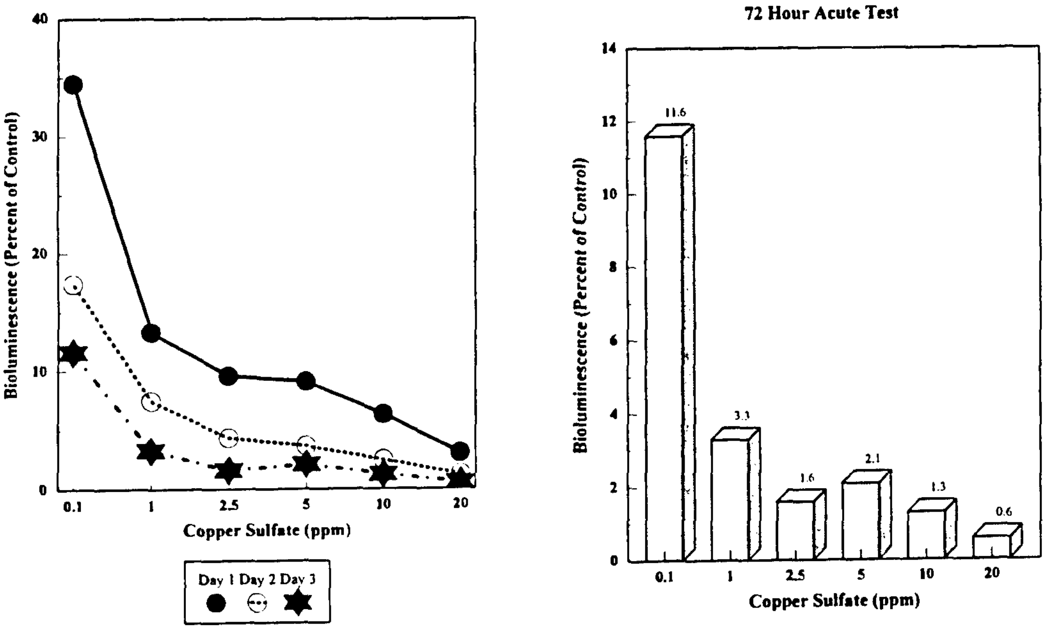


FIGURE 6

Copper sulfate range finding test on bioluminescence inhibition in *G. polyedra*. The left plot presents the day to day effect of copper sulfate concentrations while the right plot displays the end point inhibition following 72 hours of exposure. Range of copper sulfate concentrations used: 10 µg/L - 2000 µg/L.

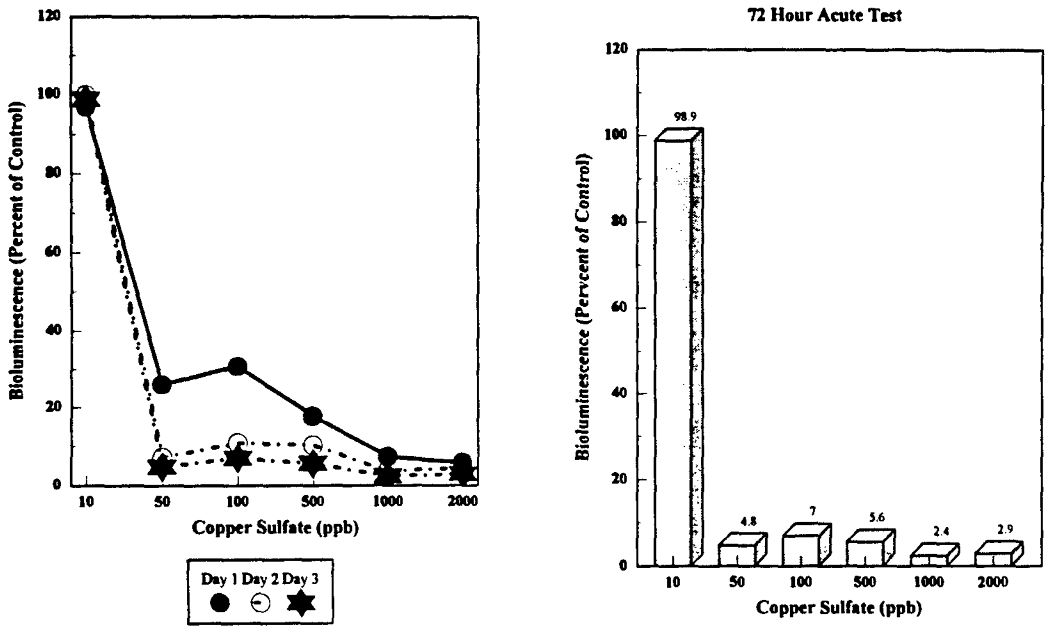
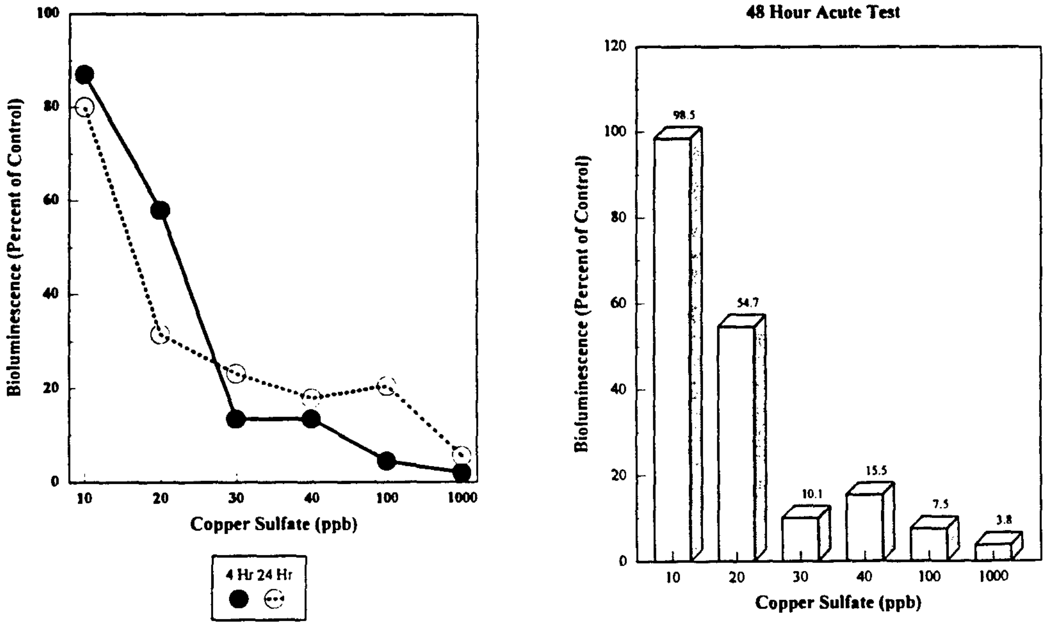


FIGURE 7

Copper sulfate acute test on bioluminescence inhibition in *G. polyedra*. The left plot presents the day to day effect of copper sulfate concentrations while the right plot displays the end point inhibition following 48 hours of exposure. Range of copper sulfate concentrations used: 10 µg/L - 1000 µg/L.

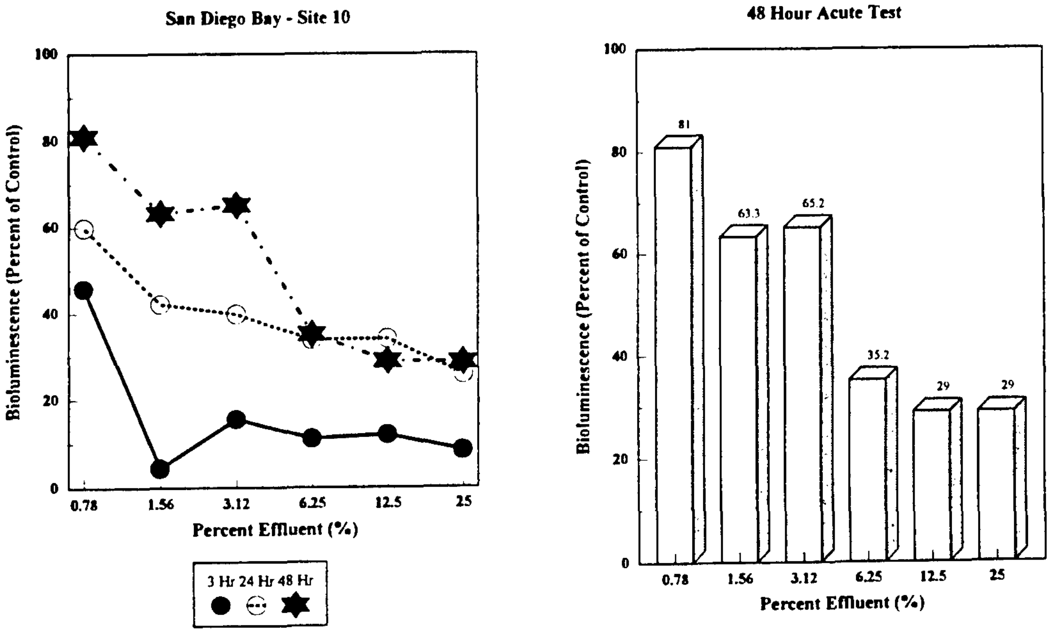


Storm Drain effluent effects

Storm drain effluents, particularly following the "first flush" during a storm can be toxic [4]. For example, an effluent was collected in San Diego Bay and a 48 hour acute test was conducted. A series of dilutions of the storm drain effluent were prepared which ranged from a mixture of 0.78% to a 25% effluent mixture. Toxicity was observed after 3 hours of exposure. However, inhibition of bioluminescence decreased over time at the lowest effluent concentration (0.78%) indicating that an early measurement at 3 hours is probably not indicative of a real toxicity, but rather a stabilization of the cells bioluminescent capacity. A 50% reduction in light output was observed between the 3.1% and 6.2% effluent concentration at 48 hours. While this sample was not analyzed for metals and oils, previous work has demonstrated that 100's of parts-per-billion copper and zinc are found in storm water runoff which exceed the toxicity threshold for *G. polyedra* [4].

FIGURE 8

Storm drain effluent test on bioluminescence inhibition in *G. polyedra*. The left plot presents the day to day effect of the storm drain effluent dilutions while the right plot displays the end point inhibition following 48 hours of exposure.

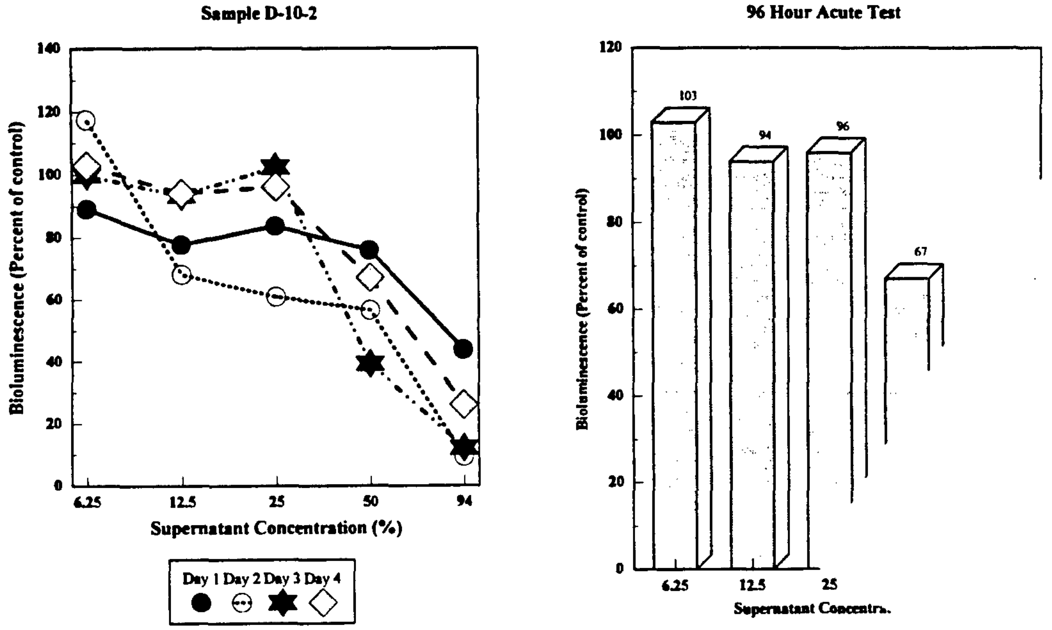


PAH Contaminated Sediment leachate effects

The object of this study was to observe potential toxic effects from a leachate prepared from a sediment-water slurry. Sediment known to have high levels of PAHs (poly aromatic cyclic hydrocarbons ~ 200 ppm) were collected and stored at 4°C for approximately 7 months. A preliminary leachate was prepared by mixing 10 grams of

FIGURE 9

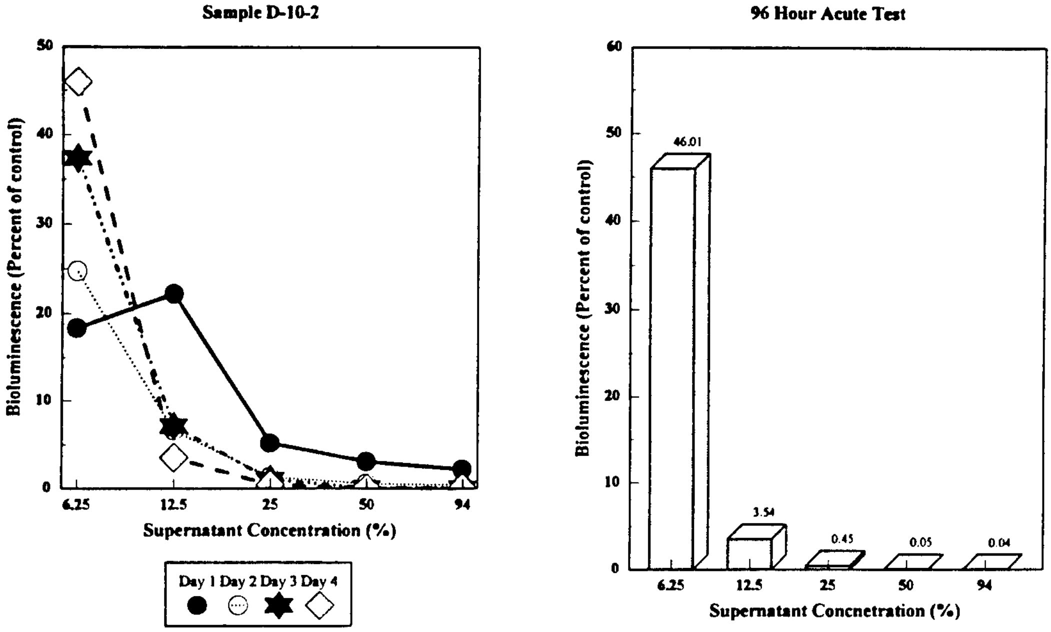
Contaminated sediment elutriate test on bioluminescence inhibition in *G. polyedra*. The left plot presents the day to day effect of the sediment elutriate dilutions while the right plot displays the end point inhibition following 96 hours of exposure.



sediment into 1 L of filtered seawater and letting stand for 18 hours at room temperature (22-23°C). The sediment was allowed to settle while the supernatant was siphoned off and used as a 100% solution. Cells were distributed at leachate concentrations from 6.2% to 94%. Bioluminescence inhibition was measured at the 50% and 94% supernatant concentration after 24 hours exposure. An IC_{50} was observed between these two concentrations at 96 hours exposure. A 37% reduction in light output was observed at the 50% leachate concentration (Figure 9). A heavier sediment to water elutriate mixture was prepared with the same leachate concentrations [7]. Almost total light inhibition was measured by 48 hours at supernatant concentrations of 12.5% and greater. More than 50% of the light was lost at our lowest leachate concentration of 6.25% (Figure 10). It is not clear if the toxicity was due to dissolved PAHs, the level PAHs present in the leachate or to the presence of other potentially toxic heavy metals.

FIGURE 10

Contaminated sediment elutriate test on bioluminescence inhibition in *G. polyedra*. The left plot presents the day to day effect of the sediment elutriate dilutions while the right plot displays the end point inhibition following 96 hours of exposure.



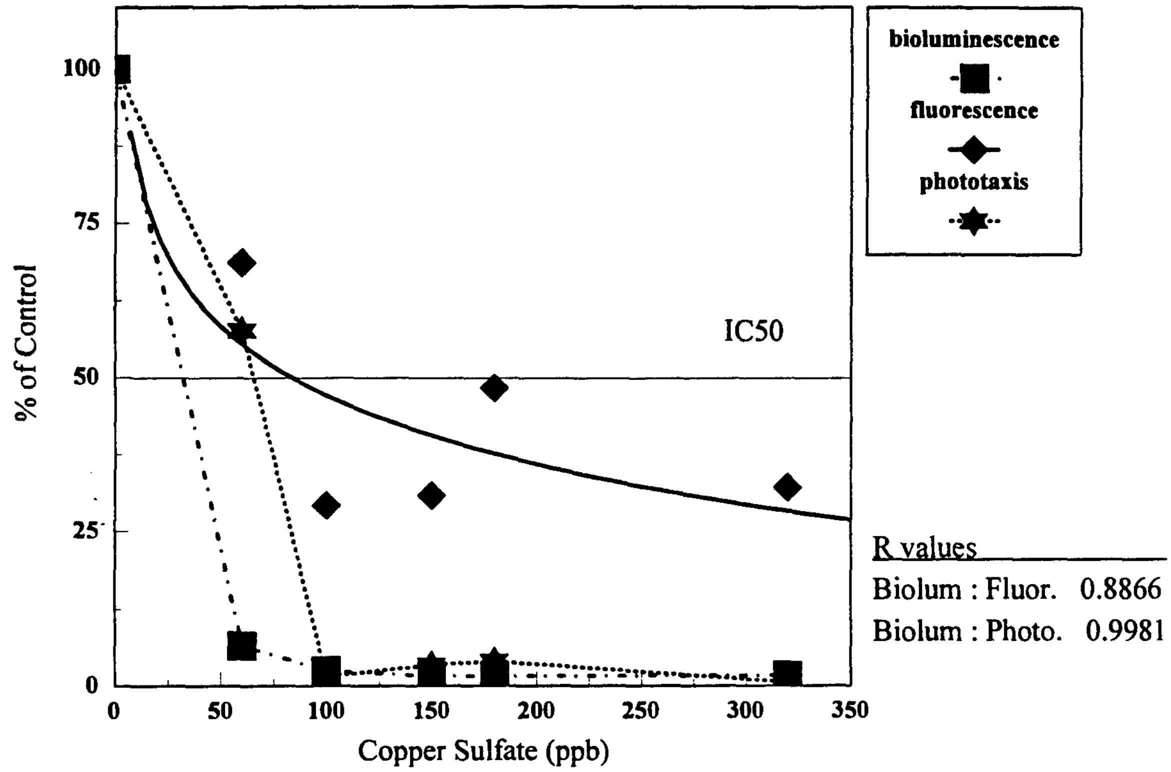
Relationship of bioluminescence to other toxicity indicators in G. ployedra

We also conducted a bioassay which integrates the phototaxis behavior of the cell and the ability of the cell to conduct photosynthetic activitities as well as its ability to produce bioluminescence. Although the migration of *G. polyedra* to and away from a light source can be easily and accurately monitored, little is known about the effects of toxicity on phototaxis behavior. The quantification of cell densities at the meniscus of each test chamber provides an estimate of phototaxis response. Alternatively, chlorophyll fluorescence is a measure of living plant biomass. If the cell cannot migrate in the water column to an appropriate light level, they cannot conduct normal photosynthesis and manufacture proteins for tissue growth. Consequently, this 48 hour bioassay measured three supportive indicators: cell distribution, bioluminescence, and chlorophyll-a fluorescence, making it a more thorough and confident assessment of the effects by copper sulfate.

The number of cells at the meniscus dropped off markedly between 60 and 100 μg/L copper sulfate with an estimated EC_{50} value (50% effect concentration) of 65 μg/L. Bioluminescence and chlorophyll fluorescence has similar IC_{50} values of 70 and 78 μg/L copper sulfate, respectively (Figure 11). Phototaxis was the most sensitive stress indicator to copper exposure while chlorophyll fluorescence was the least sensitive indicator. High correlation coefficients (r) were calculated for bioluminescence and Chl fluorescence and bioluminescence and phototaxis (Figure 11). These results indicate that copper sulfate inhibited bioluminescence, Chl fluorescence, and the phototaxis behavior of *G. polyedra* at comparable exposure levels within a 48 hour exposure.

FIGURE 11

Effect of copper sulfate on *G. polyedra* bioluminescence, chlorophyll fluorescence, and phototaxis. The end point inhibition is plotted at 48 hours of exposure. Phototaxis had an EC_{50} value of 65 µg/L copper sulfate, bioluminescence had an IC_{50} value of 70 µg/L copper sulfate while chlorophyll fluorescence had an IC_{50} value of 78 µg/L copper sulfate.



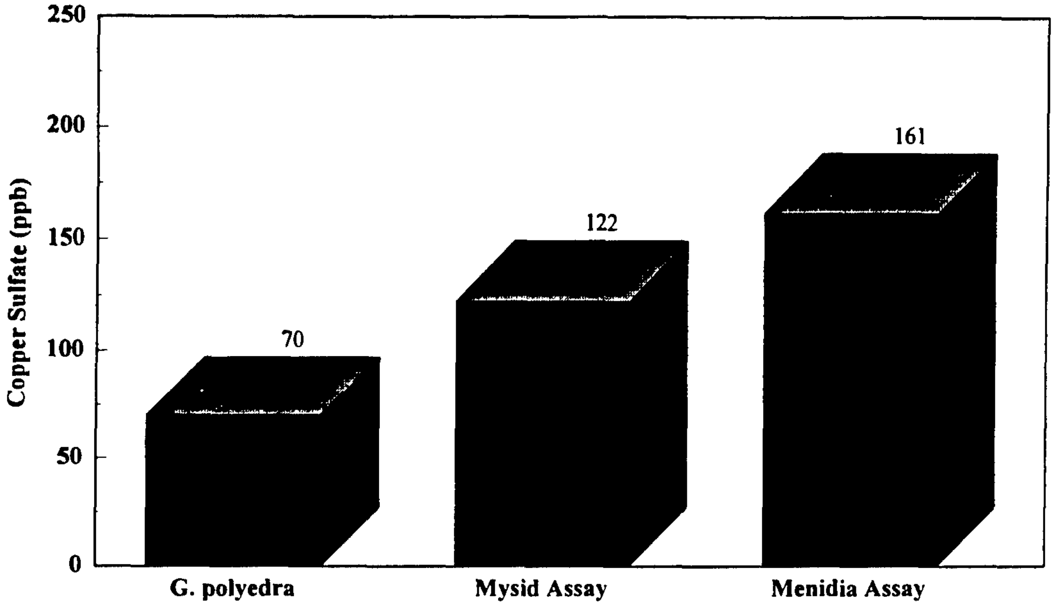
R values	
Biolum : Fluor.	0.8866
Biolum : Photo.	0.9981

Comparison of QWIKLITE endpoints to other standard bioassays

Two other standard bioassays used in our laboratory using copper sulfate as a toxicant have been compared with QWIKLITE. Both the mysid shrimp (*Mysidopsis bahia*) and the minnow (*Menidia beryllina*) 4 day acute survival tests have been conducted with similar concentrations of copper sulfate. The IC_{50} for the QWIKLITE (*G. polyedra*) and the LC_{50} (concentration of a toxicant required to kill 50% of the tested population) are similar in magnitude, the QWIKLITE endpoint being as sensitive as the shrimp and fish acute bioassays (Figure 12).

FIGURE 12

Toxicity endpoints for the QWIKLITE (*G. polyedra*), the mysid shrimp (*Mysidopsis bahia*), and the minnow (*Menidia beryllina*) acute bioassay tests. All endpoints are either an IC_{50} for the QWIKLITE or the LC_{50} for the shrimp and minnow as µg/L copper sulfate.



CONCLUSIONS

Protection of aquatic species requires prevention of unacceptable effects on populations in natural habitats. Toxicity tests are conducted to provide data to predict what changes in viable numbers of individual species might result from similar exposure in the natural habitat. Bioluminescent dinoflagellates have demonstrated comparable sensitivity to other standard bioassays such as mysid shrimp, silverside minnows, and marine algae. The immediate advantage of using this assay would be to evaluate acute effects, chronic effects, and sublethal effects to marine phytoplankton and other marine organisms from exposure to metals, effluent discharges, industrial discharges, organics, and contaminated sediments. The entire bioassay (4 or 7 day test) requires 3 hours to assess the dinoflagellate stock concentrations (microscopic counts), make dilutions of experimental material being tested, and delivery (pipetting) to cuvettes. Daily testing requires less than 1 hour. Finally, the QWIKLITE bioassay system is suited for assessing a wide variety of toxins and at sites where remediation is necessary, whether it be soil or in an aquatic environment. The

QWIKLITE bioassay system can quickly assess the progress of reducing contamination effects which, in the end, translates into reduced labor and overhead costs for conducting bioassays.

ACKNOWLEDGEMENTS

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POLLUTION PREVENTION IN INDUSTRIAL STORMWATER MANAGEMENT

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ABSTRACT

About 30 percent of identified cases of water quality impairment are attributable to stormwater discharges. Congress amended the CWA to require the Environmental Protection Agency (EPA) to establish requirements for stormwater discharges. In 1990, EPA published the permit application rquirements for certain categories of stormwater discharges associated with industiral activity, and discharges from municipal separate storm sewer systems. The industrial stormwater management program emphasizes pollution prevention and reflects a heavy reliance on best management practices (BMPs) to reduce pollutant loadings and improve water quality. Planning, organization, assessment and implementation of pollution prevention are discussed. Assessment of pollutant sources and identification of BMPs are analyzed. Activity-specific and site-specific BMPs are also provided.

INTRODUCTION

The "National Water Quality Inventory, 1990 Report to Congress" indicates that roughly 30 percent of identified cases of water quality impairment are attributable to stormwater discharges. Even after the 1972 amendments to the Federal Water Pollution Control Act (FWPCA, or CWA for Clean Water Act) established the National Pollution Discharge Elimination System (NPDES), efforts to improve water quality traditionally have focused on reducing pollutants in discharges of industrial process wastewater and from municipal sewage treatment plants. Efforts to address stormwater discharges under the NPDES program have generally been limited to certain industrial categories with effluent limitations for stormwater.

In 1987, in response to the need for comprehensive NPDES requirements for discharges of stormwater, Congress amended the CWA to require the Environmental Protection Agency (EPA) to establish phased NPDES requirements for stormwater discharges. To implement these requirements, beginning at the end of 1990, EPA published the permit application rquirements for certain categories of stormwater discharges associated with industiral activity, and discharges from municipal separate storm sewer systems. Stormwater discharge permits provide a mechanism for monitoring the discharge of pollutants to waters of the United States and for establishing appropriate controls.

The industrial stormwater is the stormwater discharge which is associated with industrial activity. It is the discharge from any conveyance which is used for collecting and conveying stormwater and which is directly related to manufacturing, processing or raw materials storage areas at an industrial plant. The facilities which are engaging in "industrial activity" include: those subject to stormwater effluent limitations guidelines, new source performance standards, or toxic pollutant effluent standards, and those for lumber & wood products, paper, chemicals, petroleum refining, leather, primary metals, fabricated structural metals, ship building, mining and oil & gas operations, hazardous waste treatment, storage, or disposal, landfills, land application site and open dumps that receive industrial waste, recycling facilities, steam electric power generation, transporatation, sewage treatment works, construction, and other light industrial facilities.

The industrial stormwater management program emphasizes pollution prevention and reflects a heavy reliance on best management practices (BMPs) to reduce pollutant loadings and improve water quality.

POLLUTION PREVENTION REQUIREMENTS

Pollution prevention is considered to be the most important requirement of the industrial stormwater permit. Stormwater pollution prevention plans consist of a series of steps and activities to identity sources of pollution or contamination on site, and select and carry out actions which prevent or control the pollution of stormwater discharges. Each industrial facility covered by the permit must develop a plan, tailored to the site-specific conditions, and designed with the goal to control the amount of pollutants in stormwater discharges from the site. Each facility will select a pollution prevention team from its staff. The team will be responsible for developing and implementing the plan. The permit requires that the plan contain a description of potential pollutant sources, and a description of the measures and controls to minimize waste in stormwater.

BEST MANAGEMENT PRACTICES

BMPs are measures or practices used to reduce the amount of pollution entering surface water, air, land, or groundwaters. BMPs may take the form of a process, activity, or physical structure. Some BMPs are simple and can be put into place immediately, while others are more complicated and require extensive planning or space. They may be inexpensive or costly to implement.

The measure and controls of pollution prevention in stormwater must include good housekeeping or upkeep of industrial areas exposed to stormwater, preventive maintenance of stormwater controls and other facility equipment, spill prevention and response procedures to minimize the potential for and the impact of spills, testing of all outfalls to insure there are no cross connections, and only stormwater is discharged, and training of employees on pollution prevention measures and controls, and record keeping.

The permit also requires that facilities indentify areas with a high potential for erosion and the stabilization measures or structural controls to be used to limit erosion in these areas, and implement traditional stormwater management measures such as oil-water separators, vegetative swales, and detention ponds where they are appropriate for the site. Facility personnel must inspect the plant equipment and industrial areas on a regular basis. At least once a year a more thorough site compliance evaluation must be performed by facility personnel.

ACTIVITY-SPECIFIC SOURCE CONTROL BMPs

There are specific BMPs for different industrial activities that may contaminate stormwater. The activities that can contaminate stormwater and the specific BMPs which are required to control the pollution are briefly described for common industrial activities:

FUELING STATIONS

The fuel station activities that can contaminate stormwater include spills and leaks that happen during fuel or oil delivery, spills casued by topping off fuel tank, rainfall on the fuel area or stormwater running onto the fuel area, hosing or washing down the fuel area, and leaking storage tanks. The BMPs for fueling station are installing spill and overflow protection, discouraging topping off of fuel tanks, reducing exposure of the fuel area to storm- water, using dry cleanup methods for the fuel area, using proper petroleum spill control, and encouraging employee participation.

VEHICLE AND EQUIPMENT MAINTENANCE

Activities that can contaminate stormwater are engine repair and service which include parts cleaning, shop cleanup, spilled fuel, oil, or other materials, and replacement of fluids, outdoor vehicle and equipment storage and parking which include dripping engine and automotive fluids from parked vehicles and equipment, and disposal of materials or process wastes which include greasy rags, oil filters, air filters, batteries, and spent coolant, degreasers, etc. The BMPs for vehicle maintenance and repair are checking for leaking oil and fluids, using nontoxic or low-toxicity materials, draining oil filters before disposal or recycling, preventing liquid waste from pouring down drains, recycling engine fluids and batteries, segregating and labeling wastes, and using recycled products.

PAINTING OPERATIONS

The painting activities that can contaminate storm- water include painting and paint removal, sanding or paint stripping, and spilled paint or paint thinner. The BMPs for painting operations are inspecting parts prior to painting, containing sanding wastes, preventing paint waste from contacting stormwater, proper interim storage of waste paint, solvents and materials, evaluating efficiency of equipment, recycling paint, paint thinner, and solvents, and segregating wastes.

VEHICLE AND EQUIPMENT WASHING

Stormwater can be contaminated by outside equipment or vehicle cleaning and wash water discharged directly to the ground or storm drain. The BMPs are use of phosphate-free detergents, using designated cleaning areas, and recycling wash water.

LOADING AND UNLOADING MATERIALS

The activities that can contaminate stormwater include pumping of liquids or gases from barge, truck or rail car to a storage facility or vice versa, pneumatic transfer of dry chemicals to or from the loading and unloading vehicles, transfer by mechanical conveyor systems, and transfer of bags, boxes, drums, or other containers by forklift, trucks, or other material handling equipment. The BMPs are containing leaks during transfer, checking equipment regularly for leaks, limiting exposure of material to rainfall, and preventing stormwater runon.

LIQUID STORAGE IN ABOVE-GROUND TANKS

The most common causes of releases from tanks are external corrosion and structural failure, installation problems, spills and overfills and failure of piping systems. The BMPs are properly training employees, installing safeguards against accidental releases, routinely inspecting tanks and equipment, and installing secondary containment.

INDUSTRIAL WASTE MANAGEMENT AREAS

The activities causing contamination include landfills, waste piles, wastewater and solid waste treatment and disposal, land application, processes or equipment that generate dusts, vapors or emissions, outside storage of hazardous materials or raw materials, dripping or leaking fluids from equipment or precesses, and liquid wastes discharged directly onto the ground or into the storm sewer. The BMPs are conducting a waste reduction assessment, instituting industrial waste source reduction and recycling or other treatment of runoff, preventing runoff and runon from contacting the waste management area, and minimizing runoff from land application sites.

OUTSIDE STORAGE OF RAW MATERIALS, BY-PRODUCTS, OR FINISHED PRODUCTS

Causes of contamination are fuels, raw materials, by-procucts, intermediates, final products, and process residuals. The BMPs are those which properly cover or enclose materials.

SALT STORAGE FACILITIES

The activities that cause contamination are salt stored outside in piles or bags that are exposed to rain or snow, and salt loading, unloading areas located outside or in areas where spilled salt can contaminate stormwater. The BMPs include putting it under a roof, use of temporary covers, and enclosing transfer areas.

SITE-SPECIFIC INDUSTRIAL CONTROL BMPs

Site specific BMPs are those preventing pollutants on site from mixing with stormwater. They are briefly described as follows:

STORMWATER FLOW DIVERSION PRACTICES

Flow diversion structures are used to channel storm- water away from industrial areas so that pollutants do not mix with the stormwater.

Stormwater Conveyances (Channels, Gutters, Drains, Sewers)

These conveyances collect stormwater runoff and direct its flow.

Diversion Dikes

These are structures used to block runoff from passing beyond a certain point.

Graded Areas and Pavement

Land surfaces can be graded or graded and paved so that stormwater runoff is directed away from industrial activity areas.

EXPOSURE MINIMIZATION PRACTICES

By eliminating or minimizing the possibility of storm- water coming into contact with pollutants, facilities can eliminate or minimize the contamination of stormwater discharges associated with their industrial activity.

Containment Diking

These are temporary or permanent earth or concrete berms or retaining walls that are designed to isolate spills.

Curbing

Curbing is a barrier that surrounds an area of concern to contain spills, leaks, etc. and prevent their being released to the environment.

Drip Pans

These are small depressions or pans used to contain very small volumes of leaks, drips, and spills that occur at a facility.

Collection Basins

These are permanent structures where large spills or contaminated stormwater are contained and stored before cleanup or treatment.

Sumps

These are holes or low areas that are structured so that liquid spills or leaks will flow down toward a particular part of a containment area.

Covering

This is the partial or total physical enclosure of materials, equipment, process operations, or activities.

Vehicle Positioning

This is the practice of locating trucks or rail cars while transferring materials to prevent spills of materials onto the ground surface, which may then contaminate storm- water runoff. It is a simple and effective method of material spill prevention but is commonly overlooked.

Loading and Unloading by Air Pressure or Vacuum

Air presure and vacum systems are commonly used for transporting and loading and unloading materials. They are simple to use and effective in transferring dry chemicals or solids from one area to another.

MITIGATIVE PRACTICES

Mitigation involves cleaning up or recovering a substance after it has been released or spilled to reduce the potential impact of spill before it reaches the environment.

Sweeping

Sweeping with brooms, squeegees, or other mechanical devices is used to remove small quantities of dry chemicals and dry solids from areas that are exposed to precipitation or stormwater runoff. It is a low cost practice that can be performed by all employees and requires no special equipment or training.

Shoveling

Shoveling is a manual cleanup method that is simple and low in cost. It can be used to remove larger quantities of dry chemicals and dry solids, as well as to remove wetter solids and sludge. It is also useful in removing accumulated materials from sites not accessible by mechanical cleanup methods.

Excavation Practices

Excavation of released materials is typically conducted by mechanical equipment such as plows and backhoes, and can be done using a specifically designed vehicle, tractor, or truck.

Vacuum and Pump Systems

These systems are effective for cleaning up spilled or exposed materials with the benefits of simplcity and speed.

Sorbents

These are materials that are capable of cleaning up spills through the physical processes of adsorption and absorption.

Gelling Agents

These are materials that interact with liquids either physically or chemically. They interact with a material by concentrating and congealing it to become semisoid. The semisoid gel later forms a solid material, which can then be cleaned up by manual or mechanical methods. They are effective in controlling a liquid spill.

OTHER PREVENTIVE PRACTICES

Some preventive measures which can be easily implemented at industrial sites to limit or prevent the exposure of stormwater runoff to conataminants are briefly described as follows:

Preventive Monitoring Practices

These include the routine observation of a process or piece of equipment to ensure acceptable performance. They also include the chemical analysis of stormwater before discharge to the environment.

Dust Control

These are controls that prevent pollutants from entering stromwater discharges by reducing the surface and air transport of dust caused by industrial activities. They include water spraying, negative pressure systems, collector systems, filter systems, and street sweeping.

Signs and Labels

Signs and labels identify problem areas or hazardous materials at a facility. They are a good way to suggest caution and provide instructions on the use of materials and equipment. They are also a good way to organize large amounts of materials, pipes, and equipment, especially on large sites.

Security

A security system can help prevent an accidental or intentional release of materials to stormwater runoff as a result of vandalism, theft, sabotage, or other improper uses of facility property.

Area Control Procedures

These involve practicintg good housekeeping measures such as maintaining indoor or covered material storage and industrial processing areas.

Vehicle Washing

Materials that accumulate on vehicles and then scatter across industrial sites represent an important source of stormwater contamination. Vehicle washing removes materials such as site-specific dust and spilled materials that have accumulated on the vehicle.

SEDIMENT AND EROSION PREVENTION PRACTICES

Any site where soils are exposed to water, wind or ice can have soil erosioon and sedimentation problems. Erosion is a natural process in which soil and rock material is loosened and removed. Sedimentation occurs when soil particles are suspended in surface runoff or wind and are deposited in streams and other water bodies.

Vegetative Practices

These include preservation of natural vegetation, buffer zones, stream bank stabilization, mulching, matting, and netting, temporary seeding, permanent seeding and planting, sodding, and chemical stabilization.

Structural Erosion Prevention and Sediment Control Practices

These practices include interceptor dikes and swales, pipe slope drains, subsurface drains, filter fence, straw bale barrier, brush barrier, gravel or stone filter berm, storm drain inlet protection, sediment trap, temporary sediment basin, outlet protection, check dams, surface roughening, and gradient terraces.

INFILTRATION PRACTICES

These are surface or subsurface measures that allow for quick infiltration of stormwater runoff. They provide some treatment of runoff, preserve the natural flow in streams, and recharge groundwater. They can reduce the velocity of the runoff so that it will not cause damaging erosion. They can also reduce the need for expensive stormwater conveyance systems.

Vegetated Filter Strips

These are gently sloping areas of natural vegetation or are graded and artificially planted areas used to provide infiltration, remove sediments and other pollutants, and reduce the flow and velocity of the stormwater moving across the terrain.

Grassed Swales

These are vegetated depressions used to transport, filter, and remove sediments.

Level Spreaders

These are devices used at stormwater outlets to spread out collected stormwater flows into sheetflow which is a thin, even layer.

Infiltration Trenches

These consist of long, narrow excavation ranging from 3 to 12 feet deep, filled with stone, which allows for temporary storage of stormwater runoff in the open space between the stones.

Porous Pavements, Concrete Grids and Modular Pavements

These allow stormwater to infiltrate so that the speed and amount of runoff from a site can be reduced.

CONCLUSIONS

Industrial stormwater runoff is one of the major sources of water pollution. Pollution prevention through BMPs prevents the contamination of stormwater in the industrial activities at the sites, reducing environmental problems.

REFERENCES

The materials and concepts of this paper are derived from the manual entitled, "Storm Water Management for Industrial Activities - Developing Pollution Prevention Plans and Best Management Practices." EPA 832-R-92-006, September 1992.

OFF-THE-SHELF IN THE FIELD:
INNOVATIVE TECHNOLOGIES FOR NATURAL RESOURCE MANAGEMENT

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INTRODUCTION

Natural resource managers, faced with increased data requirements, have a corresponding greater need for technology to generate, process, store and display that data. Topographic Engineering Center (TEC) researchers are investigating the resource-management potential of the following tools: Multispectral digital videography, black and white digital still photography, Global Positioning Systems (GPS), laptop computers for the field, and GeoLink mapping software. Applications of these components in various combinations have been used in rangeland and wetland monitoring, red-cockaded woodpecker habitat assessment, erosion detection, and kudzu identification. These tools were selected for testing because of their immediate or near-term availability to the natural resource management community.

DISCUSSION

Limited personnel and shrinking budgets are compelling resource managers to find new techniques to complete resource management functions. At the same time, training land degradation and regulatory issues are increasing the data needed by these managers to make informed decisions.

TEC's evaluation has demonstrated that the tools examined below can reduce data collection time and improve data accuracy. While the potential for these individual tools is great, many pitfalls exist, especially hardware robustness and software usability.

System Capabilities

Digital cameras can store photos in black and white or color versions. Black-and-white images occupy approximately 180 kilobytes of disk space while color occupies approximately 500K per image. Thirty or more compressedformat images can be stored in a digital camera. The power source can be either internal battery, external battery or AC adapter. Digital cameras can be extremely portable. The DYCAM Model 3 black-and-white unit used is seven inches long, three inches wide and one inch thick. It weighs about a pound. The number of pixels per black-and- white image has been 496 by 365. Camera cost was $700 last year. Costs should drop as capabilities increase. Kodak predicts having a digital color camera on the market in the early 21st century which costs about $300 (Maney, 1995). Photos can be taken using manual or software keyboard control. Under software control, the camera must be connected to a laptop. Software-controlled photo acquisition allows for remote (i.e., tripod- or extension-mounted) operation for those shots that can not be manually acquired.

Digital images can be manipulated with rudimentary image processing software included with the camera or may easily be exported to a more sophisticated image processing package (such as ERDAS Imagine or Adobe PhotoShop) for finer analysis and manipulation. Software runs in a DOS environment, but acquired images can be exported in a TIF format to several other platforms. Import into PC-based geographic information systems (GIS) software packages accepting the TIF image format is very easily accomplished.

Digital videography combines the flexibility of selectable scale with the processing capability of satellite data. Both high spatial resolution and spectral information are available in digital multispectral videography.

A first consideration for flying digital videography is the type of platform to use. Two light-duty planes were used. The first plane was a Cessna 172, single-engine aircraft, with a hole cut in the fuselage to accommodate the camera. This aircraft costs $150/hour, fueled. The second aircraft was a Piper Aztec, twin-engine, also with a camera port cut into the fuselage for the camera. Cost for this aircraft is approximately about $450/hour. Imagery has been successfully acquired with both planes. However, a switch to the Aztec platform resulted in a) less pitch, roll, and yaw, especially in rough weather; b) a greater ability to fly a designated transect line; c) a faster aircraft for transit to and from study sites; d) greater overall safety afforded by a second engine; e) higher flying height ability for data collection (13,000 feet versus 7,000 feet); f) greater passenger and equipment capacity (five passengers versus three and room for equipment racks; and g) better image quality due to less vibration and movement of the plane.

In our experience, the Aztec has provided a platform to acquire higher-quality imagery at an hourly cost which, although much higher than the Cessna, has been justified by the many added benefits it provided. Videography could be flown from a Department of Defense (DOD) service helicopter if a proper mount or port were available.

The optical head of the camera now used is a beta-system camera. It acquires color or color-infrared imagery simultaneously in four various user-selected bandpasses. The current configuration is three visible channels with one near-infrared (IR) channel centered at 770 nanometers (nm). Resolution is controlled by altitude and focal length. Higher altitudes result in lower resolution. Image frames are 740 pixels long by 578 pixels wide. At a flying altitude of 5,000 feet above ground level and a 24-millimeter focal length, each pixel resolves a ground area (footprint) of 50 by 50 centimeters. At 10,000 feet, the resolution doubles to 100 centimeters, or one meter. There is a linear relationship between pixel resolution and flying height.

Area covered on the ground is directly proportional to pixel size. To increase the ground area covered in an image frame, the video camera needs to be flown at higher altitudes. Greater area covered on the ground is useful from several standpoints: a) fewer image frames means less processing and mosaicking of acquired imagery, b) less time, and consequently less money, is required for flying time in the air, and c) there is a greater chance of identifying multiple photo points within an image frame. With three or more photo-identifiable points, registration of the image to a geographic coordinate system can occur. An alternative to finding photo-identifiable points on the ground is the placement of GPS-located placards on the ground. If the videography system is equipped with a GPS link that geographically positions each image frame to the ground, photo-identifiable ground points and placards are not as important.

Digital video systems are available but are expensive and technically demanding to operate and process data. A must for mapping is the addition of GPS integration into the image frame acquisition process. Placards and photo identification points are not the way of the future.

Videography systems are available for purchase today. Based on our experience, digital video may be more reasonably considered truly off-the-shelf within a few years. The system we have been using still needs improvements, although it was designed and built for environmental-characterization applications. To work with videography at present requires significant investments of time and expertise to acquire reliable imagery.

Global Positioning System (GPS): Several accuracy levels are available to GPS end users. In general, greater accuracy requires increasing amounts of time, money and training. Two positioning services are provided by the Navigation Satellite Timing and Ranging (NAVSTAR) Global Positioning Survey (GPS). One is the Standard Positioning Service (SPS) with which many of us are familiar. The second is the Precise Positioning Service (PPS).

Standard Positioning Service (SPS) GPS instruments require post-processing or real-time radio links for decimeter or better horizontal accuracy. Cost of these receivers is going down quickly. They are also getting smaller and lighter. Integration of GIS into GPS technology gives managers the ability to precisely locate natural resources and attribute these resources in the field. GIS attribution schemes can be programmed in the office and added to a hand-held GPS receiver to be used in the field. Data can be positioned and attributed in the field and then immediately downloaded into a GIS. The ability to enter data into a GIS without risk of entry error is a significant improvement over having to create a data base from field notes.

GPS manufacturers have wisely chosen to quasi-standardize the operation of the keypad so that use of one receiver is similar to the use of many others. Decimeter-level positioning can now be achieved with systems costing $10,000 or less. For inventory of natural resources at decimeter-level horizontal accuracy, post-processing or radio links are necessary.

A radio position-enhancement link can give a natural resource manager guaranteed return to a preselected location. With no radio link, 100-meter accuracy aids but does not guarantee relocating monitoring sites.

Precise Positioning Service (PPS) GPS receivers are easy to use and increasingly affordable. Training costs are minimal; the authors were self-taught in one day. PPS receivers definitely qualify as a technology that will continually get used after purchase because they are not difficult to use and are rugged and small. A Rockwell International Precision Lightweight GPS Receiver (PLGR) model, the authorized military hand-held unit, can achieve 10-meter absolute positioning or navigation accuracy. This level of accuracy is probably acceptable for most (but not all) resource management situations. Neither post-processing nor real-time radio link is required to acquire the position. Precise Positioning Service GPS requires that a decryption module be added to the receiver, thereby allowing it to interpret the encrypted DOD P-code. This allows the unit to decipher satellite information to position the GPS to within +-10 meters on the ground. It is this deciphering of the satellite data that distinguishes this type of unit from the SPS receivers.

Inventory of a resource is accurate only to the acquirable horizontal accuracy. In our investigations, accuracies have ranged between 10 and 20 meters, depending on the region of the country, local landscape, etc. Navigating back to a site for later monitoring can be achieved at the same level of horizontal accuracy. Even with a 20-meter radius, finding a flagged stake in the ground should be fairly simple. Transect end points can be easily programmed into the PPS GPS. The receiver can be used to direct the user to move left or right to stay on track to the target location. This proves especially useful when walking a transect that crosses an impenetrable area that must be bypassed. Distance and direction back to the original transect is continuously recorded, allowing the user to complete the transect on the other side of the impassable area.

Access to a PPS unit is limited to U.S. and allied military forces, but DOD does authorize PPS access to other government and selected private-sector users provided appropriate security requirements and other selection criteria are met (Department of Army, 1994).

GeoLink is a commercially available GPS/GIS/imagery integration software package. The attractive feature of this software package, in brief, is its advertised ability to view GPS positions in real time as an annotated cursor position on an image background and to record GIS attribute data about the position in the field. The software is hardware-independent and accepts input from any GPS system. Attribution of GIS data types can be predefined prior to going into the field for data acquisition.

Our experience with this software running on a 486 laptop has been that the GPS functionality was good. There was no noticeable degradation of horizontal accuracy when processing the data through the GeoLink software. The GIS attribution capability was achievable, and data input into the predefined attribute schemes was smooth. Presentation of imagery background data has been poor. This may be because of several reasons: software limits of only 13 gray scales or color channels; loss of image clarity when displaying images on a laptop display screen approximately nine inches in size; and image degradation during the rectification/rotation operation.

Our main GeoLink goal was field-classifying remotely sensed images. This has not yet been possible. Original high-quality images, once imported into GeoLink, became poor replicas of the originals. Registering the images into geographic space was a major challenge. Fortunately, map backgrounds did not suffer the same level of display degradation visited on our images. We feel that with improved image-display capabilities, GeoLink can provide resource managers with the ability to field-classify remotely sensed images.

An **active-color-screen, 486 laptop PC** has been our platform for digital videography, black-and-white, digital, still-camera shots, and GeoLink software. It worked successfully in the aircraft with the digital video camera and fairly successfully in the field with the black and white digital camera. Using the lap-top to attempt to classify imagery in the field, however, was a failure.

For field work with a laptop, a frame backpack is sold that allows the computer to be mounted onto a rigid tray in front of the user. This backpack configuration is a great deal better than carrying the laptop. Current backpack cost is about $300. The major disappointment with a laptop in the field (particularly a color laptop) has been that the screen is almost invisible in direct sunlight. Black-and-white displays are better for viewing outdoors but they, too, are not easy to see. Active-screen laptops use battery power quickly; four hours of use before recharging can be expected. An additional battery and/or a car-battery converter are recommended. Collecting data in the field and directly importing the data into the computer is a real advantage. Because of the difficulty with display visibility in direct sunlight, laptop work outdoors should be concentrated in areas of shade or even inside a vehicle.

Case Studies

TEC has been evaluating the preceding tools at several project locations: Jornada Experimental Range (JER), New Mexico; Fort Benning, Georgia; and Cedar Run, Virginia. Applications for which we applied these tools are discussed for each site.

Jornada Experimental Range (JER), New Mexico- (Digital B&W Camera, Laptop PC, GeoLink) The black-and-white, still, digital camera was used at JER to demonstrate a capability to record one-meter-square vegetation quadrat data along a transect. Historically, JER quadrat data were sketched and recorded on graph paper. The digital camera was used to acquire both overhead-looking and oblique shots. A laptop operated the camera shutter for the overhead shots due to the height of the camera over the ground (approximately 13 feet). Surrounding scenery shots were taken and were very useful, although color would have been a more impressive medium.

A problem that needed to be corrected for the successful use of the camera was adjusting the proximity of an external battery cable to the laptop/camera serial cable. The power cable was taped together with the serial cable and caused the camera image data to be corrupted on export from the camera into the laptop. Once the battery and serial cables were separated, camera images were imported successfully into the laptop.

JER quadrat images of mesquites and black gramma grasses were easily imported into a commercial image-processing package. An unsupervised clustering algorithm successfully assigned the vegetation types to separate groups in a bitmap format. Unfortunately, the clustered groups could not be output as a vector product as desired. Had vector products been achievable with the image processing package used, they would have been imported into a GIS and, given the same quadrat over different dates, change-detection evaluation could occur. This technique will again be attempted given newly received image processing software. The benefits being pursued are a permanent digital record, an accurate change detection evaluation, and an ability for junior field personnel to collect images for senior personnel to evaluate in the office.

A scanned aerial photo scene was displayed on a laptop with the hope that some degree of better understanding of the imagery could be realized in the field. The scale of the imagery (1:60,000), the poor quality of the imagery as displayed by the GeoLink imagery module, and the difficulty in seeing the laptop display in sunlight made this task an impossibility.

Cedar Run, Virginia- (Digital Videography, Digital Camera, PPS GPS, GIS/GPS) Cedar Run is a man-made wetland site. Seasonal digital videography has been successfully flown over the site using a Cessna flying at 3,500 and 5,000 feet above ground level. Image frames have been classified using supervised techniques based on ground spectra reflectance data. Wetland vegetation has been shown to have a particular reflectance signature that can be acquired from ground-based and airborne-based measurements using digital classification. Image processing software is "trained" to cluster the digital signatures for various vegetation types within the videography image frame. Next, the software interprets the entire frame and assigns codes to particular vegetation groups. For Cedar Run, vegetation groups were classified, mapped, and field-validated. In general, agreement between screen-based and field-based vegetation mapping was good. Quantitative classification errors are now being compiled.

Precise Positioning System GPS was used at Cedar Run to position placards at ten-meter horizontal accuracy for future registering of image frames. Placard size and color against rock and grass backgrounds were evaluated. At 5,000 feet, both white and blue 18-inch squares were visible and spectrally distinguishable on the image frames. The GPS performed without problems acquiring positions in an averaging mode.

Digital camera shots of wetland community plants (i.e., cattails, rushes, etc.) and general shots of the wetland area were taken. The shots were taken with an external battery source attached and with the internal battery. Thirty-two images were taken and upon review were judged very acceptable. Our experience has been that the internal battery has a very short life (approximately two hours) before it needs to be recharged.

Fort Benning, Georgia (Digital Videography, PPS GPS) Fort Benning has been the site of recent investigations into delimiting a) preferred red-cockaded woodpecker habitat (longleaf pine), b) kudzu plants, and c) erosional areas.

Leaf-off digital videography flights over a Fort Benning test site have been flown at 5,000 and 7,000 feet above ground level in a Cessna. Late March flights were flown over the same test site at 5,000 and 10,000 feet above ground level in a Piper Aztec. Resolution of the imagery picture elements collected are 50, 70 and 100 centimeters, respectively. This high degree of spatial resolution allows for a high-resolution vegetation community classification. Vegetation-mapping flights over unexploded ordnance areas or the like present favorable opportunities for high spatial digital videography systems. Special sites requiring high spatial understanding might best be mapped using digital videography as a supplement to other data sources (i.e., SPOT, NHAP, Landsat).

Investigations are ongoing as to the ability to distinguish longleaf from loblolly and shortleaf pine species. Ground-collected radiometric readings show measurable differences in the spectral signatures at certain wavelengths. Expectations are high for airborne-acquired imagery to depict these same spectral differences.

Differentiating kudzu from other background vegetation shows promise, especially with the late-March imagery. All vegetation was "greening" up at that time except the kudzu. Both the visual figure/ground relationship of kudzu against other vegetation and the high spectral signature differences of kudzu versus other plant species make remote kudzu characterization an anticipated reality. Once delimited, kudzu eradication management decisions can be made. Erosional areas are identifiable based on the high spatial capability of the camera. Mapping significant erosional gullies appears possible with stereo coverage from a digital video system.

Investigations will soon begin at TEC to see if high-level digital elevation matrices can be compiled from stereo digital videography image frames. We anticipate that meter-level elevation postings may be derived. Lack of a rigorous photogrammetric model for our digital multispectral video (DMSV) would mean that the newly created postings would not be absolutely correct in their location, but in comparison to the alternative use of a digital elevation model (DEM) with 30-100-meter postings, a DMSV-generated DEM looks quite attractive. For special erosional area studies, this might greatly facilitate erosion models that rely on slope, aspect, and run factors.

Precise positioning service GPS was used at Fort Benning for positioning ground placards to register the videography image frames. It also was used to identify areas of erosion and kudzu. Either point data or polygonal data can be recorded. Polygonal data might best be collected if walking a boundary of kudzu or an erosion depositional area. Point data might be the center of a kudzu area or erosional area. The transect to be flown for the digital videography flight was walked on the ground using the navigation routing feature of the GPS. Placards were dropped in clearings and notes taken regarding the landscape. Time required for on-the-job training of Benning personnel in the use of this technology was very short.

Experiments with using the PPS receiver in a Cessna aircraft for waypoint navigation were attempted over Fort Benning and Cedar Run. Waypoints were established for navigation and programmed into the receiver. The reception of the signal was fine in the aircraft. Logistically, however, because the GPS operator was not the pilot, it was an unworkable situation. Waypoints changed too quickly for adequate communication between the pilot and the GPS operator. Later flights in the twin-engine Aztec equipped with conventional aircraft GPS operated by the pilot proved efficient. The preferred solution at present is onboard aircraft GPS such as we used in our second mission flown over Fort Benning.

CONCLUSIONS

Each of the aforementioned tools can be used in the natural resource management community. They can augment any current practices used for data inventory and monitoring. The tools vary in price and usability. Of the tools we evaluated, several are highly recommended. A PPS GPS is very highly recommended due to price and ease of use. Federal DOD organizations should be able to secure one of these receivers and the encrypted key necessary to achieve 10-meter horizontal accuracy. A black-and-white, or preferably color, digital still camera is very highly recommended because it too is affordable and easy to use. GPS systems with the added functionality to record GIS attribution data in the field for immediate importation into geographic information data bases represents a significant advancement in data acquisition.

A digital videography system is an expensive investment and is not a simple tool to work with. This technology shows enormous potential and should be closely monitored. Our expectation for the DOD community would be either group purchase of such a technology, whereby the equipment and training costs could be shared between installations, or a purchase by a single installation with numerous applications identified to justify the cost (again, costs of technologies such as these are coming down rapidly).

GeoLink software did not perform as hoped, due to the imagery background incapabilities. Digital map backgrounds were fine, GPS positioning was acceptable, and the attribution capability was programmable and workable without flaws. If there are future improvements to the background imagery module of this software package, a resource manager could conceivably annotate large-scale imagery in the field using the GPS and GIS attribution capability resident on GeoLink. Again, however, a remaining weak link to this field data acquisition methodology is the laptop computer. The laptop's screen is not going to get much larger, if at all; sunlight continues to "wash-out" color monitor visibility so black-and-white displays are a must; and the laptop itself is clumsy to use in the field.

Integrating and creatively applying technologies that are already on the market is an effective step to quickly transferring tools to the natural resource managers. While research and development (R&D) for better natural resource management technology continues, tools that can be used today are being demonstrated and shown to be effective for particular applications. In essence, TEC and other Corps of Engineers R&D labs can act as "technology scouts" for the natural resource manager who often has neither the time nor the funding to do these types of investigations. Sharing our experiences with commercial-off-the-shelf technologies may assist resource managers in their selection and usage of appropriate technologies to assist in the overall management process.

NOTE: TEC does not endorse any particular vendor or product mentioned in this paper.

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INTEGRATED NATURAL RESOURCES MANAGEMENT PLANS (INRMPs): A CURRENT INITIATIVE IN DEFENSE NATURAL RESOURCES MANAGEMENT[1]

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INTRODUCTION

We are beginning to see how devastating human activities have affected natural systems in the United States. A recent study of endangered natural communities in the United States lists 126 ecosystems that have declined by 70 percent or more since European settlement began, mostly in California, the Midwest, Northeast, and South.[2] Ecosystems categorized as critically endangered have experience over 98 percent decline, those classified as endangered, as much as 98 percent decline, and those listed as threatened, as much as 84 percent decline. The study concluded, "A continually expanding list of endangered species seems inevitable unless trends of habitat destruction are reversed soon through a national commitment to ecosystem protection and restoration." The report suggests that integrated conservation plans be developed for all ecosystems. These "need not be restricted to pristine sites, which are now almost nonexistent. Rather, management and, where possible, restoration plans for native biodiversity in partially disturbed sites should be considered."

The Department of Defense (DoD) manages over 25 million acres of land. Many millions more are managed by components of the National Guard. The primary use of these lands is in support of the defense of the United States. Trees, stable soil, and a natural environment are important to the military mission, directly affecting the state of readiness. Timely natural resources management is important to ensure sustainable quality and usefulness of training and testing lands. Thus, it is not surprising that the DoD is one of the major federal agencies managing land and natural resources.

The interior parts of most installations have been isolated from the impacts of urban development. Many date back to the beginning of the civil war. A few installations date back to the time of the revolutionary war. Some of these military lands are home to a rich assemblage of native fauna and flora. Although many installations devote a sizeable portion of natural resources management to the production of upland game species, fish, agricultural crops, and selected trees, they provide the shelter and refuge necessary for the resting, feeding, and nesting of threatened wildlife such as neotropical migratory birds.

Neotropical migratory birds nest in the United States and Canada and migrate to the tropical regions of Mexico, Central America, South America, and the Caribbean for the winter. Over half of all bird species nesting in the United States are neotropical migratory birds, including many waterfowl, birds of prey, shorebirds, and songbirds. Precipitous declines in neotropical migrants have occurred over the last decade, with over 70 percent decline noted for some states in the eastern United States.[3] The implementation of sound Integrated Natural Resources Management Plans (INRMPs) is instrumental to the successful protection and recovery of such threatened species and leads to sustainable biodiversity.

The focus of integrated natural resources management represents a shift in terms of managing forests as dynamic natural systems, instead of managing product-producing programs focusing on fish and wildlife, timber, and crops or protecting endangered species and soil. Professional natural resources managers are beginning to think of themselves as part of an overall natural resources organization rather than just within a fish and wildlife, forestry, outdoor recreation, or land management unit.

GOVERNMENT'S VIEW TOWARD ECOSYSTEM MANAGEMENT

The administration's FY 1995 budget proposal included $610 million in discretionary spending for ecosystem management initiatives.[4] The initiatives entail pilot ecosystem management restoration efforts: (1) the old-growth forests of the Pacific Northwest, (2) south Florida, including the Everglades and Florida Bay, (3) the urban watershed of the Anacostia River in Maryland and the District of Columbia, and (4) Alaska's Prince William Sound, damaged by the March 1989 oil spill.

The budget report states that the administration is considering (1) managing along ecological boundaries, (2) ensuring coordination among federal agencies and increased collaboration with state, local, and tribal governments, the public, and Congress, (3) using monitoring, assessment, and the best science available, and (4) considering all natural and human components and their interactions.

In 1993, the White House Office on Environmental Policy, established an Interagency Ecosystem Management Task Force to implement an ecosystem approach to environmental management. Ongoing efforts focus on examining major issues that influence the effectiveness of ecosystem management, such as the budget process, legal authorities, and information management. An important prerequisite for implementation of a national ecosystem management initiative involves identification of "the priority to be given to the health of ecosystems relative to human activities when the two conflict."[4]

All four of the primary federal land management agencies are using or will soon be using an ecosystem approach in managing their lands and natural resources. The Forest Service has a new policy of multiple-use ecosystem management on national forests and grasslands and will be conducting large-scale regional assessments: Mid-Atlantic, Columbia River, and Southern Appalachia.

The Bureau of Land Management has adopted principles of ecosystem management to guide its management of the public lands and their natural resources. The United States Fish and Wildlife Service is developing its policies and strategy for biodiversity management and overall ecosystem management. The National Park Service is developing its ecosystem management strategy and policies, focusing on comprehensive regional ecosystem management and restoration through new partnerships, alliances, and coalitions.

One agency which is active in controlling soil and wind erosion on many Army installations is the Natural Resources Conservation Service (NRCS), formerly the Soil Conservation Service (SCS). This agency has been active for over one-half century in providing natural resources management to private agricultural land users throughout the United States. Evolving from basic soil erosion control strategies, its current program of technical services focuses on watershed and overall ecosystem management.

The NRCS has developed an ecosystem-based nine-step planning strategy involving problem identification, determination of objectives, inventory of resources, analysis of resource data, formulation of alternatives, evaluation of alternatives, decision-making, plans implementation, and plan evaluation. The planning process recognizes that boundaries are assigned to ecosystems for convenience to facilitate analysis or manipulation and not to suggest that ecosystems function solely within such boundaries.

The United States Army Environmental Center (USAEC) and the NRCS have executed a Memorandum of Understanding (MOU) to facilitate Army - NRCS cooperative efforts. The MOU serves as the authority for an Army installation to execute a specific interagency agreement with a NRCS state office to develop and implement ecosystem management plans on a reimbursable basis.

HISTORY OF SIKES ACT AND PENDING AMENDMENTS

Beginning in 1960, the Sikes Act provided for coordination among state and federal fish and wildlife agencies and military installations. In 1968, an amendment established hunting and fishing programs on the installations. A 1974 amendment identified the need to control off-road vehicle traffic and plan for the management of fish and wildlife and corresponding habitats. Provision for the protection of threatened and endangered species on military lands was added in 1982. The last amendment in 1986, requires the use of trained professionals to guide the development of comprehensive management planning of all natural resources.

Major revisions to the Sikes Act failed to pass in 1994 due to last minute political maneuvering that had nothing to do with the H.R. 3300, which was passed by the House of Representatives and went through the Senate Environment and Public Works Committee. This bill has been re-introduced in 1995. The bill would change the Sikes Act to require INRMPs in place of the presently required Cooperative Fish and Wildlife Management Plans. It would also add to the required elements within these plans as shown below (* = Existing Sikes Act law; + = Proposed 1995 revision language):

- * Fish and wildlife habitat improvements.
- * Range rehabilitation for support of wildlife.
- * The control of Off-Road Vehicles.
- * Specific habitat improvements and protection for T&Es.
- * Wetland protection, restoration, and creation.
- + Consideration of conservation needs for all biological communities.
- + Establishment of specific natural resources management goals, objectives, and time-frames for proposed actions.
- + Needs for fish and wildlife management, land management, forest management, and wildlife-oriented recreation.
- + The integration of, and consistency among, the various activities under each INRMP.
- + No net loss in the capability of installation lands to support the military mission.
- + Sustained use by the public to the extent that such use is consistent with the military mission and the needs of Fish and Wildlife Management.
- + Professional enforcement of natural resources laws.

The Sikes Act has other provisions that relate to the implementation of an INRMP. These provisions include:

- Regular review of an INRMP and its effect, not less often than every five years.
- Installation Commander authorization to collect, spend, administer, and account for fees involved with the sale of special installation hunting and fishing permits.
- Provisions for spending hunting and fishing permit fees exclusively for the protection, conservation, and management of fish and wildlife, including habitat improvement, and related activities in accordance with the INRMP.
- Exemption from procurement of services under Office of Management and Budget Circular A-76 and any of its successor circulars.
- Priority for contracts involving the implementation of an INRMP in coordination with state and federal agencies having responsibility for conservation of fish and wildlife.
- Cooperative agreements with states, local governments, nongovernmental organizations, and individuals to implement an INRMP which are exempt from the Economy Act which requires lengthy justifications.
- Authority to enforce all federal laws relating to the conservation of natural resources on federal lands with respect to violations of those laws which occur on military lands.
- Requirement for sufficient numbers of professionally trained natural resource management and natural resources law enforcement personnel to be available and assigned responsibility to implement an INRMP.

USAEC's INRMP GUIDELINES INITIATIVE

For most installations, Army regulations (e.g., AR 200-3) require Integrated Natural Resources Management Plans (INRMPs) to be used as planning and operations tools for installation programs. Existing guidance for preparing these plans is outdated by changes in laws and natural resources management policies. An ecosystem management approach to natural resources management to better protect biodiversity and meet other needs must be more effectively incorporated within installation INRMPs.

The USAEC has implemented an initiative to develop new guidelines for the preparation of INRMPs and to apply these guidelines in the development of four INRMPs for Army installations, together with supporting National Environmental Policy Act (NEPA) documentation. The new guidelines will be consistent with Army policy, federal laws, and national natural resources management philosophies.

MILITARY MISSION AND INRMPs

The primary land use activity on an installation is its mission. It is the reason for the installation's existence. INRMPs are not intended to interfere with mission-related activities. Often, implementation of INRMPs will enhance mission capability by providing improved training conditions. On active ranges, testing, and training lands, natural resources management activities are conducted in harmony with, and complimentary with, military activities or they are not conducted at all.

The INRMP Guidelines emphasize that the concept of "no net loss in the capability of the land to support the military mission" is a major goal of the natural resources program. In this light, the Army's Integrated Training Area Management (ITAM) program should be an integral part of an INRMP to provide direct support to the military mission.

Training often involves repetitive use of land by heavy wheel and track vehicles, resulting in a marked effect on soil stability, vegetation stress, wildlife movement, water quality, and cultural resources. Construction of sediment basins, vegetated filter strips, diversion terraces, hardened roads and stream crossings are activities incorporated into INRMPs that are value added features which strengthen the military mission.

LINKING NEPA TO INRMP DEVELOPMENT

The Administrative Procedure Act (APA; 5 U.S.C.: 701-706) is an omnibus statute providing the waiver of sovereign immunity and right to recourse in federal courts. "The APA tells courts that they can only set aside administrative decisions of agencies when they find that the agency's actions, findings, or conclusions were: (a) arbitrary and capricious; (b) an abuse of discretion; or (c) otherwise not in accord with the procedures required by law."[5] In simple terms, federal agencies need to ensure that relevant factors are considered during decision-making and that procedural rules under relevant statutes and regulations are followed.

As a signer of an INRMP, the Army becomes a decision-maker relevant to land use and conservation management. Thus, the Army makes administrative decisions in INRMPs, not merely managing the performance of contractors. Since there is no enforcement provisions under the APA until the agency has made a decision, a substantial waste of resources can result from unstructured decision-making.

Only an "administrative record can demonstrate whether the agency considered relevant factors, properly exercised its decision, and followed an appropriate procedural path."[5] Documentation, such as the preparation of Environmental Assessments (EAs) or Environmental Impact Statements (EISs), under NEPA can provide such an administrative record. Such structured paths to decision-making, entailing data gathering, scientific analyses, consultation and coordination, and public disclosure and review, provide a solid foundation and documentation for INRMP decisions to be based on a rational, thorough, deliberative decision-making process.

The 5-year land use plans embedded within the INRMPs can be interpreted to constitute a commitment to a major federal action. Such actions defined within NEPA (Section 1508.18, and implementing regulations) require NEPA documentation.

PREPARING INRMPs: AN EXERCISE IN CONSENSUS BUILDING

The *first step* in the process of preparing an INRMP involves gathering and reviewing pertinent background information such as:

- Mission Statement and Plans
- Natural Resources Management Plans
- Cultural Resources Management Plans
- Master Plan(s)
- Endangered Species Management Plans (ESMPs)
- Fauna and Flora Inventories
- Wetland Delineations
- Natural Heritage Database
- Land Condition Trend Analysis surveys (LCTAs)
- Natural Communities, Sensitive Species, and Habitat Studies
- Forestry Inventories and Forest Management Plans
- Native Plant Seeding Program
- Landscaping Plans
- Cooperative Fish and Wildlife Management Plans
- Game Census Data and Game Management Plans
- Pest Management Plans
- Installation and Local Soil Surveys
- Stormwater and Soil Erosion Management Plans
- Water Quality Assessments
- Watershed Management Plans
- Integrated Training Area Management Implementation Plans
- Unit Leaders Environmental Guidebook
- Soldier Environmental Handbook or Field Card
- Installation Environmental Impact Statements (EISs)
- Recent Environmental Assessments (EAs)

The *second step* is to meet with installation individuals involved or affected by INRMPs. Examples of these individuals or their equivalent include:

- Chief, Environment and Natural Resources Management Division
- Chief, Natural Resources Section
- Chief, Regulatory Branch
- Chief, Fish and Wildlife
- Chief, Forestry Branch
- Chief, Conservation Branch
- Chief, Game Enforcement Branch
- Chief, Outdoor Recreation Branch
- Installation ITAM Coordinator
- Director of Planning, Training, and Mobilization
- Chief, Range Control Operations
- Installation Master Planner
- Director of Personnel and Community Activities
- Chief, NEPA Coordinator
- Chief, Cultural Resources
- Chief, Real Property
- Environmental Awareness Coordinator
- Installation Public Affairs Officer
- Provost Marshall

Examples of external individuals to be contacted are:

- Local state representative of its Department of Wildlife and Fisheries
- Local state game supervisor
- Regional representative of the United States Fish and Wildlife Service
- Local representative of the NRCS
- Representative of a nearby federal park, memorial, or forest
- Representative of a nearby state park or state forest
- Representative of nearby federal, state, or local wilderness area
- Coordinator of any local or regional ecosystem management program

These meetings with installation personnel should focus on clarifying their perceived role and plans for their particular program. External interviews focus on perceived concerns and aspirations with respect to the objectives of the installation's natural resources management program.

The *third step* in the INRMP preparation process is to take time to assimilate the gathered information and arrange it within the format delineated in the INRMP guidelines. Questions are formulated to fill information gaps, and ideas for specific plans are articulated, focusing on the beneficial effects of synergism across resource management areas.

The *fourth step* is to meet again with installation personnel to fill information gaps and to identify collaborate efforts which share common goals. This is the most important step in INRMP development. It focuses on consensus building and attainment of feelings of unanimity in the approach to natural resources management.

It is important to capture the holistic nature of the proposed plans and benefits of integration in meeting shared goals and overall enhancement of ecosystem management objectives. Notation should be made of any intended outreach efforts to coordinate and integrate installation INRMP activities with local, state, or regional ecosystem management initiatives.

By choice, a subsequent meeting can be held wherein stakeholders representing all installation parties review the salient aspects of the draft INRMP. This meeting also can be useful in identifying and removing inconsistencies and in setting priorities for natural resources management activities to be implemented within each year of the 5-year plan.

NEPA documentation enters the process at this stage. The NEPA document evaluates alternatives (e.g., no action, more intense natural resources management, less intense natural resources management). Subsequent draft reviews and revisions of the INRMP lead to the final approval and commitment to the 5-year INRMP following provision for public review of the NEPA documentation.

OVERALL INRMP STRUCTURE AND SALIENT FEATURES[6]

An *Executive Report* and a statement of *Goals and Policies* are all encompassing introductions. These indicate, in a general way, what and why natural resources management is being done. Costs and benefits are also reviewed.

Initial chapters describe the status of conditions at the installation with regard to those features which affect natural resources. Many of these considerations are similar to the descriptions of "affected environments" in NEPA documents.

A *Ecosystem Status Summary* is a means to quickly determine the overall status of ecosystems at the installation in terms of soil, water, and biodiversity trends. This part of the INRMP summarizes the effects of these trends on military training options and the production of renewable products from the land. This part represents a conversion from the status of natural resources to natural resources management.

A discussion of *Land Management Units* is both a status description and also the beginning of the change from descriptions of status to management plans. A section dealing with *Ecosystem Management - General* describes the overall management philosophy and sets the stage for succeeding sections.

Subsequent sections describe the ecosystem management options being considered or planned for use during the next five years. These sections are the heart of the INRMP, representing the "what we are going to do (or not do)" to manage the installation's natural resources.

Additional sections describe how the natural resources management program relates to other programs intimately tied to the management of such resources. All of the other programs have compliance implications. Specifically, these sections note how the natural resources management program will support these programs as well as comply with the laws associated with them.

Particular sections dealing with *Biopolitical Issue Resolution* and *Implementation* describe how an installation intends to resolve conflicts and implement the INRMP. These sections help identify constraints to implementation of the INRMP in terms of politics and sociological barriers and present a point-in-time snapshot with predictions of the future. Priorities are identified for activities within the 5-year planning period, along with staffing requirements.

ISSUES

During the development of INRMPs, several issues tend to become commonplace:

1. Natural resources management personnel have become accustomed to focusing only on the objective of treating natural resources as solitary products (e.g., trees, crops, game) and single species needing protection (e.g., endangered species) rather than on ecosystem management.

Ecosystem management requires that utilization of resources within ecosystems be allowed only if the overall ecosystem integrity is not compromised. Thus, the production of timber, quail, red-cockaded woodpeckers, soybeans, and other "product-oriented" natural resources must occur within this basic "bottom line". While not compromising the military mission, installation natural resources managers must begin to think in terms of managing installation pieces of land with biological and other essential natural functions involving soil and water, not just producing products.

2. A need exists for better integration of the installation's mission, the mission's objectives, and the mission's schedule and INRMP goals.

Program loyalties can be very strong and all-encompassing. Protective attitudes can hinder integration among natural resource program areas and testing and training programs. The consensus building feature of the INRMP preparation process can contribute significantly to breaking down such barriers.

3. Natural resources management tends to operate independently from cultural resources management.

Natural resources management plans often require the construction of new roads to facilitate access to hunting and fishing areas, and so forth. It is important for INRMPs to take note of possible detrimental impacts on cultural resources (e.g., prehistoric and historic sites and areas of interest of native American Indians).

4. Reluctance exists to the formation of partnerships.

Partnerships with private or public landowners adjacent to an installation can be an invaluable mechanism for the protection and stability of an ecological community on an installation. Various types of incentives, environmental awareness, stewardship, and public acclaim are some of the grounds for providing legitimacy and encouragement for such agreements.

INITIATIVE STATUS

The USAEC is preparing guidelines for the development of INRMPs and is testing these guidelines at four Army installations (Fort Knox, KY; Fort Polk, LA; Fort Lee, VA; and Umatilla Army Depot Activity, OR). In support of this INRMP decision-making process, NEPA documentation is being prepared concurrently with the INRMPs. This testing effort is expected to be completed in 1996.

CONCLUSIONS

For most installations, Army regulations require Integrated Natural Resources Management Plans (INRMPs) to be used as planning and operations tools for installation programs. Existing guidance for preparing these plans is outdated by changes in laws, pending amendments, and natural resources management policies. An ecosystem management approach to natural resources management to better protect biodiversity and meet other needs must be more effectively incorporated within installation INRMPs.

The USAEC has taken the initiative to develop new guidelines for the preparation of INRMPs and to apply these guidelines in the development of INRMPs for four Army installations (Fort Knox, Fort Polk, Fort Lee, and Umatilla Army Depot Activity). To support the decision-making process, NEPA documentation is being prepared. The new guidelines will be consistent with Army policy, federal laws, and current national natural resources management philosophies.

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1. The information in this paper reflects opinions of the authors and is not to be regarded as Army policy.

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6. Note that the INRMP Guidelines are not policy, but support Army policy regarding natural resources management on Army lands.

RIPARIAN ZONE MANAGEMENT AND RESTORATION TRAINING UNDER THE LEGACY PROGRAM, U.S. DEPARTMENT OF DEFENSE

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INTRODUCTION

Riparian zones occur throughout the United States between aquatic and upland habitats and are common landscape features on many Department of Defense (DoD) lands. These zones are important because they provide erosion control by regulating sediment transport and distribution, enhance water quality, and produce organic matter for aquatic habitats. Although riparian zones typically comprise only a small proportion of the total land surface on DoD lands, they are extremely rich in plant and animal life and are critical to the environmental quality and biodiversity of the regional landscape.

Riparian ecosystems on DoD lands are subject to a variety of impacts, including those resulting from military training activities, forest management, grazing, fire, installation housing, and construction activities. These impacts may be cumulative over time and can threaten the integrity of entire landscapes. Thus, it is important for DoD land managers to understand the function of riparian systems and develop procedures to protect, manage, and restore these valuable resources.

In 1992, the DoD Legacy Resource Management Program funded a work unit at the U.S. Army Engineer Waterways Experiment Station (WES) entitled "Design of Special Training Sessions on Riparian Zone Restoration and Management." The objective of the work unit was to provide state-of-the-science information on riparian zone ecology, restoration, and management to DoD natural resources personnel through development of regional training workshops. Study tasks included:

1. Synthesize existing information on riparian zone ecology, restoration, and management.
2. Identify sources of expertise on riparian ecosystems.
3. Coordinate with DoD land managers to determine information and training needs.
4. Design a curriculum on riparian zone management tailored to DoD lands.
5. Develop regional training sessions for installation personnel.

This paper presents the results of the Legacy riparian zone work unit from 1992 through 1994. Development of regional training sessions, the workshop notebook, and other products and activities are described. Future research and management needs of installation personnel are also discussed.

TRAINING SESSIONS

A curriculum and riparian zone training program was developed for DoD installation personnel from 1992-93, and a workshop was conducted in Billings, Montana, during June 1994. The workshop included both classroom lectures and field demonstrations/exercises during 5 consecutive days. To address the complex issues of riparian zone ecology, restoration, and management, several instructors with a diversity of experience and expertise in riparian ecology were chosen. These instructors included employees from WES; U.S. Natural Resources Conservation Service (formerly the Soil Conservation Service); Colorado Division of Fish and Wildlife; Montana Department of Fish, Wildlife, and Parks; and 3 private consulting firms. Natural resource personnel representing 23 DoD installations or facilities attended the workshop. Classroom facilities and field study sites were provided by ZooMontana, located southeast of Billings, MT (Figure 1).

FIGURE 1

Natural resource personnel conducting field exercises along Canyon Creek, ZooMontana, as part of the DoD Legacy Riparian Workshop, Billings, MT.

Course content focused mainly on riparian zones in the northwestern United States, although supplementary information from other regions was also presented when appropriate. To complement the training workshop, a training notebook was developed and distributed to participants. This notebook provided a detailed literature review on a variety of topics and included strategies and techniques for addressing riparian zone issues. The workshop and accompanying notebook served as products for the DoD Legacy work unit. A summary of information contained in each notebook section is provided below.

Overview of Riparian Zones

Riparian zones may be characterized generally as linear areas along rivers and streams that are subject to occasional flooding[1]. They are considered among the most diverse, dynamic, and complex biological systems on earth, contributing significantly to regional biodiversity[2] by providing essential habitat for a wide variety of plant and animal species (Figure 2). Additionally, these corridors provide erosion control by regulating sediment transport and distribution, enhance water quality, produce organic matter for aquatic habitats, and provide numerous wildlife benefits.

A substantial amount of literature has been written on riparian zones, especially since 1975, but much of this information is contained in state reports and symposia that are unavailable to most field personnel. Installation personnel need specific answers regarding restoration and management techniques, but studies are often poorly designed and published results are often contradictory. Furthermore, most guidelines for determining existing and potential impacts on riparian ecosystems are inadequate[4].

The introductory section of the notebook provided a general overview of riparian ecology, including riparian zone definitions, why riparian zones are important ecosystems, current issues in riparian ecology, and physical and biological characteristics (including regional differences). In addition, apparent problems associated with terminology were discussed.

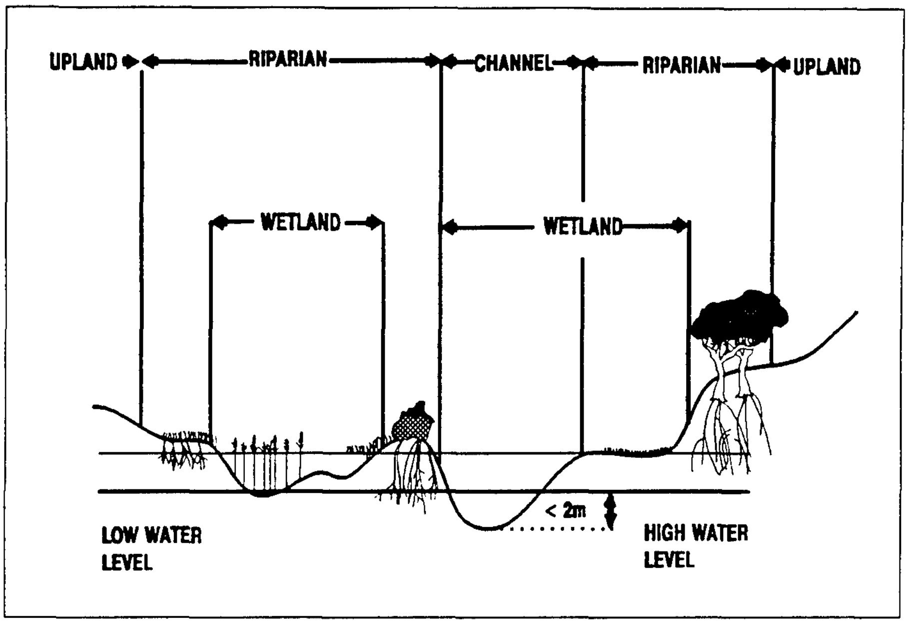
Riparian Classification

A variety of hierarchical-classification schemes for riparian vegetation have been proposed and used on a regional or local basis, mostly in the western U.S.; these schemes typically attempt to identify and classify riparian communities based on major vegetation types, hydroperiod, and geomorphology[3]. Regional schemes often classify riparian vegetation into discrete units to facilitate their study, predict the distribution of plant and animal communities, determine the effects of water and land management upon these communities[3], and describe and document community diversity as a basis for sound management[4]. However, no consistent classification scheme exists for riparian zones.

A national riparian classification scheme[5] that is compatible with the U.S. Fish and Wildlife Services' wetland classification scheme[6] has been developed to reflect ecological differences of ecosystems associated with ephemeral, intermittent, and perennial waters. A review of riparian classification schemes, including both national and regional perspectives was provided in this section.

FIGURE 2

Riparian zones occur adjacent to rivers and streams. They often extend beyond the "wetland" boundaries established by most wetland definitions. They are a diverse and dynamic component of the landscape, and have many important ecological functions[3].



Riparian Functions, Values, and Trends

The structure, functions, and values of many wetland systems have been intensively investigated. However, riparian zones have only recently been fully recognized as important ecosystems[7]. Riparian zones provide a variety of benefits, including stabilizing stream channels; providing erosion control by regulating sediment storage, transport, and distribution; enhancement of water quality; producing organic matter for aquatic habitats; serving as nutrient sinks for the surrounding watershed; improving the quality of water leaving the watershed; providing water temperature control through shading; reducing flood peaks; serving as key recharge points for renewing ground water supplies; and providing wildlife habitat[8].

Riparian zones and their associated aquatic systems suffer greatly from past and present land-use practices, especially overgrazing, and nonpoint-source pollution from timber removal and agricultural runoff[9]. Estimates of the percentage of riparian zones that have been altered in the United States ranged from 70-90%[2,8,9,10], making them among the most drastically altered ecosystems. By about 1980, an estimated 4-6 million ha of riparian habitat remained in the United States[8].

This section of the notebook provided information designed to distinguish between functions and values and how they apply to riparian zones. The national and regional status of riparian zones, including distribution, abundance, and trends was discussed. During this and other sessions, natural resource personnel were strongly encouraged to discuss riparian zone issues (e.g., impacts, restoration, management) on their installations.

Riparian Ecology: Fluvial Geomorphology

Riparian and aquatic ecosystems are interdependent ecological entities. Riparian zones are the result of hydrologic and geomorphic conditions where water, energy, and materials from aquatic systems converge in the narrow floodplain. Conversely, the riparian zone influences the physiochemical and biological characteristics of the aquatic system through water and nutrient exchange and organic export[12]. The formation of watersheds, and both the upland and riparian landforms associated with watersheds, is mostly determined by the interdependent factors of geology, climate, valley gradient, soils, and vegetation[13].

In this section, riparian/aquatic interdependence, some of the important ecological processes that occur in riparian zones, and those processes that occur in upland (watershed) and aquatic habitats that affect the riparian zone were summarized. Principles and processes of fluvial geomorphology and hydrology were discussed as they relate to both the riparian zone and the surrounding watershed. Key ideas were illustrated in the lecture by examples of both good and poor management.

Riparian Ecology: Vegetation

Riparian zones are characterized by the presence of vegetation that requires free or unbound water or conditions that are more moist than normal. Benefits of riparian vegetation include stream shading, stabilization of stream banks with extensive root systems, provision of wildlife habitat, and building of stream banks by trapping sediment. Plant species composition varies within riparian zones because plant communities differ in their ability to obtain water along the moisture continuum from mesic to more xeric portions of the riparian zone. Riparian plant communities reflect the complex interactions of physical controls (e.g., climate, geomorphic setting), as well as biological interactions and various types of disturbances. The most obvious controlling influence is flooding, which can eliminate many plant species and favor dominance by species that are able to tolerate periods of inundation.

This chapter provided a general understanding of riparian vegetation, successional processes in riparian zones, and recommendations for riparian buffer zones and corridors. Specific topics addressed included vegetation-moisture gradients; composition, structure, and diversity of vegetation; regional variation; plant succession; ecological attributes of vegetation; riparian buffer zones and corridors; ecotones and edge; influence of disturbance on vegetation; and phreatophyte problems.

Riparian Ecology: Fauna

Riparian ecosystems provide year-round habitat for many species of mammals, reptiles, amphibians, and birds, as well as breeding sites, wintering areas, and stop-over habitat for an exceptional variety of migratory birds. Numerous studies have shown that a variety of wildlife species use riparian habitat disproportionately more than other habitats. For example, riparian zones in the western U.S. constitute <1% of the total land area, yet these areas are used by more species of breeding birds than any other habitat in North America[7]. For example, in the Blue Mountains of Oregon and Washington, riparian zones were the most important wildlife habitat[14]. Two-hundred eighty-five (75%) terrestrial species either required riparian zones year-round or were directly dependent on them for a portion of their lifecycle. Some wildlife species move into riparian habitats from uplands during dry periods. Many aquatic species use riparian zones during flooding[15].

Information from this section included an introduction to the ecology of riparian fauna (birds, mammals, herpetofauna, fish, and aquatic invertebrates). For avian, mammalian, and herpetofaunal communities, specific topics addressed were habitat characteristics; seasonal use and importance; characteristic species; use vs. riparian zone width; influence of riparian zones on adjacent habitats; importance of adjacent habitats; and impacts of habitat modification.

Riparian Ecology: Special Topics

The realization that habitat loss and fragmentation are serious problems impeding biological diversity (commonly referred to as biodiversity) management has spawned larger-scale approaches (e.g., ecosystem and landscape levels) to the preservation of biodiversity[16]. River systems and their associated riparian zones contribute significantly to landscape ecology and regional biological diversity[2,17], and provide one means by which a landscape approach to the preservation of biodiversity can be achieved. Riparian zone diversity is maintained by natural disturbance regimes occurring over a variety of spatial and temporal scales (e.g., floods, fire, landslides, debris torrents, and channel migration). These disturbances create a wide array of vegetal communities in various successional stages that subsequently provide diverse wildlife habitat[2].

Riparian zones are extremely important for some rare, endangered, and endemic species. Of the 276 species listed as threatened or endangered by the U.S. Fish and Wildlife Service (USFWS) in 1980, 80 species (29%) were at least partially dependent on riparian habitats[8]. Riparian zones on military installations are often important habitat for these species. For example, a project is underway to restore riparian habitat for the least Bell's vireo (*Vireo bellii pusillus*), a Federally listed endangered species, at Camp Pendleton Marine Corps Base, California.

This section provided basic information on selected topics related to riparian ecology and management. The importance of riparian zones in protecting biodiversity, including genetic, species, ecosystem, and landscape diversity was addressed. The value of riparian communities to threatened, endangered, and sensitive species was also discussed.

Inventory and Monitoring

The collection of appropriate data is necessary to inventory and monitor riparian zones for management programs. The primary purpose of an inventory is to locate and quantify riparian flora and fauna, and broadly classify vegetation. General inventory data can be used as a starting point for identifying more intensive inventory needs[18]. These data are useful for obtaining information on evaluating the response of riparian zones to land-management practices and the level of habitat quality achievable through improved management[4].

This section provided information on design and application of methods that are appropriate for monitoring and censusing animals in riparian zones, such as birds (point counts, spot-mapping, mist netting), mammals (trapping, pitfalls), herpetofauna (pitfalls), and fish (electroshocking). Inventory and monitoring of riparian vegetation was also addressed. Several of these techniques were demonstrated during field exercises.

Impacts to Riparian Zones

Human activities can significantly alter the ecology of riparian and wetland ecosystems. Impacts result primarily from land clearing and drainage[19], hydrologic modifications such as stream channelization and dams[15], agricultural practices, timber management, and various types of pollution[20]. Wetlands and riparian zones of agriculture-dominated landscapes may be influenced by herbicide and pesticide use, nitrogen and phosphorus runoff, sedimentation, livestock grazing, and burning practices. Some of these activities may be beneficial when conducted in a carefully planned and controlled manner (e.g., controlled grazing and prescribed burning); however, most agricultural operations are not designed for the benefit of wetlands.

This section was designed to provide information on the variety of land-use practices that impact or influence riparian zones. Because impacts to both aquatic systems and the watershed can subsequently influence the riparian zone, the emphasis of this section was on the landscape approach. Impacts that were addressed included silvicultural practices, agricultural and grazing practices, flood control and channelization, urbanization and recreation, fire, and specific military impacts.

Military training may have dramatic impacts on riparian habitats. Although several studies have been conducted to determine the effects of different types of military vehicles on soils and vegetation[21,22,23], few studies specifically addressed the influence of these impacts on riparian zones. Continuous heavy vehicle use along streamsides may also result in erosion problems and impacts to aquatic resources, especially when buffer zones have not been established. Additional research is needed to assess the impacts of military training to riparian zones.

Restoration Strategies

The need for innovative restoration techniques for degraded riparian zones on installations was identified during the workshop. Information was provided on restoration strategies and techniques for riparian zones, including assets, limitations, and specific factors to consider in project design. Bioengineering, the combination of native vegetation and low-cost building materials, was suggested as the preferred strategy for restoring and stabilizing riparian ecosystems. This practice provides wildlife habitat, buffers adjacent land-use impacts, and is cost-effective, aesthetically pleasing, and self-sustaining. Specific techniques described included plant fiber rolls, wattling bundles, geotextile mats, willow/fence combinations, and crib structures. Additional topics addressed included assets, limitations, and factors to consider when using planted vegetation, stream flow characteristics, bank geometry, site preparation, vegetation types, and revegetation techniques, including plant procurement and costs.

A case-study was presented that demonstrated how bioengineering was successfully used to restore riparian zones on Tinker Air Force Base, Oklahoma. A section of Canyon Creek, ZooMontana, which was restored using various bioengineering methods, provided an excellent field demonstration site (Figure 3).

Management Strategies and Techniques

Riparian management typically focuses on managing or restoring a stable zone of riparian vegetation adjacent to the aquatic system for the enhancement of water quality and wildlife habitat[24]. Evaluation, design, and implementation of management strategies in riparian zones rely on many considerations, such as successional stage of existing vegetation, geographic location, soils, water regime, topography, and fauna.

Riparian condition is often a product of the biogeochemical processes occurring among aquatic, riparian, and terrestrial communities[25]. In general, management applied to any one of these ecosystems may subsequently affect the other ecosystems. This is especially true when management occurs in upland areas because results of the action (positive or negative) will ultimately be realized at lower-elevation sites. Since upland, riparian, and aquatic ecosystems are interdependent, management practices should be viewed in light of the impacts they will have on the entire landscape of a region[25].

State-of-the-science techniques for managing riparian zones, including watershed management, forest management, grazing/livestock management, and wildlife and fisheries habitat management were presented in this section. Specific techniques described were snag management, buffer zone designs, corridor development, planting methods, control of exotic species, wetland restoration, erosion control, and site protection.

CONCLUSIONS

A Legacy project on riparian zone ecology, restoration, and management was conducted from 1992 through 1994. The primary objective of the study was to develop regional training sessions tailored to natural resource needs on DoD military installations. Work unit tasks were to (1) synthesize information on riparian zone ecology, restoration, and management, (2) identify sources of expertise on riparian ecosystems, especially at the regional level, (3) coordinate with DoD land managers to determine information and training needs, (4) design a curriculum on riparian zone technology tailored to DoD lands, and (5) develop regional training sessions for installation personnel.

FIGURE 3

Canyon Creek site before restoration (top photo) and immediately after grading and application of bioengineering techniques (bottom photo).

Work completed in 1992 and 1993 included a background search and synthesis of riparian technology, development of curriculum and lesson plans, selection of preliminary regional training sites, and completion of the draft training notebook. The training notebook focused on the Pacific Northwest region and included the following chapters: (1) Overview of riparian zones; (2) riparian classification; (3) riparian functions, values, and trends; (4) riparian ecology - fluvial geomorphology; (5) riparian ecology - vegetation; (6) riparian ecology - fauna; (7) riparian ecology - special topics; (8) inventory and monitoring; (9) impacts to riparian zones; (10) restoration strategies; and (11) management strategies and techniques. A glossary of technical terms was also provided. Other products and activities for the work unit included the development of an extensive topical and regional literature review; this resulted in a literature base of approximately 2,500 references that was made available to workshop participants.

A regional training workshop was conducted in Billings, Montana on 13-17 June 1994. Twenty-three personnel from military installations, primarily from the northwestern states, attended the workshop. Results of the workshop evaluation showed that the training was well-received and of considerable value to installation personnel. Benefits to DoD installations include:

1. Improved capability to manage riparian resources in various military settings.
2. Enhanced water quality and reduced erosion in streamside habitats affected by military activities.
3. Increased biodiversity and improved habitat for a variety of species, including threatened and endangered plants and animals.
4. Cost-effective habitat restoration using bioengineering techniques.
5. Increased knowledge of management/restoration strategies and techniques for various riparian zone settings.
6. Increased understanding of land use impacts on riparian ecosystems and their associated landscapes.
7. Extensive partnering with other agencies, organizations, and universities to accomplish riparian zone restoration and management objectives on DoD lands.

Development of additional regional workshops will depend on approval and funding from the Legacy Program or other sources. Although only one workshop was completed under the 1992-94 project, the course curriculum and training notebook will continue to be updated as more information becomes available. Potential sites being considered for future workshops include White Sands Missile Range, NM, Camp Ripley, MN, Fort Leavenworth, KS, and Fort Drum, NY. Additionally, contacts have been made with a variety of federal and state agencies, universities, conservation organizations, and private firms to locate instructors for future courses. A team of partners appropriate for the region of concern will be assembled for each workshop. DoD personnel will also be invited to present case studies of riparian restoration and management projects on their installations.

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INTEGRATED VEGETATION DATA COLLECTION

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INTRODUCTION

Data collection and management are costly, time-consuming components of any mapping project. Vegetation mapping, given the frequently complex nature of many plant-community mosaics, can be extremely costly. Topographic Engineering Center (TEC) biologists and cartographers are working on combining remote sensing, geographic information systems (GIS), geostatistics and ground and aerial multispectral, digital cameras into a flexible data-gathering system. This system can be used by resource managers to compile baseline vegetation data, monitor changes and predict changes based on various training and management decisions. Current methods -- quadrats, transects, etc. -- work effectively in relatively small areas but are expensive and technically demanding on the large, often enormous tracts of Army installation land.

DISCUSSION

The methodology TEC envisions integrates available technology into a cycle of vegetation data acquisition and evaluation. Four primary components make up this cycle: (1) An initial **imagery source** that is readily available and capable of analysis; (2) **statistical protocols** for evaluating the imagery to determine a sampling scheme for ground truth; (3) airborne, high-spatial-resolution **digital multispectral videography** missions flown over the defined sample points; and (4) a suite of **ground truth** techniques for vegetation characterization and collection of imagery training data (see Figure 1: Technology Integration).

Vegetation Data Acquisition Technology Components

(1) Imagery Source: SPOT and Landsat imagery are both commercially available, well-accepted imagery products.

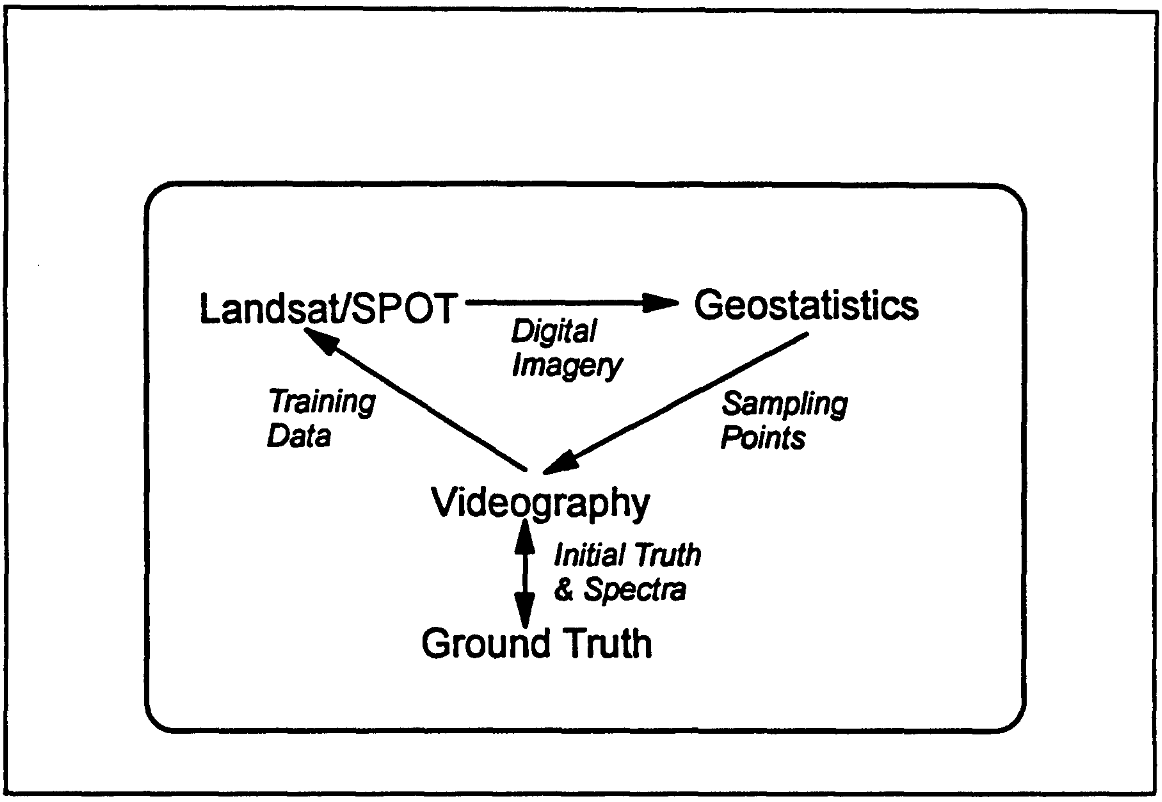

Figure 1: Technology Integration. This cycle can be repeated and should result in improvement in data quality.

Spatial resolution varies from 10-30 meters. Spectral resolution is relatively broad. Both products have been generated for at least the last eight years, making short-term change detection possible.

(2) Statistical Protocols: Funding limitations often mean that enormous military bases must be characterized using relatively small amounts of data. Determining which sites to visit on an installation to best characterize the overall vegetation is not an easy task. A broad-brush approach is to statistically review imagery of an entire area of interest (for example, an entire installation or an area of selected interest within an installation's fenceline, etc.). The premise behind this idea is that relatively homogeneous areas will require fewer ground sampling sites while heterogeneous areas will require a great many sampling points. Without a preliminary global evaluation of an area, significantly different areas may not be sampled. This has been cited as a shortcoming of the Army's Land Condition Trend Analysis (LCTA) program, whereby transects have been selected for continued monitoring that may not be fully representative of an entire installation's vegetation diversity.

Vegetation/terrain will dictate the number and location of the recommended sampling sites. Classical statistics, demanding 100 or more points for large sample populations for example, are replaced by the more flexible and earth science-related geostatistics. Geostatistics are presently being investigated to determine if the geo-spatial characteristics (i.e., topological relationship to other like pixels and their digital value) of imagery pixels can be used to better infer the most representative sampling points to be visited for ground-truthing purposes. The use of geostatistics has been successfully explored in other geographical venues, such as soil type characterization and mineral evaluation (Badr et al., 1993; and Rendu, 1978).

(3) Digital Multispectral Video (DMSV): This emerging technology provides multiple channels of digital data at spectral bands of the researcher's choosing. A video system we currently are using uses four bands, 25 nanometers (nm) wide and centered on 450, 550, 650 and 770 nm, respectively. Band selection is controlled by choice of filters. This system has not been demonstrated as an effective mapping system to date, due to its lack of a sophisticated internal global positioning system (GPS) component. However, for individual pixel mapping, especially considering 10-30 meter SPOT and Landsat data, DMSV imagery can acquire high-resolution spatial and spectral data about selected pixel locations identified as sampling points. Sufficient ground control must exist to geo-locate DMSV images. This ground control can be photo-identifiable points on the imagery and/or ground control placards positioned in the area prior to imaging.

(4) Ground Truth: Numerous ground truth techniques and technologies have been, or can be, used for natural resource management. These techniques can serve to validate and train both the DMSV imagery and the original SPOT or Landsat scenes. Many of the suggested techniques/tools are cited below:

* Global Positioning Systems (GPS)- GPS data points can be collected in the field or tied to photo-identifiable points on satellite images. GPS is essentially now a utility, with short learning times, low prices and increasing accuracy. For most natural resource needs, decimeter- or meter-level accuracy is sufficient.

Several types of GPS are available today. To most accurately identify a ground position, differential GPS resolves ground position to sub-meter-level accuracy. With sub-meter-level accuracy, there is high assurance that a field characterized ground location resides within an imagery sampling pixel of 10 (SPOT panchromatic) to 30 meter (Landsat TM) dimension.

* Quadrats: Squares, circles, polygons or rectangles whose measurements are chosen to provide a representative sample of a study area's vegetation, can also be used to "train" imagery. Randomly selected sample points

can be geo-referenced with GPS and then censused. The vegetation within the quadrat is then used to associate pixel patterns in an image to vegetation patterns throughout an image.

* Transects: Point-to-point lines on the ground are used to establish ground traverses over an area to be characterized for vegetation and habitat. Transects can be used to collect large amounts of vegetation or habitat data, but must be chosen carefully to be truly representative of the study area. Quadrats may be chosen at regular or random points along a transect.

* Radiometers: These instruments are used to identify vegetation stands for image "training." Training an image means identifying known plant communities on the ground at an exact geographic position and collecting the plant's reflective spectra at that position. The spectra information is then used to find imagery pixels with similar characteristics.

* Digital cameras: We are developing the use of digital hand-held cameras to shoot vegetation quadrats for later species and abundance analysis. Image processing routines for vegetation classification and subsequent conversion to vector products for import into a GIS also are being researched and developed. This evolving technique is expected to reduce field time and reduce identification errors caused by a lack of central quality control. Change detection analysis will be achieved by comparing identical quadrats of different dates. Digital quadrat data will be readily recoverable in the future. Compilation of data from 1-meter quadrat data vegetation polygons into complete data layer arrays without void areas is to be investigated using geostatistical principles of interpolation.

Technology Integration

Components of the system described herein have been used for several research projects. All the components work independently; their smooth integration is expected to take some iterative research and development. We are moving toward joining the technologies together into a system flexible enough for the many management jobs Army resource managers must handle.

Imagery scenes from conventional sensors, such as Landsat or SPOT, are acquired for the proposed project area. Unsupervised classifications can be run on this imagery to coarsely categorize urban, water, soils and vegetation areas. Once all vegetation has been classified as a single cluster group, geostatistical analysis of the vegetation image pixel digital numbers occurs.

Topological relationships of these digital numbers, considering both distance between pixels and their actual values, are examined using geostatistical software.

Variograms of the data are generated that show the scale and pattern of spatial variation. Sampling locations needed for collection of ground truth training data are designated. Homogeneous areas on the imagery demand fewer sampling locations than do the very heterogeneous area. There is no predefined number of sampling points needed for training any imagery scene as is the convention in mathematical statistics. Each image uniquely determines the points. A listing of sampling points is generated identifying the latitude and longitude (or UTM coordinate). For ground truthing sample points, a question arises as to how to most efficiently visit the sites. Typically, an issue such as proximity to roads immediately comes into play as does dispersion of the points across the landscape. A GIS package could conceivably be used to recommend the best routes to visit all the sampling sites.

An alternative to this traversing on-the-ground would be to use an aircraft that could navigate to the sampling points and acquire high-resolution images of the ground for later photo interpretation. The imagery acquired could be simply visible or could be multispectral. Digital multispectral imagery would facilitate image processing and therefore spectral interpretation of vegetation data. Again, a GIS could be used to determine the airborne routes to visit the sampling sites. Because imagery provides area coverage while ground sampling provides point coverage, buffering the aircraft route and highlighting the image frame width would be effective for designing a sampling collection route.

All sample sites would be flown with digital multispectral videography. GPS must be directly linked to the image frames. Navigation to the sampling sites would be done with an aircraft-quality, onboard GPS. Following imagery acquisition, interpretation of the images would occur in the office using standard photo-interpretation skills and image-processing software. The imagery would be initially classified as to vegetation type.

A percentage of the total sample sites would need to be field-checked on the ground both for verification of the interpreted vegetation types and to collect spectra, or reflectance measurements, of the vegetation within an image frame. This spectra and field checking would be used to improve the initial vegetation classifications for the sample sites. A digital multispectral vegetation classification for each of the sampling sites would then be generated.

GPS can be used to navigate to a single sample point site. Digital videography has a pixel resolution that can now exceed 1-meter even at an altitude of 10,000 feet. However, because the ultimate goal is to pass information back to the original SPOT or Landsat scene (train the image), consideration must be given to interpreting an area the size of a SPOT or Landsat pixel (10-30 meters). Techniques used to interpret the vegetation within a 10-30 meter pixel could include quadrats and/or transects. Collection of oblique digital camera shots of the area from the ground would be beneficial for interpretation of the vegetation and for later inclusion in a GIS as an analog image. Collection of digital camera shots of a quadrat, taken from a nadir position (directly overhead) above the quadrat, would be equally useful and could be used for time series analysis in the future. Radiometers would be used to collect plant spectra for training DMSV image frames.

Once the digital multispectral video image frames have been classified and the classifications improved by field work, the information is then ready to be passed to the original SPOT or Landsat scene. The DMSV images train the SPOT or Landsat scene for a supervised vegetation (maximum likelihood classification) using image processing software.

CONCLUSIONS

The benefit to this vegetation mapping schema is that there is an optimal exploitation of small-scale (SPOT and Landsat) and large-scale (DMSV) data sets. Local-level information is passed back up the scale to the more regionalized imagery. For large project ares, this is very appealing. Selection of appropriate sampling locations is equally appealing, especially if there is a quantitative methodology to their selection. This proposed integration of technologies, therefore, has a great deal of potential and is actively being researched as to its utility for the natural resource management community.

The integrated data approach is being investigated with aerial photography, SPOT, Landsat, and DMSV image sources. As new satellites with high-resolution sensors begin to supply imagery, these images will constitute a rapidly growing archive of high-resolution (sub-meter to 5-meter resolution) data that can be used with the techniques described here. In fact, one of the valuable byproducts of developing DMSV as a data source may be learning how to best exploit such high-resolution images. Satellite images may become an inexpensive, technically non-intimidating data source with frequent repeat visit times.

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ECOLOGICAL RISK ASSESSMENT AT FORT ORD: COMPARISON OF MODELED EXPOSURE CONCENTRATIONS WITH ACTUAL CONCENTRATIONS FOR ECOLOGICAL RECEPTORS

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INTRODUCTION

The purpose of ecological risk assessments under Superfund has been to evaluate whether the "environment" has been, or potentially could be, adversely affected by chemicals that originated at a Superfund site. There has been, until recently, little guidance in the preparation and performance of ecological risk assessments for Superfund sites. EPA has provided general guidance in their Risk Assessment Guidance for Superfund, Volume II[1]. This was followed in 1992 with the publication of the Framework for Ecological Risk Assessment[2] EPA has provided additional information through the ECO Updates[3-7], and papers have been published in the open literature summarizing approaches to ecological risk assessments[8]. Individual states have also developed guidance, some of which are generally consistent with the EPA approach (e.g. Cal EPA - DTSC).

An Ecological Risk Assessment was conducted as part of a Remedial Investigation/Feasibility Study (RI/FS) at Fort Ord, California, a 28,000 acre former military (light infantry) training installation on the National Priorities List. Fort Ord is also on the base closure list, and the schedule for completing the RI/FS was driven by the Panetta Bill, which mandates that federal Superfund sites on the base closure list must complete the RI/FS within 36 months from listing on the NPL. Located along the coast near Monterey, California, Fort Ord is characterized by landfills, small arms and high explosive target ranges, airfields, maintenance yards, and motor pools. Forty-one individual source areas were identified for evaluation. Current plans call for the facility to be transferred to various public and private agencies with various proposed future land uses, ranging from state parks and wildlife reserves to college campuses with associated residential facilities.

Ecological risk assessments often use measured soil concentrations to model potential exposures of various organisms to chemicals and to assess potential risks. In this study, soil concentration data collected during the RI at Fort Ord were used to estimate uptake and tissue concentrations in plants. For inorganic chemicals, a single chemical-specific plant uptake factor was used to model uptake into plants; for organics, a regression equation based on pesticides was used. Potential exposures of herbivores to chemicals were estimated using this modeled plant uptake and these modeled exposure doses were then used to estimate potential exposure doses in predators.

For this ecological risk assessment, possible chemical impacts due to soil contamination were estimated in plants and rodents using a phased approach. In Phase 1, a screening assessment was conducted using only soil concentration data and a modeling approach to estimate potential exposures. Plant, rodent, and fox concentrations were predicted using chemical uptake and exposure modeling based on soil data. The second phase incorporated actual measured data from each of the sites for both plants and rodents (e.g., biota samples analyzed for chemical constituents). The remainder of this paper discusses the use of modeled (Phase 1) and field data (Phase 2) to estimate potential ecological effects and the results of these different approaches on risk estimation. A list of keywords and their definitions is provided at the end of this paper.

METHODS

Fort Ord is a 28,000 acre former military (light infantry) training installation located along the Pacific Coast near Monterey, California. Fort Ord is characterized by landfills, small arms and high explosive target ranges, airfields, maintenance yards, and motor pools. Forty-one individual source areas were initially identified for evaluation. The ecological risk assessment for these sites was performed in a manner consistent with the Framework for Ecological Risk Assessment developed by EPA[2]. The problem formulation consisted of the identification of a subset of sites that needed further evaluation and data gaps for those sites. There were fifteen sites that were eliminated because they were essentially paved or otherwise lacked a suitable habitat for ecological receptors.

For the remaining 26 sites, conceptual models were formulated and endpoints were identified. On the basis of the habitats, chemicals, and species present at these sites, two basic conceptual models were formulated, one for coastal sites and one for inland sites. Information obtained during chemical site characterization and preliminary habitat surveys performed during the problem formulation were used to identify specific data needed to evaluate the endpoints. A sampling plan was developed to address any data gaps and to provide sufficient information to adequately evaluate the endpoints. On the basis of societal values, the health of endangered and special-status species was chosen as one assessment endpoint. These species could not be directly sampled and evaluated because that would be in violation of the endangered species act. Therefore, the conceptual models were used to identify surrogate species to be evaluated as measurement endpoints. These surrogate species included wild oat (*Avena fatua*), hottentot fig (*Carpobrotus edulis*), deer mouse (*Peromyscus maniculatus*), and gray fox (*Urocyon cinereoargenteus*).

The assessment of endpoints was phased. Data collection of biota was deferred to Phase 2 pending the results of a Phase 1 screening assessment using only measured soil data and modeled biota data. In this way, additional sampling could be further focused on specific "problem" sites and endpoints and unnecessary sampling of biota could be limited. The approaches and methods used in these two phases are discussed below.

Phase 1

In Phase 1, a screening assessment was conducted using an exposure modeling approach. Soil data collected as part of site characterization efforts were used for the screening assessment. Chemicals evaluated in the screening assessment were metals, pesticides, and dioxin congeners. For metals, concentrations at each site were compared with basewide-specific background concentrations by depth and soil type. Those metals detected at sites above appropriate background concentrations were identified as chemicals of potential concern (COPCs) and evaluated in Phase 1. Dioxins were detected in soil at 2 sites and were evaluated at both. A variety of congeners were detected. Detected congeners were converted to 2,3,7,8-TCDD toxicity equivalent quotients (TEQs) for analysis. Receptors evaluated in Phase 1 included most of the surrogate species identified above, except for the hottentot fig. For these receptors, exposures were modeled using soil data. This paper focuses on the exposures estimated for lead, zinc, and OCDD, one dioxin congener. The methods used during Phase 1 are summarized below.

Plants

For plants, a chemical-specific plant uptake factor developed by Baes et al.[9] for individual metals was used to convert soil concentrations to modeled plant tissue concentrations. The authors developed separate element-specific factors for reproductive (Br) and vegetative (Bv) portions of plant tissues based on measured data in crop plants. Because the species evaluated in this assessment may eat both types of plant parts, a weighted-average of these factors were used to estimate plant metal concentrations. Based on information from the literature, it was assumed that 75 percent of ingested plant material was seeds (i.e., reproductive portions) and 25 percent was shoots (i.e., vegetative portions). For the two metals discussed in this paper, lead and zinc, Br values provided by Baes et al. are 0.009 and 0.045, respectively[9]. Bv values for lead and zinc provided by Baes et al. are 0.90 and 1.5, respectively[9]. Taking the weighted average of these values results in plant uptake factors for lead and zinc of 0.0178 and 1.04, respectively. These values were multiplied by the measured soil concentrations at each site to estimate plant tissue concentrations.

For dioxins, a regression equation developed for pesticides by Travis and Arms[10] was used to estimate plant tissue concentrations. This equation describes a relationship between soil-to-plant transfer factors for vegetative tissues and octanol-water partition coefficients (Kow). Specific plant uptake factors or equations have not been developed for dioxin congeners.

The regression equation developed by Travis and Arms[10] is as follows:

$$\log Bv = 1.588 - 0.578*(\log Kow) \qquad \text{(Equation 1)}$$

The equation developed by Travis and Arms[10] was based on chemicals with log Kow values ranging from 1.75 to 6.15. The majority of log Kow values were above 4. The range of Kow values for dioxin congeners is 5.91 to 11.54[11]. The range of log Kow values for OCDD is 7.46 to 8.6[11]. Therefore, the equation may not adequately describe the relationship between soil concentrations and plant uptake for dioxins because the majority of dioxin log Kow values are higher than those on which the equation is based. However, the equation was developed using mainly hydrophobic chemicals, and was considered to be the most relevant equation available for dioxins. For these reasons, and because pesticides were also detected in soil at Fort Ord sites, use of the Travis and Arms equation was considered appropriate for this screening assessment. The only dioxin congener consistently detected along transects at both sites was octachlorodibenzodioxin (OCDD). Therefore, this evaluation was limited to OCDD. Using a log Kow for OCDD of 9.05, the resulting plant uptake factor (Bv) is 0.000227.

Mammals

Exposures were estimated in Phase 1 for both the deer mouse and gray fox using soil data. For the deer mouse, dietary intake was modeled using the maximum soil concentration at each site and intake assumptions from the literature[12]. For this conservative screening assessment, it was assumed that the entire home range of the mouse was within the maximally contaminated area of a site.

For the gray fox, dietary intake was modeled using the maximum soil concentration, dietary intake assumptions from the literature[12], and a factor relating intake to body burden in mice, which is necessary to obtain an exposure point concentration (EPC) for the fox that is assumed to eat deer mice at the site. Similarly to the deer mouse, it was conservatively assumed that the entire home range of the fox was within the maximally contaminated area of a site. Because the home range of a gray fox is much larger than the acreage of most evaluated sites, this is a very conservative assumption. In this way, if no problems were identified for the fox using the model, actual exposures would likely be much lower and no further evaluation in Phase 2 would be necessary.

A variety of exposure pathways and routes were included in the exposure model for each receptor. For both receptors, the following pathways were evaluated:

- Ingestion of and dermal contact with soil
- Ingestion of plants containing chemicals based on plant uptake model discussed above.

Additionally for the gray fox, ingestion of deer mice was evaluated. This pathway includes a three-tiered model (soil to plant, plant to deer mouse, deer mouse intake to deer mouse body burden). As a result, uncertainty associated with the gray fox exposure model is expected to be substantial.

One equation combining all exposure pathways for a given receptor was developed for estimating exposure for each receptor. The general equation used for both deer mouse and gray fox exposure is as follows:

$$LADD = \frac{EF * ED * (Cp * IRp) + (Cs * IRs) + (Cs * AF * SA * DAF) + (Cm * IRm)}{BW} \qquad \text{(Equation 2)}$$

Where:

LADD = Lifetime average daily dose (mg/kg/day; modeled)
EF = Exposure frequency (days exposed/365 days; assumed to be 1.0)
ED = Exposure duration (years exposed/years lifetime; assumed to be 1.0)
Cp = Concentration in plant (mg/kg; modeled)
IRp = Plant ingestion rate (kg/day; assumed)
Cs = Soil concentration (mg/kg; measured maximum)
IRs = Soil ingestion rate (kg/day; assumed)
AF = Adherence factor for soil on skin (kg soil/cm^2/day; assumed)
SA = Surface area of exposed skin (cm^2; assumed)
DAF = Dermal absorption factor (unitless fraction; assumed to be 1.0)
Cm = Chemical concentration in deer mouse (mg/kg; modeled)
IRm = Deer mouse ingestion rate (kg/day; assumed)
BW = Body weight (assumed).

The (Cm * IRm) term is applicable only to the gray fox, since this pathway is for consumption of deer mice. For estimating the deer mouse LADD, these values are assumed to be zero.

The following assumed values not provided above were used for deer mice. For IRp, this assessment assumed the entire diet of a deer mouse consisted of plants from the site, although information suggests deer mice also feed on invertebrates[12]. The median food consumption rate of 0.005 kg/day reported by EPA[13] was used for this variable. No information on soil ingestion (IRs) was found for the mice. An inadvertent soil ingestion rate for deer mice was calculated based on the assumption that a certain percentage of the total intake of food is soil. Data for larger foraging mammals such as sheep, cattle, and deer indicate that inadvertent soil ingestion typically represents 1 percent of total ingestion. To account for potential soil ingestion while grooming, this value was increased to 3 percent of the plant ingestion rate, or 0.00015 kg/day. The amount of soil adhered to skin (AF) used in this assessment was 1.0 mg/cm^2/day[14]. This value is considered by EPA to represent a reasonable upper value for humans[14]. The surface area of exposed skin (SA) was assumed to be 10 percent of the total surface area of the deer mouse based on analogy to comparable estimates for the muskrat[15]. The total surface area was calculated assuming that surface area is equal to $BW^{2/3}$ times a factor of ten[16,17]. The body weight reported for mice ranges from 0.015 to 0.035 kg[13]; the midpoint of this range was used for BW in this assessment (0.025 kg). Using this value for BW, a value of 8.55 cm^2/day was used for SA.

The following assumed values not provided above were used for the gray fox. For IRp and IRm, this assessment assumed the diet of a gray fox consists of both plants and small mammals. The typical vegetative portion of the diet includes manzanita berries, cherries, and coffee berries. In this assessment, the gray fox was assumed to consume 2.25 kg food/week, which is a value used for the red fox[12]. This value was used to calculate an average total daily ingestion rate of 0.32 kg/day. For this assessment, it was assumed that the entire diet of the gray fox consists of deer mice and plants from the site. Although no information on food distribution were available for the gray fox, it has been stated that the fox is a "wonderful mouser"[18]. Therefore, it was assumed that 60 percent of the diet is deer mice and 40 percent is plants. Using this information, values of 0.13 kg/day and 0.19 kg/day were used for IRp and IRm, respectively. No information on soil ingestion (IRs) was found for the gray fox. Using the same approach discussed for deer mice, an inadvertent soil ingestion rate of 3 percent of the plant ingestion rate, or 0.0039 kg/day, was used for the gray fox. The amount of soil adhered to skin (AF) was the same as that used for the deer mouse (1.0 $mg/cm^2/day$)[14]. The surface area of exposed skin (SA) was assumed to be 10 percent of the total surface area of the fox, as discussed above for the deer mouse. Using the same surface area to body weight relationship discussed for the deer mouse, and assuming the body weight of a gray fox is 5.25 kg[12], a value of 301.9 cm^2/day was used for SA.

The chemical concentration in deer mice was estimated from the calculated LADD. In the Phase 1 assessment, the lifetime average daily dose was assumed to be equal to the body burden in the deer mice. That is, the total uptake and elimination of chemicals from the deer mice was assumed to be at steady state and the body burden was assumed to be equal to the exposure dose. Other authors[19] have used a factor of ten percent to estimate the bioavailability of all metals to meadow voles and deer mice (i.e., chemical concentration in tissues was assumed to be 10 percent of the LADD). This Phase 1 assessment used the more conservative approach that assumed 100 percent of the dose was bioavailable.

Phase 2

In Phase 2, collection of biota and additional soil samples was conducted to address data gaps and further evaluate potential "problem" sites based on the results of Phase 1. The approach for field sampling used collocated sampling of all media along predefined transects. Generally 4 transects were defined per site; large sites had more transects (up to a maximum of 10 on a site). Transects were designed to encompass all habitats at a site and ranged across chemical concentration gradients in soil to provide typical concentrations for exposure by biota. With this overriding goal, transects were restricted to areas containing vegetation to ensure the availability of all types of biota for sample collection. To prevent depleting a specific stand of plants, no more than 50 percent of the stand was sampled. Because this strategy resulted in insufficient plant material for chemical analysis, plant samples were collected from a number of stands along a given transect and composited, resulting in one plant sample per transect. Surface soil samples were collected from each location where plants were sampled and were also composited to provide one soil sample per transect. All plant and soil samples were individually sealed in labeled plastic bags and stored at 4°C until received by the analytical laboratory.

Small mammals were trapped by placing 20 large folding aluminum Sherman live traps (3" x 3.5" x 9") prebaited with a mixture of rolled oats and peanut butter along each transect. Baited traps were placed along the transects late in the afternoon and were checked the following morning. Trapping was continued at each site for 2 nights, or until at least four individuals of the same species were collected, whichever came first. Individuals were identified by species, sex, and age class, placed in plastic bags, sealed, and euthanized in a cooler of dry ice. Specimens were stored at 4°C until received by the analytical laboratory.

Biota were analyzed for the same chemicals that were identified in soil. All samples were analyzed for metals. However, due to sample size limitations, not all individual small mammals could be analyzed for all types of organic chemicals. Dioxins were detected in soil at two sites, but were only analyzed in mammal tissue at one of the sites; no rodents were successfully collected at the other site. Plants were analyzed for dioxins at both sites. However, plants and small mammals were not collected and analyzed for dioxins along the same transects at either site.

Transects were also defined at reference locations for each habitat where biota were collected. The same sampling approach was used at the reference locations to estimate background concentrations of metals in plant and mammal tissues.

RESULTS

Modeled and measured plant concentrations from Phases 1 and 2, respectively, are compared with soil concentrations for lead, zinc, and OCDD in Figure 1. The predicted plant concentrations using the plant uptake models from Phase 1are presented along the right axes, and the measured concentrations from biota analyzed during Phase 2 are presented along the left axes. Background soil concentrations of lead and zinc are included to put the detected concentrations in perspective. The average measured concentration detected during Phase 2 is also plotted. The predicted concentrations are a straight line because the soil and plant concentrations are directly related by one factor. Measured concentrations are indicated by the points, and adjacent points are connected. For both lead and zinc (Figures 1a and 1b, respectively), both measured and modeled axes use the same scale, but the soil concentration ranges are different. For OCDD (Figure 1c), the predicted concentration axis uses a scale approximately 30 times smaller than the measured axis. For lead and zinc, the measured plant concentrations were 0.7 and 0.8 times the modeled concentrations, respectively, across the range of detected soil concentrations. For OCDD, the measured plant concentrations were much greater than the modeled concentrations (ratio of measured to modeled of 187; Figure 1c).

Modeled and measured deer mouse concentrations from Phases 1 and 2, respectively, are compared with soil concentrations for lead, zinc, and OCDD in Figure 2. The predicted deer mouse LADDs using the exposure model from Phase 1 are presented along the right axes, and the measured concentrations from biota analyzed during Phase 2 are presented along the left axes. The average measured concentration detected during Phase 2 is also plotted. The predicted concentrations are a straight line because the soil and plant concentrations are directly related by one factor that combines all the intake values in Equation 2. For both lead and zinc (Figures 2a and 2b, respectively), both measured and modeled axes use the same scale, but the soil concentration ranges are substantially different, and are different from the scale used in Figure 1. For OCDD (Figure 2c), the predicted concentration axis uses a scale approximately 30 times smaller than the measured concentration axis. For lead and zinc, the measured whole-body concentrations were 0.3

FIGURE 1.
Comparison of Plant and Soil Concentrations.

FIGURE 1a. Lead

Ratio Actual/Modeled = 0.7

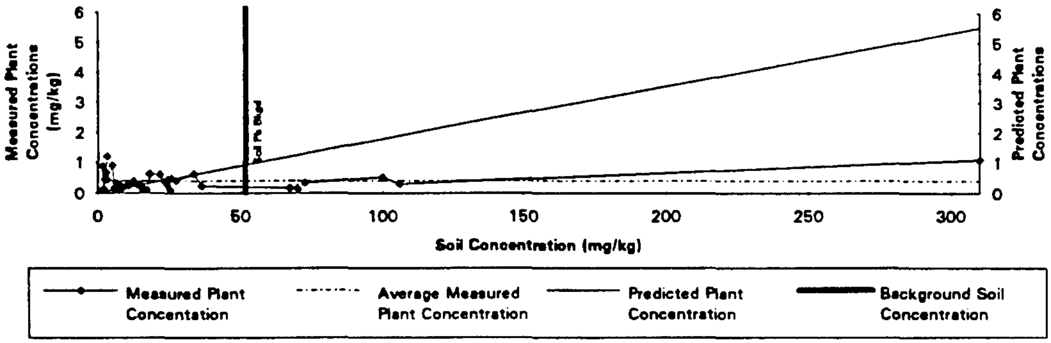


FIGURE 1b. Zinc

Ratio Actual/Modeled = 0.8

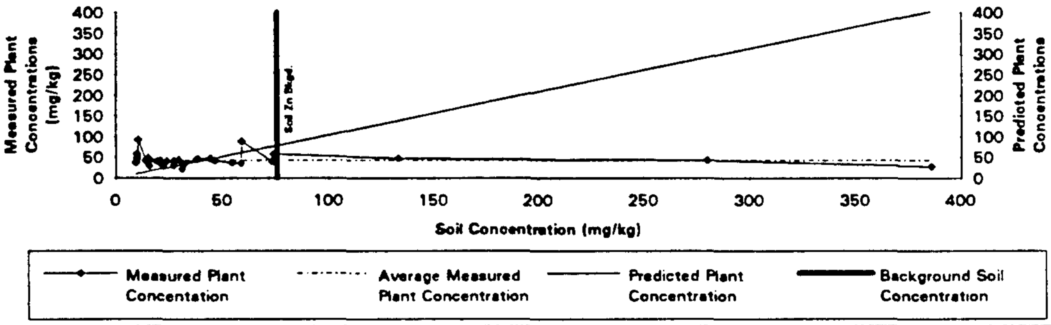


FIGURE 1c. OCDD

Ratio Actual/Modeled = 187

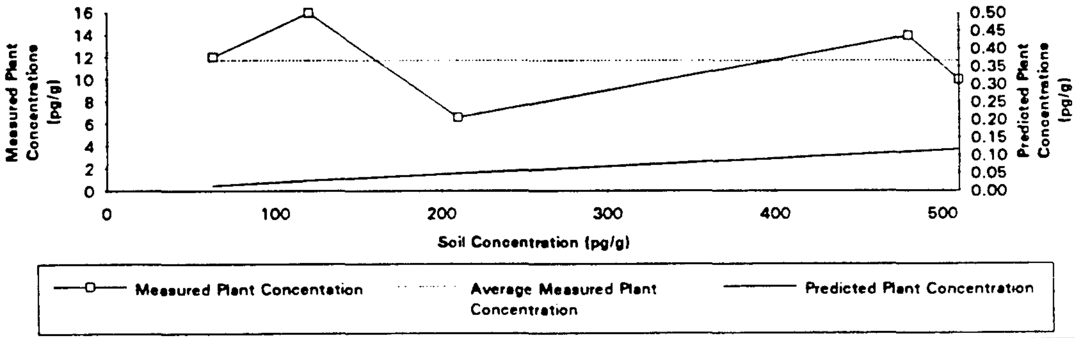


FIGURE 2.
Comparison of Mammal and Soil Concentrations

FIGURE 2a. Lead

Ratio Actual/Modeled = 0.3

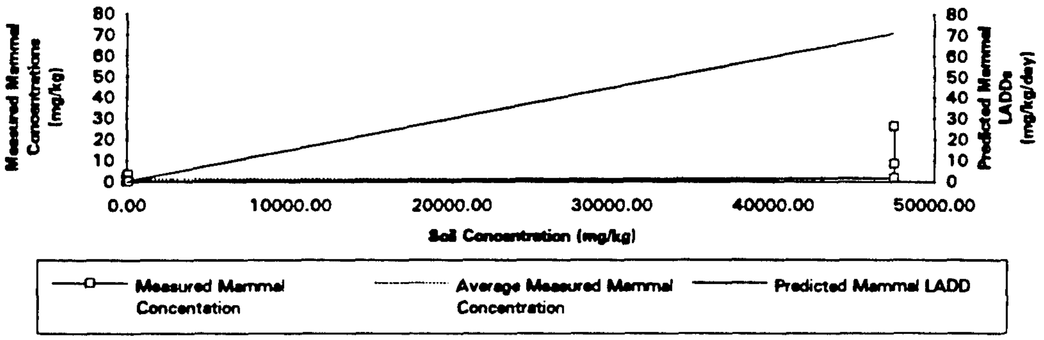


FIGURE 2b. Zinc

Ratio Actual/Modeled = 2

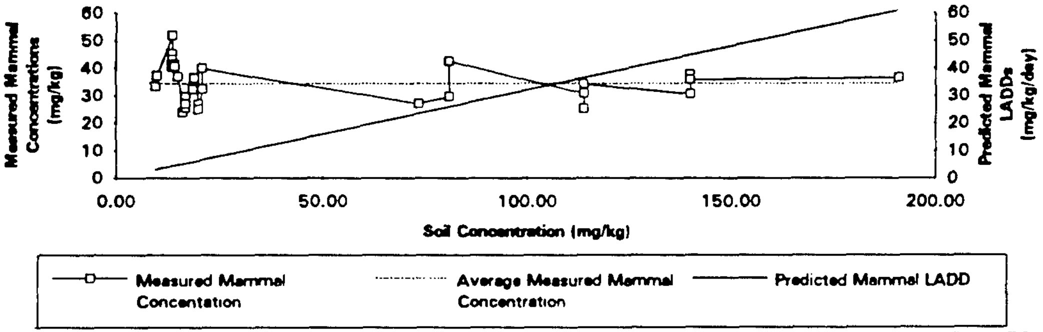
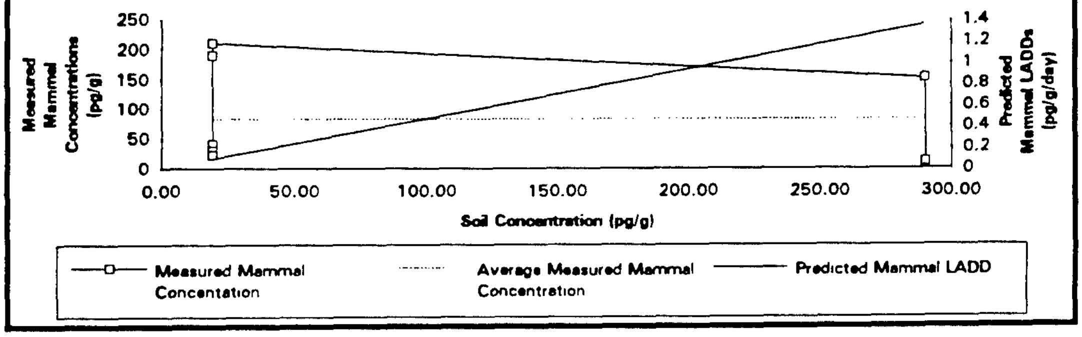


FIGURE 2c. OCDD

Ratio Actual/Modeled = 147



and 2 times the modeled LADDs, respectively, across the range of detected soil concentrations. For OCDD, the measured whole-body concentrations were much greater than the modeled concentrations (ratio of measured to modeled of 147; Figure 2c).

The majority of measured data points for lead and zinc were from soil concentrations less than 100 mg/kg. Figure 3 presents the zinc data for plants and deer mice for soil concentrations less than 100 mg/kg on an expanded scale. Although not shown here, lead data indicate similar patterns to zinc using this expanded scale.

DISCUSSION

For lead and zinc, the plant uptake and deer mouse exposure models consistently overpredict measured concentrations at high concentrations and slightly underpredict concentrations at low concentrations (Figures 1 and 2). For plants, the measured concentrations for all soil levels of lead and zinc above background were less than the modeled concentrations (Figures 1a and 1b). As shown on Figure 3, the model begins to overestimate actual plant tissue concentrations for zinc at approximately 40 mg/kg in soil, which is about half the background soil concentration of 75.8 mg/kg. For deer mice, the model begins to overestimate actual body burdens just above a soil concentration of 100 mg/kg. Because the models are linear, the overestimation of actual exposures increases with the soil concentration. Therefore, at very high soil concentrations, the models may grossly overestimate actual exposures. This indicates that the kinetics of uptake and depuration of lead and zinc in plants and deer mice are not linear, but are sublinear at high concentrations. Because ecological risk assessments focus on concentrations substantially in excess of background, this indicates that the screening models used in Phase 1 are likely to substantially overestimate actual exposures, and therefore risks.

A different pattern is seen for OCDD. Across the range of detected soil concentrations, the measured concentrations in plants were consistently greater than that predicted from the plant uptake model (Figure 1c), by approximately 2 orders of magnitude. This implies that the equation developed by Travis and Arms[10] is not appropriate for use with dioxins. For deer mice, a similar pattern was observed (note the different scales used for modeled and measured values in Figure 2c). Because the exposure model for deer mice includes a plant dietary intake term, and the diet of a deer mouse was assumed to be only plants, it follows that because the plant uptake model underpredicts actual concentrations, so will the deer mouse exposure model. In spite of this underestimation of plant and deer mouse concentrations by the model, modeled LADDs for the gray fox based on modeled plant and mouse concentrations are higher than those based on measured plant and mouse concentrations for half of the detected soil concentrations. This may in part be due to the lack of dioxin analyses performed for deer mice for some soil concentrations. This underscores the importance of collected appropriate data for all biota if risk management decisions are to be made based on the data.

FIGURE 3.
Comparison of Biota and Soil Zinc Concentrations Less Than 100 mg/kg

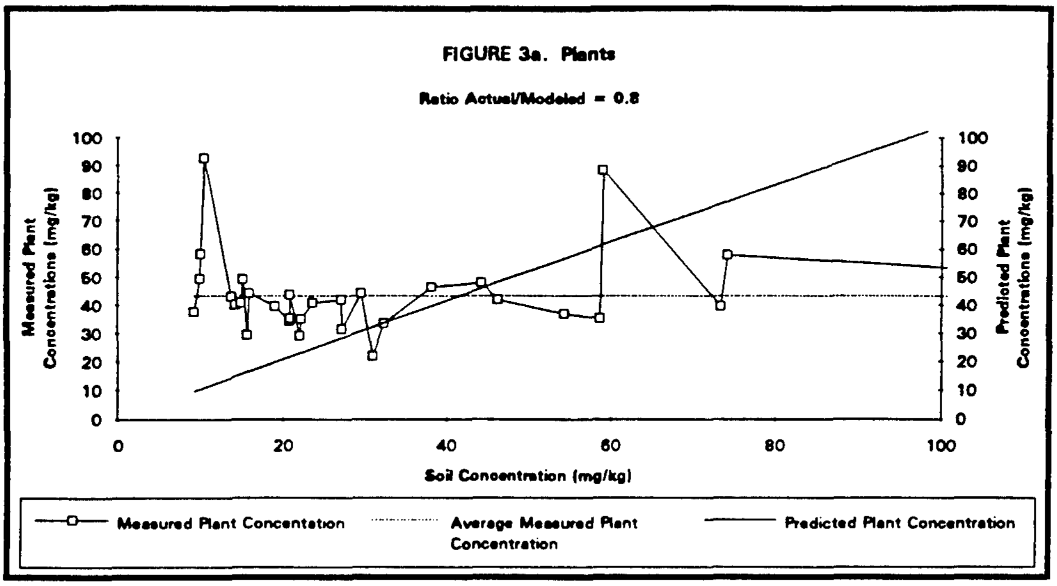


FIGURE 3a. Plants

Ratio Actual/Modeled = 0.8

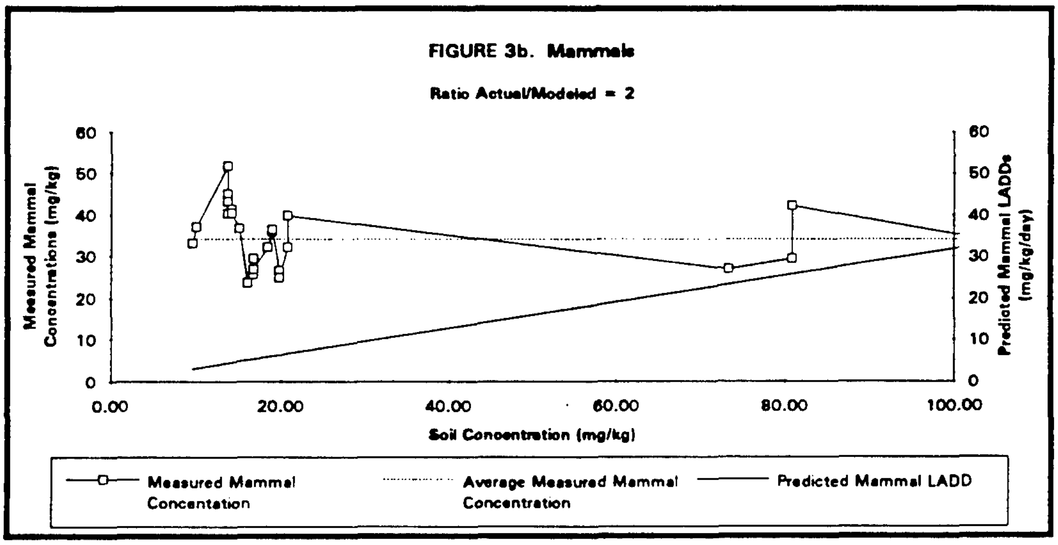


FIGURE 3b. Mammals

Ratio Actual/Modeled = 2

CONCLUSIONS

This evaluation demonstrates the importance of using multiple approaches to estimate exposure and risk for ecological receptors. A weight-of-evidence approach should be used to evaluate endpoints, as recommended by EPA[2,8], to decrease the likelihood of misinterpreting data using only one approach. In this assessment, use of only measured soil data and modeled exposures would lead to overestimating exposures and risks to receptors for lead and zinc, and underestimating exposures and risks to receptors for OCDD. One way to address the uncertainty associated with a given approach as well as the variability of data is to provide a range of risks for a given endpoint using quantitative methods such as Monte Carlo analysis.

Given that the models tend to overpredict actual exposures at high concentrations for metals, for most contaminated sites, modeling can provide a conservative screen but would result in excessive cleanup in the absence of field data on biota. Therefore, focused collection and analysis of biota should be considered prior to basing risk management decisions on risk assessment results based solely on modeling. The added cost in collecting and analyzing these data may result in substantial cost savings in remediation.

ACKNOWLEGEMENTS

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KEY TERMS

2,3,7,8-TCDD: 2,3,7,8-Tetrachlorodibenzo-p-dioxin.

Assessment endpoint: An explicit expression of the environmental value that is to be protected.

Collocation: Samples collected at the same location along the same transect.

Conceptual model: Describes a series of working hypotheses of how stressors (e.g., chemicals) might affect different parts of the ecosystem. The conceptual model also describes the ecosystem potentially at risk, the relationship between measurement and assessment endpoints, and exposure scenarios.

Exposure: The process by which the temporally and spatially distributed concentrations of a chemical in the environment are converted to a dose.

Exposure pathway: The course a chemical agent takes from a source to an exposed organism describing the unique mechanism by which a receptor is exposed to chemicals at or originating from a site.

Exposure point concentration (EPC): The concentration of a chemical at the location of potential contact between a receptor and a chemical agent.

Exposure route: The way in which a chemical agent comes in contact with a receptor (e.g., by ingestion or dermal contact).

Lifetime average daily dose (LADD): The total estimated dose, in mg/kg/day, that a receptor is estimated to be exposed to daily for its entire lifetime.

Measurement endpoint: A measurable ecological characteristic that is related to the valued characteristic chosen as the assessment endpoint.

Monte Carlo analysis: A technique used to obtain information about the propagation of uncertainty in mathematical simulation models. The distribution of the output values can be used to determine the probability of occurence of any particular value given the uncertainty in the parameters.

Societal values: Societal values and concerns can range from protection of endangered or commercially or recreationally important species to preservation of ecosystem attributes for functional reasons (e.g., flood water retention by wetlands) or aesthetic reasons.

Toxicity equivalents (TEQs): TEQs are used to compare the relative toxicity of individual dioxin and furan congeners to 2,3,7,8-TCDD.

Transect: A line traversing a site that is used to locate sampling stations.

Uptake: The rate at which a receptor takes up a chemical. The rate is expressed as the unit mass of chemical per unit mass of receptor.

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COMPLIANCE FOR CONTINUING MISSION

ULTRA-VIOLET / ELECTRON BEAM DETOXIFICATION OF NITROGLYCERINE / PROPYLENE GLYCOL DINITRATE WASTE WATER

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1.0 INTRODUCTION

Three production facilities at the Naval Warfare Center, Indian Head Division (NSWC-IHD) produce wastewater containing nitrate esters; (1) the Moser facility where trimethylol ethane trinitrate (TMETN) and triethylene glycol dinitrate (TEGDN) are manufactured; (2) the Biazzi plant where trinitroglycerin (NG) and propylene glycol dinitrate (PGDN) are manufactured; and (3) the NG propellant extrusion facility where high pressure water is used to extract NG propellant chips from the extrusion press. The concentration of nitrate esters in these wastewater streams is reduced by filtering the wastewater through activated carbon. This method, albeit effective in reducing the nitrate ester concentration to below limits of detection, does not destroy the nitrate esters, but transfers it from the water to the carbon. The nitrate esters are then destroyed by mixing the spent carbon with coal and feeding the mixture to the NSWC-IHD powerhouse for energy recovery (with the permission of the Maryland Department of the Environment).

In an effort to define a cost effective method to treat these complex waste streams, NSWC-IHD has undertaken a series of studies comparing the performance and cost of two advanced oxidation treatment processes, (a) peroxide enhanced ultra-violet oxidation, and (b) electron beam (EB) processing. Photolysis of hydrogen peroxide by UV light creates hydroxyl radicals, OH•, a powerful oxidizing species. This forms the basis for the UV/peroxidation treatment of nitrate ester contaminated water. Electron beam treatment of aqueous solutions produces not only the hydroxyl radical, but hydrogen radicals, H•, and the solvated electron, e_{aq}^-, both strong reducing species.

A prior study performed at NSWC-IHD showed that UV/peroxidation treatment had limited effectiveness on "washwaters" containing carbonate, sulfate, and nitrate ions.[1] The limited effectiveness of the U.V. peroxide treatment was attributed to (a) carbonate ions "scavenging" the hydroxyl radicals,

$$OH\bullet + CO_3^{-2} \longrightarrow OH^- + CO_3^-$$

and (b) the strong parasitic absorption of UV light by the nitrate ion that reduces the yield of hydroxyl radicals.

The motivation behind this study was to compare the effectiveness of UV and EB treatment, to see if the EB treatment created additional "beneficial" chemistry for treating the washwaters, and to compliment the prior work performed at NSWC-IHD by performing a chemical analysis of irradiated process streams.

Four of the six wastewater process streams were treated by the Solarchem UV/peroxide system and five wastewater process streams were treated by the EB process. Following treatment, chemical analysis was performed to identify the volatile and non-volatile decomposition products to establish a mass balance. The results from the EB treatments were used to determine the facility requirements and operating costs of an industrial EB facility.

2.0 METHODOLOGY

Since nitrate esters are prone to hydrolysis in both alkaline and acidic conditions, measures were instituted to ensure that the composition of the NG and PGDN samples remained unchanged over the course of this program. The acid catalyzed hydrolysis of nitrate esters can be minimized if refrigerated at a neutral pH. For this reason, all samples were stored in sealed containers, kept away from sunlight, and refrigerated at 4 °C. Quality control checks consisting of monthly pH, nitrate ion^3, and conductivity measurements were performed on all samples. For none of the samples did the pH or conductivity change over the course of this work.

Prior to treatment, the pH, nitrate ion, and conductivity were measured. After adding inorganic salts (to simulate washwater), the pH increased. After treatment, the samples were sealed and stored at 4 °C. Quality control checks performed on these samples over the course of this program confirmed that the compositions remained unchanged.

For the characterization of the irradiation byproducts, four different chromatographic separations were performed: GC/FID for relatively low boiling point alcohols, aldehydes, and ketones; GC/MS and HPLC for the more highly associated carboxylic acids and polyols; and a second HPLC procedure for nitrate esters. The GC/FID procedure corresponds to ASTM Method D 6395, "Standard Test Method for Volatile Alcohols in Water by Direct Aqueous-Injection Gas Chromatography" and tests for the following compounds; methanol, n-propanol, ethanol, isobutanol, acetone, methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, ethyl acetate, isopropyl acetate and n-butyl acetate. Calibrations at the concentration levels 5, 50 and 500 mg/l were performed on all standards. The MDL (method detection limit) is 5 mg/l. For analysis above 200 °C, the same chromatographic column was used on a GC equipped with a mass spectrometer.

The more highly associated oxygenated hydrocarbons, such as oxalic acid and glycerol were separated by a normal phase HPLC using a bonded amino stationary phase and detected by a refractive index detector.[4] During this analysis it was found that inorganic salts created a large interfering peak, which raised the MDL of glycerol to 500 mg/l. Therefore it was necessary to desalinate the samples with an ion exchange resin.[5] After desalination, the interfering peak was successfully removed and the method detection limit for glycerol was lowered to 30 mg/l. Routine analysis consisted of running standards along with unknowns. As an additional check, the process streams were spiked with known amounts of standard materials. This insured that the chemical characteristics of the wastewater streams tested did not interfere with the sensitivity of the analysis.

Quantification of the organic nitrate concentration was performed by HPLC at the IHD-NSWC Analytical Chemistry Division. All samples, both treated and untreated, were analyzed in triplicate and calibrated against high purity analytical standards at three concentrations (0.25, 2.5 and 25 mg/l).

For the electron beam irradiated wastewater, vapor samples were collected and tested for their total organic carbon. In this procedure, a gas sample was injected directly into the capillary column of a gas chromatograph with a flame ionization detector. The capillary column used for the analysis was: DB-624, 30 m long, 0.32 mm ID and 1.8 µm film thickness.

For compounds with vapor pressures low enough to be released and lost during the irradiation, gas sensitive monitors were used. These compounds include formaldehyde, carbon dioxide, carbon monoxide, ammonia, and nitrogen dioxide. Gas sensitive monitors[6] operate under the principle of air diffusion sampling and provide a quantitative measure of the average concentration of vapor in the air sampled. Electron beam irradiation produced no detectible amounts of carbon dioxide, nitrogen dioxide or ammonia. Hydrogen gas generated during the electron beam irradiation may have interfered with the long time measurement of CO and HCHO.

3.0 RESULTS

3.1 Ultraviolet/Peroxide Treatment of NG/PGDN Contaminated Water

The photoinduced decomposition of NG transfer water was performed in a 120 kW Rayox® Reactor[7] at NSWC-IHD. This system was designed to deliver a UV dose of 500-600 kWh per 1,000 gallons and handle 4-6 gpm of NG transfer water. Although this system can only process 4-6 gpm of NG transfer water, it circulates the wastewater a rate of 120 gallons per minute through the UV processing zones and continuously aerates the wastewater during treatment. During this treatment, 1,000 ppm of hydrogen peroxide was added to the process stream and a UV dose of 600 kWh per 1,000 gallons was applied. During treatment, the pH dropped from 8.4 to 2.4, and the NG was almost completely oxidized to carbon dioxide.

Wastewaters containing PGDN were irradiated at Solarchem Environmental Systems using a 30 kW, 5 gallon batch reactor. The UV dose administered was 500 kWh per 1,000 gallons and 2,000 ppm of hydrogen peroxide was added to each process stream. The time to process 5 gallons of wastewater in the 30 kW Rayox® Reactor was 140 minutes. This treatment proved sufficient to decompose all the NG and PGDN in the transfer water. The same treatment demonstrated only limited effectiveness in degrading the nitrate esters NG and PGDN when nitrate ions and carbonate salts were present. The effect of UV/peroxide treatment on the organic concentration is given in TABLE 3-1. Other than the partially degraded nitrate ester propylene glycol mononitrate (PGMN), the only byproducts detected were acetone, glycerol and trace amounts of methanol. A mass balance performed on all the carbonaceous byproducts found in the UV treated wastewater is shown in TABLE 3-2.

TABLE 3-1
Organic Nitrate Concentration Before and After UV Irradiation

UV Process Streams @ 500kWhr/1,000 gal.	Organic Nitrate Conc.[†] mg/l Prior Treatment	Organic Nitrate Conc.[†] mg/l After Treatment
NG transfer water	83	<0.1
PGDN transfer water	111	<0.1
PGDN wash water	102	39
NG/PGDN composite water	157	67

[†] expressed as mg/l nitrogen.

3.2 Electron Beam Treatment of NG/PGDN Contaminated Water

Irradiations were performed at the University of Maryland's Laboratory for Radiation and Polymer Science with a 1 kW linac and at Irradiation Industries, Inc. (Gaithersburg, MD) with a 75 kW 2.7 MeV Dynamitron. All dosimetry was performed using radiochromic film dosimeters and are traceable to the National Institute of Standards and Technology. Irradiations were performed at five doses ranging from 50 to 200 kGy in sealed sample holders with gas sampling ports to permit the capture and analysis of the gaseous byproducts.

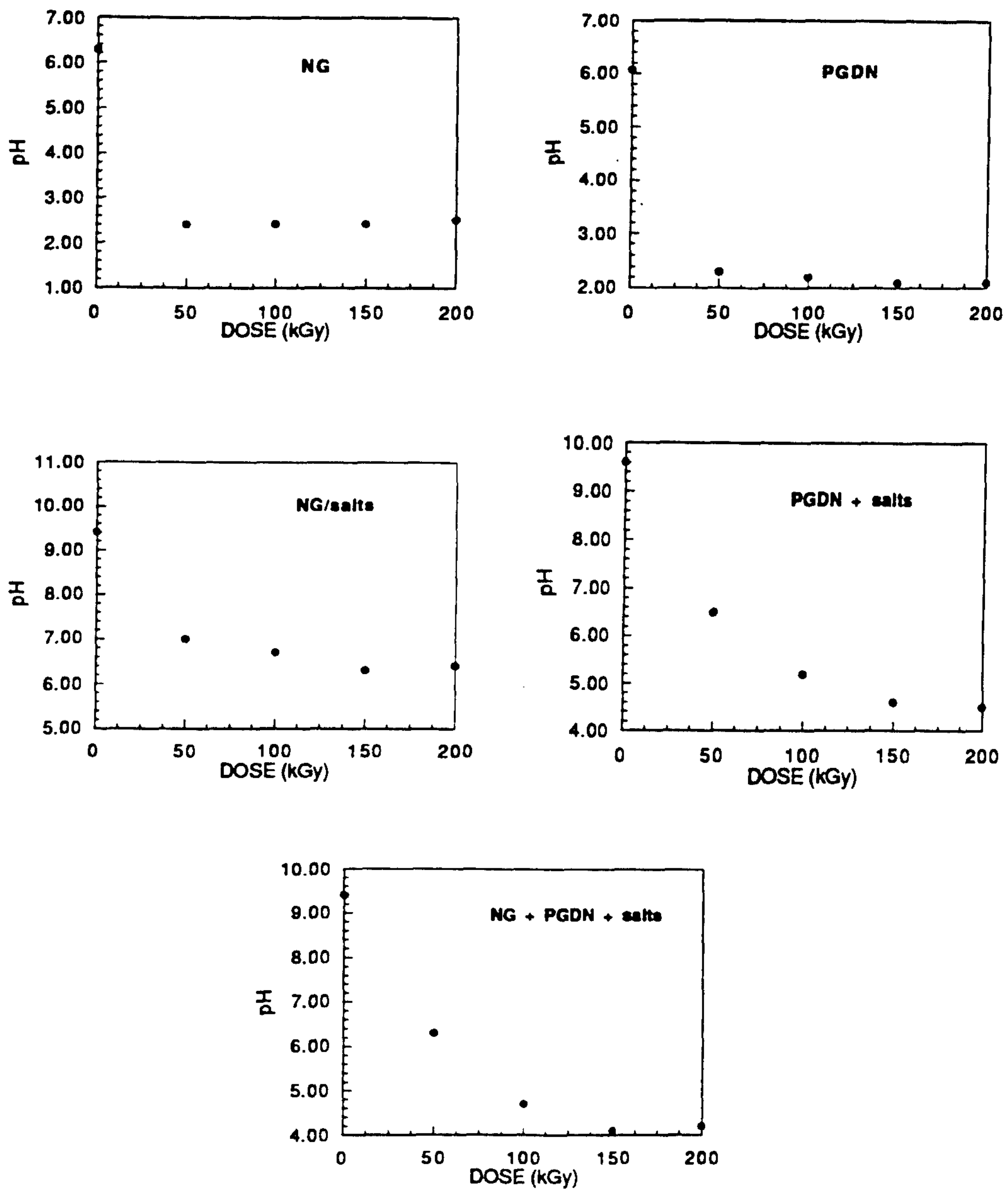
The effect of electron beam irradiation, at a dose of 200 kGy, on the organic nitrate content in the wastewaters tested, is summarized in TABLE 3-3. Only the NG transfer water was treated with a sufficient dose to reduce the organic nitrate concentration below 5 ppm (by weight of carbon). The effect of dose is shown in FIGURE 1. As the organic nitrate concentration drops, the pH drops, indicating the formation of HNO_3. The washwater pH was buffered by the carbonate salts, which decreased the extent of nitrate ester hydrolysis.

TABLE 3-2
Carbon Mass Balance for UV Irradiated Process Streams

UV/H_2O_2 Treatment
Carbon Mass Balance Table

		Organic Nitrates by HPLC (mg/l)		Solvent Screen Aqueous Byproducts by GC/FID (mg/l)		Non-Volatile Organics by HPLC (mg/l)	Carbon Dioxide (mg/l)	Total Organic Carbon by persulfate digestion (mg/l)	Total Carbon (mg/l)
Process Stream	Irradiated	NG	PGDN	Methanol	Acetone	Glycerol	(est.)		
NG transfer water	No	64	<1	<1	<1	<1	NA	110(±20)	64(±2)
	Yes	<1	<1	3	<1	<20	60	3(±2)	63(±20)
PGDN transfer water	No	<1	142	<1	<1	<1	NA	---(±-)	143(±2)
	Yes	<1	50	1	<1	<20	100	50(±20)	150(±20)
PGDN wash water	No	<1	132	<1	<1	<1	NA	---(±-)	132(±2)
	Yes	<1	47	<1	<1	<20	80	94(±20)	127(±20)
NG/PGDN/salts composite water	No	70	95	<1	<1	<1	NA	---(±-)	165(±2)
	Yes	35	36	1	46	<20	60	178(±20)	168(±20)

FIGURE 1.
EB Treated Organic Nitrate Concentration vs. Dose



The HPLC of the NG and PGDN transfer water after EB processing revealed that the decomposition of nitrate esters occurs by cleaving one nitrate ester group at a time. The compounds formed from the destruction of NG are dinitroglycerine (DNG) and MNG (mononitroglycerine). The decomposition of PGDN results primarily in the formation of PGMN. The identified byproducts in the HPLC trace of EB processed NG transfer water are MNG and DNG. The identified byproduct for the PGDN transfer water was PGMN. The only organic byproduct found was glycerol, as evidenced by the GC/MS results. A mass balance of the carbonaceous electron beam decomposition byproducts is shown in TABLE 3-4.

TABLE 3-3
Organic Nitrate Concentration Before and After EB Irradiation

EB Process Streams	Organic Nitrate Conc.† mg/l Prior to Irradiation	Organic Nitrate Conc.† mg/l After Irradiation (200 kGy)
NG transfer water	45	3
NG wash water	61	48
PGDN transfer water	117	97
PGDN wash water	102	89
NG/PGDN/salts composite water	157	144

† expressed as mg/l nitrogen.

4.0 ECONOMIC EVALUATION FOR ELECTRON BEAM DETOXIFICATION

From the treatment dose and the throughput requirements (i. e., the maximum gallons per minute) the power required to treat each of the wastewater streams can be computed using the following relationship,

$$\text{Dose (J/kg)} \times \text{Flow rate (kg/s)} = \text{Power (J/s)}.$$

These values are computed in TABLE 4-1. This calculation does not, however, account for various system inefficiencies. Assuming a 50% energy loss from incomplete beam energy utilization, the line power required to treat 2 gpm of NG wastewater with an average dose of 210 kGy is 52 kW. Similarly, the beam power required to treat 4 gpm of PGDN wastewater with an average dose of 950 kGy is 460 kW.

TABLE 3-4
Carbon Mass Balance for EB Treatment Process Streams.

EB Treatment
Carbon Mass Balance

		Organic Nitrates(mg/l)					Non-Volatile Organics (mg/l)	Total Carbon (mg/l)
Process Stream	Irradiated	NG	PGDN	DNG	PGMN	MNG	Glycerol	
Process Stream #1 NG transfer water	No	37.6	1.0	<0.1	<0.1	<0.1	<1.0	38±1
	Yes	<0.1	<0.1	<0.1	3.0	<0.1	30±10	33±10
Process Stream #2 NG wash water	No	51.9	<5.0	<5.0	<5.0	<5.0	<1.0	52±5
	Yes	48.2	<5.0	<5.0	<5.0	<5.0	14±10	62±10
Process Stream #3 PGDN transfer water	No	4.2	142.2	<0.1	<0.1	<0.1	<1.0	146±10
	Yes	1.4	76.5	0.8	17.0	1.0	30±10	127±10
Process Stream #4 PGDN wash water	No	<5.0	132	<5.0	<5.0	<5.0	<1.0	132±5
	Yes	<5.0	121	<5.0	<5.0	<5.0	14±10	135±10
Process Stream #5 NG/PGDN/salts composite water	No	70	95	<5.0	<5.0	<5.0	<1.0	165±5
	Yes	61	83	<5.0	<5.0	<5.0	8<>20	158±10

TABLE 4-1
Production Volume of the Biazzi Nitration Facility Wastewater Streams and the Electron Beam Dose Required to Reduce the Organic Nitrogen Content to 1 mg/l

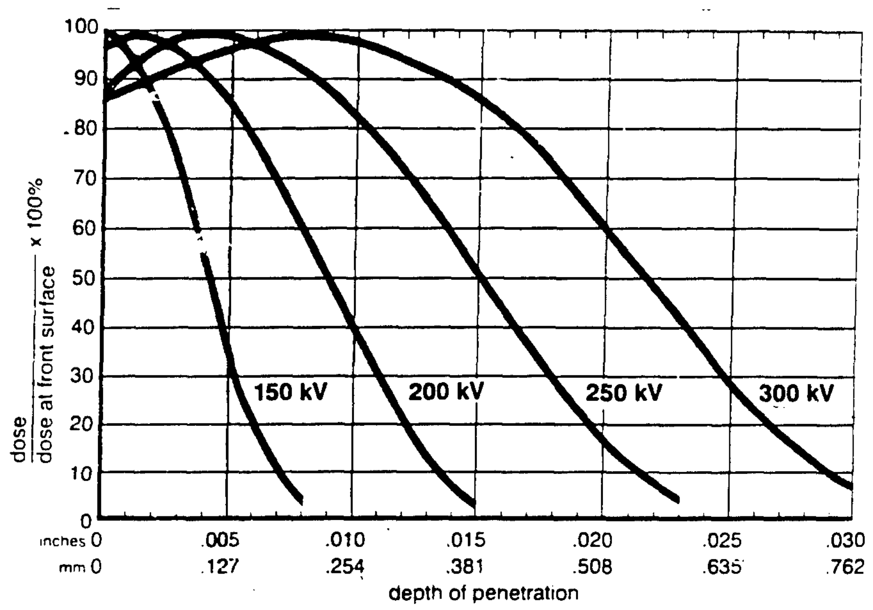
Wastestream	Volume (gal/wk)	Flow Rate (gal/min)	Dose req'd (kGy)	Power Required kW
Process Stream #1 NG transfer Water	9,000	2	210	26
Process Stream #2 NG wash water	25,000	3	7,400	1,344
Process Stream #3 PGDN transfer water	35,000	4	950	460
Process Stream #4 PGDN wash water	10,000	1	10,250	620
Process Stream #5 NG/PGDN/salts composite water	79,000	8	9,800	4,745

The beam power is the product of the beam current and the kinetic energy of the electrons produced. For example, a 10 mA beam current accelerated to a potential of 1,000 keV (1 MeV) produces 10 kW of beam power. A variety of electron beam processors, ranging in power from 1 to 100 kW are readily available.

Based on the throughput requirements, treatment dose, and standard EB designs, this evaluation recommends a 60 kW unit, which can process up to 2 gpm of NG transfer water. At least two manufacturers, Energy Sciences Inc. and RPC Industries produce low energy (300 keV) self shielded EB treatment units that deliver the requisite power. By incorporating multiple filaments, these systems are able to produce a uniform distribution of current over a wide area, and provide the user with ample processing power. The line-to-beam power efficiencies of these two types of accelerators exceeds 80% and makes these systems, the most economical choices.

The optimal thickness of the water stream can be easily determined by examining the dose distribution curve for 300 keV electrons in water. This is shown in FIGURE 2. From this profile, it can be determined that for a water thickness of 0.017 inches, the dose variation in the water is less than 15%, and approximately 60% of the total beam energy is absorbed. Therefore, to process a 2 gpm wastestream of NG (0.017" thick) with a treatment dose of 210 kGy, a 24" wide stream flowing at 94 ft/min must pass under the electron beam.

FIGURE 2.
Dose Distribution Curve (courtesy of ESI)



The full scale wastewater treatment facility, based on the above recommendations, contains a self-shielded 60 kW, 300 keV EB processor, and a process control system that adjusts the water flow and beam current to deliver the necessary treatment dose. The pumps required to maintain adequate flow into the EB processor would require only a few square feet of space and easily reside underneath or along side the processing area. As part of the overall quality control program, a personal computer is coupled to an analog-to-digital interface to continuously monitor and adjust the accelerator power and inlet/outlet flow rates. If desired, a similar system could be implemented to adjust the pH, and oxygen/ozone/hydrogen peroxide content of the process stream. The projected capital and operating costs are listed in TABLE 4-2.

5.0 DISCUSSION

Hydrogen peroxide and 500-600 kWh per 1,000 gallons of UV light completely destroyed the NG in wastewater containing no inorganic salts.[7] A chemical analysis of the UV/H_2O_2 process stream indicates that the primary chemical byproduct is carbon dioxide. The energy cost for this treatment (assuming $ 0.08/kWh) is $ 40 per 1,000 gallons. By comparison, the energy cost for EB treatment to reduce the NG concentration in the transfer water to 6 ppm is $ 35 per

TABLE 4-2
Capital and Operating Costs for 60 kW, 300 keV Electron Beam Treatment Unit (@ 2 gpm)

Capital Costs:			
Installed Beam (includes shielding)			$750,000
Optional Support Facility (includes analytical equipment)			50,000
			$800,000
Operating Costs (hourly):	hourly	/1,000 gal.	
Operator (20% time @ $20.00/hr.)	$4.00	$33.33	
Power (60kW @ $0.08/kWh)	4.88	34.67	
Chilled water (@ $1.25/k gal. hr.)	1.25	10.42	
Maintenance ($7,400/yr avg.)	1.23	10.25	
	$11.36	$88.67	

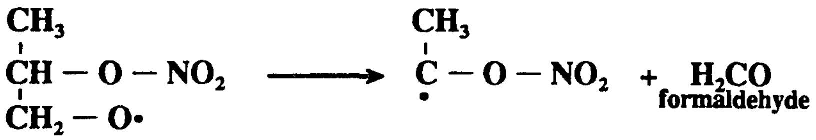
1,000 gallons. EB treatment converted the NG primarily into glycerol rather than carbon dioxide. The EB treatment dose required to destroy NG in the transfer waters was insufficient to completely destroy PGDN in both transfer and wash waters (containing the cations K^+, Ca^{++}, Na^+, cations and nitrate, sulfate and carbonate anions). In general, the UV/peroxide treatment was more effective at destroying the nitrate esters than the EB treatment. Aside from the byproducts carbon dioxide and glycerol, the PGDN process stream produced trace amounts of methanol. After irradiation, the composite water also contained acetone.

Although the experimental conditions for the UV and EB treatment are similar in that the pH was allowed to fall during treatment. The differences in the extent of reaction and nature of the byproducts produced may be attributed to the presence or absence of oxygen during treatment. In the UV irradiated process streams oxygen was continuously replenished while being recycled in the Solarchem batch reactor. This was not the case during the EB treatment where sealed vessels were irradiated to allow the capture of vapors.

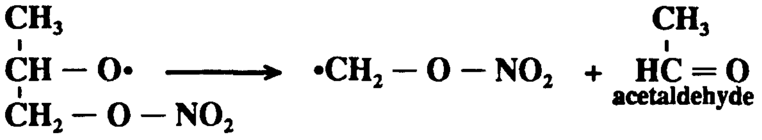
5.1 UV/H_20_2

The decomposition of the nitrate esters are favored both energetically and entropically by the creation of the compounds CO_2, N_2, H_2, CO, NO, and H_2O which all have large negative heats of formation. With the addition of a minimal amount of thermal energy, the driving force for the pyrolysis of nitrate esters causes explosions. Fortunately, a controlled method is available to destroy the nitrate esters NG and PGDN when they are in dilute solution. As in the thermal pyrolysis of nitrate esters, the destruction of nitrate esters in dilute solutions by, UV light or ionizing radiation, is initiated by the formation of free radicals. In the presence of oxygen, free radical decomposition reactions can lead to the formation of carbon dioxide, acetone, and methanol. These reactions may occur instantaneously or sequentially. Other reactions of greater or lesser importance may also contribute to the degradation of NG and PGDN, but since detailed spectroscopic and kinetic measurements are not available, no temporal or totally conclusive reaction mechanism can be assigned.

Photolysis of hydrogen peroxide generates hydroxyl radicals, OH•, initiates the decomposition of nitrate ester molecules by cleaving the O-NO_2 bond,[8] and produces NO_2 and the alkoxy radical, RR'CH-O•. The NO_2 produced reacts quickly with OH• to form nitric acid which lowers the pH. The alkoxy radical can, (a) undergo unimolecular decomposition of the alkoxy radical into an aldehyde, R-CH=O, and alkyl radical, •HCR-ONO_2, (5-1, 5-2) or, (b) abstract hydrogen to form a hydroxyl group. Abstraction of hydrogen by the photolyzed nitrate ester accounts for the conversion of PGDN to PGMN. The alkyl radical •CH_2-ONO_2, can either undergo unimolecular decomposition to form formaldehyde and NO_2. Similarly, •CH(CH_3)-ONO_2 produces acetaldehyde and NO_2.



$$\begin{array}{l}CH_3\\ \mid\\ CH-O-NO_2\\ \mid\\ CH_2-O\bullet\end{array}\longrightarrow\begin{array}{l}CH_3\\ \mid\\ \underset{\bullet}{C}-O-NO_2\end{array}+\underset{\text{formaldehyde}}{H_2CO}\qquad(5\text{-}1)$$



$$\begin{array}{l}CH_3\\ \mid\\ CH-O\bullet\\ \mid\\ CH_2-O-NO_2\end{array}\longrightarrow\bullet CH_2-O-NO_2+\underset{\text{acetaldehyde}}{\begin{array}{c}CH_3\\ \mid\\ HC=O\end{array}}\qquad(5\text{-}2)$$

The aldehyde byproducts (formaldehyde and acetaldehyde) are oxidized by molecular oxygen to form percarboxylic acids, R-(C=O)-O-OH, which are unstable and decompose readily to form carboxylic acids. Hydroxyl radicals compete with the peroxidation reaction by abstracting hydrogen form the aldehyde to form an acyl radical, R-C=O•. The methyl-acyl radical, CH_3-C=O•, decomposes into a methyl radical, CH_3• and carbon monoxide. Bimolecular reaction between these two radicals terminates any further reaction because it produces the relatively oxidation resistant compound, acetone. The composite wastewater had the highest concentration of nitrate esters which increased the probability of the bimolecular reaction and was the only process stream that contained a significant quantity of acetone. Bimolecular reactions between a methyl radical and a hydroxyl radical produce methanol. Methanol is oxidized to carbon dioxide through the formation of formic acid. It is found as a byproduct because of incomplete oxidation.

In summary, UV light and hydrogen peroxide act in synergy to destroy nitrate esters by producing nitrogen dioxide and an alkoxy radical. Cleavage of the carbon chain occurs by a free radical chain mechanism where unimolecular decomposition of the alkoxy radical produces aldehydes and alkyl radicals. Aldehydes are readily oxidized with great ease by a free radical chain mechanism that involves the addition of molecular oxygen or the hydroxyl radical to form carboxylic acids. The byproduct formic acid is further oxidized by molecular oxygen or hydroxyl radicals to carbon dioxide which terminates the reaction sequence. Other termination reactions include the bimolecular reaction of the methyl radical with the alkoxy radical to produces the relatively oxidation resistant compound acetone. Glycerol is produced by the acid catalyzed hydrolysis alone and does not require the photolysis of the nitrate ester molecule.

5.2 EB Treatment

In the EB treatment of nitrate ester contaminated wastewater, high energy electrons deposit their energy in water molecules and nitrate ester molecules through a series of ionizations and excitations. Since the fraction of energy absorbed by the nitrate ester molecules is proportional to its weight percent, which was very low (approximately 500 ppm), the primary pathway to the to the destruction of nitrate esters involves reactions between nitrate ester molecules and the products formed by the excitations and ionizations of water molecules. A small fraction of the energy (approximately 3%) is absorbed by the anions (SO_4^-) and cations (Ca^{+2},Na^+). These inorganic species are spectator ions and do not participate in any chemical reactions.

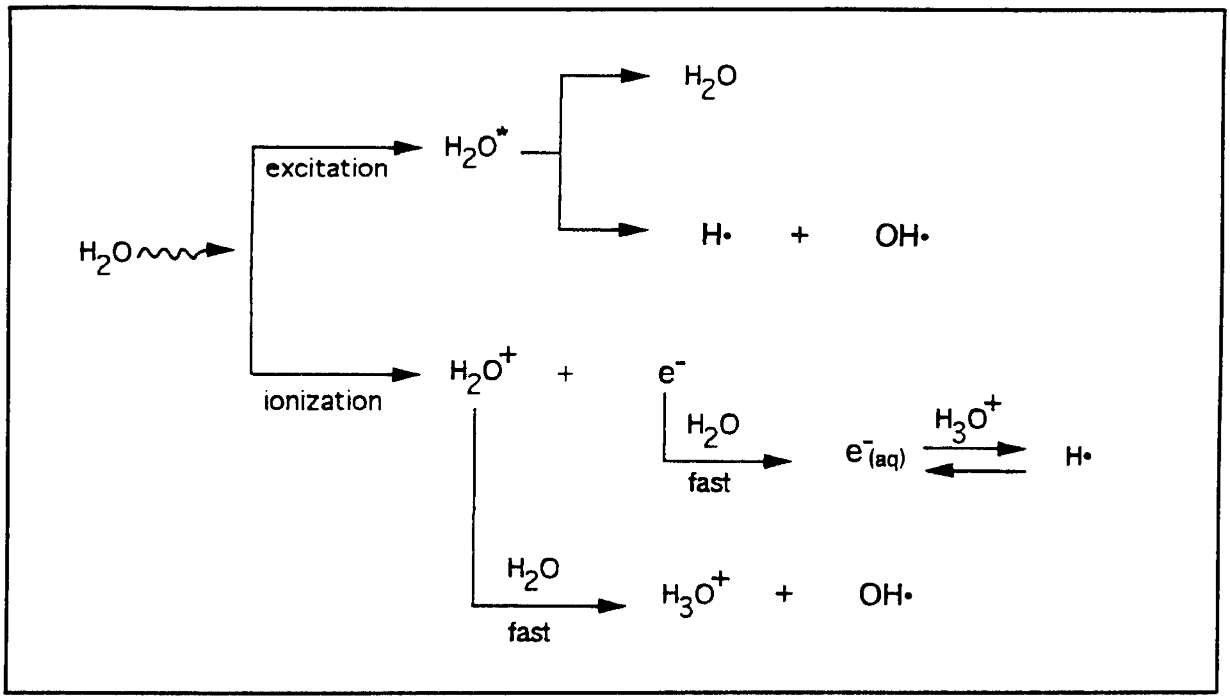
High energy electrons cause ionizations and excitations of water as shown in FIGURE 3. Ionization of H_2O liberates electrons and creates H_2O^+. The liberated electron is rapidly solvated to create the redox species e^-_{aq}, which has a relatively long lifetime, on the order of milliseconds. H_2O^+ is very unstable and reacts with the surrounding water to form the hydronium ion, H_3O^+ and the hydroxyl radical, OH•. Redistribution of the energy in electronically excited water molecules, H_2O^*, creates hydrogen radicals, H• and hydroxyl radicals, OH•.

It is possible that the solvated electron, e^-_{aq}, a reducing agent, reacts with the nitrate ester molecule to cause the simultaneous formation of a free radical (RR'CH-O•), and reduces the nitrate group to a nitrite ion, NO_2^-. Although no experimental work has been performed to test this hypothesis, supporting evidence is available from the known interaction of the solvated electron with methyl nitrate, in which the nitrite group readily accommodates the solvated electron.[9] The nitrite group is then oxidized by hydroxyl radicals to form nitric acid.

The alkoxy radical formed by the interaction of the solvated electron with the organic nitrate can a) combine with a hydrogen radical or b) abstract a hydrogen atom from water in the surrounding media. This process would lead to the complete hydrolysis of NG to produce glycerol. The conversion of PGDN to glycerol involves an intermolecular hydrogen abstraction which frees the primary carbon to react with a hydroxy radical, thus providing a pathway to the complete hydroxylation of the molecule.

Because the irradiations performed in this study were under nearly anaerobic conditions, the dose required to oxidize the nitrate ester was increased considerably and dose rate effects were not observed. It is expected that had the process streams not been irradiated under anaerobic conditions the oxidation process would have gone to completion.

FIGURE 3
Effect of High Energy Electrons on Water



CONCLUSIONS

Earlier work at NSWC-IHD that demonstrated the effectiveness of UV/peroxide treatment to destroy nitrate esters in production waste streams. This work confirmed that the UV/peroxide process reduced the organic nitrate concentration to less than 1 ppm by converting the toxic contaminant to carbon dioxide, methanol, acetone, and glycerol.

Evaluation of oxygen depleted EB treated waste water confirmed that the only byproduct was non-toxic glycerol. Both UV/peroxide and EB remediation processes reduced the organic nitrate concentration to less than 1 ppm with approximately a 75% reduction in operating costs.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support, cooperation, and guidance of Charles R. Painter (NSWC-IHD) throughout the course of this work. We also thank Professor Joseph Silverman (University of Maryland) for his contributions to the radiation chemistry of this work and Dr. Chester Clark for valuable discussions related to the production and demil of energetic materials.

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AN EVALUATION OF PHYSICAL/CHEMICAL TREATMENT VERSUS BIOLOGICAL TREATMENT FOR TREATMENT OF PROPELLANT PRODUCTION WASTEWATER CONTAINING 2,4-DINITROTOLUENE

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ABSTRACT

2,4 Dinitrotoluene (DNT) is used in the production of propellants at the Radford Army Ammunition Plant (RAAP) in Radford, Virginia. 2,4-DNT is a RCRA toxic waste that is a suspected carcinogen and has also been linked to heart disease by some studies. The existing biological wastewater treatment plant (BWTP) at RAAP receives wastewater that contains 2,4-DNT from several propellant production operations. The U.S. Army Environmental Center (USAEC) is conducting a pilot-scale field demonstration project at RAAP to evaluate two potentially applicable technologies for treating the 2,4-DNT wastewater at the point of generation (i.e., upstream of the BWTP). This paper discusses these technologies and presents a preliminary evaluation of the information collected to date. The USAEC is conducting this program to support environmental compliance activities at RAAP. Pending changes in Virginia's wastewater regulations are expected to place increasingly stringent limits on discharges of 2,4-DNT.

BACKGROUND

The Radford Army Ammunition Plant (RAAP), located in Southwest Virginia, is a Government Owned Contractor Operated (GOCO) Army installation operated by Alliant Techsystems (Alliant) (formerly Hercules, Inc.). 2,4-DNT is a plasticizer used in the manufacturing process of single- and multi-base propellants to reduce hygroscopicity, improve mechanical properties, alter thermochemistry and burning rate, and facilitate solvent removal. Slug flows of 2,4-DNT enter the wastewater stream via discharge from several batch production operations including water-dry, wet screening, and solvent recovery. The existing wastewater treatment facility operates as a central BWTP and receives wastewater from all operations for treatment prior to discharge into the New River under a National Pollutant Discharge Elimination System (NPDES) permit. Previous studies have indicated that the BWTP influent wastewaters contain up to 75 mg/L of 2,4-DNT.

The current daily discharge limits for 2,4-DNT are 113 µg/L (average) and 285 µg/L (peak). The 113 µg/L level was established based on the quantitation limit of the analytical methods available at the time current regulations were proposed. Improvements in the analytical methods have since lowered detection levels to the range of several parts per billion. The potential exists for discharge limits to become more stringent. For example, discharge requirements as low as 25 µg/L have been implemented in Australia. The chronic toxicity reference level for 2,4-DNT is 0.5 µg/L.

To address this situation, the U.S. Army Environmental Center (USAEC) (formerly the U.S. Army Toxic and Hazardous Materials Agency, USATHAMA) sponsored an engineering study from 1989 to 1991 by IT Corporation (IT) (formerly PEI Associates, Inc.) to identify production sources of 2,4-DNT at RAAP and to characterize the flows and concentrations of the various wastewater streams containing 2,4-DNT.[1] Limited bench-scale testing of various treatment technologies was also conducted during this study. It was noted that 75 percent of the 2,4-DNT-bearing wastewater originated from the water-dry process. In this process, excess 2,4-DNT is leached from the propellant along with high concentrations of ethanol and ether. The wet screening operations and solvent recovery operations were estimated to contribute 18 and 7 percent of the 2,4-DNT load to the BWTP, respectively.

This preliminary study concluded that interception and pretreatment of the 2,4-DNT-bearing wastewater upstream of the BWTP was an option that could significantly reduce the 2,4-DNT load to the BWTP concentrations above the proposed regulatory limit. Design flow rates and concentrations were established at 125 gpm at 75 mg/L of 2,4-DNT, 500 mg/L of ethanol, and 10 mg/L of ether. The study concluded that both granular activated carbon (GAC) and ultraviolet (UV) oxidation technologies should be effective for the treatment of 2,4-2,4-DNT. It was also concluded that biodegradation of 2,4-DNT is another technology warranting further studies.

Subsequently, the U.S. Army Construction Engineering Research Laboratory (USACERL), in association with the University of Cincinnati (UC), investigated the feasibility of using an anaerobic fluidized bed bioreactor (AnFBR) with GAC to treat 2,4-DNT containing wastewater.[2] A bench-scale study was performed with both simulated wastewater and actual 2,4-DNT wastewater generated by the water-dry process at RAAP[3]. The USACERL study concluded that AnFBR offered favorable prospects for treatment of water-dry wastewater. The by-product of anaerobic degradation of 2,4-DNT was found to be 2,4-Diaminotoluene (2,4-DAT). It was believed that 2,4-DAT would be aerobically degraded in the BWTP.

The current USAEC pilot-scale demonstration project was initiated in 1993 with IT and Alliant. The objectives of this effort are to select and evaluate the two most potentially suitable technologies for pretreating the 2,4-DNT water-dry wastewater at RAAP. This effort is intended to support design of a full-scale system if one or both technologies is proven at pilot-scale. A literature search was conducted to identify historic and current technologies suitable for removal of 2,4-DNT from wastewater. Successful bench-scale treatment of 2,4-DNT, or an analogous compound, in wastewater was used as the minimum criteria necessary for further consideration. The literature search identified six technologies suitable for further evaluation. Preliminary budgetary cost estimates of full-scale systems for the selected technologies were also prepared based on the wastewater flows and concentrations obtained in the earlier IT study. As illustrated in Table 1, an evaluation of these technologies resulted in the decision to field demonstrate both a UV Oxidation system and an AnFBR system followed by a Rotating Biological Contactor (RBC) unit.

PILOT-SCALE DEMONSTRATIONS

The pilot-scale demonstrations of UV/Oxidation and AnFBR were conducted in Building No. 1672 at RAAP. Wastewater for these demonstrations was obtained from the water-dry process during the manufacture of single-base propellants containing 2,4-DNT. The wastewater was intercepted at Manhole No. 32 (MH 32), which is adjacent to Building No. 1672. (Wastewater flowing through MH 32 contains water-dry effluent and possibly other wastewater

TABLE 1

Preliminary Technology Evaluation Matrix for Pre-Treatment of DNT in Wastewater at Radford Army Ammunition Plant

Treatment Technology	Refractory Compounds	DNT Treatment	Pilot Testing Recommendation	Comments
Anaerobic Fluidized Bed Bio-Reactor (AnFBR)	Successful	Successful	Recommended	• Proven Ability to degrade 2,4-DNT in RAAP Wastewater. • Biodegradation of carbon is advantageous.
Ultra-Violet Oxidation with Ozone/Hydrogen Peroxide	Successful	Successful	Recommended	• Proven Ability to degrade 2,4-DNT. • Vendor literature claims to remove 2,4-DNT with ozone based system.
Rotating Biological Contactor (RBC)	Successful	Successful	Recommended	• Proven ability to remove 2,4-DNT in RAAP wastewater. • Application in series with an AnFBR system would simulate pretreatment followed by aerobic treatment. Information from pilot-scale test could potentially be used to improve operation of RAAP BWTP.
Granular Activated Carbon (GAC)	Successful	Successful	Not Recommended	• Proven ability to remove 2,4-DNT in wastewater. • Adequate information available from other sources to allow full-scale design without a pilot-test possible.
Anaerobic Batch Sequencing Reactor (AnBSR)	Not Tested	Not Tested	Not Recommended	• Not sufficiently different from AnFBR to warrant separate demonstration.
Aerobic Sequencing Batch Reactor (SBR)	Successful	Not Tested	Not Recommended	• No evidence in literature to show success in 2,4-DNT removal. • Technology not sufficiently different from RBC technology to warrant separate demonstration.

flows.) Collection of the water-dry wastewater was coordinated with production operations to minimize contamination by other wastewaters. Descriptions of the technologies evaluated and the results of the pilot-scale tests are discussed in this section.

UV OXIDATION PILOT TEST

Technology Background - UV Oxidation uses ultraviolet radiation in combination with oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2), or both, to produce hydroxyl radicals.[4] Hydroxyl radicals are second only to fluorine in their oxidation potential[5] and have been shown to be effective in the treatment of industrial wastewater contaminated with semivolatile compounds.[6,7] Ho has shown that UV radiation and H_2O_2 will degrade 2,4-DNT in aqueous solutions.[8] The following reaction pathway was suggested for photooxidation of aqueous 2,4-DNT solutions with UV/H_2O_2:

> 2,4-DNT → 2,4-dinitrobenzyl alcohol → 2,4-dinitrobenzaldehyde → 2,4-dinitrobenzoic acid → 1,3-dinitrobenzene → 3-nitrophenol + dinitrophenols (+NO_3^-) → dihydroxynitrobenzenes → trihydroxynitrobenzenes → nitromuconic acid derivatives (+NO_3^-) → maleic acid + nitro- and hydroxymaleic acid derivatives + glyoxal + glyoxylic acid → oxalic acid + formic acid (+ NO_3^-) → CO_2 + H_2O

Complete mineralization of 2,4-DNT to carbon dioxide and water is theoretically possible. However, examination of the reaction intermediates indicates that several species are also biodegradable. Therefore, destruction of the 2,4-DNT to a biodegradable intermediate may increase the effectiveness of treatment of the wastewater by the existing aerobic biological wastewater treatment plant.

Pilot-test Equipment - The UV Oxidation equipment used in the tests was an Ultrox Model P-650 pilot-scale system. The system consisted of four main units:

- A 650-gallon UV reactor
- An ozone generator with accompanying air compressor, filter, and dryer
- A hydrogen peroxide feed tank and pump
- An ozone decomposer.

A schematic of this UV Oxidation system is shown in Figure 1. A process flow diagram for the system is shown in Figure 2. The reactor had a total volume of 650 gallons and was partitioned by weirs into six cells of equal volume. Wastewater entered the reactor at the bottom of Cell 1 and exited at the bottom of Cell 6. Each cell contained 12 low-pressure UV lamps totaling 780 watts (W) for a maximum of 4.68 kW of UV light (with a wavelength of 254 nm). All, one-half, or none of the UV lamps in each cell could be turned on or off to provide variable intensities of UV radiation.

Oxidants used during testing were O_3 and H_2O_2, both individually and in combination. H_2O_2 was metered into the system at the wastewater inlet. O_3 was bubbled into each of the six reactor cells in equal amounts. The off-gas, including any unreacted O_3, was treated for destruction of O_3 prior to discharge to the atmosphere.

Sampling and Analysis - During a series of test runs, analytical samples were withdrawn from the following locations (shown on Figure 2):

• SP2	Untreated wastewater influent
• SP4	Cell 2
• SP6	Cell 4
• SP9	Effluent Sample.

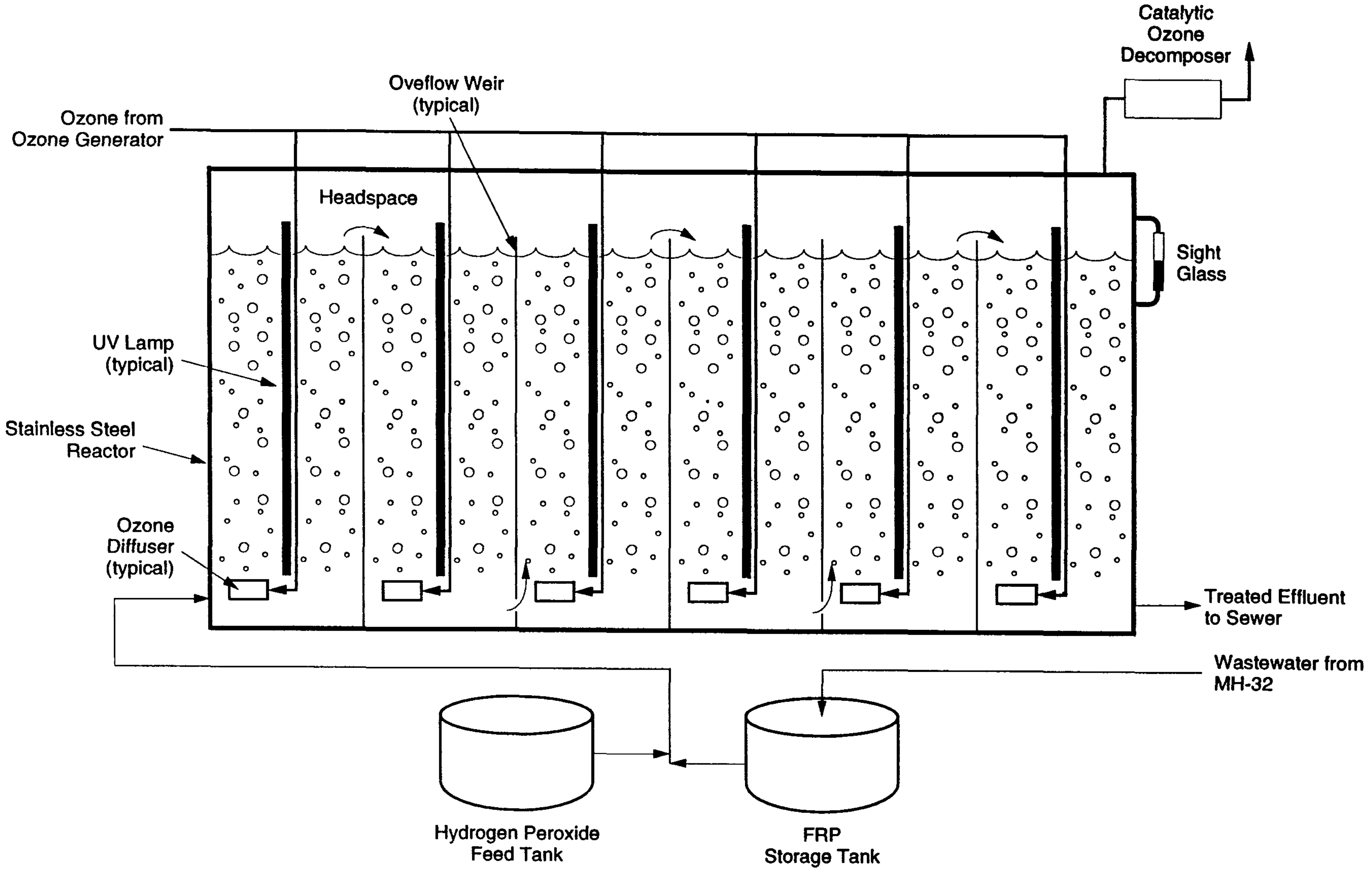


Figure 1. Process flow diagram – Ultrox Pilot UV/Oxidation Test System.

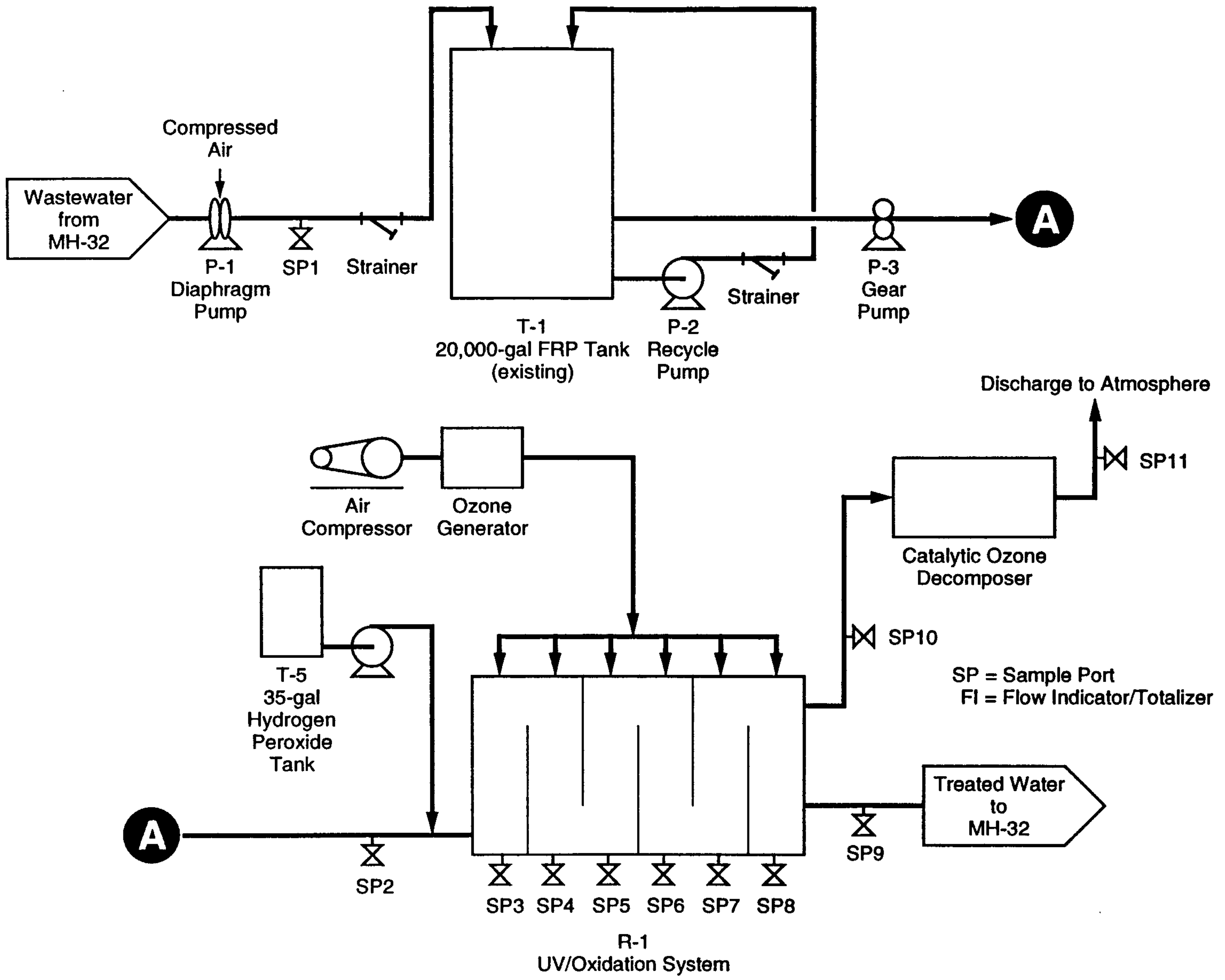


Figure 2. Process flow diagram – UV/Oxidation Pilot-Test System.

TABLE 2

Test conditions for UV Oxidation pilot tests.

Run No.	Wastewater Flowrate (gpm)	Hydrogen Peroxide Flowrate (ml/min)	Total Ozone Flowrate (cfh)	Total Oxidant Dosage (mg/l)	UV (Percent of Lamps On)
1	5	21	0	440	100
2	5	0	500	420	100
3	5	5	380	420	100
4	2.5	5	380	840	100
5	1.5	7	500	1,900	100
6	2.5	2.5	190	420	100
7	2.5	5	380	840	50
8	1.5	5	380	1,400	100
9	Batch[1]	5	380	2,300	100

[1] Wastewater was recirculated within reactor at 5.5 gpm with hydrogen peroxide and ozone being added continuously.

Prior to the initiation of sampling, the system was operated for a period equal to three residence times to allow the system to reach steady-state conditions. Three samples were then taken during each run at 30-minute intervals from the sample ports identified above. During one run (Run No. 5), an additional sample was taken from Cell 5 (SP7) to provide additional data for assessing destruction of 2,4-DNT across the reactor. The samples were analyzed for the following parameters: 2,4-DNT, ethanol, ether, COD, hardness, alkalinity, TSS, turbidity, iron, and manganese.

Results - Test conditions used for each run are shown in Table 2. The O_3 and H_2O_2 doses used for Runs 1, 2, and 3 were selected based on the available literature and vendor recommendations. Subsequent dose rates and retention times were determined based on the results of these initial runs. During the final run (Run 9), the test unit was operated in a batch mode to significantly extend retention time so that the maximum destruction of 2,4-DNT could be estimated.

The analytical results from the nine test runs conducted are summarized in Table 3. Zero-, first-, and second-order kinetic rate expressions were evaluated to express the observed rate of 2,4-DNT destruction.

Figure 3 presents a graph of 2,4-DNT concentrations vs. time for all nine runs. The plots for Runs 1, 2, and 3 are straight lines, suggesting zero-order reaction kinetics. The results of these runs show that the greatest destruction was achieved when O_3 and H_2O_2 were used in combination. The plot for Run 4 (which had twice the retention time and oxidant dosage as Run 3) is linear for 2,4-DNT concentrations to approximately 24 mg/L, at which point the slope of the graph changes significantly. This indicates a shifting-order reaction. Approximately 97 percent of the influent 2,4-DNT was destroyed during this run. However, a significant concentration of 2,4-DNT (3.73 mg/L) remained in the effluent.

A new batch of wastewater was collected for Run 5. Water-dry wastewater is generated in batches during propellant production. Production of M-14 propellant is not continuous and is determined by military need. This, combined with wastewater storage capacity limited to 20,000 gallons, resulted in the need to use multiple batches of water during testing. This wastewater contained almost ten times more ethanol than the wastewater used during Runs 1 through 4 (960 mg/L vs. 98 mg/L, on average). Although the resident time and oxidant dosage for Run 5 was increased from that used for Run 4, the plot for Run 5 shows a significantly slower rate of 2,4-DNT destruction than that observed during Run 4. Because the UV Oxidation reaction is not selective in the destruction of organics, the increase in ethanol concentration lowered the rate of 2,4-DNT destruction. Oxidant was consumed as it reacted with the increased concentration of ethanol in addition to the 2,4-DNT.

Runs 6 and 7 were designed to evaluate, respectively, the effect of lower oxidant dosage rates and the effect of UV light intensity on 2,4-DNT destruction. These runs were performed with the same residence time as Run 4, but with one-half the oxidant dosage and one-half the UV light intensity. The plot for Run 6 indicates a shifting-order reaction. The 2,4-DNT destruction was less than observed in Run 4 (67% vs. 97%), indicating that higher oxidant dosages are required to achieve higher 2,4-DNT destruction. During Run 7, less 2,4-DNT destruction occurred than in Run 4 (70% vs. 97%), indicating decreased destruction with decreased UV intensity.

The test conditions for Run 8 combined those parameters from the previous runs that were shown to maximize destruction of 2,4-DNT. The plot for Run 8 indicates a shifting-order reaction and a 2,4-DNT destruction of 97 percent. The effluent 2,4-DNT concentration was 1.6 mg/L, however, which is significantly higher than the target effluent concentration (i.e., detection limit of 100 μg/L).

The objective of Run 9 was to evaluate the maximum potential for the reactor to destroy 2,4-DNT. The reactor was operated in a closed-loop mode (effluent redirected to influent) to provide a batch mode of operation. Run 9 achieved a level of treatment that resulted in

TABLE 3

Summary of UV/Oxidation Analytical Test Results.

Run No	Wastewater Flow Rate (gpm)	Sampling Point	Time (min)	DNT Conc. (mg/L)	Alcohol Conc. (mg/L)	Ether Conc. (mg/L)	COD Conc. (mg/L)	pH	DNT Destruction	Rate Equation
1	5	Influent	0.00	123.67	102.30	61.20	628.33	7.12		
		Cell 2	32.50	116.00	102.33	66.57	711.33	7.11		
		Cell 4	75.83	110.33	100.37	63.27	711.00	7.05		
		Effluent	130.00	108.00	96.97	60.67	706.33	6.96	13%	Zero-order
2	5	Influent	0.00	101.77	101.78	54.3	589	7.03		
		Cell 2	32.50	86.73	75.53	31.17	512.67	5.14		
		Cell 4	75.83	67.93	50.17	14.43	460	4.24		
		Effluent	130.00	47.17	31.83	4.44	408.33	3.90	54%	Zero-order
3	5	Influent	0.00	111.13	96	53.33	559.67	6.93		
		Cell 2	32.50	88.4	73.67	30	552.67	5.52		
		Cell 4	75.83	59.6	43.33	12.33	477.33	4.30		
		Effluent	130.00	36.17	24	3.2	417.67	3.75	67%	Zero-order
4	2.5	Influent	0.00	117	93.33	87	598.33	3.97		
		Cell 2	65.00	74.33	57.67	31	486.67	4.65		
		Cell 4	151.67	23.53	19	2.93	343.67	3.55		
		Effluent	260.00	3.73	3.2	0	254.33	3.25	97%	Shifting-order
5	1.5	Influent	0.00	112.33	964.33	74.33	2700	6.73		
		Cell 2	108.33	81.67	711	24.67	2383.33	4.13		
		Cell 4	252.78	52	446.33	5.33	2275	3.47		
		Cell 5	325.00	43	368.67	2.67				
		Effluent	433.33	33.67	283.33	1.3	1958.33	3.18	70%	Zero-order
6	2.5	Influent	0.00	64.33	351.67	40	1029	6.76		
		Cell 2	65.00	49	302	30.33	992.67	5.22		
		Cell 4	151.67	29.33	246.33	16.77	908.67	4.62		
		Effluent	260.00	21.33	197.33	8.7	837.33	4.29	67%	Shifting-order
7	2.5	Influent	0.00	64.67	356	43	991.83	6.63		
		Cell 2	65.00	47.67	246	18.63	921.67	4.59		
		Cell 4	151.67	32.33	147.33	5.9	782.83	4.04		
		Effluent	260.00	19.33	71	1.43	667	3.72	70%	Zero-order
8	2.5	Influent	0.00	60.5	320	28.33	967.67	6.05		
		Cell 2	65.00	27.33	152.33	7.8	860.33	4.11		
		Cell 4	151.67	8.77	39	0	642	3.66		
		Effluent	260.00	1.63	6.07	0.42	470.67	3.44	97%	Shifting-order
9	5.5	Cell 6	0.00	59.9	297	28	948	5.58		
		Cell 6	120.00	24.8	150	4.1	773	4.17		
		Cell 6	240.00	8.2	36	0	619	3.74		
		Cell 6	360.00	0.99	2.3	0.49	495	3.48		
		Cell 6	480.00	0.1	0	0	330	3.42		
		Cell 6	600.00	0	0	0	179	3.33		
		Cell 6	720.00	0	0	0	55	3.16	100%	First-order

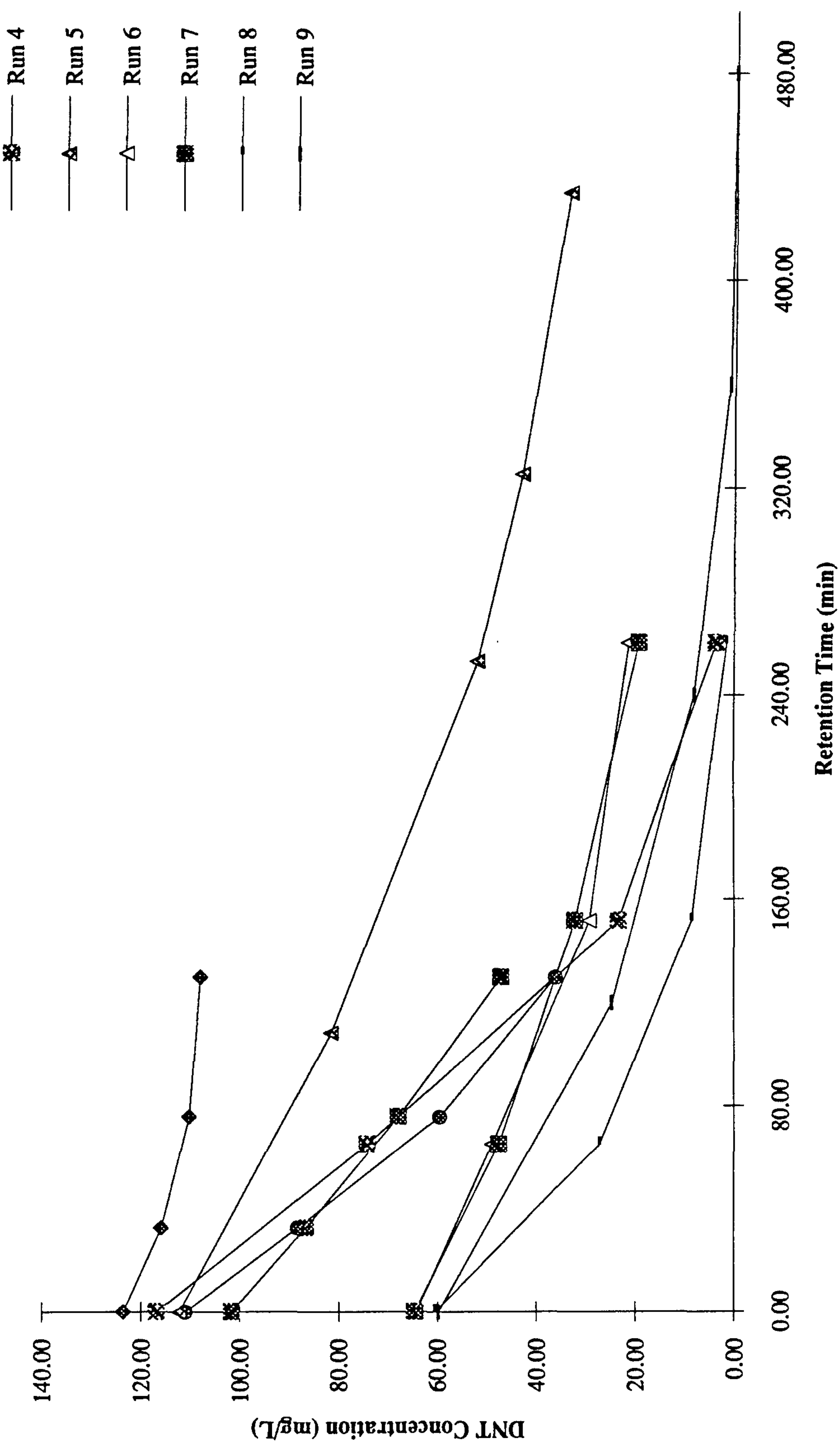


Figure 3
DNT Concentration vs. Retention Time
Runs 1 - 9

nondetectable levels of 2,4-DNT in the effluent at a retention time of 600 minutes.

The COD levels in the effluent did not decrease during the tests in levels that corresponded to the decreasing levels of 2,4-DNT, ethanol, and ether in the reactor. This was attributed to the formation of by-products of 2,4-DNT destruction. Limited attempts to identify potential by-products tentatively indicate that the most likely compounds formed were 2,4-dinitrobenzaldehyde and 2,4-dinitrobenzoic acid.

Conclusions - The results of Runs 1 through 9 indicate that destruction of 2,4-DNT to nondetectable levels is possible with this technology. However, the rate and extent of 2,4-DNT destruction were impacted by the presence of other organic compounds (e.g., ethanol, ether) that may be present in the wastewater. The composition of water-dry wastewater was shown to be highly variable and could contain high concentrations of ethanol. Therefore, it may not be cost-effective to design a treatment system to produce effluent with nondetectable levels of 2,4-DNT under all circumstances.

An evaluation is necessary to estimate the maximum concentration of 2,4-DNT that could be effectively processed by the BWTP. Then, the application of an upstream UV Oxidation system could be designed to reduce 2,4-DNT levels in water-dry wastewater to levels consistent with this limitation. The pilot tests indicate that, under most circumstances, approximately 70 percent of the 2,4-DNT could be reliably destroyed in a UV Oxidation system.

ANAEROBIC FLUIDIZED BED REACTOR (AnFBR) AND ROTATING BIOLOGICAL CONTRACTOR (RBC) PILOT TESTS

Technology Background - An AnFBR system consists of a vertical tank containing GAC. Untreated wastewater and a recycle stream from the reactor is fed to the reactor from the bottom with sufficient velocity to fluidize and expand the bed volume by a factor of approximately 1.5. The function of the GAC in the AnFBR system is to 1) provide a substrate to support microbial growth and 2) to capture, through adsorption, surge loads of 2,4-DNT. During periods of low flow or low 2,4-DNT concentration, the 2,4-DNT adsorbed on the carbon bed desorbs and is degraded by the bacteria, thus regenerating the carbon bed. The contact time required for effective treatment depends on the 2,4-DNT concentration and on the presence of other competing metabolites and is one of the variables that were evaluated during the demonstration. A portion of the column effluent is recycled to maintain the bed in a fluidized state and to permit the wasting of sludge/carbon as necessary. Methane gas is generated by the anaerobic biological activity in the reactor and is discharged from a vent in the top of the reactor to the atmosphere.

Pilot-test Equipment - The AnFBR demonstration system was manufactured by Envirex, Ltd. Figure 4 shows a schematic of the Envirex system. The system consists of a 15-foot-tall, 20-inch-diameter reactor column with a bed volume of approximately 187 gallons and containing approximately 380 lb of GAC. The influent wastewater flow rate was controlled by a needle valve and passed through two basket strainers to remove any solid 2,4-DNT. An in-line water heater was used to maintain the reactor temperature at 95°F.

Biomass growth on GAC particles reduces the particle density and causes it to float. When the particle reaches a height of 11 feet in the reactor, it is removed from the reactor and enters a settling tank. The particle exits the bottom of the settling tank via a pinch valve that shears the biomass from the carbon. The carbon is then returned to the reactor and the biomass is wasted.

The Envirex system also contains feed systems for nutrients, supplemental ethanol, and sodium hydroxide. The nutrients are fed into the influent line to ensure the presence of essential micro nutrients. Ethanol is also fed into the feed line and acts as a co-substrate for 2,4-DNT transformation. This supplemental ethanol was required to ensure that sufficient ethanol as a food source was present to establish a healthy consortium of micro-organisms during startup and the initial phases of testing. The sodium hydroxide is fed into the recycle line and is used to control pH. System pH tends to fall because of production of organic acids.

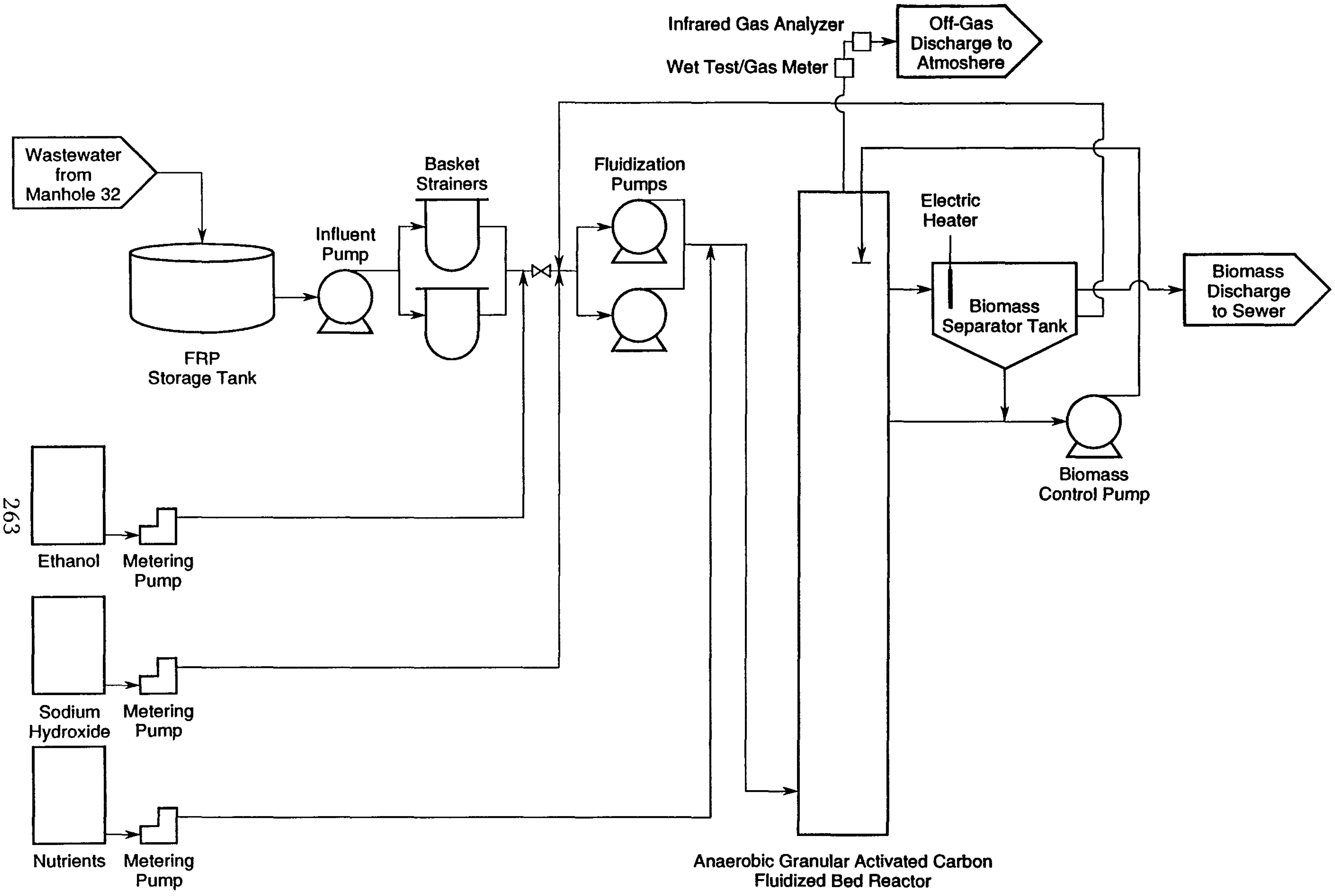


Figure 4. Process Flow Diagram – Envirex System.

The Envirex system was acclimated on an influent feed of clean water dosed with nutrients and ethanol to provide metabolites for growth of the microorganisms. The ethanol feed was adjusted to maintain a COD loading rate of approximately 10 kg COD/m^3 GAC per day. Numerous problems, primarily related to equipment operation, were experienced during the start-up phase. This lead to a longer start-up time than anticipated and required reactor reinoculation with anaerobic sludge from a POTW three times during the start-up period.

The pilot-scale RBC unit was previously used at RAAP in the mid-1970s to establish the operating and design parameters for the existing BWTP. The unit is a 0.5-m "Bio-Surf®" pilot unit produced by Autotrol Corporation. The unit measures 72 in. long, 28 in. wide, and 24 in. high. It has four cells separated by removable bulkheads, and each cell contains a bank of nine 18-5/8-in.-diameter corrugated polyethylene discs. Influent to the RBC enters the first cell and follows a serpentine path to successive cells. The discs are approximately 35 percent submerged. The volume of the unit is approximately 34 gallons at 35 percent submersion. The discs are rotated at approximately 12 rpm for an industry standard of a tip speed of approximately 1 ft/sec. Flow rates, retention times, and rotational speed can be varied.

Sampling and Analysis - Samples were drawn from the influent and effluent of the AnFBR and the effluent of the RBC. These samples were analyzed for ethanol, ether, 2,4-DNT, 2,4-DAT, acetic acid, propionic acid, sulfate, sulfide, and COD. In addition, the Envirex system was equipped with a Programmable Logic Controller (PLC) that recorded several parameters including the influent and recycle flow rates, system pH, and dissolved oxygen. The off-gas rate and composition were measured with a wet-test gas meter and an Infrared Gas Analyzer, respectively. Other parameters that were monitored manually included the flow rates of nutrients, supplemental substrate (ethanol), and pH buffer solution.

Results - As a result of equipment problems resulting in a prolonged start-up, only two test runs have been completed to date. Both tests were performed at 0.4 gpm and under similar conditions to observe system performance at the same retention time but at different influent wastewater compositions. The current available data permits a preliminary, qualitative evaluation of the AnFBR system.

The AnFBR system uses two competing phenomena to remove 2,4-DNT from the wastewater. These phenomena are adsorption on the GAC and biodegradation by the microbial population. The degree of removal by adsorption on GAC can be measured directly through analysis of DNT on samples of carbon from the bed. Several such samples have been collected; however, results of analysis are not yet available.

Under anaerobic biological conditions, 2,4-DNT is transformed to 2,4-DAT. Removal of 2,4-DNT by biodegradation can be estimated by the formation of 2,4-DAT in the reactor. However, both 2,4-DNT and 2,4-DAT are adsorbed on activated carbon. Therefore, it is difficult, initially, to gauge the true rate of biodegradation of 2,4-DNT from the concentration of 2,4-DAT in the effluent. Table 4 shows the influent and effluent concentrations for ethanol, ether, acetic acid, COD, 2,4-DNT, and 2,4-DAT during the two test runs. As shown in this table, ethanol was totally degraded during the second test run, with a corresponding increase in acetic acid production. All influent 2,4-DNT was also removed by the system, resulting in nondetectable concentrations in the effluent. A corresponding increase in 2,4-DAT concentration was observed in the effluent. Figures 5 and 6 show graphs of the influent 2,4-DNT concentration (in mmol/L) versus effluent 2,4-DAT concentrations (also in mmol/L). During the first test run, only detectable concentrations of 2,4-DAT were observed in the effluent. Thus, during this test run, either the microbial population had not grown sufficiently to degrade all the influent 2,4-DNT to 2,4-DAT, or adsorption on the GAC was accomplishing 2,4-DNT removal and masking 2,4-DAT production.

During the second test run, the 2,4-DAT concentration had increased substantially to approach that of the influent 2,4-DNT concentration. This trend shows that the effluent 2,4-DAT concentration will approach that of the influent DNT concentration showing complete transformation of 2,4-DNT

TABLE 4
Summary of AnFBR and RBC Analytical Results

		AnFBR Feed						AnFBR Effluent						RBC Effluent					
Run No.	Date	Alcohol* (mg/L)	Ether (mg/L)	Acetic Acid (mg/L)	COD* (mg/L)	DNT (mg/L)	DAT (mg/L)	Alcohol (mg/L)	Ether (mg/L)	Acetic Acid (mg/L)	COD (mg/L)	DNT (mg/L)	DAT (mg/L)	Alcohol (mg/L)	Ether (mg/L)	Acetic Acid (mg/L)	COD (mg/L)	DNT (mg/L)	DAT (mg/L)
1	1/31/95	144	64	53	763	159	0.251	584	6.4	786	2,100	0.111	0.43	5	ND	412	1,388	< 0.01	ND
	2/1/95	136	61	47	763	154	0.244	567	8.3	817	2,138	0.11	ND	3.2	ND	420	1,475	< 0.01	ND
	2/2/95	147	63	52	788	152	0.056	445	9.9	768	1,888	0.117	ND	1.9	ND	433	1,350	< 0.01	ND
	2/3/95	138	71	47	625	151	0.22	464	15	922	1,950	0.113	ND	1.7	ND	539	1,300	< 0.01	ND
	2/6/95	144	63	55	675	169	ND	152	14	1,031	1,325	< 0.1	ND	ND	ND	485	588	< 0.01	ND
	2/7/95	140	69	54	650	169	ND	263	16	852	1,375	< 0.1	ND	ND	ND	566	863	< 0.01	ND
	2/8/95	138	60	47	725	162	ND	ND	17	451	625	< 0.02	ND	ND	2	101	150	< 0.02	ND
	2/9/95	132	57	49	750	162	0.028	143	19	670	1,025	< 0.02	ND	ND	ND	365	475	< 0.02	ND
	2/10/95	136	68	48	728	151.1	0.652	675	24	678	1,700	0.006	< 0.01	32	2.5	451	1,313	< 0.01	0.08
	2/13/95	135	61	56	728	150.4	0.812	672	29	652	1,800	< 0.006	0.21	17	3.3	306	1,400	< 0.01	0.29
	2/14/95	132	63	55	725	148.9	0.887	690	37	648	2,125	0.006	0.41	14	ND	305	1,375	< 0.01	0.38
	2/15/95	141	67	54	670	145	1.006	739	31	690	2,200	0.008	0.49	69	4.5	233	1,250	0.009	0.49
	2/16/95	140	61	55	655	148	0.994	919	38	574	2,450	0.01	0.74	35	8.8	284	2,010	0.008	0.72
2	4/21/95	254	126	25	1,114	159.5	0.326	ND	122	557	842	< 0.05	22.06	ND	0.8	4.9	165	< 0.05	18.47
	4/24/95	248	119	24	1,068	144.58	0.504	ND	124	259	576	< 0.05	25.04	ND	ND	3	60	< 0.05	3.53
	4/25/95	249	116	22	1,089	198.3	0.5	20	130	567	962	< 0.05	26.89	ND	2	132	293	< 0.05	25.13
	4/26/95	247	117	24	1,039	176.3	<0.10	45	124	624	1,023	< 0.05	26.71	ND	6	137	315	< 0.05	25.40
	4/27/95	248	121	24	1,090	213	0.453	47	132	620	1,047	< 0.05	28.93	ND	6	75	228	< 0.05	25.38
	4/28/95	248	121	25	1,042	168.01	0.54	36	131	611	1,028	< 0.05	27.70	ND	2	22	168	< 0.05	25.73
	5/1/95	239	116	33	1,094	204.65	3.3	ND	132	563	919	< 0.05	35.31	ND	2	44	229	< 0.05	31.18
	5/2/95	234	111	26	1,027	205.68	1.11	ND	134	618	979	< 0.05	35.13	ND	2	5	189	< 0.05	28.44

* - Supplemental alcohol was added to the system at a rate equivalent to 5 kg COD/m3 bed/day for Run1 and Run 2 respectively.
Therefore, COD and alcohol concentrations in the feed to the AnFBR is higher than that present in the wastewater.

Figure 5
DNT Disappearance and DAT Appearance in the AnFBR System
During Test Run 1

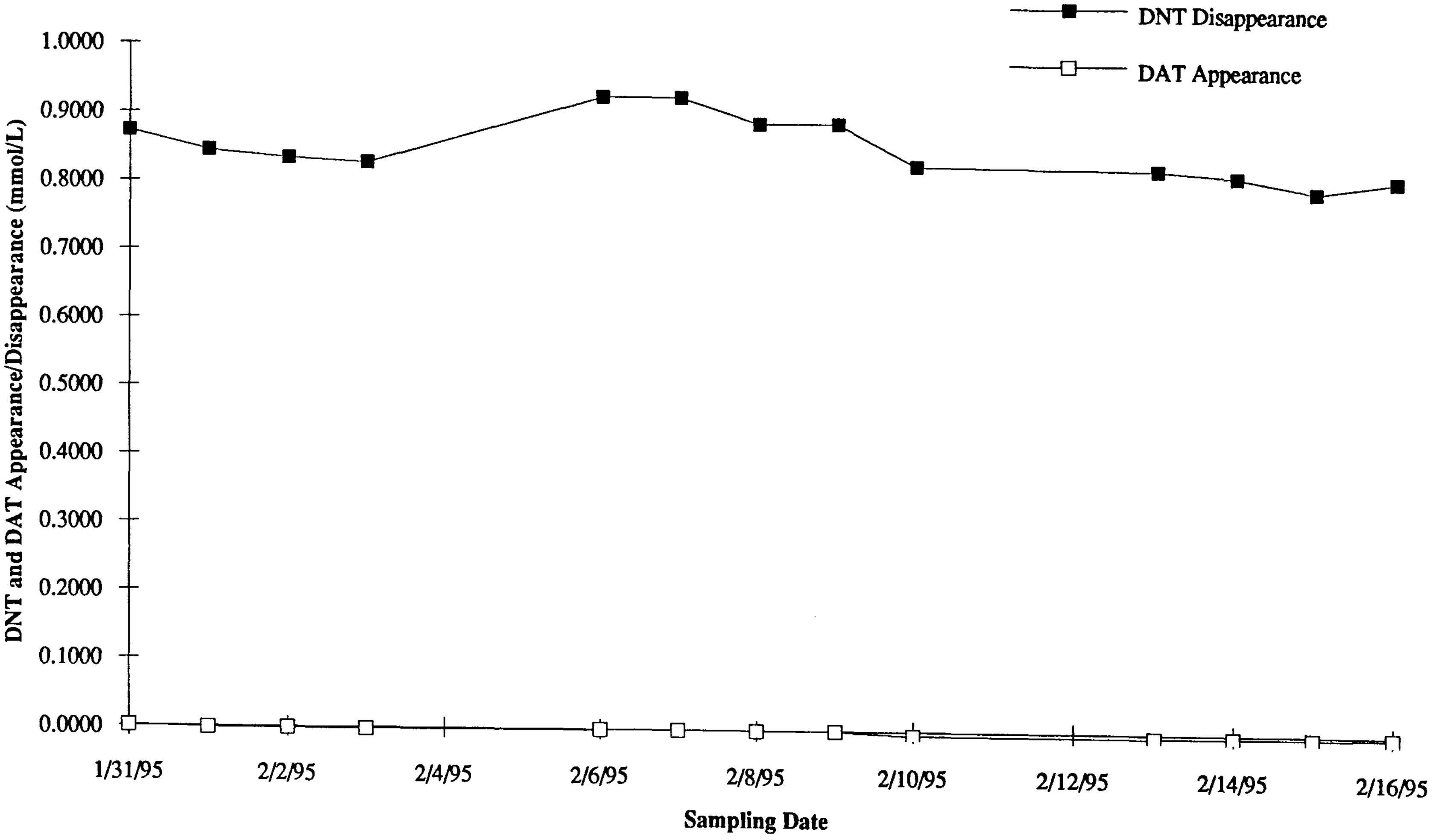
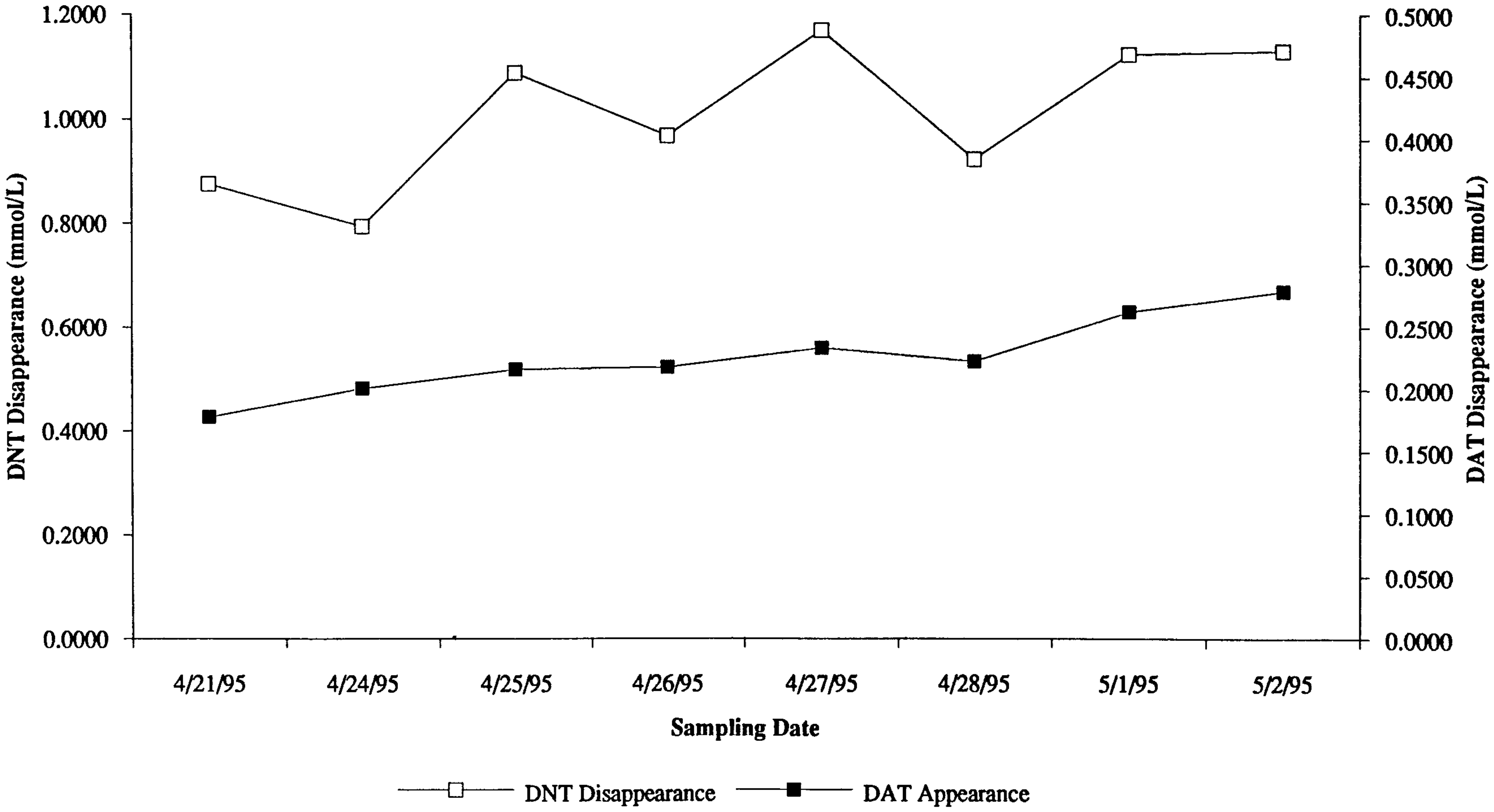


Figure 6
DNT Disappearance and DAT Appearance in the AnFBR System
During Test Run 2



to 2,4-DAT.

Also, as can be seen from Table 4, the RBC effluent 2,4-DNT and 2,4-DAT concentrations were non-detectable. This shows that the RBC can successfully degrade 2,4-DAT aerobically.

Conclusions - The two test runs conducted to date do not provide sufficient quantitative data to permit an evaluation of system performance. The preliminary results indicate that AnFBR technology has the capability to degrade 2,4-DNT to 2,4-DAT and produce an effluent with nondetectable levels of 2,4-DNT. The RBC system has also demonstrated the ability to remove the 2,4-DAT generated and the residual ethanol and ether in the AnFBR effluent. During each test run completed, supplemental ethanol was used as a substrate for biomass growth. Future tests will evaluate the ability of the system to achieve 2,4-DNT removal with the ethanol in the water-dry wastewater alone. Other tests to be conducted will evaluate system performance at higher flow rates (and correspondingly lower residence times). A full-scale system can then be sized based on the results of these test runs.

CONCLUSIONS

Completion of the technology demonstrations are intended to support the selection and design of an appropriate system for control of 2,4-DNT at RAAP. Participants involved in such decisions will include personnel from the USAEC and Alliant at RAAP, the Army Production Base Modernization Agency (PBMA), and the Army Industrial Operations Command (IOC) Headquarters. The final decision of the appropriate course of action will consider many factors including performance, reliability, economical, and regulatory factors. For the purposes of this paper, the following criteria are discussed in evaluating the two treatment technologies: effluent quality, commercial availability, operability, and flexibility.

The performance of UV Oxidation was found to be dependent on the concentrations of ethanol and ether present in the wastewater. During the pilot tests, this system was unable to reduce 2,4-DNT concentrations to the detection limit except at very high oxidant dosages and extended residence times. The target effluent load (113 µg/L 2,4-DNT) was difficult to achieve in the presence of ethanol and ether. However, the system consistently removed more than 65 percent of the 2,4-DNT in the wastewater. An evaluation of the BWTP is required to determine if this removal rate would permit the bioplant to meet anticipated discharge standards.

The tests performed on the AnFBR indicate the system is capable of achieving the target effluent quality. However, these test runs have been performed at a flow rate of 0.4 gpm (i.e., retention time of 12 hours). Further testing at increased flow rates reduced retention times (as necessary) to fully evaluate the system's ability to produce acceptable effluent at economical equipment sizes.

The AnFBR system also produces 2,4-DAT in the effluent. Although 2,4-DAT has been shown to be aerobically biodegradable and there are no current regulatory standards for its discharge, the ability to degrade 2,4-DAT requires confirmation. The pilot-scale RBC succeeded in reducing the 2,4-DAT in the AnFBR effluent to nondetectable levels. Thus, the pilot-tests indicate the feasibility of aerobic 2,4-DAT removal in the BWTP.

A pretreatment system installed to intercept the wastewater released from the water-dry and wet screening operations could intercept over 90 percent of the 2,4-DNT influent loading to the BWTP at a common point in the underground sewer system (e.g., MH 32).[1] The remaining 2,4-DNT loading to the BWTP would result from the solvent recovery and propellant coating operations. An earlier study also observed that approximately 0.18 million gallons of wastewater per day (MGD) passes through MH 32 versus the 1.28 MGD treated at the BWTP.[1] Based on this observation, it is recognized that it would be much more efficient to pretreat wastewater passing through MH 32. Also, since less than 15 percent of the wastewater flowing into the BWTP is attributable to water being discharged through MH 32, there is essentially an 85 percent reduction of the 2,4-DNT concentration upon entering the BWTP. As already noted, the BWTP also reduces the 2,4-DNT wastewater even further as a result of aerobic biodegradation. The degree of 2,4-DNT reduction required by the pretreatment to attain the 113 µg/L average and 285 µg/L peak discharge levels in the effluent of the BWTP must be determined.

One advantage of the AnFBR is that it is anticipated to have the capacity to withstand significant variations in influent DNT concentrations because of the adsorptive capacity of the activated carbon.

One aspect of the AnFBR is that the alcohol and ether that pass through the system will be consumed in the treatment process and will not be passed onto the BWTP (see chart of results). The RBCs in the BWTP depend on minimal levels of COD in the wastewater to maintain healthy biomass. When these levels drop to below minimal levels, supplemental alcohol must be added. Thus, it is not necessarily desirable to remove the alcohol from the wastewater. Both the UV/Oxidation and the AnFBR systems reduce alcohol levels in the demonstrations.

Both systems tested are currently available commercially. Commercial availability is a measure of the technical maturity of a technology. UV/Oxidation systems are widely available commercially through a number of vendors. This technology has been implemented on numerous wastewater streams. A relatively high degree of experience in the industry is pertinent to the operation and maintenance of such systems. Several vendors currently offer these systems in a wide variety of configurations to suit various process needs. AnFBR technology is currently available from a limited number of vendors. Compared with UV/Oxidation, AnFBR is an emerging technology. Because the degree of documented experience with AnFBR is less than with UV/Oxidation, it would likely be more difficult to start up and troubleshoot the AnFBR system.

One advantage of the AnFBR over conventional aerobic activated sludge systems is that there is no buildup of sludge requiring management. One of the disadvantages of the AnFBR system is that it has a very tall reactor column (15 feet in the pilot test equipment), which necessitates a proportionally tall building and large entrance way. By contrast, the UV/Oxidation system has dimensions of and is easier to get in and out of a building.

Many operational upsets have been associated with the AnFBR system because of complications with the inflow pump, alcohol delivery pump, pH control solution pump, and the main control system. Although the system, as tested, was computer controlled, the system required significant operator attention. As is typical of biological systems, the AnFBR system required significant time for reacclimation following upsets which can be caused by variation in influent quality, temperature, and other variables. By contrast, the mechanical UV/Oxidation system can be started and brought on-line quickly and is very adaptable to changing wastewater influent characteristics.

Final results of the ongoing field demonstration at RAAP will be available in October 1995 under final report number SFIM-AEC-ETD-CR-95048. Copies may be obtained by mailing a request to: Commander, U.S. Army Environmental Center, ATTN: SFIM-AEC-ETD (Mr. Edward Engbert), APG, MD 21010-5401. Additional information may also be obtained by contacting Mr. Edward Engbert at 410-612-6867.

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MEETING NATIONAL ENVIRONMENTAL POLICY ACT REQUIREMENTS USING A PROGRAMMATIC APPROACH

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INTRODUCTION

The Department of Defense (DoD) is owner and controller of contaminated properties subject to remedial action mandated by the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (PL 96-510).[1] In order to accomplish remediation of these properties, DoD has established the Defense Environmental Restoration Program (DERP). One major problem relating to the DERP has been the availability of suitable technologies and processes for remediation of explosive contamination. While numerous processes and technologies exist which are applicable to conventional contaminants, there is limited experience with substances unique to DoD facilities and installations.

The lack of facilities for accomplishing field testing and development of new processes has resulted in a restriction of new technologies development and a hindrance to the speed of accomplishing remedial actions. In addition, lack of proven new technology raises significant questions relative to the cost-effectiveness of processes used for these actions.

Working with the U. S. Environmental Protection Agency, the U. S. Army, U.S. Navy and U. S. Air Force established a joint program to enhance the testing and evaluation of innovative technologies. The program is called the DoD/National Environmental Technology Demonstration Program (D/NETDP, sometimes called the National Test Sites Program), which is funded through the Strategic Environmental Research and Development Program. Although programs are integrated and linked, lead services have been established to better focus and manage research and development activities. The Army has responsibility for projects related to energetics and heavy metals contamination, the Air Force for petroleum, oils, and lubricants (POL) contamination, and the Navy for solvent contamination.

The Army's Demonstration Program, managed by the Army Environmental Center (AEC) at Aberdeen Proving Ground, Maryland, involved establishing test facilities at Volunteer and Louisiana Army Ammunition Plants (AAP). The program at Volunteer AAP will address technologies for addressing trinitrotoluene (TNT) contamination, but could be expanded to include soils contaminated with heavy metals. The program at Louisiana AAP will address technologies for explosives of all types associated with the load, assemble and pack operations of ordnance production and heavy metals associated with metal forming and other operations.

This paper presents environmental guidance and information in a generic fashion where possible. However, a greater understanding is achieved if a practical frame of reference is available to see how each concept applies in the real world. To fill this need, frequent references are made to and excerpts appear from the EA prepared for the D/NETDP activities planned at Volunteer AAP, the location for which the EA has been finalized. It is not the intent of this paper to give a "how to" workbook for completing an EA; we expect readers will be knowledgeable in completing various sections of an EA for proposed projects of a traditional nature. The paper will instead focus on three areas which differ from the conventional approach: developing a strategy for complying with NEPA, evaluation of yet unknown actions under an umbrella document designed for tiering such evaluations, and the analysis of alternatives in such a way that provides reasonable and defensible input to decision makers. Table 1 contains an outline of the topics covered in the Volunteer AAP EA, but only the components listed in the previous sentence will be addressed in this paper.

STRATEGY FOR COMPLYING WITH NEPA

The Volunteer AAP EA is part of an overall plan for complying with the National Environmental Policy Act consistent with Council on Environmental Quality regulations (40 CFR 1500-1508) and with Department of the Army Regulation 200-2, "Environmental Effects of Army Actions."[2,3] The nature and extent of environmental review for the Demonstration Program was discussed on February 18, 1994, with representatives of U. S. EPA Region IV's Environmental Policy and Federal Activities Offices. Agreement was reached in that meeting that, based on the nature of the Demonstration Program, an EA was the appropriate level of review.[4] It was further agreed that, since specific technologies to be tested would not be known until a later date, a "programmatic" style of environmental review would be conducted initially and reviews of specific projects would be conducted once selected for inclusion in the Demonstration Program. AR 200-2 encourages tiered analyses for programs such as this one to avoid repetitive discussions of issues and sharper focusing on key issues associated with each demonstration.

The approach described above was discussed briefly on June 30, 1994, with several representatives of state and local regulatory agencies.[5] That briefing was held as a courtesy to regulatory agency and local government officials that would be contacted during the program or who have an interest in the program at Volunteer AAP. Comments and suggestions obtained from individuals attending that briefing were incorporated into or addressed in the EA.

The EA focused exclusively on the direct impacts of establishing the Demonstration Program at Volunteer AAP and actions at that installation associated with preparations for hosting demonstrations. The EA did not address specific technology demonstrations (or site characterization activities conducted specifically for a demonstration), since the identities of such demonstrations were not yet known. However, the EA contained baseline environmental information to support and facilitate the project-specific reviews. The EA also described the process by which demonstration-specific environmental reviews would be accomplished.

TABLE 1

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Actions associated with setting up infrastructure and laboratories in support of the program were addressed separately for their compliance with NEPA requirements. Those activities were determined to be categorical exclusions and a Record of Consideration reflecting that determination was filed at Volunteer AAP. To provide the reader with basic information about the types of tests which MAY be conducted as part of the Demonstration Program, the EA described general categories of technologies from which future demonstrations are likely to come. The "may" was emphasized because program sponsors hope that innovative approaches will be proposed for testing which may not compare exactly with the general descriptions provided.

EVALUATION OF DEMONSTRATION PROJECTS

Each candidate demonstrator is required to submit environmental information to the AEC D/NETDP program manager for meeting NEPA requirements. Information to be submitted includes process flow diagrams, identification, qualification and quantification of all waste streams, test plans and schedules, monitoring plans and resource requirements. Each applicant is required to identify how all wastes will treated, released, or disposed of during and at the completion of tests. The applicant is required also to identify any environmental permits they anticipate needing for their test and describe how existing environmental permits at Volunteer AAP might be affected during the test.

Cumulative effects, impacts resulting from the proposed test in combination with other tests currently being conducted within the program, must be addressed. The baseline environmental conditions for assessing impacts from a new project are the conditions that exist at the time of acceptance into the Demonstration Program. For example, the environmental review for approved test number three would use EA-described baseline environmental conditions associated with tests one and two.

For each test, the environmental information provided by the applicant will be assessed by the Demonstration Program manager, or an AEC-designated representative qualified to perform such reviews. The amount of documentation and the level of evaluation effort for each test-specific environmental review will depend on the degree of controversy and potential effects of the proposed test.

AR 200-2 provides for three possible outcomes for each NEPA evaluation: Categorical Exclusion (CX), Environmental Assessment (EA) and Environmental Impact Statement (EIS). The lowest level of review occurs when a proposed action is categorically excluded from further environmental review. AR 200-2 Appendix A lists typical categorical exclusions and screening criteria to assist in decision making. This outcome is reserved for actions having minimal or no individual or cumulative effect on environmental quality, no environmental controversy, and actions deemed to be similar to excluded actions previously examined. For actions fitting the requirements and guidance for being categorically excluded, or if the action is covered under an existing EA or EIS, a Record of Environmental Consideration (REC) would be completed and documentation used in supporting the CX decision attached.

The second outcome is the preparation of an environmental assessment. An EA assures compliance with NEPA if a CX is not appropriate. Whether public input is sought during the preparation of an EA depends on the extent of impacts, magnitude of the project, and/or the expected level of public interest. The EA must contain sufficient information for the decision maker to determine whether an EIS is required or a Finding of No Significant Impact (FNSI) can be issued. If no significant impacts are identified, a FNSI, with the EA or a summary of the EA attached, is issued and made public at least 30 days prior to initiation of the proposed test.

If an EIS is deemed necessary, a Notice of Intent to prepare such a document is published, public scoping is initiated, and preparation of an EIS is begun. EISs involve substantive public involvement and input at several stages and may result in significantly longer preparation and review times than EAs. Chapter 6 of AR 200-2 provides detailed guidance for preparing and processing EISs. If at anytime during the review process an EIS is judged to be the appropriate course of action, the demonstration proposal would be rejected and no testing performed at Volunteer AAP.

ANALYSIS OF ALTERNATIVES

The purpose of this section of an EA is to identify and discuss the potential alternatives considered and addressed for a proposed action. NEPA regulations require the identification and analysis of reasonable alternatives to the proposed action that could potentially avoid or reduce adverse effects to the environment. This section is arguably the most important in the entire EA since it provides information needed by decision makers as intended by the original NEPA legislation. In this section of an EA, the writer must consider all reasonable alternatives to the project, and alternatives to any and all portions of the project. Justification should be presented for carrying out the proposed project and the proposed action completely described. A universe of reasonable alternatives must be considered. If any alternatives prove to be reasonable based on economic or engineering criteria and would meet the need for action, they must be evaluated for their impacts to the environment.

Identifying reasonable alternatives consists of questioning whether the goals or products of the proposed action could be accomplished in another way, with possibly fewer impacts to the environment. For the Volunteer AAP EA, alternatives were required to meet the following criteria:

- Meet AEC's requirements for carrying out technology demonstrations in the program;
- Be technically feasible and implementable within the required time frame;
- Provide some environmental advantage to lessen, minimize, or avoid potential adverse effects compared with the proposed action; and
- Be relatively cost-effective.

For the Volunteer AAP EA, potential alternatives included (1) alternative means for satisfying the Army's need for acquiring the information needed for characterizing the effectiveness of remedial technologies, (2) alternative installations for conducting the demonstration program, (3) alternative areas of Volunteer AAP for conducting the program, and (4) alternative means of obtaining contaminated material for use in the demonstration program. A discussion of how these alternatives were considered and addressed for The D/NETDP activities planned for Volunteer AAP may be found in the EA.[6]

To provide a basis for identifying and evaluating alternatives, the proposed project must be well-defined at this point since it is only an alternative being considered by the decision maker. It is important that the proposed project be clearly described so that alternatives identified later can be contrasted with it. The EA writer should devote the space necessary for the reader to completely understand all aspects of the proposed action and its ramifications. However, it is not necessary to include lengthy technical information to describe the proposed action; rather it should be concise and easily understandable. All direct actions associated with the project or program should be described.

Direct actions for the Volunteer AAP program consisted of preparing the affected area to accept demonstrations; however, the identity of specific demonstration projects was not known since the program had not progressed to the point where projects had been selected. In order to provide the reader with some information about what projects could be expected at Volunteer, a generic description was presented of the categories of technologies in a research and development stage or currently available for treating explosives contaminated soils and groundwater. Although not all-encompassing, most innovations usually come from small changes in conventional approaches. By reading this section, one will be able to acquire a reasonably accurate understanding of what kinds of projects could be expected.

The EA should also present, to the degree known, the methodology that will followed during the execution of the program. It would be appropriate to describe the criteria for selection of candidate technologies (or at least refer to documents with such information), typical test parameters, the expected "road map" to be followed during projects, generic information about how waste streams would be handled, regulatory permits would be obtained or modified, etc. The typical schedule for projects and other documents that either have been or will be developed in connection with the program should be described so the reader can obtain additional information if needed.

The discussion of alternatives should be logical and decisions about whether an alternative is reasonable (and therefore deserves analysis later for its environmental consequences) and be scientifically defensible. Analyses must be objective and open minded. Arguments must be presented in a concise and clear manner. Decision models are useful for narrowing choices and options in an objective manner. This section should be easily understandable by the layman. There should be sufficient information to allow a reader to reach the same conclusions as the EA writer did relative to reasonable alternatives to the project. The EA should avoid the appearance of alternatives "justification" or pre-selection of alternatives. Once all alternatives have been considered, the reasonable alternatives must be evaluated for their potential environmental impact, and compared with the proposed action. The results of the alternatives analysis can be summarized in a table such as Table 2 which is taken from the Volunteer AAP EA.

CONCLUSIONS

An environmental assessment is appropriate for proposed U. S. Army actions which are of low controversy and potential environmental impact, such as the DoD's National Environmental Technology Demonstration Program. An assessment can be prepared to address a suite of future actions whose identities are not yet clearly defined but can be generically described as a type of action. This approach provides a vehicle addressing any direct environmental impacts associated with the proposed action, while describing how future sub-activities of a program will be evaluated for environmental impact. While RCRA-

TABLE 2

Summary of Alternatives Considered in the EA

1	Alternative Means for Satisfying the Need for the Project	
	• Potential Alternatives	a) Rely on research conducted in the private sector
	• Alternative to be Assessed	a) Proposed project
2	Alternative Installations	
	• Potential Alternatives	a) Alabama Army Ammunition Plant b) Cornhusker Army Ammunition Plant c) Iowa Army Ammunition Plant d) Joliet Army Ammunition Plant e) Lonestar Army Ammunition Plant f) Milan Army Ammunition Plant g) Mississippi Army Ammunition Plant
	• Alternatives to be Assessed	a) Proposed project
3	Alternative Areas of Volunteer AAP	
	• Potential Alternatives	a) Ordering of sourcing activities by drainage basin
	• Alternatives to be Assessed	a) Proposed project
4	Alternative Soil and Groundwater Sourcing Methods	
	• Potential Alternatives	a) Interim storage of sourced materials
	• Alternatives to be Assessed	a) Proposed project
5.	No Action Alternative	a) Proposed project

sanctioned actions associated with the cleanup of contaminated facilities and lands may not be subject to NEPA reviews, programs aimed at testing technologies or equipment which have not yet gained regulatory approval for use at a particular location must receive appropriate attention to minimize or avoid environmental impacts.

Early meetings with Environmental Protection Agency and regulatory agency representatives can help in decisions about the level of evaluation and documentation needed for a particular proposed action. This approach creates opportunity for team building and buy-in for projects and prevent late stage disagreements or confrontations. Permitting and NEPA-related activities are often on the critical path for most projects and delays incurred here will be felt later. A well written environmental assessment can be a valuable tool for communicating with interested groups and stakeholders, even when the action does not warrant significant interaction with those stakeholders.

Key components of an appropriate environmental review are the consideration all alternatives to the proposed action and evaluation of reasonable alternatives to the proposed action. Addressing environmental impacts in an open minded and unbiased way may lead to identifying mitigation actions and project modifications which will reduce overall environmental impacts and ensures meeting the letter and the spirit of NEPA requirements. At the very least, analysis of alternatives provides a means for crystallizing the result to be achieved by action and defining how an action can be conducted with the least impact to the environment.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions made to the preparation of the Volunteer AAP D/NETDP environmental assessment by H. Ray Threlkeld, P.E. Mr. Threlkeld, formerly of the Tennessee Valley Authority, is currently employed with Quantum Engineering Corporation, Loudon, Tennessee.

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DEVELOPMENT OF A RACT PROPOSAL FOR THE U.S. ARMY GARRISON OF FORT INDIANTOWN GAP

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ABSTRACT

The Clean Air Act Amendments of 1990 (CAAA-90)[1], Sections 182(b)(2) and 182(f)(1), require states establish a Reasonably Available Control Technology (RACT) program for facilities defined as major stationary sources (MSS) of volatile organic compounds (VOC) and/or nitrogen oxides (NO_x). The Pennsylvania Department of Environmental Resources (PADER) required each MSS facility submit a RACT proposal by July 15, 1994[2]. After PADER approval of the RACT proposal, the facility is obligated to implement the RACT program no later than May 31, 1995. The U.S. Army Garrison of Fort Indiantown Gap (FTIG) is subject to the new RACT program requirements because of its *potential* to emit 100 tons or more per year of NO_x and 50 tons or more per year of VOC. *Potential* NO_x emissions indicate that the combustion units (boilers, furnaces and space heaters) are the only source of NO_x emissions. *Potential* VOC emissions indicate that the inactive landfill and motor gasoline (MOGAS) dispensing operations are the two most significant sources of VOC emissions. This paper presents the approaches and strategies used to prepare a NO_x RACT proposal and a VOC synthetic minor option at FTIG.

INTRODUCTION

-FTIG Background

The U.S. Army Garrison of Fort Indiantown Gap (FTIG) is located in a rural area in the southern portion of central Pennsylvania. FTIG is located 23 miles northeast of Harrisburg, PA; 46 miles west of Reading, PA; and 14 miles northwest of Lebanon, PA (see Figure 1). The Blue Mountains, a portion of the Appalachian chain, form the northern boundary of FTIG and gently rolling farmlands lie to the east, west, and south of the installation. FTIG is comprised of approximately 19,200 acres of land; 17,800 of which are leased to the Federal Government by the Commonwealth of Pennsylvania. The installation is 11 miles long, seven miles wide, and encompasses three lakes. All the installation's buildings and facilities, and a majority of its land, lie in the northwest corner of Lebanon county which includes the townships of East Hanover and Union. The western portion of the installation's firing range extends into Dauphin County.

FTIG is a subinstallation of Fort Drum, New York, and is under the command of the U.S. Army Forces Command (FORSCOM). Two agencies are permanently located at the installation:

- the U.S. Army Garrison Headquarters of FTIG (HQ, FTIG); and
- the Pennsylvania Department of Military Affairs (PADMA)

. The two agencies are separate entities; neither tenant having jurisdiction over the other. The FTIG Garrison Headquarters is responsible for all U.S. Army owned and leased property, logistics, and support to reserve component training and tenant activities. Tenants of FTIG Garrison Headquarters include: the Health Services Command (HSC), the U.S. Army Readiness Group, the Headquarters of the Senior Army Advisor to the Pennsylvania Army National Guard, the 56th Ordnance Detachment (Explosive Ordnance Disposal), and the 79th and 99th Army Reserve Command (ARCOM).

-Regulatory Reviews

Concentrations of criteria pollutants near ground-level are routinely monitored by the U.S. Environmental Protection Agency (EPA). To protect human health and the environment, the National Ambient Air Quality Standards (NAAQS) were promulgated by the EPA in the Clean Air Act Amendments of 1977. The NAAQS represent a maximum concentration of a pollutant that should not be exceeded anywhere in the United States. There are two types of NAAQS; primary and secondary. Primary standards are designed to protect human health, while secondary standards protect public welfare. TABLE 1 presents the criteria pollutants and their associated health-based standards. The threshold levels are based on studies of epidemiological, health, and environmental effects conducted by the EPA. It is important to note that the NAAQS only provide target levels for concentrations of criteria pollutants in the atmosphere; they do not regulate pollutant emission rates for individual sources.

Currently, ground-level ozone is the most prevalent air pollution problem encountered by the majority of industrialized urban areas in the United States. Numerous studies indicate that ozone (O_3, smog) is a byproduct of photochemical reactions involving VOC and NO_x. To achieve compliance with the ozone NAAQS, strategies for reducing VOC emissions were prioritized. However, the 1990 Amendments also mandated reductions of NO_x emissions because NO_x is now recognized as an ozone precursor (a smog-forming chemical).

A geographic area that meets or does better than the primary NAAQS is called an attainment area; areas that fail to meet the primary NAAQS are called nonattainment areas. To meet ozone NAAQS, new or modified major sources located in attainment areas are subject to best available control technology (BACT) requirements. In a nonattainment area, the lowest achievable emission rate (LAER) and reasonably available control technology (RACT) requirements must be applied to new or modified major sources and existing major sources, respectively.

Attainment of the ozone NAAQS is a statewide dilemma for Pennsylvania. The Pennsylvania Environmental Quality Board amended Chapters 121 and 129 of the PA Code on November 15, 1993. The amendments now require facilities to determine if they are a Major Stationary Source (MSS) for VOC and/or NO_x . According to Pennsylvania's regulations, facilities with the *potential* to emit 100 tons or more per year of NO_x or 50 tons or more per year of VOC are subject to the new RACT requirements. The Pennsylvania Department of Environmental Resources (PADER) required each MSS facility submit a RACT proposal by July 15, 1994. After PADER approval of the RACT proposal, the facility is obligated to implement the RACT program no later than May 31, 1995.

-Procedures

The original objectives of the project were to assist FTIG in submitting the required air information management system (AIMS) data forms and to evaluate the applicability of the new RACT program requirements established by PADER. The project involved the following tasks:

- Performance of the CY93 Air Emission Inventory (AEI) of FTIG;
- Calculation of the *actual* and *potential* emissions for criteria pollutants and hazardous air pollutants (HAPs) regulated under CAAA-90;
- Preparation of a NO_x RACT proposal; and
- Formulation of a VOC synthetic minor option.

AIR EMISSIONS INVENTORY

-Field Survey

After review of the CY92 Emission Statement for Fort Indiantown Gap[3], PADER requested the following sources be updated and inventoried for calendar year 1993:

- all combustion units;
- surface coating operations (excluding architectural painting);
- MOGAS dispensing operations;
- degreasing operations;
- municipal wastewater treatment plant;
- the inactive landfill; and
- swimming pools.

The field survey was conducted according to the U.S. Army Environmental Hygiene Agency (USAEHA) AEI Protocol[4]. The air emission sources listed above were investigated and relevant information was recorded on data collection forms. The raw data collected during the field survey were used to calculate *actual* and *potential* emissions for each source.

EMISSION CALCULATIONS

-Calculation of Actual Emissions

Emissions of NO_x, VOC, other criteria pollutants, and the hazardous air pollutants (HAPs) were calculated for the Emission Statement using the EPA emission factors provided in AP-42[5] or a mass balance approach. The *actual* VOC and NO_x emissions for 1993 were 25.77 tons per year (TPY) and 21.71 TPY, respectively. The *potential* VOC and NO_x emissions for 1993 were 53.32 TPY and 256.87 TPY, respectively. The total *actual* and *potential* emissions of other criteria pollutants and total HAPs for 1993 were summarized in TABLES 2 and 3, respectively. For instance, the *actual* and *potential* HAPs emissions for 1993 were 9.03 TPY and 45.70 TPY, respectively. The following sections briefly describe the air emission sources located at FTIG.

A. **All combustion units** - The main heating plant, Building 14-501, housed three No. 6 fuel oil fired boilers (2 units at a capacity of 41 MMBtu/hr each and 1 unit at a capacity of 25.1 MMBtu/hr). The boilers produced steam for many of the buildings at FTIG. In addition, hundreds of smaller boilers, furnaces, or space heaters (all less than 10 MMBtu/hr in capacity) fueled by coal, No. 1 fuel oil, or liquid propane gas, were scattered throughout FTIG. The annual *actual* emissions of criteria pollutants from the operation of combustion units were estimated by multiplying the actual fuel usage by the appropriate emission factors contained in AP-42.

B. **Surface coating operations** - The types of surface coating products used at FTIG in 1993 included primers, enamels, lacquers, spray paints, stencil and marking inks, limited quantities of Chemical Agents Resistant Coating (CARC) paints, and thinners. All products were applied with a brush and/or roller; or by spray can (aerosol). No spray paint booths were used at FTIG. The *actual* VOC emissions were estimated using a mass balance approach. This method assumed that all the volatile components of the paints were released to the atmosphere (water and non-VOCs were not included in the VOC emissions). The amount of particulate matter released was estimated based on the solids content of the paints; and the transfer efficiency of the application method.

C. **MOGAS dispensing operations** - Emissions from MOGAS storage tanks are in the form of organic vapors that are derived from tank breathing (due to pressure and temperature changes) and working losses (from filling and emptying). Emissions from fuel dispensing operations arise from the evaporation of spills and vehicle tank filling. Emissions from storage tanks and fuel dispensing operations at FTIG were calculated by multiplying the annual throughput by emission factors provided in AP-42.

D. **Degreasing operations** - FTIG utilized fourteen small cold cleaner degreasers (ranging in size from 6 to 40 gallons in capacity) in 1993. All the degreasers used Safety-Kleen Solvent 105, except for one 6-gallon capacity unit that used immersion cleaner. All degreasers were serviced by Safety-Kleen, a private contractor that routinely collected and recycled used solvent, and delivered fresh solvent. Emissions from cold cleaner degreasers are volatile organic vapors derived from evaporation processes. *Actual* VOC emissions from degreasing operations were estimated using a mass balance approach.

E. **Municipal wastewater treatment plant** - A municipal wastewater treatment plant, installed in the 1940's, is located in Building T4-162, near Biddle Drive. During 1993, the plant was operated eight hours a day by a state certified operator with Type 3, Class D certifications. The operator performed sampling and analyses on site as required by the National Pollutant Discharge Elimination System (NPDES) permit. The maximum capacity of the plant is a flowrate of 2 million gallons per day (MGD). Anaerobic digestion processes occur in six Imhoff tanks. The organic materials in the sewage (expressed as BOD_5) and the sludge generated under anaerobic conditions are biologically converted to methane (CH_4), carbon dioxide (CO_2), Nitrogen (N_2), and other VOC. *Actual* emissions were estimated by multiplying the *actual* wastewater treatment rate by the emission factors contained in the EPA publication, "Procedures for the Preparation of Emission Inventories for Carbon Monoxide and Precursors of Ozone, Volume I, General Guidance for Stationary Sources, EPA-450/4-91-016"[6]. It should be noted that this reference only provides emission factors for industrial wastewater. The EPA assumes that domestic wastewater treatment plants accept an average of approximately 16 percent of the total effluent from industrial sources.

F. **An inactive landfill** - An inactive sanitary landfill, approximately 100 acres in size and equipped with no gas collection system, is located in Area 24 of FTIG. The landfill was opened in 1942 and was designed to receive solid wastes generated by the installation. Due to the difficulty in obtaining a state landfill permit, the use of the landfill was discontinued on October 1, 1982. The exact type and amount of waste disposed of in the landfill was estimated by a USAEHA Landfill Study[7]. The study indicated that the inactive landfill was primarily used for co-disposal of municipal solid waste (MSW) and other organic materials, such as: domestic waste, sewage sludge, industrial liquid waste, and scrap metal. Air emissions, such as carbon dioxide (CO_2) and methane (CH_4), are generated as the landfilled waste materials decompose through biodegradation processes; however, non-methane organic compounds (NMOC) (e.g., halogenated hydrocarbons and VOC) are also emitted. VOC and HAPs emissions from the landfill were determined using the EPA Landfill equations in AP-42, 4th edition, Section 2.7[5]. Default values were assumed whenever site-specific data were unavailable.

G. Swimming Pools - Two outdoor swimming pools (an adult pool and a children pool) were open during the summer season, a total of 98 days in 1993 (May 31 through September 6, 1993). Emissions from swimmimg pools are the chlorine gas (Cl_2) that are derived from chlorination processes. The *actual* chlorine gas emissions were estimated using a mass balance approach. Due to the lack of the residual chlorine concentrations, a very conservative method was used to estimated chlorine gas emissions. The method assumed that all chlorine content in the commercial bleach solution was emitted to the atmosphere as chlorine gas.

-Calculation of Potential Emissions

The *potential* emissions were calculated using the same methods described above for *actual* emissions; however, it was necessary to estimate *potential* fuel usage or *potential* paint/chemical usage. The methodologies used for estimating *potential* fuel usage or *potential* paint/chemical usage for various sources are as follows:

A. All combustion units - *Potential* throughput was calculated by multiplying the rated capacity of each combustion unit by the number of hours in a year (8760 hours/year), divided by the heating value of the type of fuel used (e.g., 150,000 Btu/gal for No. 6 fuel oil)[8].

B. Municipal wastewater treatment plant - *Potential* emissions were estimated by multiplying the *potential* wastewater treatment rate by the same emission factors used to estimate *actual* emissions. The *potential* wastewater treatment rate was equal to the maximum design capacity of the plant, which was 2 million gallons per day.

C. An inactive landfill - VOC and HAPs emissions from the landfill were determined using the EPA Landfill equations in AP-42, 4th edition, Section 2.7[5]. Default values were assumed whenever site-specific data were unavailable. Because operation of the landfill was discontinued on October 1, 1982, *potential* emissions were equal to *actual* emissions.

D. All other operations - For surface coating, degreasing operations and MOGAS dispensing operations, the *potential* chemical usage or throughput was derived by extrapolation of the *actual* chemical usage/throughput to a 24 hours per day, 365 days per year time period. *Potential* chemical usage or throughput was estimated by multiplying the *actual* chemical usage or by the ratio of the number of hours in a year (8760 hours/year) to the *actual* hours of operation in 1993.

E. Swimming Pools - *Potential* chlorine gas emissions were estimated by multiplying the *actual* chlorine gas emissions by the ratio of the number of days in a year (365 days/year) to the *actual* days of operation in 1993 (98 days/year).

-Applicability of RACT Requirements

Fort Indiantown Gap is located in an O_3 non-attainment area classified by the EPA as "marginal". According to Pennsylvania's regulations[2], facilities located in nonattainment areas with the *potential* to emit 100 tons or more per year of NO_x or 50 tons or more per year of VOC are subject to the new RACT requirements. The *potential* VOC and NO_x emissions from FTIG in CY93 were 53.32 TPY and 256.87 TPY, respectively. Therefore, FTIG was subject to the RACT requirements and was required to submit a RACT proposal by July 15, 1994.

PREPARATION OF A NO_x RACT PROPOSAL

-Introduction

RACT is defined as a control technology generally recognized to be technically and economically achievable for a majority of existing similar sources. The EPA has issued control technology guidelines (CTGs) for a number of VOC and NO_x source categories. The guidance documents provide proposed control measures for RACT. The RACT proposal for FTIG was carried out in accordance with the "Guidance Document on Reasonably Available Control Technology for Sources of NO_x Emissions"[9], prepared by PADER, dated March 11, 1994. In addition, PA Title 25, Subchapter 129.93 regulations provide a number of presumptive RACT standards for various sources (such as boilers and storage tanks). "Presumptive RACT" refers to specific control technology standards, as well as testing, monitoring, recordkeeping, and recording requirements outlined in PA Title 25 Subchapter 129.93 for various types and classes of NO_x sources. Because of the small heat inputs of the combustion units (all of capacities less than 50 MMBtu/hr) located at FTIG, presumptive NO_x RACT standards were utilized in development of the NO_x RACT proposal for FTIG. Therefore, the cost analyses of NO_x RACT alternatives were not performed.

-Presumptive NO_x RACT

Several presumptive NO_x RACTs have been identified by PA Title 25 Subchapter 129.93. The following describes the presumptive NO_x RACTs selected for the FTIG combustion units:

A. For Combustion Units with Maximum Heat Inputs Between 20 MMBtu/hr and 50 MMBtu/hr:

Combustion units with maximum heat inputs equal to or greater than 20 MMBtu/hr, but less than 50 MMBtu/hr, are located at the Main Heating Plant (Building 14-501) of FTIG. There are no combustion units with maximum heat inputs equal to or greater than 50 MMBtu/hr. The presumptive RACT described in Subchapter 129.93(b)(2) requires all units located in Building 14-501 conduct an annual tune-up of their combustion processes. The tune-up should include, at minimum, the following:

- inspection, adjustment, cleaning or replacement of fuel-burning equipment, including the burners and moving parts necessary for proper operation as specified by the manufacturer;

- inspection of the flame pattern or characteristics and adjustments necessary to minimize total emissions of NO_x, and to the extent practicable minimize emissions of carbon monoxide (CO); and

- inspection of the air-to-fuel ratio control system and adjustments necessary to assure proper calibration and operation as specified by the manufacturer.

In addition, all adjustments conducted on an annual basis must be recorded in a permanently bound log book. This log book must contain at a minimum the following information:

- the date of the tuning procedure;
- the name of the service company and technicians;
- the final operating rate or load;
- the final CO and NO_x emission rates;
- the final excess oxygen rate; and
- other information required by the applicable operating permit.

The operator of the combustion units must make the annual adjustments in accordance with the EPA document entitled "Combustion Efficiency Optimization Manual for Operation of Oil and Gas-Fired Boilers."[10] The operator must also maintain certification records for the type of fuel used. The certification records must contain values for the nitrogen content of the fuel as well as the sampling method and sampling protocol.

B. For Combustion Units with Maximum Heat Inputs less than 20 MMBtu/hr:

Besides combustion units located in Building 14-501, hundreds of smaller boilers, furnaces, or space heaters (all of capacities less than 10 MMBtu/hr) fueled by coal, No. 1 fuel oil, or liquid propane gas, were scattered throughout FTIG. Among these units, only two coal-fired boilers with heat inputs of 2.7 and 5.4 MMBtu/hr are regulated by PA Code Title 25 Subchapter 127.14 and have operating permits. As described in Subchapter 129.93(c)(1), the presumptive RACT emission limitations for boilers and other combustion sources with individual maximum heat inputs less than 20 MMBtu/hr are the installation, maintenance and operation of the units according to manufacturer specifications.

FORMULATION OF A VOC SYNTHETIC MINOR OPTION

-Background

CY93 total *actual* and *potential* VOC emissions, presented in TABLES 2 and 3, were 25.77 TPY and 53.32 TPY, respectively. The *potential* VOC emissions were slightly greater than the VOC major source threshold of 50 TPY. The primary source of the *actual* and *potential* VOC emissions at FTIG was the inactive landfill. It is important to note that the *actual* and *potential* VOC emissions from the inactive landfill will decrease versus time according to the calculations performed using the EPA Landfill equations in AP-42[5]. A preliminary RACT analysis, including cost analysis, was conducted for the inactive landfill to identify and evaluate applicable control technologies, such as a flaring system and carbon adsorption. According to the results of the cost analyses, none of the control technologies were economically feasible for FTIG; the costs ranged from $9,700/ton to $12,000/ton. WCFS suggested FTIG file a synthetic minor application in place of a RACT proposal for VOC sources. The synthetic minor approach was economically as well as technically feasible for FTIG.

-Synthetic Minor Strategies

Synthetic minor is a term applied to a facility that would normally be a MSS facility but whose owner agrees to limit its emissions through federally enforceable conditions (e.g., a cap on production rates, maximum hours of operation, maximum fuel throughputs, sulfur content of fuels used, etc.). Permits issued to facilities choosing the synthetic minor approach will become federally enforceable only when the EPA approves Pennsylvania's State Implementation Plan (SIP). As of April 1994, the EPA has yet to approve Pennsylvania's SIP.

The total amount of gasoline dispensed at FTIG during 1993 was 499,491 gallons. TABLES 2 and 3 indicate a large difference between the *actual* and *potential* VOC emissions from MOGAS dispensing operations for 1993 (3.25 TPY versus 15.60 TPY). In 1992, the *actual* VOC emissions from MOGAS dispensing operations were 3.65 TPY. The decrease in *actual* VOC emissions from 1992 to 1993 was expected because of the conversion from gasoline to diesel fueled vehicles at FTIG. Because of the facility's reduction of the *actual* VOC emissions, application of a federally enforceable condition for MOGAS dispensing operations (e.g., gasoline throughput limitation) was recommended.

The *potential* VOC emissions from MOGAS dispensing operations can be lowered considerably by implementing enforceable operating limitations on the amount of gasoline dispensed and installing Stage II vapor controls systems. Stage II vapor control systems with a control efficiency of approximately 90 percent were installed at the PX MOGAS station (Building 9-66) in January of 1994. The fuel throughput limitations coupled with the Stage II vapor controls will reduce the facility-wide *potential* VOC emissions below 50 TPY, thus changing the facility from a major to a minor VOC source status.

-Development of Enforceable Conditions for Synthetic Minor

Maintenance of operational flexibility, curtailment of managerial burden, and reduction of *potential* VOC emissions for FTIG were the three major concerns during the development of the throughput limitations for the MOGAS dispensing operations. CY93 *potential* VOC emissions of 15.60 TPY for all MOGAS dispensing at FTIG were calculated based on 2.4 million gallons of gasoline per year being pumped through MOGAS dispensing stations with Stage I vapor controls. The proposed *potential* VOC emissions for the MOGAS dispensing operations was 9.33 TPY. This number was estimated based on a limitation of 3.5 million gallons of gasoline per year at gasoline stations equipped with Stage I and II vapor controls, such as the PX gas station at Building 9-66; and a limitation of 0.6 million gallons of gasoline per year at gasoline stations equipped with only Stage I vapor controls, such as all other FTIG MOGAS dispensing stations combined.

The installation of Stage II vapor controls at the PX gas and the gasoline throughput limitations at FTIG would result in a new facility-wide *potential* VOC emission of 47.05 TPY, as is presented in TABLE 4. This value is below the 50 TPY major source threshold for VOC, and therefore, FTIG would be classified as a minor VOC source.

-Recordkeeping and Reporting Requirements

All MOGAS dispensing stations at FTIG are required to maintain monthly, quarterly, and annual records of the amount of gasoline dispensed at each fueling station. The records will be kept on-site in permanently bound log books, readily available for inspection by PADER personnel. All records of gasoline dispensed at FTIG will be summarized in an annual report to PADER. The report will indicate the monthly, quarterly, and annual gasoline usage and ensure that the *potential* VOC emissions from the MOGAS dispensing operations will remain below 9.33 TPY, and the facility-wide *potential* VOC emissions for FTIG will remain below 47.05 TPY.

CONCLUSIONS

The results of this study also indicated that the *potential* SO_x and HAP emissions at FTIG may classify the facility as a major source. As stated in 25 PA Code Section 127.203, each major source facility will be required to obtain a Title V Operating Permit no later than November 27, 1995. However, with proper planning, a synthetic minor permit application can be filed to avoid applicability of New Source Review (NSR), Prevention of Significant Deterioration (PSD), Reasonably Available Control Technology (RACT), and Maximum Achievable Control Technology (MACT) provisions. Proper planning should encompass all aspects of air pollution emissions at FTIG including: technical evaluations of processes, pollution control devices, pollution prevention opportunities, and financial planning to ensure allocation of sufficient budget resources for permit applications.

ACKNOWLEDGEMENTS

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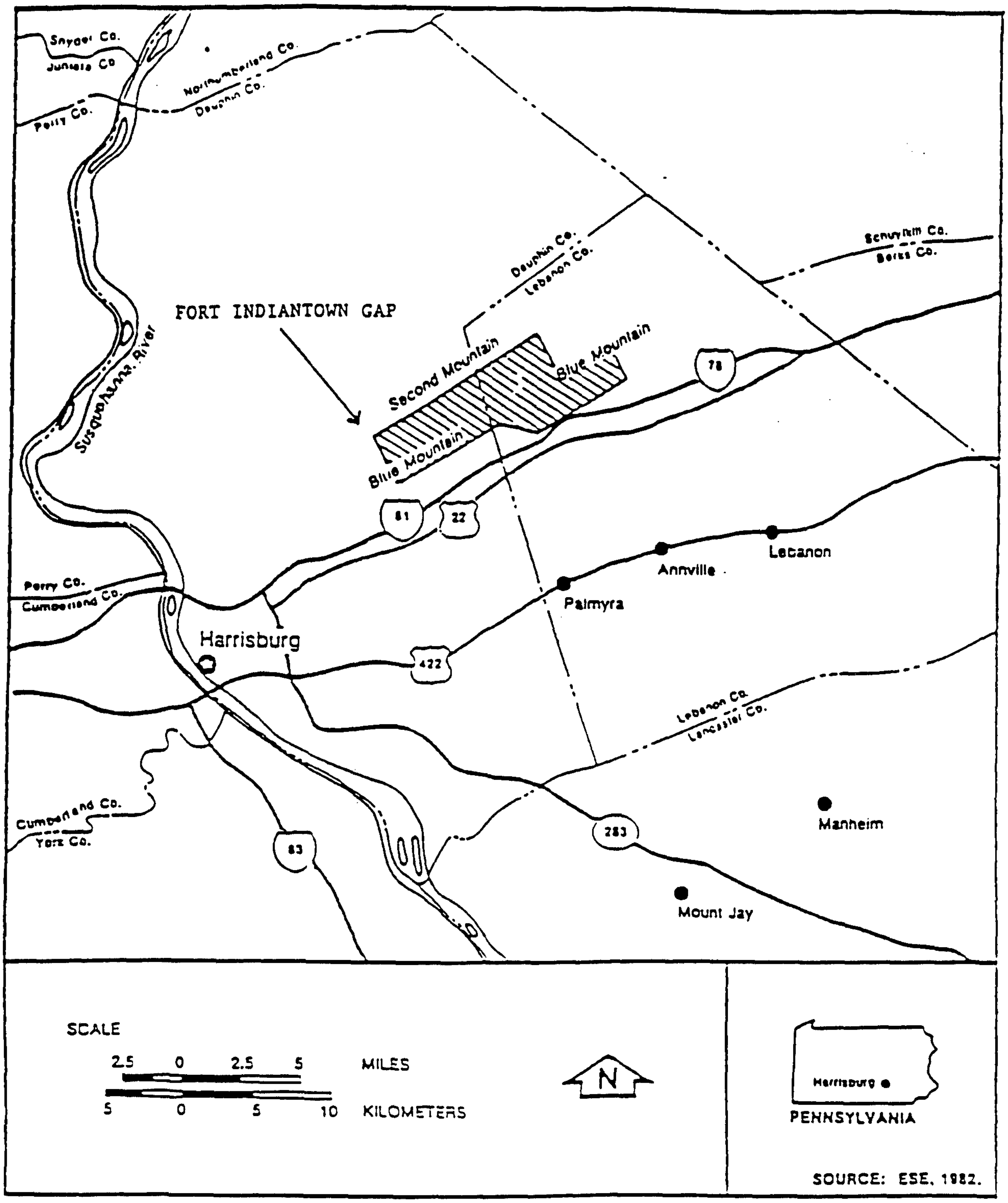
FIGURE 1

Location Map of Fort Indiantown Gap, PA



SOURCE: ESE, 1982.

TABLE 1 National Ambient Air Quality Standards

Criteria Pollutant	Averaging Period	Primary NAAQS ($\mu g/m^3$)	Secondary NAAQS ($\mu g/m^3$)
PM10 (Particulate matter)	Annual	50	50
	24-hour	150	150
SO_2 (Sulfur dioxide)	Annual	80	---
	24-hour	365	---
	3-hour	----	1,300
NO_2 (Nitrogen dioxide)	Annual	100	100
O3 (Ozone)	1-hour	235	235
CO (Carbon monoxide)	8-hour	10,000	10,000
	1-hour	40,000	40,000
Lead	Quarterly	1.5	1.5

TABLE 2

Fort Indiantown Gap, PA, Air Emissions Inventory
Criteria Pollutants and HAPs Emissions Summary

1993 Actual Emissions (TPY)

Source Description	VOC (TPY)	NOx (TPY)	CO (TPY)	SOx (TPY)	PM10 (TPY)	TSP (TPY)	Total HAPs (TPY)
Boilers/Furnaces/Heaters	0.52	21.71	3.47	82.65	3.89	11.52	3.75
Surface Coating Operations	0.29	-	-	-	-	0.05	0.13
MOGAS Dispensing Operations	3.25	-	-	-	-	-	1.61
Degreasing Operations	1.70	-	-	-	-	-	0.05
Wastewater Treatment Plant	2.94	-	-	-	-	-	1.41
Inactive Landfill	17.07	-	-	-	-	-	0.87
Swimming Pools	-	-	-	-	-	-	1.22
TOTAL (TPY)	25.77	21.71	3.47	82.65	3.89	11.57	9.03

Note:

"-": not available or not applicable.

TABLE 3

Fort Indiantown Gap, PA, Air Emissions Inventory
Criteria Pollutants and HAPs Emissions Summary

1993 Potential Emissions (TPY)

Source Description	VOC (TPY)	NOx (TPY)	CO (TPY)	SOx (TPY)	PM10 (TPY)	TSP (TPY)	Total HAPs (TPY)
Boilers/Furnaces/Heaters	5.83	256.87	41.79	793.01	34.38	95.05	28.75
Surface Coating Operations	1.24	-	-	-	-	0.19	0.53
MOGAS Dispensing Operations	15.60	-	-	-	-	-	7.72
Degreasing Operations	7.16	-	-	-	-	-	0.21
Wastewater Treatment Plant	6.42	-	-	-	-	-	3.09
Inactive Landfill	17.07						0.87
Swimming Pools	-	-	-	-	-	-	4.53
TOTAL (TPY)	**53.32**	**256.87**	**41.79**	**793.01**	**34.38**	**95.24**	**45.70**

Note:
"-": not available or not applicable.

TABLE 4

Fort Indiantown Gap, PA, Air Emissions Inventory
Proposed Synthetic Minor Option for VOCs sources at FTIG

VOC and NOx Potential Emissions (TPY)

Source Description	VOC Potential	NOx Potential
Boilers/ Furnaces/Heaters	5.83	256.87
Surface Coating Operations	1.24	-
MOGAS Dispensing Operations	**9.33**	-
Degreasing Operations	7.16	-
Wastewater Treatment Plant	6.42	-
Inactive Landfill	17.07	-
TOTAL (TPY)	**47.05**	**256.87**

Note:
"-": not available or not applicable.

ULTRAVIOLET DISINFECTION AT ARMY WASTEWATER TREATMENT PLANTS

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Most U.S. Army wastewater treatment plants (WWTPs) currently disinfect domestic wastewater using chlorination, while a great number of these installations still do not dechlorinate. In the past few years, U.S. Environmental Protection Agency (EPA) and state regulatory agencies have incorporated stringent total chlorine residual (TRC) limits for wastewater effluent. As a result, recent and pending amendments to disinfection limits will force U.S. Army WWTPs to change their disinfection processes. In turn, the Army has investigated UV disinfection as an environmentally-friendly alternative to chlorine disinfection. Disinfection procedures from 28 Army WWTPs have been examined by interviewing installation personnel and reviewing National Pollutant Discharge Elimination System (NPDES) permits to determine the nature of the disinfection dilemma. This paper examines current Army WWTP disinfection practices and solutions to disinfection problems, and offers information on ultraviolet (UV) disinfection to assist facility managers and related personnel in choosing effective disinfection processes that will meet discharge limitations. A similar study (reference 1) examines UV disinfection at publicly-owned treatment works (POTWs) throughout the U.S.

Rules and regulations for wastewater disinfection are established by the EPA or states with EPA approved programs under the NPDES, which is established under the Clean Water Act (CWA). Taking into consideration receiving stream classifications and water quality criteria, many state agencies have adopted site-specific water quality standards for TRC and fecal coliform (FC) limitations. These standards are continually updated. Some regulators have recently adopted EPA Water Quality Criteria in their permits; the chlorine concentration acutely toxic to fresh water aquatic organisms is 0.019 mg/L, and the chronic concentration is 0.011 mg/L. Consequently, newly issued permits are specifying extremely low or nondetectable (<0.1 mg/L) TRCs. A few facilities, such as Red River Army Depot and Milan Army Ammunition Plant, have schedules for meeting interim and final permit limits.

Red River Army Depot's EPA permit specifies a TRC of 0.019 mg/L after the first 3 years. A TRC of between 1 and 4 mg/L is specified for the first 3 years. This limit was derived from Texas Administrative Code (TAC) 309.3 (g), which specifies a minimum TRC of 0.5 mg/L and maximum TRC of 4 mg/L for a minimum detention time of 20 minutes. The new permit writer has agreed to drop the detention time requirement since FC limits will directly regulate disinfection efficiency. However, the Red River Army Depot's permit also contains effluent biomonitoring requirements.

This permitting procedure can create disinfection dilemmas through permit violations of toxicity limits. Although Red River Army Depot's interim TRC limits provide sufficient time for design, construction, and implementation of dechlorination or alternate form of disinfection, high interim TRC levels can cause violations in toxicity tests. While the permit allows dechlorination of biomonitoring samples prior to analyses (to protect test species), dechlorination of Red River's effluent at current operating TRCs has contributed to in-stream toxicity. Therefore, use of dechlorinating agents could contribute to toxicity test failures. If so, permittees could be subject to performing toxicity reduction evaluations.

In order to meet TRC and toxicity limits while effectively disinfecting wastewater, installations can modify WWTPs in the following ways: add dechlorinating equipment for use at the existing chlorine contact chamber, retrofit existing chambers with UV disinfection, or construct a new disinfection system. Since many Army installations are switching from chlorine to UV disinfection, the following paragraphs will compare and contrast chlorine and UV. Alternate forms of disinfection including ozonation, chlorine dioxide, bromine chloride, and electron beam and gamma radiation are not widely used, and thus will not be discussed.

Chlorination chemistry is discussed in detail in reference 2. The chlorination process forms halogenated organic compounds that are possible carcinogens, mutagens, or toxins and can threaten quality of downstream water supplies. Acute and chronic in-stream toxicity has been associated with wastewater chlorination. In one study, (reference 3), complete mortality of fathead minnows was observed in TRC concentrations of 0.1 mg/L. This study suggested that synergistic toxic effects can be attributed to pollutants such as TRC, ammonia nitrogen (NH_3-N), and dissolved oxygen (DO).

Dechlorination chemistry is also discussed in detail in reference 2. Dechlorinating agents used most frequently include sulfur dioxide (SO_2), salts, and activated carbon. Storage or dissipation of chlorinated effluents is also a widely used method, although chlorination by-products can threaten water quality. Chemical dechlorinating agents are normally injected and mixed into chlorinated effluents after or in the last part of the chlorine contact chamber. While active dechlorinating agents react to remove all or part of the chlorine residual, chlorination by-products remaining in wastewater following dechlorination are possible causes of effluent toxicity.

In fact, dechlorinating agents such as SO_2 have been investigated as possible toxicant sources (references 4 and 5). For example, Milan Army Ammunition Plant's WWTP uses chlorine gas and SO_2 to meet new (1994) TRC limits of 0.011 mg/L (average monthly) and 0.019 mg/L (maximum daily). Toxicity tests performed by the U.S. Army Center for Health Promotion and Preventive Medicine (Provisional) [USACHPPM (Prov)] confirmed no toxicity before the disinfection process, and acute toxicity following the chlorination/dechlorination process (allegedly caused by processes within the chlorine contact chamber). Possible by-products are discussed in detail in reference 3. The USACHPPM (Prov) is currently performing pilot UV studies at Milan Army Ammunition Plant and Red River Army Depot in order to determine whether UV can provide effective disinfection and eliminate toxicity.

Based on results of these pilot studies, UV systems may be installed at these facilities. Wastewater is passed through UV light which irradiates the water. The UV light distorts microbial DNA, resulting in death and mutations of offspring. Light is transmitted by mercury vapor lamps encased in Quartz or Teflon sleeves and operates at a wavelength of 253.7 nm (most effective operating between 250 and 270 nm). Ultraviolet systems include closed shell reactors, open channel reactors, and non-contact Teflon reactors. Open channel UV systems (most frequently used) generally work better than closed shell reactors. An open channel system with banks of lamps inserted into the channel rovides easy access to the unit for operations and maintenance (O&M). While O&M of UV units are generally less labor intensive than chlorine systems, site-specific problems can hinder efficient use of UV. Prior to installing a UV system, the following factors should be considered.

Fouling is the most common hindrance of UV systems. When substances such as oil and grease, calcium, magnesium, and iron accumulate on the lamp sleeves, lamp transmissibility and intensity (indicated on system control panels) decrease. Degree, rate, and causes of fouling are site-specific and can be determined by pilot testing. In any case, UV lamp sleeves require regular manual cleaning in addition to any automatic cleaning systems provided. Periodic immersion in a tank of cleaning solution or hand-washing is necessary to avoid excessive fouling. All UV operators should obtain replacement banks of lamps for use during cleaning. Available cleaning solutions include organic acids (citric, oxalate), inorganic acids (sulfuric, muriatic), detergents, degreasers, caustic cleaners, or ammonia based cleaners. At Redstone Arsenal, lamp sleeves are effectively cleaned by immersion in dip tanks.

Total dissolved solids (TDS) and total suspended solids (TSS) should also be considered prior to installing UV systems. The amounts of solids in wastewater determines the amount of UV light that penetrates and effectively disinfects wastewater. One manufacturer recommends TSS concentrations of less than 15 mg/L for optimum disinfection efficiency. Theoretically, filtration prior to disinfection is desired but not required. Without filtration, secondary levels of treatment are attainable: Fecal coliform (FC) < 200-400 (colonies per 100 mL). With filtration, tertiary levels are attainable: FC < 14/100 mL. A general rule of thumb is provided: as the degree of wastewater treatment increases, UV transmittance also increases.

In addition, sufficient reduction in FC levels must occur in order to achieve optimum UV treatment. Fecal coliform concentrations before disinfection can be estimated based on the degree of treatment received. For primary, secondary, and tertiary effluents, expected FC concentrations (colonies/100 mL) are 10^6 to 10^7, 10^4 to 10^5, and 10^3 to 10^5, respectively (reference 6). A 4-logarithm reduction in FC levels sufficiently meets FC limits of 200 in most WWTPs. Dose required to achieve this degree of treatment is approximately 30,000 uW-s/cm^2, based on a transmittance of 65% and 30 mg/L TSS. Once a design dose is determined, the number of UV lamps required can be determined using manufacturers dose-response information. For UV transmittance <65% or TSS levels >30 mg/L, multiplication factors (to adjust number of lamps needed) are available from manufacturers.

Ultraviolet lamps also need replacement when they age or are no longer capable of producing the intensity required to disinfect wastewater effectively. Approximate replacement age is every 12 months, but this requirement varies widely at each site. For example, Blue Grass Army Depot installed a UV system in 1990, and replacement bulbs have reportedly not been used yet.

Photoreactivation is another consideration for UV systems. This phenomenon involves enzymatic repair of bacteria damaged by UV light and allows for subsequent replication of the organism. Photoreactivation requires exposure to light at wavelengths between 300 and 500 nm, or sunlight. The U.S. Army Environmental Hygiene Agency completed a performance evaluation of the Redstone Arsenal UV disinfection system in April 1991 (reference 7). The unit's design and performance criteria were met and excellent coliform results were obtained. Also, photoreactivation tests were performed, and the results indicated that photoreactivation is not problematic since UV design criteria accounts for some photo repair. In fact, UV systems are typically designed with a safety factor of 2.0 times or greater so that UV dose delivered is twice that to destroy E. coli.

To determine whether UV is operationally feasible, and to decrease problems associated with scale-up, pilot testing is recommended. Ongoing UV pilot testing at Red River Army Depot is discussed as follows. It is widely recognized that chlorination and UV are both effective against pathogens, but preliminary USACHPPM (Prov) study results at Red River Army Depot indicated that UV was a more efficient bacterial inactivator than chlorine. Fecal coliform levels were lower following UV than they were following chlorination. As anticipated, no toxicity was found in two samples of UV effluents.

Advantages of using UV versus chlorine disinfection are evident, as follows. UV disinfection: does not cause in-stream toxicity; requires minimal maintenance; discharges no residuals or chemical by-products; does not chemically or physically alter treated effluent; requires no transport, storage, or handling of chemicals; is generated onsite; safety considerations are not as intensive; and is effective in treating certain viruses, parasitic worm ova, and cysts (giardia) that are resistive to disinfection by chlorination. Disadvantages of UV include: requires auxiliary power, additional O&M electrical costs, lamp sleeve cleaning, and use of coliform tests to gauge UV effectiveness.

Furthermore, chlorine system O&M problems include: chemical storage, handling, transport, and safety; difficult to operate due to lack of state-of-the-art systems; measurement limitations associated with chlorine and dechlorination demand; time delays reliability; and process dynamics. For plants with fluctuating flow, this type of disinfection is difficult to control without flow-paced or demand-paced equipment. For example, McAlester Army Ammunition Plant (MAAP) installed a dechlorination facility after a state regulatory office proposed to issue a compliance agreement which would impose fines for noncompliance with TRC limits. At the time, the state recommended constructing a dechlorination facility, because information regarding UV was not readily available. Since implementation, MAAP has experienced operational difficulties with the dechlorination system. The unit operates by presetting the chlorine feed rate based upon an average flow rate. Plant operators must continually reset the unit to account for wide fluctuations in flow. In most plants with similar equipment, to decrease the amount of time spent manually adjusting equipment, dechlorination doses are often preset to over-treat. The disadvantage (other than the obvious labor intensive equipment problems) is that excess SO_2 can also contribute to in-stream toxicity. McAlester Army Ammunition Plant is currently investigating retrofitting UV into an existing process.

Both UV and chlorination/dechlorination are cost competitive. Reference 1 contains cost information for UV systems, including capital and O&M expenses (electrical power, replacement of parts, and labor). Costs vary as a result of unique site conditions. Costs for chlorination/dechlorination can be found in reference 8. A common contention is that UV operating costs are prohibitive; however, costs of chlorination/dechlorination chemicals coupled with associated safety concerns nullify this argument.

Refer to Table 1 for wastewater disinfection methods at several U.S. Army Materiel Command (AMC), Forces Command (FORSCOM), and U.S. Army Training and Doctrine Command (TRADOC) facilities. Table 1 identifies facilities that switched (or are planning to) from chlorine disinfection to UV disinfection. The following paragraphs detail problems encountered with meeting new TRC limits and individual solutions to these problems.

Installations can be categorized as follows: installations that chlorinate only, installations that chlorinate/dechlorinate, installations that recently switched from Cl_2 to UV, installations that currently chlorinate with or without dechlorination that plan to get UV within the next year, and installations that chlorinate and plan to install dechlorination within the next few years.

Installations that only chlorinate their effluent normally have either relatively high TRC limits or none at all. Furthermore, these permits sometimes specify high FC limits, which allows installations to meet limits using little or no disinfection.

Defense Distribution Region East chlorinates only. Their permit specifies a seasonal (October through April) FC limit of 100,000 colonies per 100 mL (100,000/100). As derived from Pennsylvania Title 25, Section 95.7 (reference 9), summertime FC must meet a geometric average limit of 200/100 and less than 1000/100 in 10% of samples tested. No TRC limit or toxicity tests are specified; however, the permit contains a statement requiring the permittee to institute steps to reduce or eliminate adverse negative water quality impacts if they occur.

The Fort Hood North WWTP also chlorinates without dechlorinating. The TRC permit limit of between 1.0 and 4.0 mg/L was derived from TAC 309.3 (g). No toxicity tests are required.

The following installations switched from Cl_2 to UV disinfection due to compliance agreements in permits or impending low TRC limits. Blue Grass Army Depot installed UV as a proactive approach after learning that the state regulatory agency planned to impose a stringent TRC limit in the renewed permit. In 1992, Jefferson Proving Ground retrofitted UV lights into the existing chlorine contact chamber as a result of a compliance agreement. Capital costs for a 0.25 million gallon per day system (design flow) were $29,600. To date, toxicity tests confirm that the effluent is nontoxic, and the facility is closing in September 1995. Also, Fort McCoy uses chlorine and SO_2 but plans to construct a new UV system due to impending low TRC limits. The current TRC limitation is 0.037 mg/L, and toxicity testing will commence in 1996.

The Aberdeen Proving Ground Edgewood Area (APG-EA) and Aberdeen Area (APG-AA) chlorinate/dechlorinate. These areas use chlorine and SO_2 to meet a nondetectable (<0.1 mg/L) TRC limit. The system works well for them, and toxicity test results have been nontoxic at APG-EA and toxic due to NH_3-N at APG-AA.

TABLE 1
Disinfection Methods at Army WWTPs

Installation	$Cl_2/DeCl_2$	UV	TOX***	TRC Limit (mg/L)
Anniston AD	Yes/no	No*	nontoxic	None
APG-AA	Yes/SO_2	No	NH_3-N	<0.1
APG-EA	Yes/SO_2	No	nontoxic	<0.1
BlueGrass AD	No	Yes	not reqd	None
Ft Bragg	Yes/no	retrofit*	Cl_2-toxic	None
Ft Campbell	No	Yes	nontoxic	None
DDRE	Yes/no	No	not reqd	None
Holston AAP	Yes/no	No	not reqd	2.0 proposed
Ft Hood	Yes/no	No	not reqd	1-4.0
Iowa AAP	Yes/no	No	toxic	None
Indiana AAP	Yes/no	No	toxic	1.0
Jefferson PG	No	retrofit	nontoxic	report
Joliet AAP	Yes/no	retrofit dechlorination	not reqd	.75 1st 2 yrs .05 3rd yr
Kansas AAP	Yes/no	No	not reqd	.01
Ft Lewis	Yes/no	No	nontoxic	0.5 violation
Longhorn AAP	Yes/bids**	No	Cl_2-toxic	1-4.0
Louisiana AAP	Yes/design**	No	toxic	report
McAlester AAP	Yes/SO_2	No*	nontoxic	<0.1

See footnotes on page 8.

TABLE 1 (Continued)

Installation	$Cl_2/DeCl_2$	UV	TOX***	TRC Limit (mg/L)
Ft McClellan	No	Yes	nontoxic	None
Ft McCoy	Yes/SO_2	bids*	1996	.037
Milan AAP	Yes/SO_2	pilot*	toxic	.011/.019
Mississippi AAP	Yes/sulfite	No	nontoxic	.02/.03
Ft Pickett	Yes/SO_2	No	toxic	.02
Ft Polk	Yes/NaThio	No	nontoxic	.09
Red River AD	Yes/no	pilot*	Cl_2-toxic	1-4.0 1st 3 yrs .019 4th yr
Redstone	No	Yes	not reqd	no limit
Sharpe AD	Yes/SO_2	No	nontoxic	.02
Vint Hill Farm	No	Yes	not reqd	no limit

* denotes installations planning to switch to UV.

** denotes installations planning to add a dechlorination process.

*** denotes whether toxicity monitoring is required and if results of any biomonitoring were toxic or nontoxic.

Fort Bragg currently chlorinates with or without dechlorination but plans to install UV within the next few years. No TRC limit has been specified in the permit. Toxicity tests have confirmed chlorine as a toxicant; therefore, installation of dechlorination or UV must be decided. The installation plans on retrofitting of UV banks into the existing chlorine contact chamber. The state regulatory agency is expected to impose a new TRC limit of 0.017 in 1996 when the current permit expires.

The following installations chlorinate but plan to install dechlorination facilities within the next year. Longhorn Army Ammunition Plant is pursuing dechlorination to meet their new TRC limit. However, acute and chronic toxicity have been attributed to chlorine. In addition, Louisiana Army Ammunition Plant chlorinates without dechlorinating. While sources of acute toxicity are being investigated, Cl_2 is the suspected toxicant. Only TRC monitoring is required in the permit. A dechlorination system is currently being designed. It is unclear whether the toxicity will disappear upon implementing dechlorination. These cases could parallel Milan's disinfection dilemmas.

CONCLUSIONS

Ultraviolet disinfection is currently the most promising form of wastewater disinfection for U.S. Army WWTPs, since it can eliminate effluent toxicity and meet TRC permit limits without causing violations in other discharge limits. Within the next few years, while several installations still only chlorinate, impending stringent NPDES permit limits for TRC and toxicity will force Army WWTPs to employ dechlorination or alternate forms of wastewater disinfection (UV). Awareness of the disinfection dilemma from Army WWTP experiences can ease transitions from chlorination to UV or dechlorination, and subsequently aid facility managers and related personnel in complying with new NPDES permit limitations.

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USING AN INFORMATION SYSTEM TO MEET HAZARDOUS WASTE MANAGEMENT NEEDS

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Abstract

Lawrence Livermore National Laboratory (LLNL) is a large quantity RCRA hazardous waste generator. LLNL also generates low level and transuranic radioactive waste that is managed in accordance with the Department of Energy (DOE) orders. The mixed low level and mixed transuranic waste generated must be managed to comply with both RCRA regulations and DOE orders. LLNL's hazardous and radioactive waste generation is comprised of 900 generators who contribute to nearly two hundred waste streams. LLNL has a permitted EPA treatment and storage (TSD) facility for handling RCRA hazardous waste that is operated by LLNL's Hazardous Waste Management (HWM) division. Radioactive and mixed wastes are also handled at this facility. The generators can store their waste for up to 90 days at some 52 waste accumulation areas (WAA) at LLNL. A generator of hazardous waste must submit a waste disposal requisition for review by HWM before their waste is approved for pickup. Once the requisition is approved, HWM will pickup the waste and bring it into its facility for storage. RCRA waste can be stored for up to one year before it is either shipped for disposal or treated at HWM's aqueous waste treatment farm.

In HWM we have developed an information system, the Total Waste Management System (TWMS), to replace an inadequate "cradle to grave" tracking of all the waste types described above. The first phase of this system became operational at the end of September 1994. The goals of this system are to facilitate the safe handling and storage of these hazardous wastes, provide compliance with the regulations and serve as an informational tool to help HWM manage and dispose of these wastes in a cost effective manner. The key to success in utilizing

TWMS is ensuring the accuracy and completeness of the data entered into the system. The information on the requisition is entered into TWMS where it is validated and checked for consistency before the requisition is finally approved. All hazardous wastes that are brought into the HWM facility are in a container with a unique bar-code affixed to them. A bar-code scanner with input capability is used to identify all transactions performed on a container and/or its waste. This information is downloaded to TWMS at the end of each working day and is checked for consistency. We will describe the TWMS in more detail and discuss the benefit of having a system that is integrated into the various facets of HWM's operations.

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Introduction

Lawrence Livermore National Laboratory Overview

LLNL is owned by the Department of Energy (DOE) and is jointly operated by the University of California and the DOE. The Laboratory was established in 1952 to conduct nuclear weapons research. Since 1952, other major programs including magnetic fusion energy, laser fusion and laser isotope separation, biomedical and environmental sciences, and applied energy technology have been added. LLNL is a research laboratory with all the infrastructure necessary to support its operations and more than 10,000 personnel. Employees conduct research in a variety of settings; the programmatic research includes the areas of chemistry and material science, computer science and technology, biological sciences, engineering, and physics.

LLNL is composed of a main site and Site 300. The main site is located approximately 40 mi east of San Francisco, California, at the southeast end of the Livermore Valley in southern Alameda County, adjacent to the city of Livermore. Nearly 6 million people live within 50 miles of the main site; of these, approximately 57,600 people live within the city of Livermore. Site 300 is located in the sparsely populated hills of the Diablo Range, 15 mi southeast of the main site.

Prior to 1942, the main site property was part of the Wagoner Ranch and used for grain production and cattle grazing. In 1942, the U.S. Department of the Navy bought the property to be used for a Naval Air Station (NAS) and an adjoining ancillary gunnery range. Initially the facility was used as a flight-training base. By mid-1945, large volumes of assembly and repair work, principally overflow from Alameda Naval Air Station (NAS), were performed on the property. This activity continued until October 1946 when the NAS was deactivated.

In September 1952, the site was established as the Livermore Branch of the University of California Radiation Laboratory. Subsequent names of the site include the Ernest O. Lawrence Radiation Laboratory (in 1958) and the Lawrence Livermore Laboratory (in 1971). In December 1979, the Congress renamed the site the LLNL

Hazardous Waste Management Activities

LLNL presently operates five Hazardous Waste Management Facilities at the Livermore main site. These are the Area 514 Facility, Area 612 Facility, Building 233 Facility, Building 693 Facility, and Building 419 Facility. The Area 514 and 612 Facilities include treatment and storage units for hazardous and mixed wastes; the Building 233 Facility is a container storage unit for hazardous and mixed wastes; the Building 693 Facility is a container storage unit for hazardous wastes, but will eventually be used for the storage of both hazardous and mixed wastes; and, the Building 419 Facility includes inactive treatment units, which are awaiting regulatory closure.

LLNL's main site is currently operating its hazardous waste management activities under the interim status standards of the California Code of Regulations, Title 22, Part 66265. LLNL has submitted a RCRA Part B permit application to the State of California for continued operation and expects a final permit in FY 95. Under interim status, the main site receives hazardous and mixed wastes from Site 300 and the off-site satellite operations at 2020 Research Drive, Almond Avenue and the Livermore Airport. No other off-site locations are currently allowed to send hazardous or mixed wastes to the LLNL main site.

LLNL also operates two hazardous waste management units at Site 300. These units are only used for the treatment and long-term storage (i.e., greater than 90-day storage) of hazardous wastes. Mixed wastes generated at Site 300 are limited to storage periods of 90 days or less. The waste is then either taken to the main site for treatment and/or long term storage or sent to commercial facilities for treatment and/or disposal.

Hazardous waste management operations at LLNL are subject to federal, State of California, regional, and local environmental laws and regulations. Hazardous and mixed waste operations at LLNL sites include the safe and proper handling, treatment, packaging, storage, and disposition of all hazardous and mixed wastes generated by LLNL. Mixed wastes can be chemically or physically treated at the Livermore main site. Existing treatment for mixed wastes includes: neutralization, flocculation, chemical reduction and oxidation, precipitation, separation, filtration, solidification, size reduction, shredding, adsorption, and blending. Mixed wastes are currently treated in the Building 513 Solidification Unit, the Area 514 Waste Water Filtration Unit, and the Area 514 Waste Water Treatment Tank Farm Unit.

LLNL has requested regulatory agency approval to add centrifugation and evaporation treatment units as well as to increase current treatment operations for mixed wastes. Also, mixed wastes are stored in appropriate units at the Livermore main site for extended periods until they can be shipped to an approved off-site treatment and/or disposal facility.

Hazardous Waste Management Division

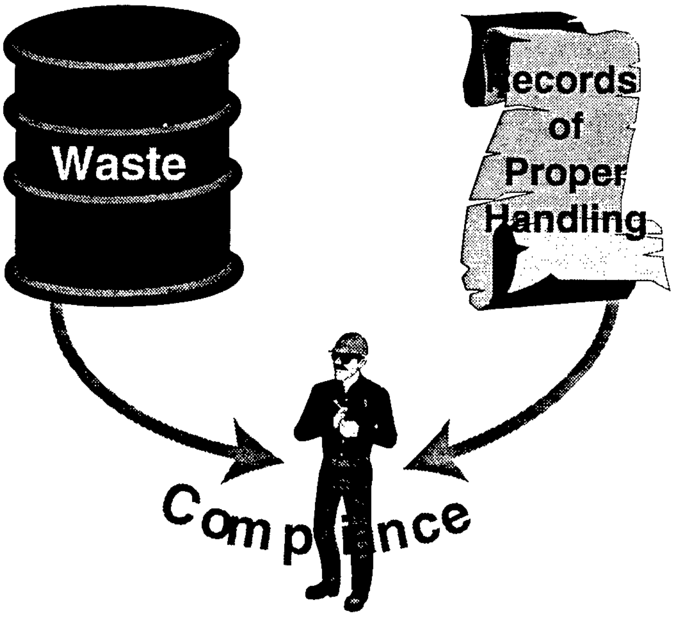
The Hazardous Waste Management (HWM) Division is Lawrence Livermore National Laboratory's (LLNL) focus for the implementation of technologies necessary to manage all hazardous, radioactive, and mixed wastes generated at all LLNL facilities. HWM is continually developing and improving methods for managing wastes to assure minimal environmental impact. The Division's responbilities include investigation of new, innovative, and more cost-effective methodologies for waste handling, stabilization, treatment, disposal, and regulatory compliance. To discharge its waste management responsibilities, HWM Division maintains expertise to:

- Track and document hazardous, radioactive, and mixed wastes for the Livermore Site and Site 300.
- Process, store, package, treat, and prepare waste for shipment to licensed offsite treatment storage, and recycling facilities.
- Ensure that LLNL meets the federal, state, and local regulations regarding the permitting and compliance of HWM facilities.

The Livermore Site has four active HWM facilites where hazardous, low-level, transuranic radioactive, and mixed wastes are treated and stored. LLNL does not produce high-level radioactive waste.

FIGURE 1

The Two Parts of Compliance



A generator of waste is required to fill out a waste disposal requisition before HWM will take possession of the waste. The generator provides information as to the source producing the waste, a chemical and physical description including chemical and/or radiological constituents and the quantity of waste. In addition, the generator provides data regarding the container enclosing the waste, the hazardous waste labeling of the container, the container location and other administrative information.

The Total Waste Management System is the "cradle-to-grave" tracking system that facilitates the fulfillment of LLNL's records, reporting, and information compliance responsibilities as well as assisting in strategic and tactical waste management planning. The aggregate of required information to TWMS is provided in two parts, manual data entry of waste disposal requisitions coupled with the Waste Inventory System (WIS), a transaction based field data application implemented through bar code scanners. WIS is a functional sub-system of TWMS and serves as the introduction point for most physical waste handling information.

Waste Inventory System

The Hazardous Waste Management (HWM) Waste Inventory System (WIS) is the "point-of-action" system and the information link between the waste and records of proper handling. WIS serves as the "front-end" to TWMS, the LLNL Regulatory Compliance Waste Information System.

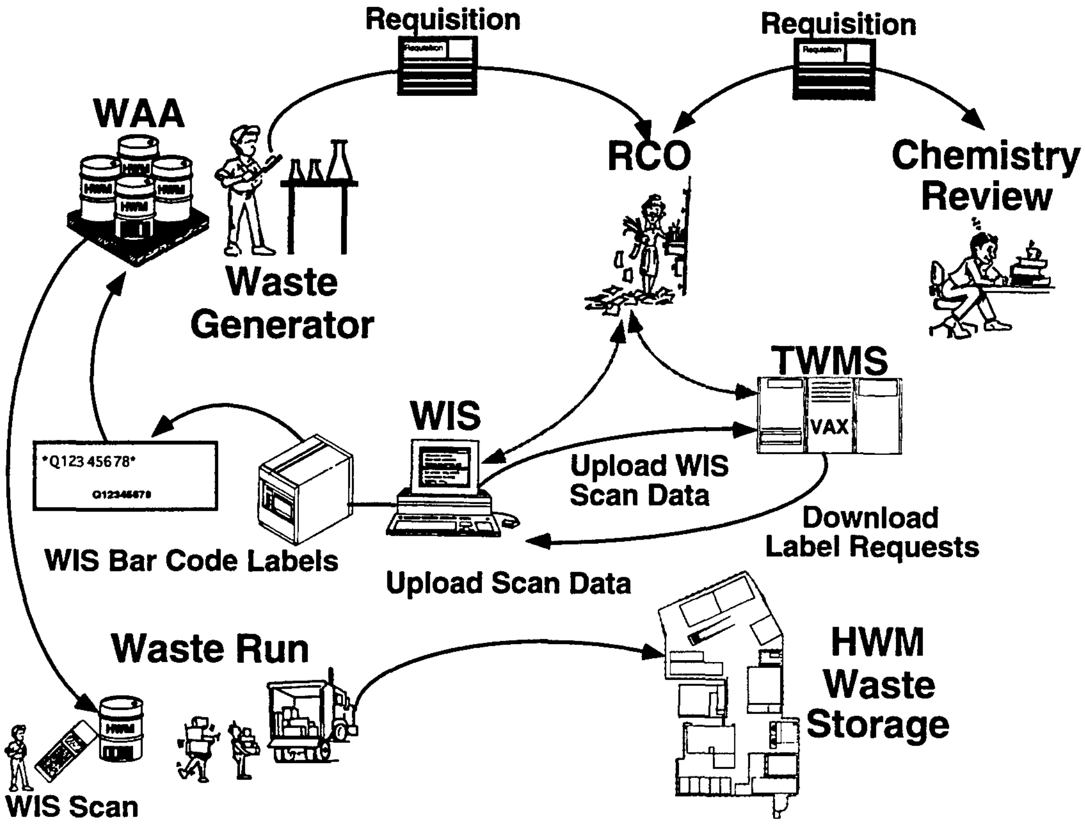
WIS provides the following capabilities:

- Collection of information concerning waste container transactions as they are performed
- Printing of a wide variety of bar code labels
- Providing HWM Waste Operations staff the ability to track status of waste containers in the storage area
- Serving as the primary source of container tracking information to the Total Waste Management System (TWMS) database

Using an automated design, WIS replaces the paper previously used for recording waste transactions, manual entry of information, and the manual recording of physical inventories.

FIGURE 2

WIS Relationships to HWM Waste Receival Operations

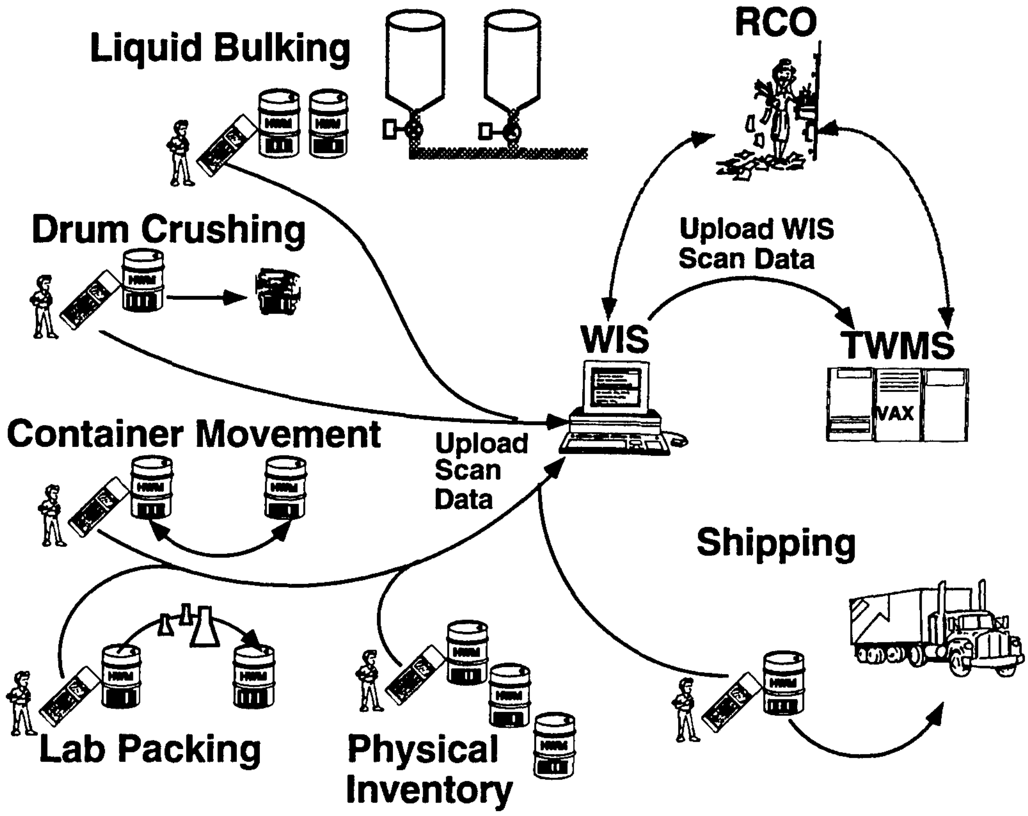


Generators submit Waste Disposal Requisitions to HWM for review and approval. After approval, the Requisition Control Office (RCO) uses WIS to print container bar code labels that get issued with the approved requisition. The labels are affixed to the container as part of pre-waste-run activities.

During the waste run, technicians collect container information using WIS Scanners by entering various transaction codes and scanning the bar code label of the container being transferred to the HWM yard. Technicians in HWM receiving areas use WIS Scanners to record waste arrival at HWM and its storage in the appropriate area. After receival of new waste containers, technicians perform a number of operations in the course of processing and disposing of the waste.

FIGURE 3

Typical Operations Tracked by WIS



Scanner information is uploaded by RCO using the WIS Workstation. At the end of each day, that day's container transactions are transferred to the TWMS database.

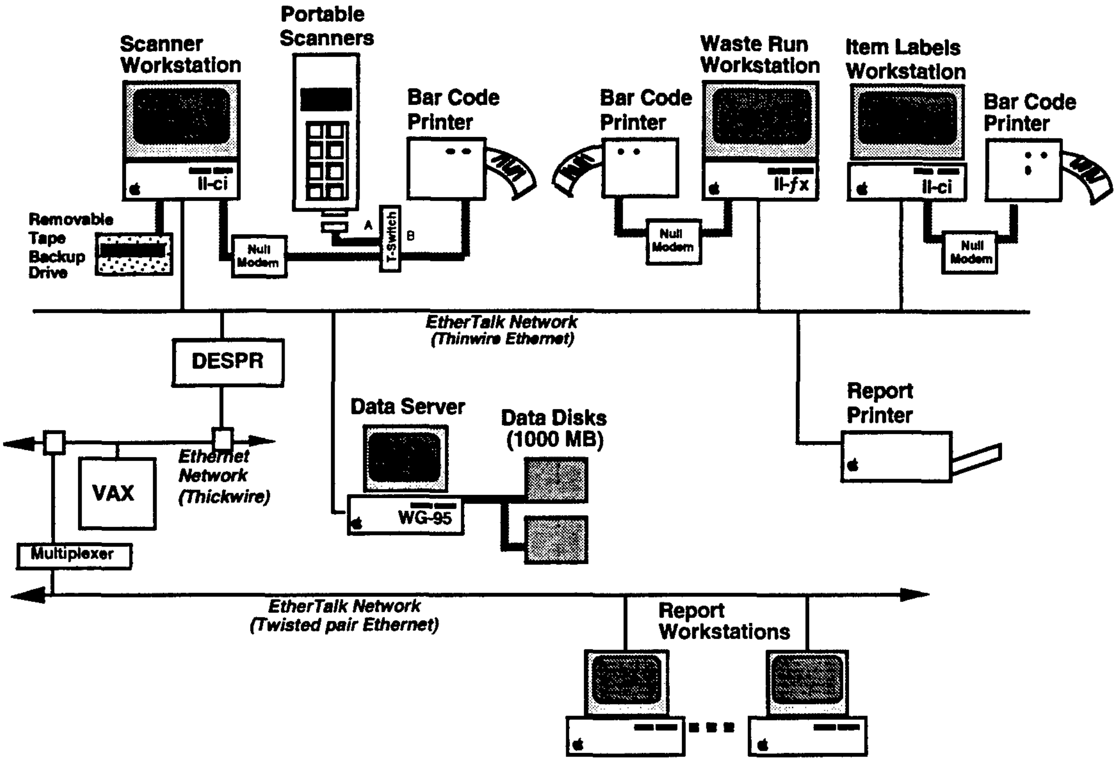
The WIS design employs a number of features to increase the assurance of highest data quality:

- Bar-coded container identifiers avoid hand-keying mistakes.
- Non-scanned identifiers are keyed *twice.*

- Pick-lists in Scanner and Workstation avoid free-form entry.
- Scanner and Workstation data entries are validated.
- Uploaded Scanner information is archived in "raw" form to mirrored disk drives.

FIGURE 4

WIS Hardware: Portable Scanners, Bar Code Printers, Report Printers, Workstation Computers, a Database Server, and a Network

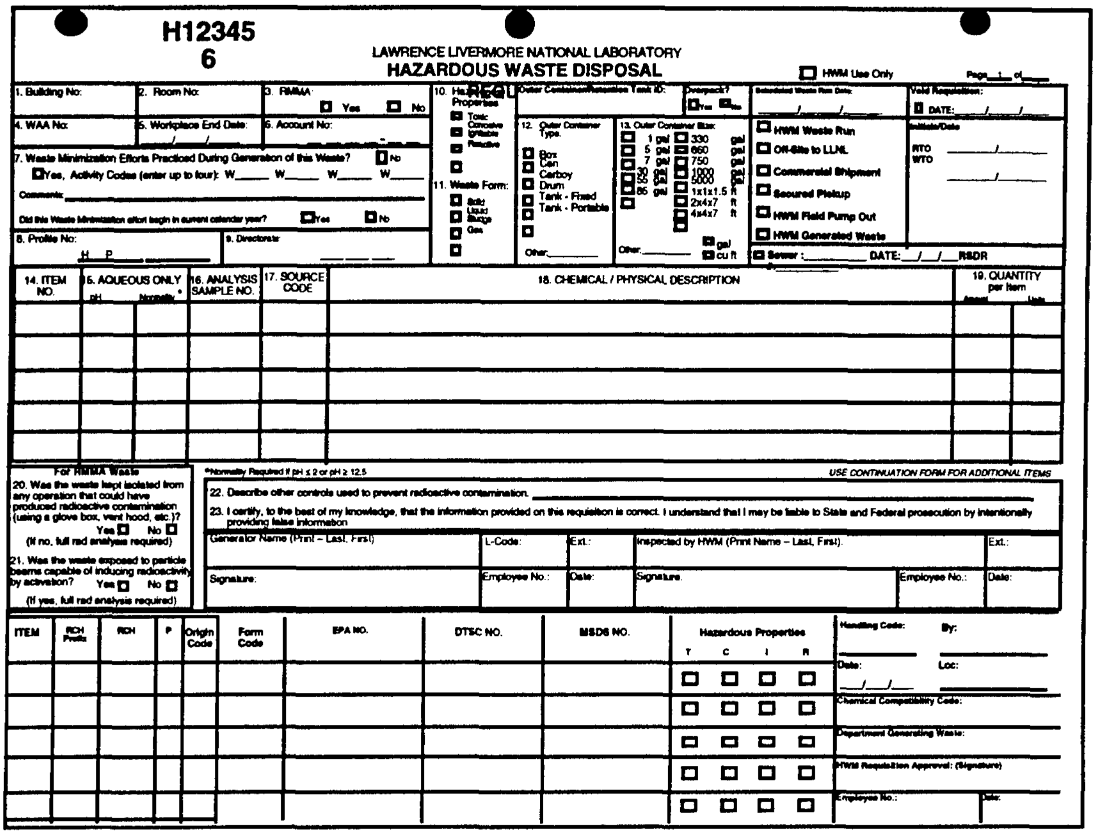


TWMS

"Cradle to grave" tracking of waste begins when a generator forwards a requisition to HWM for review and approval. The requisition number is entered into the Total Waste Management System (TWMS) database to begin monitoring the custodian of the requisition as it circulates through the review process. Other pertinent data such as the waste generation date, the location, and the size of the container are entered into TWMS. This helps HWM keep track of the generator's ninety day clock for moving the waste from their Waste Accumulation Area (WAA) and monitoring LLNL's fifty thousand gallon aggregate limit for storage of wastes at its 52 WAAs. A chemist reviews the requisition to determine if the information provided is sufficient to characterize the waste. If so, the chemist characterizes the waste according to its regulatory attributes as well as provides information relevant for safe handling and storage. If not, the chemist either requests more information from the generator or specifies a sample and analyses.

FIGURE 5

An LLNL Internal Waste Disposal Requisition is Used for Submission of Waste Information



H12345
6

LAWRENCE LIVERMORE NATIONAL LABORATORY
HAZARDOUS WASTE DISPOSAL REQU

☐ HWM Use Only

Page 1 of ___

1. Building No:
2. Room No:
3. RMMA ☐ Yes ☐ No
4. WAA No:
5. Workplace End Date: ___/___/___
6. Account No:
7. Waste Minimization Efforts Practiced During Generation of this Waste? ☐ No
☐ Yes, Activity Codes (enter up to four): W_____ W_____ W_____ W_____
Comments: ______________________
Did this Waste Minimization effort begin in current calendar year? ☐ Yes ☐ No
8. Profile No: H P______ ________
9. Directorate ___ ___ ___

10. Hazardous Properties
☐ Toxic
☐ Corrosive
☐ Ignitable
☐ Reactive
☐

11. Waste Form:
☐ Solid
☐ Liquid
☐ Sludge
☐ Gas
☐

Outer Container/Retention Tank ID:

Overpack? ☐ Yes ☐ No

12. Outer Container Type.
☐ Box
☐ Can
☐ Carboy
☐ Drum
☐ Tank - Fixed
☐ Tank - Portable
☐
☐
Other:________

13. Outer Container Size:
☐ 1 gal ☐ 330 gal
☐ 5 gal ☐ 660 gal
☐ 7 gal ☐ 750 gal
☐ 30 gal ☐ 1000 gal
☐ 55 gal ☐ 5000 gal
☐ 85 gal ☐ 1x1x1.5 ft
☐ ☐ 2x4x7 ft
☐ 4x4x7 ft
☐
Other:________ ☐ gal ☐ cu ft

Scheduled Waste Run Date: ___/___/___

☐ HWM Waste Run
☐ Off-Site to LLNL
☐ Commercial Shipment
☐ Secured Pickup
☐ HWM Field Pump Out
☐ HWM Generated Waste

☐ Sewer :________ DATE:__/__/__ RSDR

Valid Requisition:
☐ DATE:___/___/___

Initials/Date
RTO ______/______
WTO ______/______

14. ITEM NO.	15. AQUEOUS ONLY pH	Normality*	16. ANALYSIS SAMPLE NO.	17. SOURCE CODE	18. CHEMICAL / PHYSICAL DESCRIPTION	19. QUANTITY per Item Amount	Units

*Normality Required if pH ≤ 2 or pH ≥ 12.5

USE CONTINUATION FORM FOR ADDITIONAL ITEMS

For RMMA Waste
20. Was the waste kept isolated from any operation that could have produced radioactive contamination (using a glove box, vent hood, etc.)? Yes ☐ No ☐
(If no, full rad analysis required)
21. Was the waste exposed to particle beams capable of inducing radioactivity by activation? Yes ☐ No ☐
(If yes, full rad analysis required)

22. Describe other controls used to prevent radioactive contamination. ______________________

23. I certify, to the best of my knowledge, that the information provided on this requisition is correct. I understand that I may be liable to State and Federal prosecution by intentionally providing false information

Generator Name (Print – Last, First)	L-Code:	Ext.:	Inspected by HWM (Print Name – Last, First).	Ext.:
Signature:	Employee No.:	Date:	Signature. Employee No.:	Date:

ITEM	RCH Prefix	RCH	P	Origin Code	Form Code	EPA NO.	DTSC NO.	MSDS NO.	Hazardous Properties T	C	I	R
									☐	☐	☐	☐
									☐	☐	☐	☐
									☐	☐	☐	☐
									☐	☐	☐	☐
									☐	☐	☐	☐

Handling Code: ______ By: ______
Date: ___/___/___ Loc: ______
Chemical Compatibility Code:
Department Generating Waste:
HWM Requisition Approval: (Signature)
Employee No.: Date:

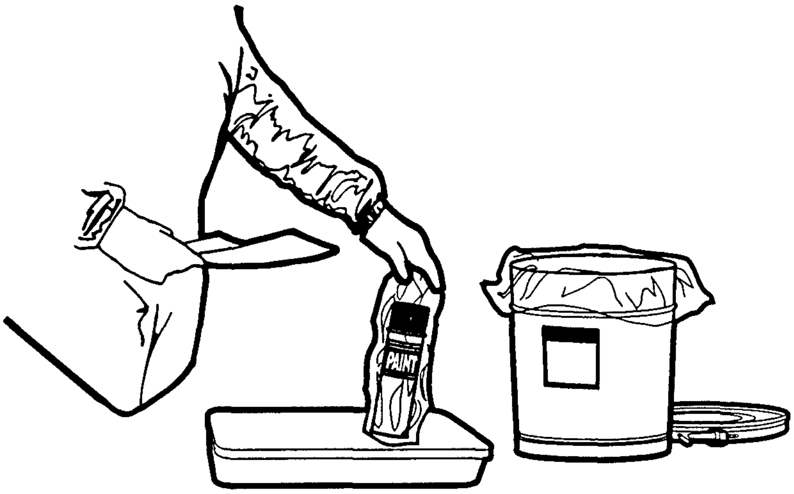
Once the chemist has approved the requisition, the waste characterization, including RCRA and state waste codes, and chemical compatibility are entered into TWMS. If a sample analysis or Material Safety Data Sheet (MSDS) information is used to characterize a waste item then a document reference number is recorded. During database requisition entry, TWMS enforces certain required entry fields with most having a set of acceptable values. This capability ensures that the data collected is complete, correct and meaningful.

Waste Operations Control accesses requisition information to determine waste handling and whether it will be shipped directly from the WAA to an off-site Treatment, Storage and Disposal (TSD) facility or brought into HWM's TSD facility. Movement and disposition of waste within the HWM facility are tracked using WIS. A unique bar-code is issued by TWMS for a given requisition and is to be affixed to the waste container.

At LLNL, a generator is allowed to package multiple waste items within a container. These generator multi-packs are brought into HWM where the container is opened and waste items within are confirmed and then bar-coded. At this point, waste is no longer associated with a requisition and instead with its container. The association of waste to a requisition is still important for regulatory reporting and waste minimization activities for quantifying sources of generation. However, for handling and disposal, it is more intuitive to associate waste to a container. All waste items handled are assumed to be within a container identified by a bar-code and all transactions involving waste and/or the container are recorded electronically in conjunction with bar-code scanning (WIS). Keeping track of container location and movement allows HWM to determine the location and quantity of waste within the HWM facility at any time. In addition, TWMS tracks combined wastes from the bulking of liquids or consolidation of solids from many containers into a single container. The inverse, splitting waste from a large container into many smaller containers, can also be tracked. TWMS tracks the movement of containers from one into another for repackaging; a process referred to as labpacking.

FIGURE 6

Labpacking at LLNL: Waste Items May be Labpacked into a New Container



TWMS provides levels of checking to ensure information integrity. Each transaction is checked to insure correct information is collected by validating each field against acceptable values. Also there are precedence rules for transactions to insure that a transaction is preceded by prerequisite transactions. For example, waste cannot be packed into a new container until the system has been notified that a new container has been brought into service.

Only acceptable transactions are processed by TWMS; unacceptable transactions are placed in a discrepancy log until they are resolved. Each day a report is printed showing transactions that were not acceptable and provides a reason for rejection. TWMS provides reports to alert HWM to conditions where a transaction was expected and did not occur. For instance, waste may be stored in a staging area for deliveries into or shipments out of HWM's 612 facility for up to 36 hours. A notification report is generated if a container is found to be in the staging area over two days. This feature allows early problem identification while information is still traceable.

Providing easy access and centralized information to HWM facilitates the selection of similar wastes for efficient and cost-effective handling and disposal. This is especially useful for HWM's aqueous treatment facility for the safe bulking of aqueous wastes that adhere to regulatory and emission limits. Once waste is bulked for treatment, the treatment farm can monitor the process in TWMS and when contaminant levels fall below wastewater discharge limits, the waste is discharged to sewer with the transaction recorded in TWMS.

For off-site disposal to a TSDF, having easy access to container waste information allows coordinated shipping and packing operations. The labpacking process is streamlined with TWMS: waste is scanned as it is unpacked and packed into a new labpack. When a labpack is complete, TWMS generates a contents packing list that a chemist reviews before approving the labpack for shipment.

Finally TWMS records the shipment of containers and associates the containers to the shipping manifest. Manifest information is currently hand entered into TWMS to provide a disposition record of a waste container. In the next TWMS development phase, the system will prepare the manifests and provide additional verification.

The benefit of collecting all information within one system is that most data necessary for preparing the EPA Biennial Report is in the database. That information includes, but is not limited to, waste stream information, EPA waste codes, California waste codes, quantities generated, waste amounts shipped off-site for disposition, waste treated on site, and amount discharged to sewer. System applications being developed include electronic file submittal to the EPA and a hard copy to keep in HWM for review. Much of the information to prepare DOE's Integrated Database request for low level waste generation and storage on site is already on the system. In fact, TWMS will minimize the effort required for such reports. In addition, the advantages of centralizing the data will help streamline operations for many years.

MATERIAL INTERACTIONS WHEN SAMPLING GROUNDWATER

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INTRODUCTION

It is important that the reported concentrations of contaminants in groundwater samples reflect true in-situ values. Thus, monitoring wells and sampling devices should be constructed of materials that do not affect contaminant concentrations or produce interferences in protocols used for analysis. Materials can affect analyte concentrations by leaching organic and inorganic contaminants from the material, or by sorbing contaminants initially present in the water and possibly desorbing these contaminants later. In addition, these materials must be able to withstand the effects of the environment in which they are placed.

Our laboratory has conducted several studies to assess the suitability of various materials currently used in monitoring wells and sampling devices. This paper will briefly review some of our older studies on the four most commonly used well casing materials (polyvinyl chloride [PVC], polytetrafluoroethylene [PTFE], and stainless steel), and then will present the results from some of our more recent studies. These more recent studies investigated the effects of high concentrations of organic solvents on rigid PVC, the suitability of four other types of casing materials for monitoring wells, and sorption of organic contaminants by sampling tubings.

PVC, PTFE, AND STAINLESS STEEL WELL CASINGS

Initial studies by our laboratory[1,2] compared sorption and leaching of organics and metals by PVC, PTFE (a Teflon fluoropolymer), and types 304 and 316 stainless steel (SS 304 and SS 316) well casings. In the first study,[1] these four materials were exposed to a solution containing ~2 mg/L of each of ten organic compounds for six weeks. This study showed that PTFE was the most sorptive of the four materials tested. Both the rate of sorption and the extent of sorption were greatest for this material. In contrast, the stainless steel casings did not sorb any of the organic solutes during the six-week study. Figure 1 shows losses of TCE by these four materials and is typical for those analytes where losses were observed. With time, sorption of organic solutes by PTFE most likely will be diminished as the casing and the well water move towards establishing equilibrium.

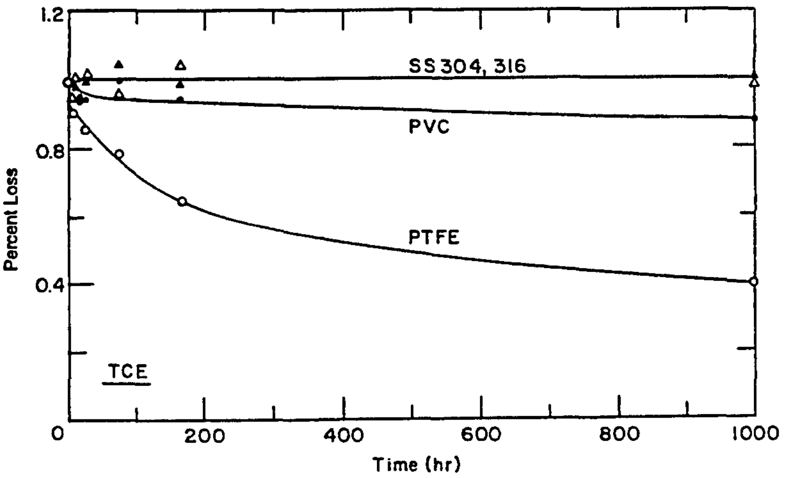

Figure 1. Sorption of TCE by the four well casing materials.[1]

In the same study,[1] these same four materials were also exposed to µg/L concentrations of As, Cr, Pb, and Cd. PTFE was the most inert with respect to sorption of metal species, while the stainless steel surfaces were the most active. We found that the two analytes that exist as anions in solution (As, Cr) were not sorbed by either plastic surface. Masse et al.[3] also observed that plastic surfaces do not tend to sorb anions. Pb was the most actively sorbed metal contaminant tested, and Figure 2 shows that even the PTFE casing sorbed some Pb.

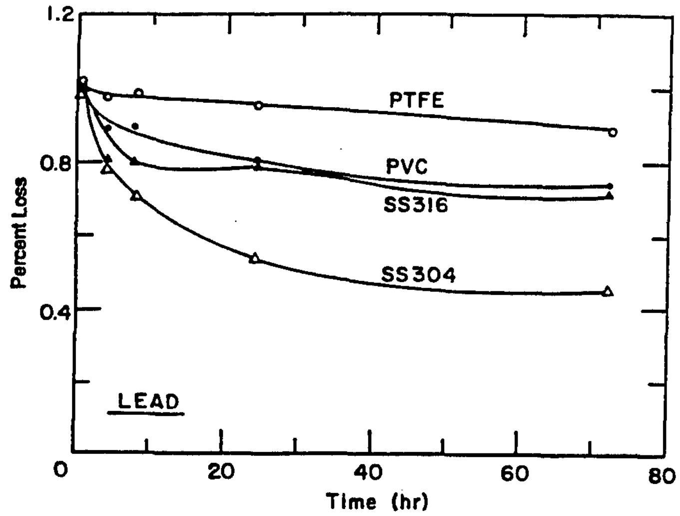

Figure 2. Sorption of lead by four casings.[1]

We[1] concluded that while PTFE would be best for monitoring inorganics, it would be worst for monitoring organic solutes. For stainless steel, the opposite was true. Overall, PVC appears to have the least impact when monitoring for both trace metals and organics. These efforts contributed to the Environmental Protection Agency modifying their guidance (for RCRA sites) to allow use of casing material that was appropriate to the site and conditions.

Because the previous study also showed that three of the materials tested (PVC, SS 304, and SS 316) leached Cd, Hewitt[2] conducted a 40-day study to determine what other metals leached from these four materials. He looked for leaching of nine metal species (Ag, As, Ba, Cd, Cr, Cu, Hg, Pb, and Se) and found that PTFE did not leach any of the nine analytes, while PVC, SS 316, and SS 304 leached significant levels of several metals. PVC leached Cr, Cd, and Pb, SS 304 leached Cr and Pb, and SS 316 leached Cr, Cd, Pb, Ba, and Cu. However, contamination was always greatest for one or both of the stainless steel casings. Concentrations of several metals increased with time in solutions exposed to the stainless steel casings, but did not when exposed to PVC casings. Hewitt concluded that these findings supported previous conclusions that stainless steel will have the greatest impact on aqueous concentrations of metals.

In the two previous studies,[1,2] Hewitt observed that the stainless steel casings rusted, and felt this might explain the observed sorption and release of metals. However, follow-up studies[4] conducted under anoxic conditions revealed similiar trends in metal concentrations even though there were no signs of rusting with these casings.

Two more recent studies on these same four materials, conducted by our laboratory, have looked at the effect of concentration on sorption of organic solutes in the µg/L and low mg/L range,[5,6] and sorption and leaching of metals under dynamic conditions.[7] The first study[5] was conducted because some regulatory agencies had expressed concern that our initial study was conducted with concentrations of organic solutes in the (low) mg/L range and that sorption might be greater at low µg/L levels. In this study, the same four well casings were subjected to the same suite of analytes as the previous study,[1] except this time the initial concentration of each analyte was ~20 µg/L (vs. 2 mg/L used in the initial study). Again we found no sorption of any of the analytes by the stainless steel casings. For the polymers, we again found that PTFE was the most sorptive, and that the relative rate and extent of sorption was the same for both concentrations of solutions.

The initial metals studies were conducted under static conditions. To more accurately simulate conditions in a monitoring well, Hewitt[7] exposed sections of well screen (made of the same four materials as previously) to flowing groundwater. He found both stainless steel screens leached Cr, Cu, and Ni. He also observed that both stainless screens showed increased signs of rusting with time, and that leached concentrations of Cr and Ni inceased with exposure time. The stainless steel screen also sorbed iron, possibly due to precipitation of ferrous hyroxide, a result of galvanic corrosion.[8]

In this study, Hewitt[7] also pumped a spiked solution containing Pb and Cd through this system to look for signs of sorption. Both polymers sorbed Pb, although less than the stainless steel screens did. For the PTFE screen, there was a slight memory effect where sorbed Pb was subsequently released to the solution, thereby giving slightly elevated Pb levels shortly afterwards. All four materials sorbed Cd and both polymers showed slight memory effects. He concluded that under dynamic conditions, PVC and PTFE had little or no influence on metal concentrations, and thus were more desirable than stainless steel when monitoring for metals.

WHEN NOT TO USE PVC

The previous studies show that PVC well casings are suitable for monitoring organic solutes and metals. It is commonly known that some neat organic solvents (pure products) can degrade PVC pipe. These organic solvents can soften and swell PVC and are referred to as swelling agents of PVC; in extreme cases they can dissolve it and are referred to as PVC solvents. PVC casings and screens should not be used if they are going to be exposed to pure product of a PVC solvent or swelling agent. However, the effects of high concentrations of these chemicals in aqueous solution are not as well understood. The purpose of our work has been to better define these effects.

The ability of a solution of a PVC solvent or swelling agent to soften PVC has been related to the activity of the analyte in the aqueous solution by several researchers.[9,10,11] For aqueous solutions, the activity of a chemical can be approximated by dividing the concentration of the compound in solution by its solubility in water. Berens[9] exposed films and powders of PVC to various (nonaqueous) solutions of PVC solvents at varying activities. He noted that at ambient temperature, rigid PVC would be softened by solvents or strong swelling agents of PVC at activities greater than 0.5. The less aggressive the solvent, the higher the activity required to cause softening.

One criticism of Berens's work is that he did not test aqueous solutions of PVC solvents and swelling agents. Our laboratory has conducted several studies[12,6,13] to confirm Berens's findings using aqueous solutions. In these studies we exposed small pieces of PVC well casing (9 × 9 × 0.8 mm) to various activity solutions of PVC solvents and swelling agents. Parker and Ranney[6] exposed the PVC test pieces to aqueous solutions of methylene chloride, with a range of activities (0.0, 0.05, 0.1, 0.2, and 0.4), for up to 20 weeks. Methylene chloride is either a solvent or a very good swelling agent of PVC.[9,10] Based on Berens's predictions, we did not expect any softening of PVC at these activities. However, we observed that there were significant changes in the hardness readings of the samples that had been exposed to activities as low as 0.1, but these changes were not large and none of these samples were noticeably pliable. Previously in the same study, we had noted that PVC samples exposed to solutions of methylene chloride with activities of 0.6 and 0.8 had larger changes in the hardness readings and were noticeably pliable after only seven days. There was no change in the hardness readings of the test pieces that were exposed to 0.05 activity solutions, even after 20 weeks of exposure.

These results seem to indicate that there is some slight change in the polymer when it is exposed to aqueous solutions of PVC solvents with activities in the 0.1 to 0.5 range. This change seems to occur in the range where diffusion of an organic in PVC goes from being purely Fickian, and thus concentration-independent and slowest, to more rapid forms of diffusion (concentration-dependent, anomalous, and finally Case II or frontal).[9,10,11,14] There is some disagreement regarding the activity level where diffusion in PVC pipe becomes greater than Fickian. Berens predicted Fickian diffusion occurs only if the activity of the solution is less than 0.25, but Vonk felt that the activity should be less than 0.1 for solvents and better swelling agents of PVC. We are currently conducting longer term studies to determine whether softening progresses at these low activities when exposure is extended for a much longer time.

Our data therefore indicate that PVC pipe can safely be exposed to solutions of PVC solvents and swelling agents that have activities less than 0.1. For methylene chloride, the upper permissible concentration would be 1900 mg/L, and for trichloroethylene it would be 100 mg/L. Thus, PVC can be used except where high concentrations of PVC solvents and swelling agents are anticipated.

In many monitoring situations, water samples will be contaminated with several organic chemicals. Because none of the literature we have found deals with the presence of two or more contaminants in the solution, we have conducted several studies[6,13] to address this issue. Our results indicate that multiple organic solutes in aqueous solution have a cumulative or interactive effect on test pieces of PVC. As an example, Table 1 shows the effect of exposing test pieces of PVC to a solution containing 18 PVC solvents or swelling agents, each at an activity of 0.05.[13] Although previous data show that a solution with one contaminant at an activity of 0.05 has no measureable effect on PVC, it is clear that the mixture of these 18 chemicals, each at an activity of 0.05, certainly did. Several of the test pieces became noticeably softened after 14 days. We are currently assessing mixtures of PVC solvents and swelling agents at even lower activities.

Table 1. Mean relative hardness (Barcol) values for the mixed-solvent study. [13]

Treatment	*1*	*3*	*7*	*14*	*21*	*42 days*
control						
$\bar{X}$	80.0	78.6	77.8	78.8	80.0	79.0
% RSD	1.3	1.9	1.4	2.4	1.5	2.4
test soln						
$\bar{X}$	74.8*	74.2*	72.0*	68.2	67.0*	65.4*
% RSD	1.7	2.4	1.4	5.2	5.3	4.1

* Values significantly different from controls at 95% confidence level.

OTHER TYPES OF WELL CASING MATERIALS

Our previous studies have shown that rigid PVC casings can be used in most, but not all, applications. It was the purpose of this work to examine several other materials that have been used as well casings or sampling pipe. In these studies we examined four different materials including two fiberglass well casing materials, fiberglass-reinforced epoxy (FRE) and fiberglass-reinforced plastic (FRP); another fluoropolymer, fluorinated ethylene propylene (FEP); and acrylonitrile butadiene styrene (ABS). We conducted a series of studies that compared these four materials with PVC and PTFE with respect to sorption and leaching of organic solutes,[15] susceptability to chemical degradation,[16] and sorption and leaching of metals.[17] In the first study,[15] these six materials were exposed to low mg/L levels of eleven organic chemicals (ten volatile organics, one nitroaromatic) for up to six weeks. Figure 3 shows that losses of m-xylene were least for FRE and PVC, greatest for ABS, and intermediate for FRP, FEP, and PTFE. These results are typical for all the analytes we tested. In all cases, neither PTFE, FEP, or FRP performed consistently better than the other.

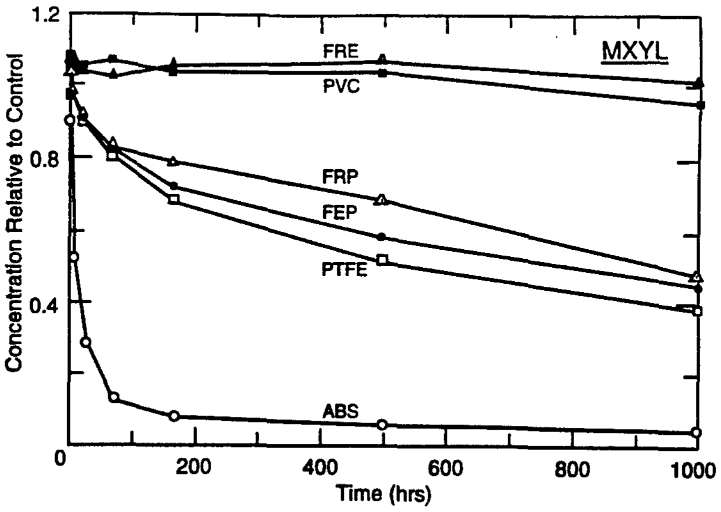

Figure 3. Sorption of m-xylene by six polymeric casings.[15]

During this study, we noticed spurious peaks in a number of the (HPLC) chromatograms. This indicates that several of these materials (ABS, FRP, FRE) leached contaminants, although the PTFE and PVC samples did not. The ABS samples leached the most contaminants (11 by the end of the study). The FRP samples leached five contaminants and the FRE samples leached only one contaminant by the end of the study.

To determine the ability of these six materials to withstand extreme environments, test pieces of these same six materials were subjected to twenty-eight neat organic compounds (including one acid) and to extremely acidic and alkaline conditions for up to 16 weeks.[16] The materials were observed for changes in weight and signs of physical degradation, such as cracking, swelling, softening, deterioration, and dissolution. As expected, the two fluoropolymers (FEP and PTFE) were the most inert materials, followed by FRE. By the end of the study, three organic chemicals had caused deterioration (flaking) of FRE and two others had caused weight gains of more than 10%. Highly acidic conditions also degraded this material. ABS was the most readily degraded material. All of the organic solvents degraded this polymer. FRP was more severly degraded by the organic chemicals than FRE, but was less affected than PVC.

Based on these two studies, we concluded that FRE would make an excellent material for monitoring organics and that ABS was not a suitable material for monitoring organics. The performance of FEP and PTFE was nearly identical, and thus neither of these materials was preferable to the other. FRP appeared to be less desirable than PVC.

More recently we[17] studied sorption and leaching of metals by five of these six materials. Because of its poor performance in the previous studies, ABS was not included in these studies. To test for sorption, small pieces of each material were exposed to a solution containing µg/L concentrations of As, Cr, Pb and Cd. As we found earlier for PVC and PTFE, none of the five materials tested sorbed either the As or Cr anions from solution. All the materials tested sorbed the cations (Cd and Pb) although the PVC, FRP, and FRE casings were more sorptive than the fluoropolymers.

To determine whether these materials leached metal species, small pieces of the five materials were placed in polypropylene jars containing fresh groundwater. (Jars with water but no casing served as controls.) The study ran for up to 40 days, and the samples were analyzed for 11 analytes (As, Ag, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, and Zn). We found that the fiberglass materials, especially FRP, leached more and higher concentrations of metals than the other three materials. With the exception of Cd, PVC was nearly as inactive as the fluoropolymers. However, for all five materials, concentrations of leached contaminants did not begin to approach limits set by the EPA for drinking water,[18] and were much lower than Hewitt[2] observed leaching from stainless steel casings (with the exception of Pb leaching from FRP). For monitoring metals we tentatively ranked these materials as follows:

FEP and PTFE > PVC > FRE > FRP >> SS.

Selection of a well casing material depends upon a number of criteria including, but not limited to, chemical inertness. Other criteria include the depth of the well and the strength of the materials to be considered, the amount and type of contaminants that are present, and whether the samples will be analyzed for metals, organics, or both. These studies reinforce our view that PVC is well suited for most monitoring situations. FRE may be especially useful in deep wells, where in the past only stainless steel could be used because of its superior strength. However, unlike stainless steel, FRE will not be subject to corrosion and should have much less impact on metal species than stainless steel casings and screens. Like stainless steel, PTFE and FEP, FRE may also prove to be useful in wells where high concentrations of PVC solvents are encountered and PVC can not be used.

SAMPLING TUBING

While the previous studies focused on well casing materials, this study focuses on sampling tubings. This study was conducted because there is concern in the monitoring industry that groundwater samples may interact with the tubing as it is pumped to the surface. This problem may be exacerbated in instances where slow-rate pumping methods are used.

Recently, we completed a study[19] that investigated sorption of organic solutes by 20 different polymeric tubings. The tubings were filled, so there was no head space, with a solution that contained low mg/L levels of eight organic chemicals. The study ran 72 hours. We found that three rigid fluoropolymers, FEP, FEP-lined polyethylene (PE), and polyvinylidene fluoride (PVDF), were the least sorptive tubing materials tested. Both the rate and extent of sorption were less for these materials. As an example, Figure 4 shows sorption of p-dichlorobenzene (PDCB) by the ten least sorptive tubings. This figure clearly shows that even tubings that are relatively nonsorptive can sorb analytes quite rapidly. For example, losses of this analyte to the FEP-lined PE tubing were almost 30% after only one hour.

When we examined the (HPLC) chromatograms in this study, we observed that there were spurious peaks in the solutions exposed to some of the tubings, indicating that leaching had occured. Several of the flexible tubings (polyurethane, polyamide [nylon], [flexible] PVC, polyester-lined PVC, and silicone modified elastomer) leached several

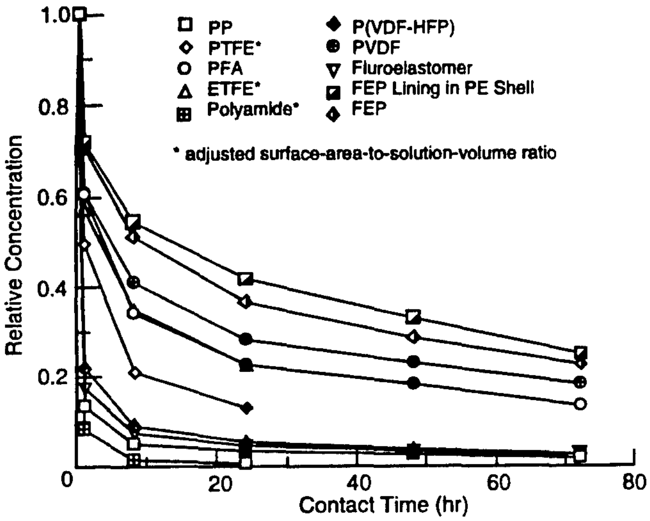

Figure 4. Sorption of PDCB by the least-sorptive tubing materials.[19]

contaminants. Only the rigid fluoropolymers and polyethylene tubings and a flexible polypropylene tubing did not appear to leach any contaminants.

We concluded that among the rigid tubings, FEP, FEP-lined PE, and PVDF were the most inert materials. Because the cost of PVDF is roughly one-half that of the FEP tubings, we would tentatively recommend using PVDF. If a flexible tubing is required, the fluoroelastomer and the P(VDF-HFP) (a copolymer of vinylidene fluoride and hexafluoropropylene) tubings were the least sorptive. However, the fluoroelastomer tubing was the most expensive tubing we tested, $870/100'. Because the cost of P(VDF-HFP) tubing is less than one-quarter of that, we tentatively recommend using P(VDF-HFP) when a flexible tubing is needed. Currently we are conducting studies under dynamic conditions to determine whether the biases we observed in this static study remain the same, increase, or disappear.

CONCLUSIONS AND CURRENT EFFORTS

Our current efforts focus on the performance of sampling tubings under dynamic conditions and decontaminating sampling devices. There has been almost no systematic study of decontamination methods and thus little justification for current decontamination protocols set by regulatory agencies.[20] Decontamination studies may allow for cost savings associated with reducing the need for dedicating sampling devices and possibly eliminating solvent rinses.

The previous studies show that materials used in well casings and sampling devices can affect analyte concentrations in groundwater samples. The purpose of this paper was to give an overview of our research findings. Individuals wishing more information should contact the authors for copies of our papers.

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CLEANUP FOR QUALITY OF LIFE

TREATING DIISOPROPYLMETHYLPHOSPHONATE (DIMP) CONTAMINATED GROUNDWATER USING A PEROXONE OXIDATION PILOT SYSTEM

by

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ABSTRACT

Advance oxidation processes (AOPs) are treatment processes that rely on the hydroxyl radical to destroy contaminants in polluted waters. Peroxone is an advanced oxidation process that utilizes the reaction of ozone and hydrogen peroxide to produce hydroxyl radicals without the requirement of ultraviolet light. The USAE Waterways Experiment Station (WES) evaluated the use of peroxone at Rocky Mountain Arsenal (RMA) for treatment of groundwater contaminated with diisopropylmethylphosphonate (DIMP) and low levels of pesticides. This evaluation was performed at RMA using a pilot scale treatment system. Results indicate that DIMP was easily oxidized to below detection limit levels. Optimization of the process indicated that a 250 mg/l hydrogen peroxide dose in four columns plumbed in series that were all sparged with 2.2% ozonated air at a rate of 2.5 scfm.

INTRODUCTION

Rocky Mountain Arsenal (RMA) is an installation of the U.S. Army which occupies more than 17,000 acres in Adams County, Commerce City, Colorado. RMA was established in 1942 and has been the site of chemical incendiary munitions manufacturing and chemical munitions demilitarization. Following World War II, Congress approved the leasing of some portions of RMA to private industry. Agricultural pesticides and herbicides were manufactured onsite from 1947 to 1982. Past military and industrial activities at RMA have resulted in the contamination of the alluvial aquifer with various organic compounds such as diisopropylmethylphosphonate (DIMP), pesticides, and volatile organic compounds.

In support of the Office of The Program Manager Rocky Mountain Arsenal (PMRMA), the USAE Waterways Experiment Station (WES) evaluated peroxone for treatment of contaminated groundwaters using a pilot scale peroxone oxidation system. These activities focused on evaluating the feasibility of using peroxone as either a pretreatment technology for the removal of organic contaminants from the influents to existing RMA systems that do not adsorb well onto activated carbon, such as DIMP, (thus reducing the activated carbon usage as a cost saving measure) or for direct remediation of the contaminated groundwater. This paper summarizes some of the results generated by this study that was recently performed at RMA by WES during August 1994.

THE PEROXONE PROCESS

Chemical oxidation processes that result in the generation of the hydroxyl radical ($OH^\cdot$) have been referred to as advanced oxidation processes (AOPs) by the American Water Works Association (Langlais et al. 1991). Commercial application of AOPs for contaminated groundwater treatment in the United States has traditionally involved UV irradiation of hydrogen peroxide, ozone, or a combination of both. In UV light based AOPs, irradiation of chemical oxidizers with ultraviolet (UV) light produces hydroxyl radicals. The hydroxyl radical is a much more powerful oxidizer than either hydrogen peroxide or ozone (Sundstrom et al. 1986).

Peroxone is an AOP that utilizes the combination of hydrogen peroxide and ozone to form the hydroxyl radical without the requirement of UV light. The results reported by Glaze et al. (1988) indicated that peroxone could effectively degrade chlorinated solvents from the groundwater. Since peroxone does not require the addition of high concentrations of chemical oxidizers and UV light, it is estimated that reductions in treatment costs as high as an order of magnitude over more traditional AOPs may be realized.

Langlais et al. (1991) present the following mechanism for the formation of the hydroxyl radical during peroxone treatment:

$$\begin{array}{rcl}
H_2O_2 + H_2O & \longleftrightarrow & HO_2^- + H_3O^+ \\
O_3 + HO_2^- & \longrightarrow & OH + O_2^- + O_2 \\
O_2^- + H^+ & \longleftrightarrow & HO_2 \\
O_3 + O_2^- & \longrightarrow & O_3^- + O_2 \\
O_3^- + H^+ & \longleftrightarrow & HO_3 \\
HO_3 & \longrightarrow & OH^{\cdot} + O_2
\end{array}$$

Discussions with French researchers indicate that some water utilities in France are currently using peroxone to treat millions of gallons per day of pesticide contaminated groundwater (Personal communication with Dr. Marcel Dore, University of Poitiers 1992). The French researchers claim that treatment costs are on the order of $0.05 per 1,000 gallons treated. Glaze et al. (1988) performed laboratory scale studies on the ability of peroxone to remove TCE and tetrachloroethylene (PCE) from a contaminated groundwater. The results proved positive enough to warrant subsequent pilot-scale evaluations (Aieta et al. 1988). Both the bench and pilot studies concluded that the reaction rate of TCE and PCE was increased by factors of 1.8 to 2.8 and 2.0 to 6.5, respectively, as opposed to those achieved by ozonation alone. Apparently, TCE was reactive toward ozone alone as well as the hydroxyl radicals formed; PCE was only reactive toward the radical species. Both studies indicated that a hydrogen peroxide-to-ozone ratio between 0.25 and 0.5 was optimal for removing TCE and PCE from the groundwater studied. The Metropolitan Water District of Southern California (1991) evaluated peroxone using pilot scale systems for treatment of 2-methylisoborneal (MIB) and trans-1,10-dimethyl-trans-9-decanol (geosmin). The District concluded that optimum hydrogen peroxide-to-ozone ratios for removal of MIB and geosmin was 0.1 to 0.2. They further conclude that peroxone was better for removal of MIB and geosmin than ozone alone due to increased hydroxyl radical production.

Researchers at the WES have recently developed a numerical model for estimating the steady-state hydroxyl radical concentrations in peroxone systems (under publication). The hydroxyl radical production and destruction mechanisms as described by the WES model are presented in the equation below,

$$[OH^{\cdot}] = \frac{(2k_6[O_3][H_2O_2]K_{H2O2}[H+]^{-1}}{(k_4[O_3])+(k_5[H_2O_2])+(k_X[X])+(k_s[S])}$$

where, X = Target Contaminant
S = Radical Scavengers
K and k = Rate Constants

The above model indicates that there are numerous chemical reactions that may occur that can remove hydroxyl radical species from a reactor fluid. Only those reactions that either result in production of the radical (shown in the numerator of the equation) and/or the destruction of the contaminant are considered beneficial (the X term in the denominator). The other reactions have an adverse impact on reaction kinetics due to the scavenging of radicals that would have been available for contaminant destructive reactions.

Based on radical production/reaction chemistry, WES has identified three predominant scavenging reactions that will most likely govern reactions within traditional AOP reactor systems when treating contaminated groundwaters. These are reactions with bicarbonate/carbonate ions, reduced cations (i.e. iron), and excessive amounts of primary oxidizers (i.e. ozone and hydrogen peroxide). Of particular interest to this study is that too much ozone or hydrogen peroxide may be added to an AOP system. Usually obtaining excessive amounts of ozone is difficult because ozonation is mass transfer limited (gas to water transfer). However, introduction of hydrogen peroxide (a liquid) is much easier and is likely a potential scavenging source in AOPs. There is an optimum dose for each oxidizer and optimum stoichiometric mass-to-mass ratios for those AOPs utilizing both oxidizers, such as peroxone. Some of the data presented in this report serve as excellent examples of these interactions.

STUDY BACKGROUND AND OBJECTIVES

In 1993, the WES evaluated the potential for three AOPs for removal of DIMP from RMA groundwaters. AOPs evaluated include UV/hydrogen peroxide, UV/ozone, and peroxone. These efforts were accomplished using one liter bench reactors. The results from this effort indicate that any time UV light was added to the hydrogen peroxide system or ozone, extremely rapid degradation rates were observed. Although the peroxone system did not have as rapid degradation as the UV based processes, appreciable degradation of DIMP was observed. The peroxone bench study indicated that hydraulic residence times (HRTs) in excess of 30 minutes will required to remove DIMP to below detection limit levels (BDLLs). Reaction of DIMP with the parent oxidizers used in the bench study, ozone and hydrogen peroxide, were found not to be reactive toward DIMP. This indicates that the primary removal mechanism for DIMP was the hydroxyl radical and/or photolysis.

The results of the bench studies for DIMP removal were considered very promising. The UV based systems had more rapid DIMP degradation rates than the peroxone systems. Unfortunately, UV based systems are more expensive than peroxone systems and are very sensitive to influent UV transmissivity. UV based systems are also susceptible to fouling of the quartz tubes which house the UV lamps. Peroxone oxidation is estimated to cost as low as an order of magnitude lower than traditional UV based AOPs and are not suspectable to problems associated with iron fouling or poor influent UV transmissivity. Therefore, further evaluation of peroxone oxidation for DIMP removal to BDLLs was initiated using a WES developed and constructed pilot scale system with the objective of evaluating the two application scenarios discussed above.

EQUIPMENT DESCRIPTION

The peroxone oxidation pilot system (POPS) used in this study was designed and constructed by the WES. The system had the capability of evaluating influent flowrates ranging from 0.5 to 15 gallons per minute (gpm). For this study a constant flowrate of 0.9 gpm was used. Figure 1 presents an illustration of the POPS unit. The system was plumbed in a countercurrent flow mode with the hydrogen peroxide dosed influent flowing downward and the ozonated gas flowing upward through the columns. Hydrogen peroxide doses was mixed with the influent using an in-line vortex mixer.

The POPS unit used a 3 lbs. per day Orec™ ozone generator capable of producing a continuous stream of air containing up to 2.5 percent ozone (wt/wt). Ozonated air was introduced into four 6 inch ID by 14 foot high, all-glass columns via ceramic spargers located on the column bottoms. A central data logging, system control unit comprised of a Gateway 486, 200 Mbyte, 50 MHz computer was used for on-screen operations analysis of process operations which was used for system operation and real-time data logging. Hydrogen peroxide was introduced into the influent stream using a metering pump to precisely dose the peroxone system with hydrogen peroxide of varying strengths (depending on the target dosage). Two IN-USA™ ozone monitors were used with the system for gas phase analysis. One unit was used to monitor ozone generator output in percent ozone (wt/wt). The other unit had multi-port capability for analyzing air phase ozone concentrations at various sampling points including column headspace, pre- and post-ozone destruct unit, and ambient air. An IN-USA™ in-line ozone monitor with multi-port capability will be used for analyzing residual ozone levels in the effluents exiting any of the four columns. Ozone exiting the columns that was not transferred into the column influents was passed through an ozone destruct system to prevent release of ozone into the ambient air. DIMP is not volatile so there were no concerns about DIMP loss via volatilization during ozonation.

APPROACH

RMA groundwater was used as the influent for this study. This influent contains DIMP at approximate levels that approach 100 ppb. The POPS unit was operated at a constant ozone feed of 2.2% ozone at a flowrate of 2.5 scfm with varying hydrogen peroxide doses into the influent added prior to entry into the first column. Influent was added to the system at a constant flowrate of 0.9 gpm which represented an approximate system hydraulic residence time (HRT) of 90 minutes (23 minutes per column). Analytical samples for DIMP analysis using gas chromatography were collected periodically after each POPS column in precleaned all-glass, one liter sample bottles. DIMP analyses was performed by the RMA Analytical Laboratory. Ozone and hydrogen peroxide concentrations exiting the columns were also recorded.

RESULTS

A DIMP concentration of BDLLs (<1.78 ug/l) was selected as a target treatment goal for comparison of process formulation performance. Tables 1 through 3 summarize the results of the POPS runs for hydrogen peroxide doses of 100 mg/l, 250 mg/l, and 500 mg/l, respectively. These data indicate that the 250 mg/l dose (Table 2) had slightly more rapid removal kinetics that the 100 mg/l dose (Table 1). The addition of 500 mg/l (Table 3) had a slight inhibitory effect on DIMP removal. The mechanism of rate inhibition is believed to be the reaction of hydroxyl radicals with the excessively high amounts of hydrogen peroxide present in the reactors (Table 3). The WES steady-state hydroxyl radical model for peroxone presented earlier illustrates how excessive amounts of either oxidizer may hinder contaminant degradation rate. In fact, the rationale for the 100 mg/l hydrogen peroxide dose to perform slightly worse than the 250 mg/l was attributed to excessive amounts of ozone present in the column which reacted with some of the hydroxyl radicals produced because of the limited amounts of hydrogen peroxide present in the columns. This effect is also illustrated in the steady-state hydroxyl radical model for peroxone systems.

In summary, all three hydrogen peroxide doses were capable of meeting the target treatment goal of BDDLs. The 100 and 250 mg/l doses reached target levels within an HRT range of greater than 23 minutes, but less than 46 minutes. This HRT supports the results of the WES bench study which predicted a HRT of at least 30 minutes would be required to meet the BDLL target. The 500 mg/l dose appeared to hinder DIMP oxidation reactions due to the excessive amounts of hydrogen peroxide present. This hindering effect is explained by the numerical model for steady-state hydroxyl radical concentrations in peroxone systems.

FURTHER EFFORTS

The results of this study were considered very encouraging. Further analysis of the applicability of the peroxone process at RMA is on-going. The 250 mg/l hydrogen peroxide dose appeared to be the optimum process formulation for the conditions evaluated to date. However, WES has generated additional data using varying ozone doses and flowrate. The steady-state [OH·] model predicts that reduced ozone and hydrogen peroxide doses may provide similar treatment efficiencies at significantly reduced treatment costs due to decreased oxidizer demands. These data are currently being evaluated and will be published when available.

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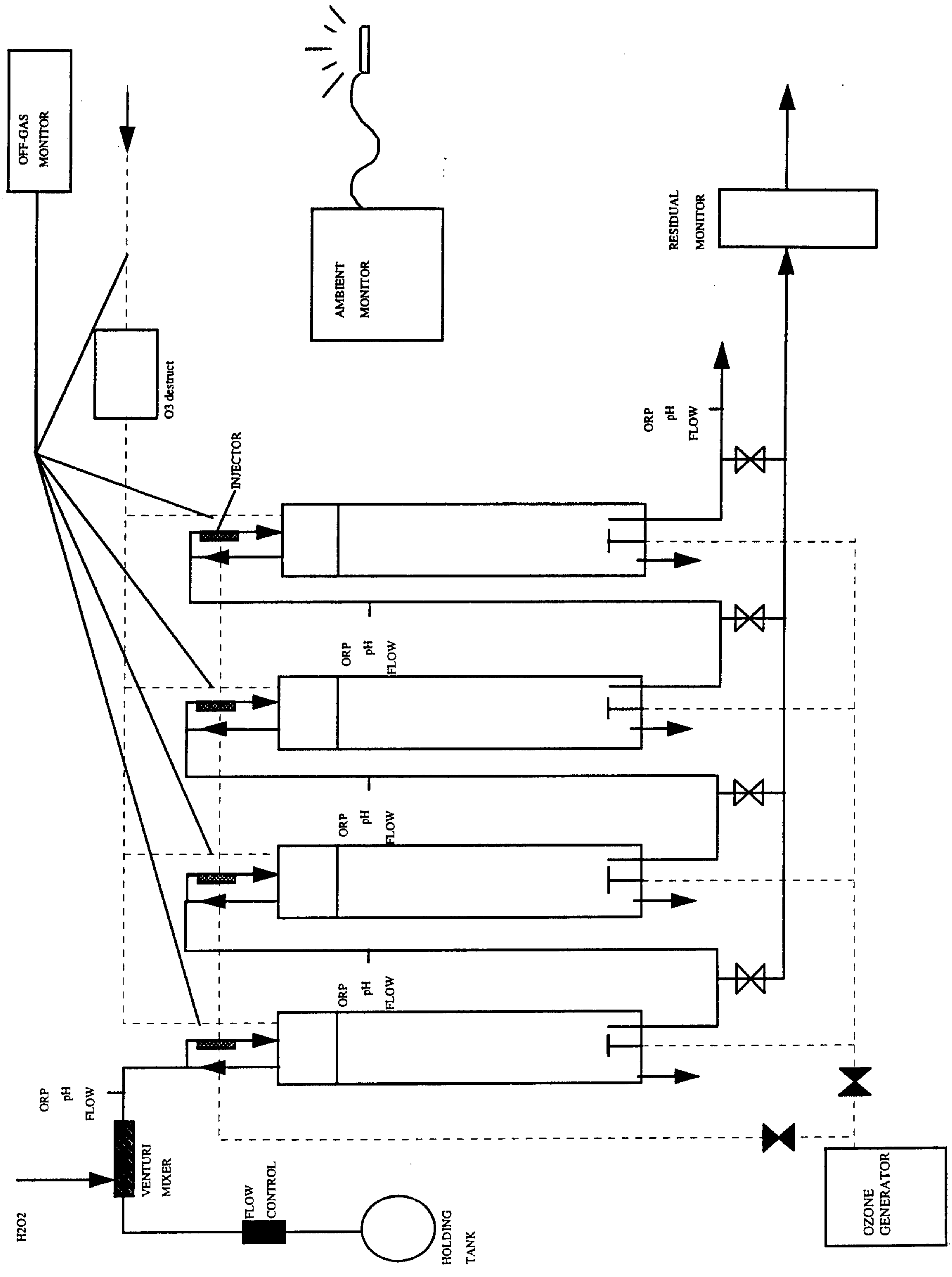
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FLOW
H2O2
VENTURI MIXER
FLOW CONTROL
HOLDING TANK
OZONE GENERATOR

Figure 1

Table 1. 100 mg/l Hydrogen Peroxide Dosed POPS Run

Sample Location*	Cummulative HRT, minutes	Water [H_2O_2], mg/l	Water [O_3], mg/l	Water [DIMP] ug/l
Influent	0	100	0	70
Column 1	23	80	0.6	14
Column 2	46	30	BDL	BDL
Column 3	69	1	0.3	BDL
Column 4	93	0.2	BDL	BDL

* - Column data based on samples collected directly after exiting the column
BDL - Below detection limit (0.1 mg/l for oxidizers and 1.78 ug/l for DIMP)

Table 2. 250 mg/l Hydrogen Peroxide Dosed POPS Run

Sample Location*	Cummulative HRT, minutes	Water [H_2O_2], mg/l	Water [O_3], mg/l	Water [DIMP] ug/l
Influent	0	250	0	65
Column 1	23	200	1.7	10
Column 2	46	125	1.2	BDL
Column 3	69	50	0.4	BDL
Column 4	93	0.2	BDL	BDL

* - Column data based on samples collected directly after exiting the column
BDL - Below detection limit (0.1 mg/l for oxidizers and 1.78 ug/l for DIMP)

Table 3. 500 mg/l Hydrogen Peroxide Dosed POPS Run

Sample Location*	Cummulative HRT, minutes	Water [H_2O_2], mg/l	Water [O_3], mg/l	Water [DIMP] ug/l
Influent	0	500	0	60
Column 1	23	500	2.0	14
Column 2	46	350	1.9	3.7
Column 3	69	275	2.0	BDL
Column 4	93	200	1.6	BDL

* - Column data based on samples collected directly after exiting the column
BDL - Below detection limit (0.1 mg/l for oxidizers and 1.78 ug/l for DIMP)

BIODEGRADATION OF NITRATE ESTERS
(Enzymatic Denitration)

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ABSTRACT

The Indian Head Division, Naval Surface Warfare Center is pursuing a program to develop biotechnologies for the treatment of nitrate ester contaminated waste. Both whole cell and enzymatic approaches are being investigated. The nitrate esters used in this investigation are nitroglycerin (NG) and propyleneglycol dinitrate (PGDN). Working with the University of Maryland at Baltimore, we are isolating the enzymes used by bacteria to denitrify nitrate esters. The goal of this technique is to develop an enzyme product capable of completely denitrating NG and PGDN. For the whole cell approach we will give a brief summary of the technologies being investigated.

The emphasis of this paper will be the joint work between Indian Head, the University of Maryland at Baltimore, and the University of Maryland Baltimore County. This work is centered on developing a denitrase enzyme product. As the result of our investigations two organisms have been isolated that are capable of denitrifying nitrate esters; *Bacillus thuringiensis/cereus* (N) and *Enterobacter agglomerans* (AT25). We will present the results on the degradation abilities of these isolates and cell-free extracts of these isolates, as well as discuss future directions of this project.

INTRODUCTION

This project will develop technologies for the biodegradation of nitrate esters. The nitrate esters (NEs) used in this investigation are nitroglycerin (NG) and propyleneglycol dinitrate (PGDN). Even though the Army has spent a considerable amount of effort investigating and developing biotechnologies for decontaminating explosively contaminated wastes, the Army's focus has been on compounds such as trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and nitrocellulose (NC). Many of the conventional treatment technologies have proven to be transferable to NEs. In biological treatment systems, the NEs are very different. The microorganisms use different enzymes to break the carbon-oxygen linkage ($C\text{-}O\text{-}NO_2$) of the study NEs as compared to the other common explosives. TNT has a carbon-nitrogen linkage ($C\text{-}NO_2$) and RDX has a nitrogen-nitrogen linkage ($N\text{-}NO_2$). NC has the same carbon-oxygen linkage as the study NEs but the polymer structure dominates the biodegradation of NC. Once the NO_2 group has been removed from the study NEs, the biosystem has only to deal with simple aliphatic polyols.

OBJECTIVES

The long-term goal of our work is to examine a potential alternative treatment strategy involving the use of enzymes (1,2). If one or more enzymes were available which denitrated NG to yield glycerol and nitrate (or nitrite), then the toxicity, explosive nature, and difficulty in degrading this waste component would be reduced. This approach may be possible based on early work by Wendt et al. (3), who studied mixed cultures from sewage sludge and observed NG was sequentially denitrated to glycerol dinitrate (GDN) and mononitrate (GMN) isomers and presumably to glycerol. To be practical for waste treatment, however, the denitration enzyme(s) must not have co-substrate requirements since few NAD(P)H- and ATP-requiring enzymes are industrially useful. With respect to the co-substrate requirement, there appear to be a few alternative reactions for denitration of NG. Cofactor-requiring reductive pathways have been reported by Servent and coworkers (4, 5), who demonstrated that the fungus *Phanerochaete chrysosporium* degrades NG with the formation of nitrite and nitric oxide. These authors reported that a glutathione transferase system is responsible for nitrite formation and a reductase system involving hemoproteins is responsible for nitric oxide formation. Alternatively, White and Snape (6) recently cited a Ph.D. thesis (7) in which hydrolytic activities were suggested to be responsible for denitration. The advantage of a hydrolytic pathway is that the simple co-substrate requirement would facilitate the development of an enzymatic strategy for transforming NG-containing wastes. To our knowledge, there have been no reports in which pure cultures have achieved complete conversion of NG to glycerol nor have there been reports on enzyme systems which can denitrate NG without the need for depletable cofactors. This basic strategy applies to the denitration of PGDN.

The specific goals of this study were to:

(a) Select and isolate microorganisms capable of denitrating NG and PGDN

(b) Characterize the fermentation processes for producing denitration activity

(c) Characterize the substrate range of whole cells

(d) Determine the degradation pathway using cell-free extracts

(e) Assess the practical aspects of enzymatic denitration.

MATERIALS AND METHODS

Materials

Analytical references of NG , 1,2-GDN, 1,3-GDN, 1-GMN, and 2-GMN were purchased from Radian Corporation (Austin, TX). [2-^{14}C]-NG and [2-^{14}C]-PGDN were purchased from American Radiolabeled Chemicals (St. Louis, MO) and had a specific activity of 55 mCi/mmole with a radiochemical purity of 99.9% at a concentration of 0.05 mCi/mL. The radioactive metabolites [2-^{14}C]-1,3-GDN, [2-^{14}C]-1,2-GDN, [2-^{14}C]-GMN, and [2-^{14}C]-glycerol were separated in our laboratory and had a radiochemical purity of 99.9%.

Isolation of Organisms with Denitration Activity

Soil and sediment samples from the Indian Head Division were taken from environments known to have been previously exposed to NE contaminants. Cultures from these samples were screened by two ways: for their ability to use NG as a sole source of nitrogen or for their ability to tolerate high, presumably toxic, levels of NEs. From these screens, 55 isolates were obtained. Each isolate was tested for its ability to degrade NEs, and the best two cultures (designated isolates N and AT25) were selected for further study. Using biochemical tests and fatty acid analysis, these isolates were identified by Industrial and Environmental Analysis, Inc. (Essex Junction, VT) as a gram positive *Bacillus thuringiensis/cereus* (isolate N) and a gram negative *Enterobacter agglomerans* (isolate AT25).

Cultivation Conditions

Seed cultures were prepared by transferring cells from slants into 250-mL flasks containing 30 mL of Luria-Bertani (LB) medium which contained: tryptone, 10 g/L; yeast extract, 5 g/L; and NaCl, 10 g/L. For seed cultures, the LB medium was supplemented with 1.5 mM NG although later studies indicated that addition of NG was not required for seed cultures. These seed cultures were grown for 10 or 15 hours at 28 °C and 180 rpm.

Flask studies were conducted by inoculating 2% of seed culture into the cultivation media. For the *Bacillus* isolate, the cultivation medium was a modified LB medium and contained: tryptone, 10 g/L; yeast extract, 5 g/L; NaCl, 10 g/L; glucose 10 g/L; and 100 mM potassium phosphate buffer (pH 7.5). For the *Enterobacter* isolate, the cultivation medium contained; malt extract, 20 g/L; yeast extract, 5 g/L; and 100 mM potassium phosphate buffer (pH 7.5).

For resting cells, a 10-mL sample was removed from the cultivation medium, and the cells were centrifuged, washed with 50 mM phosphate buffer, and recentrifuged. After discarding the supernatant, the washed cells were resuspended in 5 mL of 50 mM phosphate buffer (pH 6.8) containing 2.2 mM NG, and these cells were then incubated at 28 °C.

Work with PGDN was performed following similar procedures.

Preparation of Cell-Free Extracts

After cultivation for 24 hours, cells were harvested by centrifugation at 5,000 g. The cells were washed once and resuspended in a 1:1 ratio (cell weight to buffer volume) with a potassium phosphate buffer (100 mM, pH 7.0) containing 10 mM of the protease inhibitor, phenylmethylsulfonyl fluoride (PMSF). The cells in this buffer were then lysed by French press and fractionated by centrifugation at 30,000 g into membrane (pellet) and cytoplasmic (supernatant) fractions. The membrane fraction of the *Enterobacter* isolate was reconstituted in a 1:1 ratio (cell weight to buffer volume) with a potassium phosphate buffer (100 mM, pH 7.0). The cytoplasmic fraction of the *Bacillus* cultures had a reproducible protein concentration of 53 ± 4 mg/mL, while the protein concentration of the membrane fraction from *Enterobacter agglomerans* was not determined.

Degradation reactions with cell-free extracts were typically conducted using 100 µL extract fractions (the cytoplasmic fraction for *Bacillus* and the membrane fraction for *Enterobacter*), 100 µL NG-containing solution (final NG concentration of 3.3 mM), and 20 µL 100-mM potassium phosphate solution. In studies involving radioactivity, 2 to 20 µL of [2-^{14}C]-NG or [2-^{14}C]-PGDN (0.1 to 1 µCi) was added to the incubation mixture. Due to differences in the pH optima for the denitration reaction, the buffer for experiments with the *Bacillus* extracts was 8.0, while the buffer was 7.0 for experiments with the *Enterobacter* extracts.

Analytical Methods

Thin layer chromatography (TLC) was used for identification and separation of radioactive metabolites from [2-^{14}C]-NG degradation. Samples were spotted on silica gel plates (20 by 20 cm and 250 nm thick: EM Sciences 5721-7). The toluene/ethyl acetate solvent system (8) was used to separate NG and the GDN isomers, while the ethyl acetate/n-heptane solvent system was used to separate GMN from glycerol (8, 9). For visualization of the nonradioactive standards, the plates were sprayed with a fine mist of diphenylamine in methanol (1%), followed by detection using a UV lamp. Radioactive metabolites were visualized by scanning radioactivity on a Berthold automatic linear analyzer.

Routine analysis of NEs was performed by HPLC using a UV detector. Samples for HPLC analysis were initially treated by passing them through a solid phase extraction (C-18) column (Baxter Healthcare, Muskegon, MI) followed by elution with acetonitrile. These acetonitrile samples were then injected onto a Spherisorb 4µ ODS-2 column (length, 250 mm; diameter, 4.6 nm; MetaChem Technologies, Redondo, CA) using the acetonitrile/water mobile phases discussed above depending on the metabolites to be separated. For identification of radioactive metabolites, fractions from the HPLC were collected and analyzed by scintillation counting (Beckman LS 5801 scintillation counter).

In whole cell experiments, nitrite (and not nitrate) appeared to be the major inorganic product, and to measure the nitrite ion concentration, we adapted the colorimetric method of Ida and Morita (10). For nitrate/nitrite analysis in cell-free experiments, supernatant samples were passed through C-18 solid phase extraction column, the columns were washed with water, and all the liquid eluents were combined. The combined eluents were reduced using a Cd-Zn catalyst (11) and then nitrite was measured by the above procedure.

Cell growth in the fermentation studies was measured by optical density (OD at 610 nm) after diluting the samples tenfold.

A similar approach was used for PGDN.

RESULTS

Selection and Isolation of NG-Degrading Microorganisms

As discussed in the "Materials and Methods," 55 isolates were selected for either their ability to grow with NG as the sole nitrogen source or their ability to grow in the presence of high concentrations of NG. The two best isolates were identified as *Bacillus thuringiensis/cereus* and *Enterobacter agglomerans* (12). These isolates were also observed to be capable of degrading PGDN.

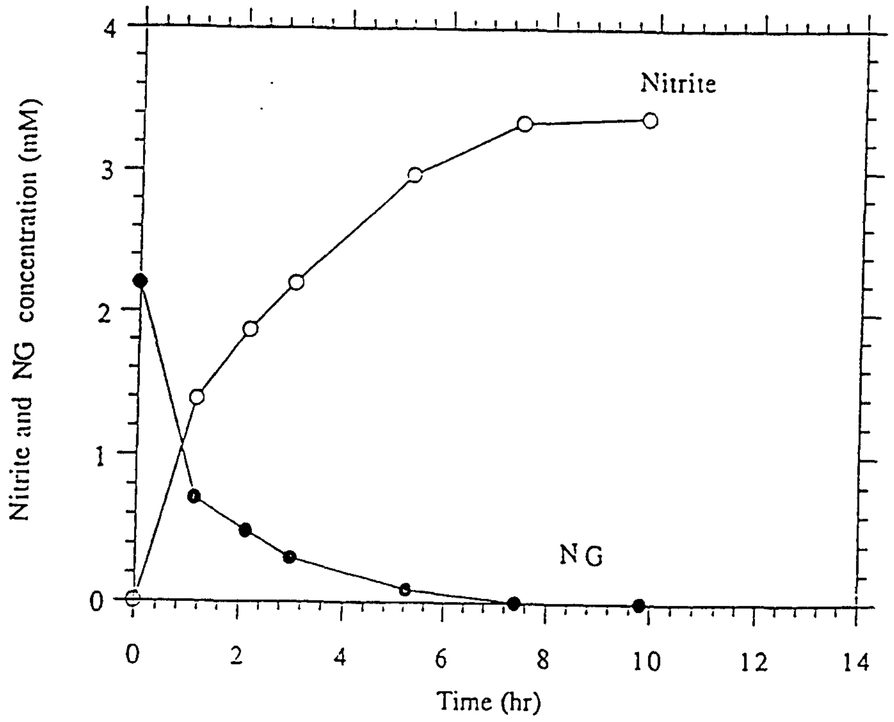
Development of Cultivation Conditions

After identifying cultures capable of denitrating NG, we investigated cultivation conditions to yield cells with high denitration activities. A resting cell assay system was developed. Using the assay system, the effects of different carbon and nitrogen sources on the denitration activity were examined as well as performing a time course of the cell growth and denitration activity.

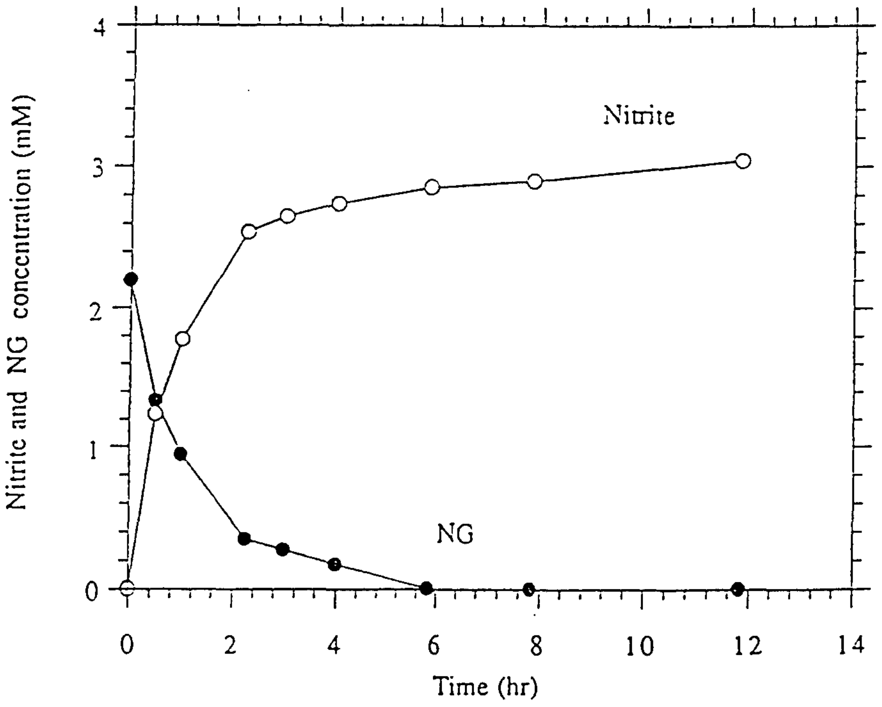
To perform medium development studies, it is necessary to have a rapid and quantitative assay for denitration activity. Since nitrite is relatively easy to analyze and since studies indicated that for resting cells, nitrite is the major inorganic nitrogen product from NG degradation, we used the release of nitrite as a rapid quantitative measure of denitration activity. To eliminate background inorganic nitrogen which could confuse the interpretation of nitrite release results and because the enzymatic activity for denitration was retained within the cells, we developed an assay method based on nitrite by resting cells (cells grown in the absence of a growth media, thus with no source of inorganic nitrite) exposed to NG. Figure 1 shows that nitrite release in these resting cells was initially rapid with the rate of nitrite release being relatively constant over the first two hours. Thus the rate of nitrite release by resting cells over an initial two-hour period served as a simple and rapid quantitative measure of denitration activity. One unit of denitration activity was defined as the formation of 1 mMol of nitrite per hour. As can be seen in Figure 1, the rate of loss of NG correlates to the rate of formation of nitrite indicating that NG loss is the result of transformation and not due to evaporation or adsorption.

To establish culture conditions which yield cells with high denitration activity, various media conditions were investigated with *B. thuringiensis/cereus* and *E. agglomerans.* As shown in Table 1, for the carbon and nitrogen sources considered, the medium containing glucose or glycerol and malt extract resulted in the highest specific denitration activities for *B. thuringiensis/cereus.* However, glucose and tryptone appear to be the best carbon and nitrogen sources for total denitration activity by this isolate. We chose to focus on the glucose and tryptone medium, and in subsequent studies we observed that initial levels of 10g/L of each of these ingredients was optimal for denitration activity.

FIGURE 1.
Time Course of NG Degradation and Nitrite Release by Resting Cells



(a) *B. thuringiensis/cereus*



(b) *E. agglomerans*

TABLE 1.
Selection of Carbon and Nitrogen Sources for *B. thuringiensis/cereus*

Carbon/Nitrogen Source[1]	Cell Growth[2] (OD_{610nm})	Denitration Activity[3] (U/L)	Specific Activity[4] (U/L-OD)
Glucose / Tryptone	9.60	1.120.120	
Glucose / Malt Extract	3.35	0.67	0.200
Glycerol / Tryptone	11.65	0.37	0.032
Glycerol / Malt Extract	4.45	0.60	0.140
Sucrose / Tryptone	10.80	0.35	0.032
Sucrose / Malt Extract	5.45	0.57	0.110

[1] All media contained 0.1M potassium phosphate buffer (pH 7.5), 10 g/L NaCl, 5 g/L yeast extract, 1.5 mM NG and 10 g/L each of the carbon and nitrogen sources.

[2] Cell growth was measured after incubation for 24 hours in the cultivation media.

[3] Denitration activity was measured in resting cells as described in the test, 4 mL of cultivation media harvested 24 hours after incubation. After centrifuging, cells were washed with 50 mM phosphate buffer (pH 6.8) and suspended in 2 mL of same buffer containing 2.2 mM NG.

[4] Specific Activity is defined as denitration activity as measured in resting cells per OD (as measured in cultivation medium at 24 hours).

For *E. agglomerans*, we conducted similar studies to identify an optimal medium for obtaining denitration activity. As shown in Table 2, glucose and tryptone appear to be the least favorable combination of carbon and nitrogen sources for denitration activity of *E. agglomerans*. After identifying glycerol and malt extract as appropriate carbon and nitrogen sources, the effects of the initial concentrations of these ingredients were examined. From this study we observed that glycerol was not necessary and 20 g/L of malt extract by itself was most appropriate for the expression of denitration activity (data not shown).

TABLE 2.
Selection of Carbon and Nitrogen Sources for *E. agglamerans*.
[Experimental conditions the same as in Table 1.]

Carbon/Nitrogen Source	Cell Growth (OD_{610nm})	Denitration Activity (U/L)	Specific Activity (U/L-OD)
Glucose / Tryptone	6.38	0.19	0.030
Glucose / Malt Extract	5.51	0.36	0.065
Glycerol / Tryptone	6.73	0.29	0.043
Glycerol / Malt Extract	5.45	0.50	0.092
Sucrose / Tryptone	7.05	0.26	0.037
Sucrose / Malt Extract	5.65	0.390	.069

To understand how denitration activity is expressed over time, we examined denitration activity of *B. thuringiensis/cereus* and *E. agglomerans* over the course of the cultivation. For both isolates, cells did not need to be exposed to NEs for expression of denitration activity and denitration activity was expressed constitutively (12).

Degradation of NG by Resting Cells

After developing improved cultivation conditions, our next goal was to better characterize the denitration reaction catalyzed by intact cells. For this we examined the loss of NG and formation of GDN and nitrite by resting cells of *B. thuringiensis/cereus* and *E. agglomerans*. Figure 2a shows the time course for denitration by resting cells of *B. thuringiensis/cereus*. The NG concentration was observed to rapidly decrease to zero by the first hour. GDN concentrations were observed to increase during the first hour reaching a maximum of 0.65 mM for 1,2-GDN and 0.62 mM for 1,3-GDN. After the first hour, the GDN concentrations were observed to slowly decrease with 1,2-GDN being completely removed by 14 hours and 1,3-GDN levels reaching 0.06 mM after 20 hours. Figure 2a also shows that nitrite formation was rapid during the first hour when NG was observed to be rapidly lost. By the first hour, the nitrite level had reached a value of 2.6 mM. After the first hour, as the accumulated GDN was degraded, an additional 1.2 mM nitrite was observed to be slowly formed.

A similar resting cell study was performed with *E. agglomerans*. As can be seen in Figure 2b, the initial 2.2 mM NG had completely disappeared by the first hour with the accumulation of up to 1.6 mM 1,3-GDN and 0.47 mM 1,2-GDN. The 1,2-GDN that had accumulated was observed to be completely removed by 6.5 hours, while the level of 1,3-GDN was observed to be reduced to 0.18 mM by 27 hours. The nitrite concentrations shown in Figure 2b also demonstrate a rapid initial formation of nitrite during the period of rapid NG loss and a slower formation of nitrite as GDN levels decreased. In summary, Figure 2 shows that NG can be readily denitrated by resting cells of both *B. thuringiensis* and *E. agglomerans*. For both isolates, denitration of the resulting GDN isomers is slower than the initial denitration of NG. Due to analytical difficulties, GMN, which is the likely denitration product of GDN, was not measured in this study.

Substrate Range for Denitration by Resting Cells

To evaluate the substrate specificity for denitration, the release of nitrite from various nitrate esters and nitro-organic compounds was tested using resting cells. Table 3 shows the results obtained for resting cells that had previously been grown on the optimal medium. The results show that resting cells of *B. thuringiensis* and *E. agglomerans* were similar in their abilities to denitrate NEs and nitro-organic compounds. Resting cells denitrated PGDN, TMETN (trimethylol ethane trinitrate), and NG. TEGDN (triethylene glycol dinitrate) did not appear to be denitrated by either resting cells. These results may be related to the fact that the chemical structures for NG, PGDN, and TMETN are quite similar, while TEGDN is structurally quite different from NG.

TABLE 3.
Nitrate release (mM) from various nitro-organics by resting cells of *Bacillus* and *Enterobacter*

	Nitrite formation	
Nitro-organic (mM)	*E. agglomerans*	*B. thuringeinsis/cereus*
1-Nitropropane (3.0mM)	0.027	0.028
2-Nitropropane (3.0mM)	0.0310.0059	
4-Nitrophenol (0.72mM)	0.0	0.017
PGDN (0.6mM)	0.15	0.28
TMETN (0.39mM)	0.77	0.34
TEGDN (0.42mM)	0.0015	0.086
NG (0.44mM)	0.30	0.50

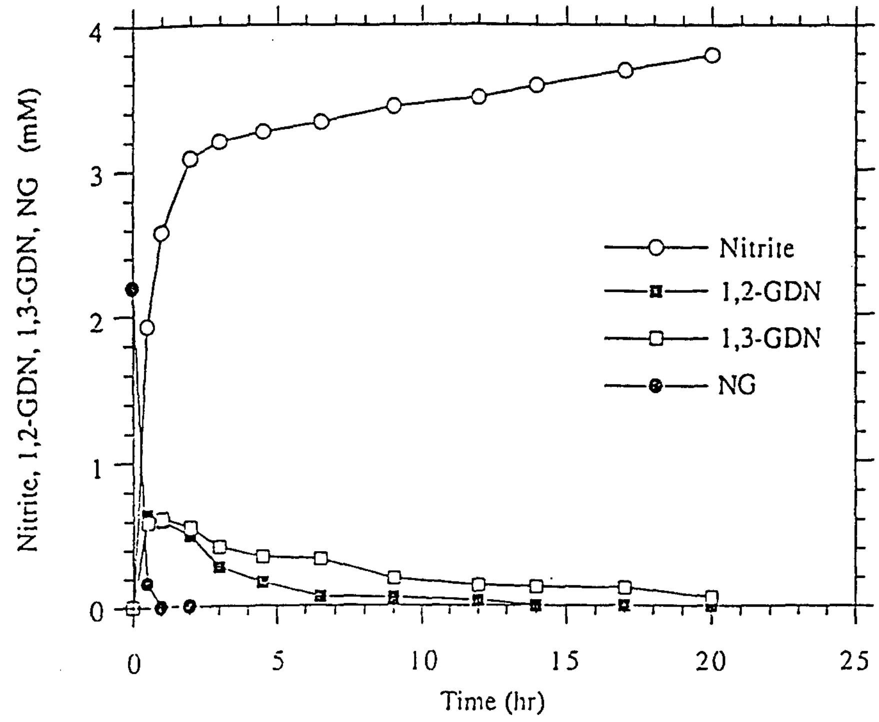
[Culture of the *Bacillus* and *Enterobacter* organisms were grown on the optimal medium. The denitration of various nitro-organics by resting cells was measured after incubation for 12 hours.]

Activity in Cell-Free Extracts

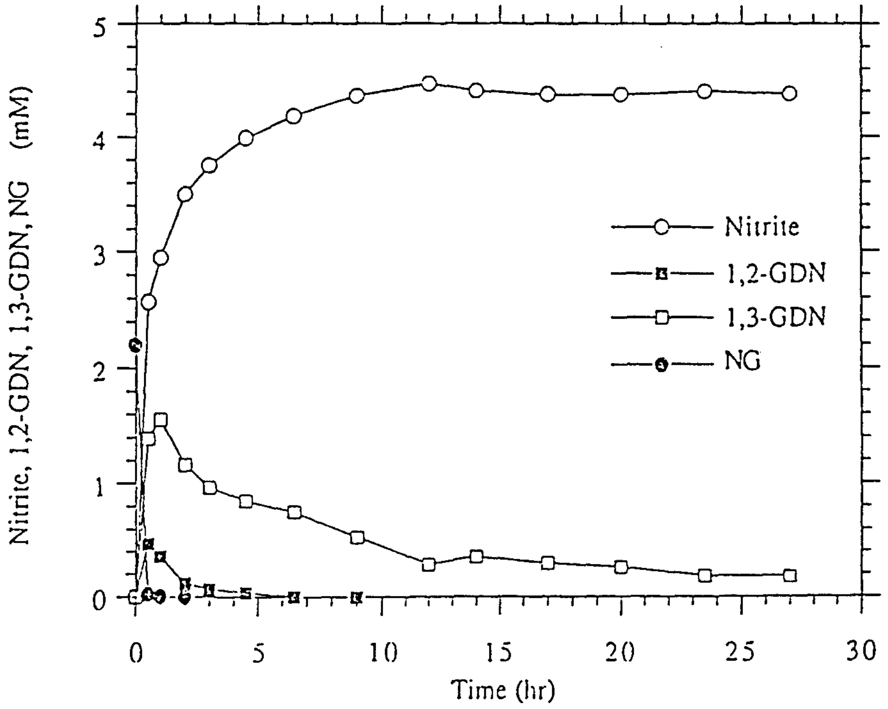
Cell-free extracts were prepared of both organisms by French press and subsequent centrifugation. For *Bacillus*, the denitration activity was found primarily in the cytoplasmic fraction, but for *Enterobacter*, a substantial portion of the activity was associated with the precipitate, or "membrane fraction." This fraction was used for all subsequent experiments with *Enterobacter*.

To determine whether dialyzable cofactors are required for denitration activity, crude, cell-free extracts were dialyzed for 3 hours against three 1-L changes of 100 mM phosphate buffer containing 1.0 mM of the protease inhibitor PMSF and assayed for denitration activity. Table 4 indicates that the loss of NG in the dialyzed extracts was comparable to the loss observed for similar extracts which had not been dialyzed. Also, Table 4 shows no loss of NG by the boiled-extract controls. Thus the results in Table 4 demonstrate that dialyzed cofactors (e.g., NAD[P]H) are not required for NG degradation by cell-free extracts from either the *Bacillus* or *Enterobacter* isolates.

FIGURE 2.
Time Course of NG degradation and Metabolite Formation



(a) *B. thuringiensis/cereus*



(b) *E. agglomerans*

TABLE 4.
Comparison of Degradation of NG with Dialyzed and Nondialyzed Fractions of the *Bacillus* and *Enterobacter* Isolates

	NG concentration after incubation (mM)	
Fraction (a)	*Bacillus* cytoplasm	*Enterobacter* membrane
Dialyzed	0.41 ± 0.04	0.13 ± 0.04
Nondialyzed	0.40 ± 0.02	0.08 ± 0.01
Control (b)	3.33 ± 0.06	3.33 ± 0.05

Metabolites from Denitration

The metabolites from denitration have been identified as published in the paper titled "Biodegradation of Nitrate Esters," proceedings 1994 JANNAF S&EPS Meeting in San Diego CA (13). NG is sequentially denitrated to form 1,2-GDN, 1,3-GDN, 1-GMN, 2-GMN, and glycerol. These metabolites were confirmed by TLC and HPLC with authentic standards and experiments using radiolabeled NG demonstrated that no unidentified compounds were generated. Similarly, experiments with radiolabeled PGDN demonstrated that 1-PGMN, 2-PGMN, and propylene glycol are the only metabolites.

Pathway for Denitration

As reported previously, we believe NG under goes sequential denitration following the pathway illustrated in Figure 3. Similar work with PGDN showed sequential denitration to propylene glycol (a paper on work with PGDN is being prepared for publication).

Extended Incubation of Cell-Free Extracts

Another goal was to demonstrate that cell-free extracts from the isolates have the ability to completely denitrate NG to glycerol. For this it was necessary to incubate the extracts with [2^{14}C]-NG over an extended period of time and to periodically add fresh cell-free extract (20 µL of extract was added nine times throughout the experiment) to the incubation mixture. For cytoplasmic extracts for the *Enterobacter* isolate, 20-µL samples were periodically removed and analyzed by TLC in both solvent systems to identify NG, both GDN isomers, GMN, and glycerol. As indicated in Figure 4, the initial NG was observed to be rapidly lost with the transient appearance of both 1,2-GDN and 1,3-GDN. The subsequent loss of GDN was accompanied by the appearance of GMN (the individual isomers were not resolved). At 30 hours, the GMN level peaked, after which it was slowly converted to glycerol. By 90 hours, all the radioactivity present on the TLC plates resulted from glycerol. Thus Figure 4 shows that NG is sequentially and completely denitrated to glycerol.

Figure 5 shows the results of a similar test with PGDN. As the PGDN disappears, the mono-nitrate products form and disappear. With the disappearance of the mono-nitrates of propylene glycol, there is a corresponding appearance of propylene glycol. This illustrates the sequential denitration of PGDN by *Enterobacter.*

Similar results were obtained were obtained with the cytoplasmic fraction of the *Bacillus thuringiensis/cereus* isolate (12,13).

Practical Aspects

In order to use the cell-free extracts in practical situations, it may be necessary to solubilize NG in organic solvents or with detergents. Therefore, we tested the effect of the reagents upon enzyme activity. These tests were run with small quantities of the radiolabeled 14-C-NG and crude *B. thuringiensis/cereus* cell-free extracts. Tables 5, 6, 7, and 8 and the explanation below discuss the results of these tests.

The effect of water-miscible organic solvents on the denitrating activity of the *Bacillus* cell-free extract was assessed by adding various amounts of ethanol:acetone (1:1) to the usual reaction system. The total volume of the reaction system was 440 µL with 10%, 25%, or 50% volume of organic solvent in the reaction vial. The reaction mixture contained 1,500 ppm, 100 µL NG, 100 µL crude *Bacillus* enzyme, 1 µL C-14-NG, 20 µL 0.1M K_2HPO_4, and pH 7 phosphate buffer to adjust the total volume to 440 µL. The reaction was incubated for 3 hours at 30 °C. Results are shown in Table 5. The tested organic solvent slowed down the reaction but did not completely inactivate it even at 50% concentration.

FIGURE 3.
Pathway for Denitration of Glycerol Trinitrate (NG)

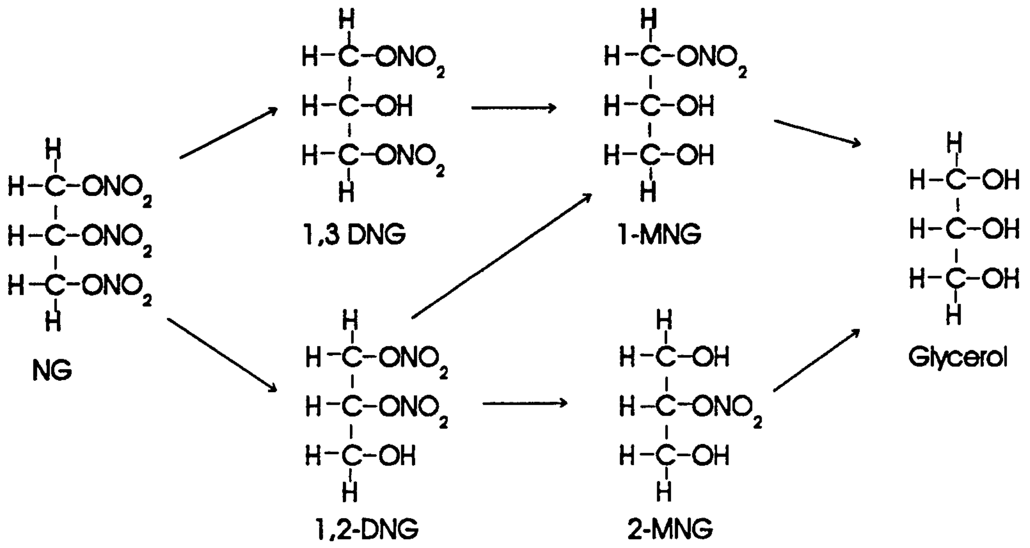


FIGURE 4.
Complete Denitration of NG by Membrane Fraction of *Enterobacter agglomerans*

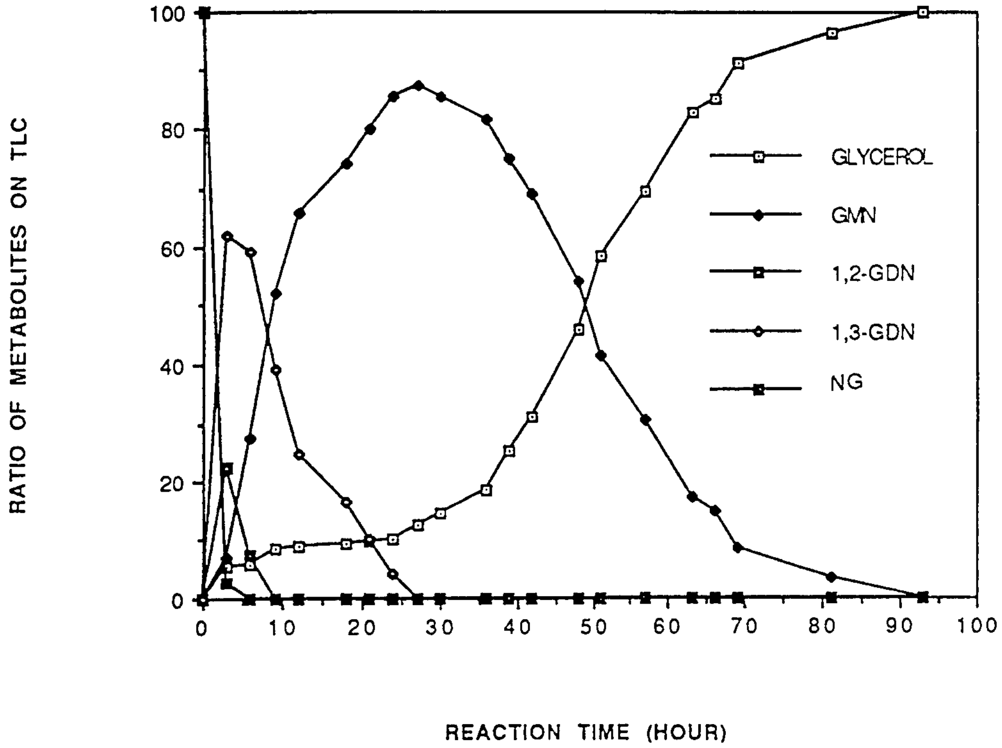


FIGURE 5.
Complete Denitration of PGDN by Membrane Fraction of *Enterobacter agglomerans*

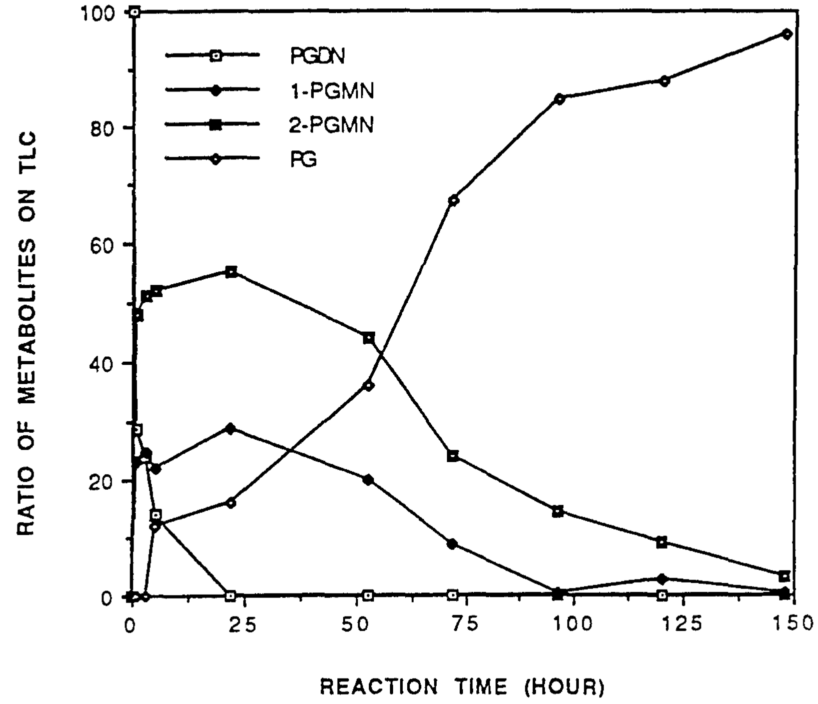


TABLE 5.
NG loss in ethanol:acetone (1:1) with water

Concentration of Organic Solvent	NG	1,2-GDN	1,3-GDN	GMN +Glycerol
0%	10%	36%	30%	24%
10%	20%	38%	23%	19%
25%	56%	16%	12%	16%
50%	80%	6%	5%	10%

In the second experiment the effect of water-nonmiscible organic solvent on the denitrating activity was assessed using $CHCl_3$. The total volume of reaction system was 440 μL (220 μL water phase and 220 μL $CHCl_3$), and all reaction conditions were the same as before. A control experiment using boiled cell-free extract was performed in parallel. Parallel samples were performed, one for scintillation counting, another one for TLC scanning. The results are shown in Table 6. The control reaction showed no breakdown of NG.

Table 6 illustrates that the 35% overall breakdown of NG observed in the chloroform:water reaction must involve either enzyme in the organic phase or NG continually partitioning into the aqueous phase. In an attempt to determine which was occurring, we performed an experiment in which the cell-free extract was added to a chloroform:water mix and after shaking, the two phases were separated and the remaining reaction components (including pure dry NG) were added. Presumably breakdown occurs in the organic phase, the enzyme is partitioning into the organic phase and degradation is occurring in both phases. One hundred μL crude *Bacillus* cell-free extract, 120 μL buffer, and 220 μL $CHCl_3$ were mixed and shaken well; then 200 μL aqueous solution and 200 µL $CHCl_3$ were added to two tubes, respectively, which contain the same amount of dry NG (0.66 mol). Incubation was for 3 hours at 30 °C.

TABLE 6.
NG loss in chloroform and water

Phase	% total radioactivity	NG	1,2-GDN	1,3-GDN	GMN +Glycerol
$CHCl_3$	71%	87%	4%	3%	4%
		*(63%)	(3%)	(2%)	(3%)
water	29%	9%	28%	26%	37%
		(2.5%)	(8%)	(7.5%)	(11%)

* number shown in percentages of each phase in each metabolite; numbers in parenthesis show the distribution in terms of total NG added.

Table 7 shows that the reaction in pure $CHCl_3$ is less than in the aqueous phase, but since the enzyme must partition into the chloroform in order for a reaction to occur, this illustrates the lipophilic nature of this enzyme. It is interesting that the degradation products lie much further toward complete degradation (GMN + glycerol) in the chloroform-based reaction. No measurement of how much of the enzyme was in the organic phase could be made.

TABLE 7.
NG loss in separated chloroform and water layers

Phase	NG	1,3-GDN	1,2-GDN	GMN + Glycerol
control (a)	100%	0%	0%	0%
water	18%	27%	19%	36%
chloroform	73%	0%	7%	20%

(a) control: reacting with boiled enzyme

The effect of detergent on denitrating activity was measured using "All" detergent. The reaction mixture contained 100 µL of 1,500 ppm NG, 100 µL crude *Bacillus* enzyme, 20 µL K_2HPO_4, and 0.5 µL C-14-NG mixed with 100 µL of three different concentrations of detergent (37.5 mg/20 mL, 75.0 mg/20 mL, and 150 mg/20 mL). The tubes were incubated 3 hours at 30 °C. Two control samples also were prepared as the same method, one with boiled enzyme and the other with detergent and no cell-free extract. The results are seen in Table 8.

TABLE 8.
NG loss with enzyme and detergent

Concentration of detergent	NG	1,2-GDN	1,3-GDN	GMN + Glycerol
control 1: NG plus detergent	100%	0	0	0
control 2: NG plus boiled enzyme	100%	0	0	0
no detergent	10%	30%	26%	33%
37.5 mg/20ml	15%	27%	22%	38%
75.0 mg/20ml	15%	25%	22%	39%
150.0 mg/20ml	14%	24%	24%	33%

This experiment indicated that there is only a slight effect of the detergent on the denitrification activity, even at the highest concentration. The detergent system shows less inhibition than that observed with organic solvent (ethanol:acetone) system.

CONCLUSIONS

Traditional physical and chemical methods for treating NG-containing wastes have their limitations and microbiological treatment methods have been suggested (14, 3). Although it would be desirable to exploit the degradative abilities of a steady-state population of microorganisms to mineralize NG and PGDN, such approaches have proven to be difficult to achieve in practice because of the difficulties of maintaining a suitable environment for biodegradation. We are considering an alternative, enzymatic approach of transforming NG to glycerol and nitrate (or nitrite) or PGDN to propylene glycol and nitrate (or nitrite). Such a biotransformation would render the wastes less dangerous in terms of toxicity and explosive nature and also yield a readily degradable glycerol or propylene glycol. We believe such an enzymatic approach could be simpler and more reliable, especially for wastes which are generated intermittently and in small volumes.

Consistent with our goal of investigating an enzymatic method for transforming NG-containing wastes, we selected two microorganisms capable of denitrating NG, and we developed fermentation conditions to optimize expression of denitration activity. For both isolates, NEs were not required for induction and denitration activity was expressed constitutively (12). Further, both isolates appeared to be capable of denitrating the related nitrate esters PGDN and TMETN, although they were unable to degrade nitophenol or nitroaliphatic compounds.

Cell-free extracts from both isolates were observed to be capable of degrading NG through a sequential denitration. Also the activity for denitration was observed to be unaffected by dialysis indicating that depletable or dissociable cofactors are not required for denitration. Finally long-term incubations indicated that cell free extracts are capable of completely converting NG to glycerol (12). PGDN was observed to be completely denitrated to propylene glycol.

With respect to waste treatment the most important observations are: cell-free extracts were observed to be capable of completely denitrating NG to glycerol and PGDN to propylene glycol; dissociable and depletable cofactor are not required for denitration; cells and cell-free extracts were observed to have a reasonable substrate range for denitrating other nitrate esters; and cell-free extracts appear to function in environments suitable for a variety of practical applications (in the presence of non-aqueous solvents and detergent).

Since the enzyme activity in the cell-free extracts appears to fit the criteria necessary for practical utility, the next step is to over produce it using recombinant DNA techniques. We initially attempted a "reverse genetics" approach of purifying the denitrase enzyme, obtaining an amino acid sequence, constructing a hybridization probe and probing a library of *Bacillus* DNA fragments. This approach encountered difficulty when the enzyme proved difficult to purify to homogeneity, so a variety of shot-gun cloning approaches are underway, along with additional effort to purify the enzyme. These approaches involve insertion of random pieces of the isolates' DNA in plasmid vectors and transformation of recipient hosts with subsequent screening of the transformant for acquired denitration activity. In a complementary approach, a *Bacillus* transposon Tn917 was inserted into various random sites in the *Bacillus* chromosome in an attempt to identify the gene through inactivation of the denitration activity. All of these approaches have been complicated by the finding that many potential hosts (e.g., *E. coli, Bacillus subtilis*) have low levels of denitrating activity that makes the screening process difficult. Currently it appears that *E. coli* transformed with *Enterobacter* fragments can be screened for dinitrating activity under carefully controlled conditions (cell mass and age of culture) and that *Streptomyces lividans* is a potential host for *Bacillus* DNA since *S. lividans* does not denitrate NG and is uniformly killed by NG at 820 ppm (therefore, a toxicity screen can be used to supplement the denitration assay). Each of these approaches is being presently pursued. Once the gene is identified it will be sequenced and cloned into a variety of over produced vectors and overproduced in either *E. coli* or *Streptomyces lividans*.

Application Development

Once we have developed a method of over-producing one of the denitrase enzymes from the organisms being investigated, we will continue with the development of applications for the denitrase enzyme. The first step will be to characterize the properties of the enzyme such as stability, rates of reaction, and chemical compatibility. Based on these results we will be able to determine which potential applications of the enzyme should be investigated. Possible applications include: a catalyst for in-situ bioremediation of NG or PGDN contaminated soil; immobilized enzymes for use in treatment of wastewater; a less toxic substitute for skunk juice for equipment decontamination. The enzyme product would be produced in a fermenter or similar vessel. The growth conditions will be manipulated to induce the production of the enzyme. At the point of maximum enzyme production, the enzyme will be separated from the organisms as a cell-free liquid or a product containing lysed (broken) cells. The engineered organism would not be released into the environment.

OTHER BIOTECHNOLOGIES UNDER DEVELOPMENT AT NSWC/IH

Indian Head Division, Naval Surface Warfare Center is pursuing several R&D programs based on biotechnologies. These programs center around the biodegradation of nitrate esters, primarily NG and PGDN. We are presently looking at branching out into other explosive compounds as well as industrial chemicals used in the manufacture of ordnance items. The primary biotechnology programs at Indian Head are listed below:

(1) Anoxic Denitrification of NG and PGDN Wastewater with High Concentrations of Inorganic Nitrate: This program is a 1-year program to pilot then demonstrate at full scale the use of a fluidized bed bioreactor to biodegrade PGDN by anoxic denitrification. This particular waste stream is contaminated with high concentrations of PGDN and inorganic nitrates, carbonates, and sulfates.

(2) Anaerobic Biodegradation of PGDN and NG: The purpose of this project is to pilot a fluidized bed bioreactor for anaerobic treatment of NG and PGDN near saturation in water. A further goal of this program is to demonstrate anaerobic biodegradation of mixed organics in the presence of NG or PGDN.

(3) Aerobic Toxicity and Biodegradability of Ordnance-Related Industrial Chemicals: The purpose of this project is to determine the effect of industrial chemicals used at Indian Head in the activated sludge domestic sewage treatment plant. Further investigation will look at the possible negative effects of mixtures of these chemicals on the sewage plant.

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SOIL PILE BIOREMEDIATION FOR RECYCLING OF PETROLEUM - CONTAMINATED SOIL

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INTRODUCTION

Waste Management Inc. treats non-RCRA petroleum-contaminated soil using a soil pile biotreatment technology termed BioSite®. Initial commercial operation occurred in 1992 at the ELDA Soil Center at the ELDA Recycling and Disposal Facility in Cincinnati. As of May 1, 1995, seven treatment facilities in four states were in operation, with an additional thirty in various stages of the permitting process and fifteen more in early planning stages. Over 500,000 tons of soil had been treated and used beneficially as of January, 1995. Uses for treated soil include daily cover and road construction at the landfill and return to the customer for use as fill material. This paper describes the methods used for construction of the soil piles, operating procedures and key results obtained for soil treatment. An investigation of the use of CO_2 monitoring to track the extent of bioremediation is also described.

PILE CONSTRUCTION

Soil piles are constructed to a predetermined capacity, which can be as much as 60,000 tons. Each pile is constructed within the permitted limits of a composite-lined landfill. The system is completely mobile and can be periodically relocated depending on the sequence of filling within the landfill. Any runoff generated during pile construction and operation is directed toward the landfill's leachate collection system which is subsequently pumped and transported to a waste water treatment facility. Petroleum-contaminated soils are delivered by truck and unloaded at the treatment site. Each pile is constructed in three foot lifts. During construction, a nutrient solution containing nitrogen and phosphorus is added to each lift. The lift is then sprayed with contaminant-specific bacterial cultures in a nutrient solution. The bacterial cultures effectively destroy organics leaving behind harmless byproducts such as CO_2 and H_2O [1,2].

The bacterial cultures are grown on-site in a mobile suspended growth bioreactor. The bioreactor includes a 1500 gallon tank heated to a minimum temperature of 75^0F. The nutrient solution inside the tank is agitated with a mixer to add additional oxygen to the solution. Initially the solution is seeded with microbes until a bacterial culture establishes in the bioreactor. The microbes are fed twice per week with a mixture of diesel fuel, gasoline, a vitamin mixture, nitrogen and phosphorus. The pH of the solution is monitored weekly to ensure that it remains within the range of 6 to 8. If the pH falls below 6, sodium bicarbonate is added to the solution during the weekly feeding until the pH stabilizes within the acceptable range.

Vacuum and pressure piping is alternated and placed at the top of each three foot lift. This procedure continues until the bioremediation pile is constructed to a predetermined capacity, typically 300 ft. long by 100 ft. wide by 18 ft. high. Vacuum is applied to the pile through a framework of perforated piping. Pressure lines for recycled air are also applied to the pile through a separate framework of perforated piping. Air is supplied through the bottom and top of the pile with yet another set of perforated piping. Air flow to each section of piping is controlled by variable position valves. During treatment, contaminants are removed while oxygen is drawn into the pile enabling the aerobic bacteria to degrade contaminants. The piping network is illustrated in Figure 1.

During construction and operation of the BioSite®, the soil pile is covered with an impermeable tarpaulin. The tarpaulin prevents unnecessary air emissions, excessive infiltration due to rainfall, moisture evaporation and loss of passive solar heat [3].

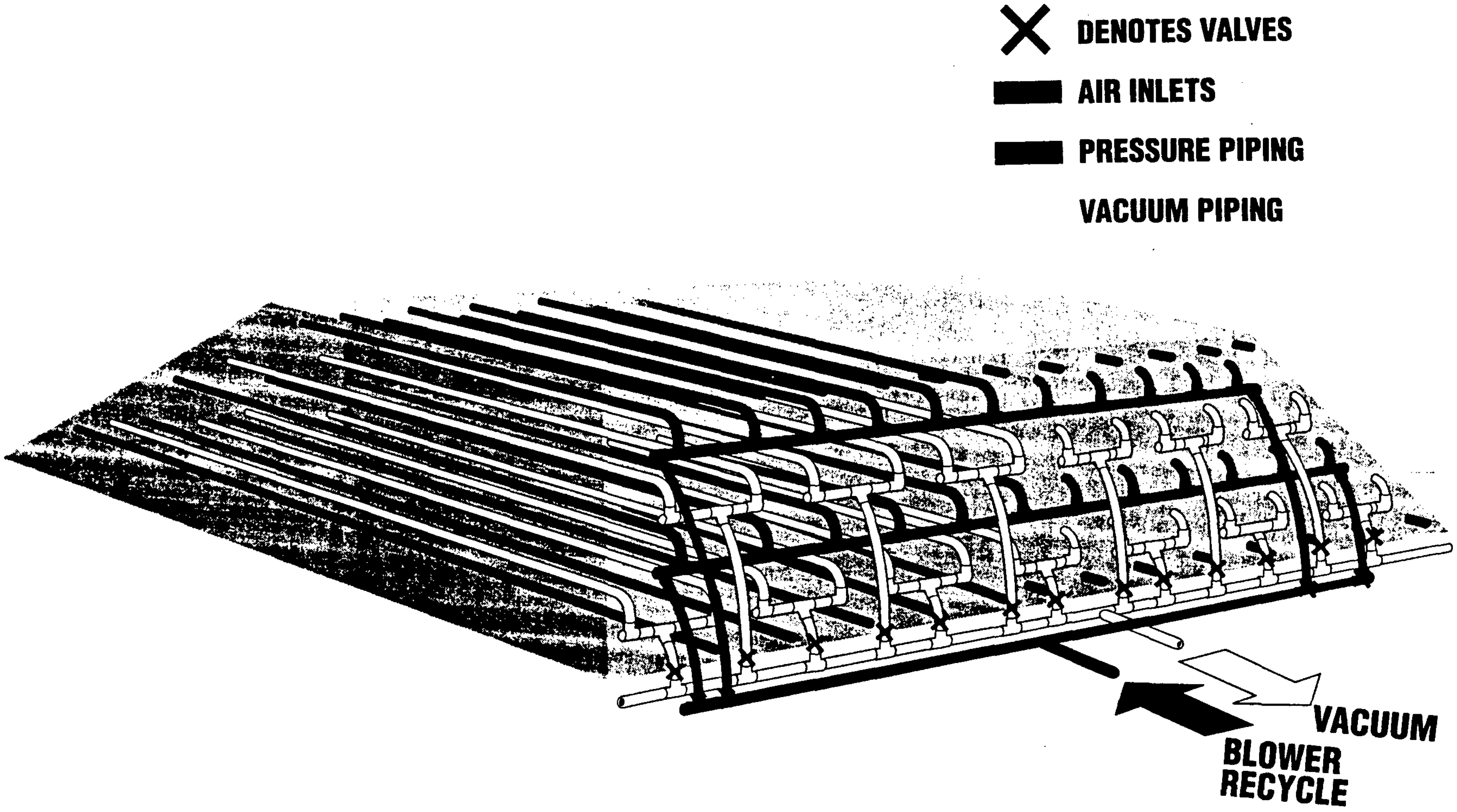


Figure 1
Piping Network

PILE OPERATION

When construction of the soil pile is complete, the piping network is connected to a mobile air emission control system and operation begins. The air emission control system removes potential air emissions and heats the recycled air for winter operation. The emission control system illustrated in Figure 2 includes a knockout drum, a vacuum blower and a carbon canister. When the system is connected and the blower is activated, emissions are monitored and treated.

The blower is used to pull a slight vacuum on the pile through the vacuum framework of piping. This causes air, which is needed for the aerobic biodegradation, to be pulled into the pile through the air inlet lines at the top and bottom of the pile. Exhaust air from the pile is first drawn through a knockout drum which knocks out any condensate accumulated in the piping network. At this point, one of two operating conditions can be used. Under the first operating condition, a portion of the blower exhaust is sent back to the pile for additional treatment and to warm the pile during winter operation. The remaining blower exhaust is sent through vapor phase granular activated carbon prior to discharge. Under the second operating condition, the entire blower exhaust stream is sent back to the pile resulting in no air emissions.

Actual measured air emissions have been extremely low. Table 1 depicts typical air emissions data from the ELDA BioSite®. At the Ridgeview site recently started up in Wisconsin [2] air emissions are monitored using a Foxboro TVA or OVA 128A. Total volatile organic compound (VOC) emissions and methane (CH_4) are measured daily for the first two weeks of pile operation and every three days thereafter at locations "a", "b", and "c" on Figure 2. Total VOCs are measured weekly at the corners and midpoints of the bioremediation pile.

PILE CLOSURE

The pile operates for approximately four to six weeks. At the end of operation the bioremediation pile is randomly sampled to ensure that the soils have reached acceptable levels. When the pile is randomly sampled a grid is established over the pile. Each grid is 15 feet square and represents soil to a six foot depth. A list of random numbers is used to select grids for sampling. The processed soil piles are randomly sampled at a minimum of one sample per 700 cubic yards. The random samples are then tested for the parameters detected and methods employed for the post testing program.

At Ridgeview, which is a typical site, processed soils can be beneficially reused as landfill daily cover, berms, road base and other features which are not located on exterior slopes if the combined diesel range organic (DRO) and

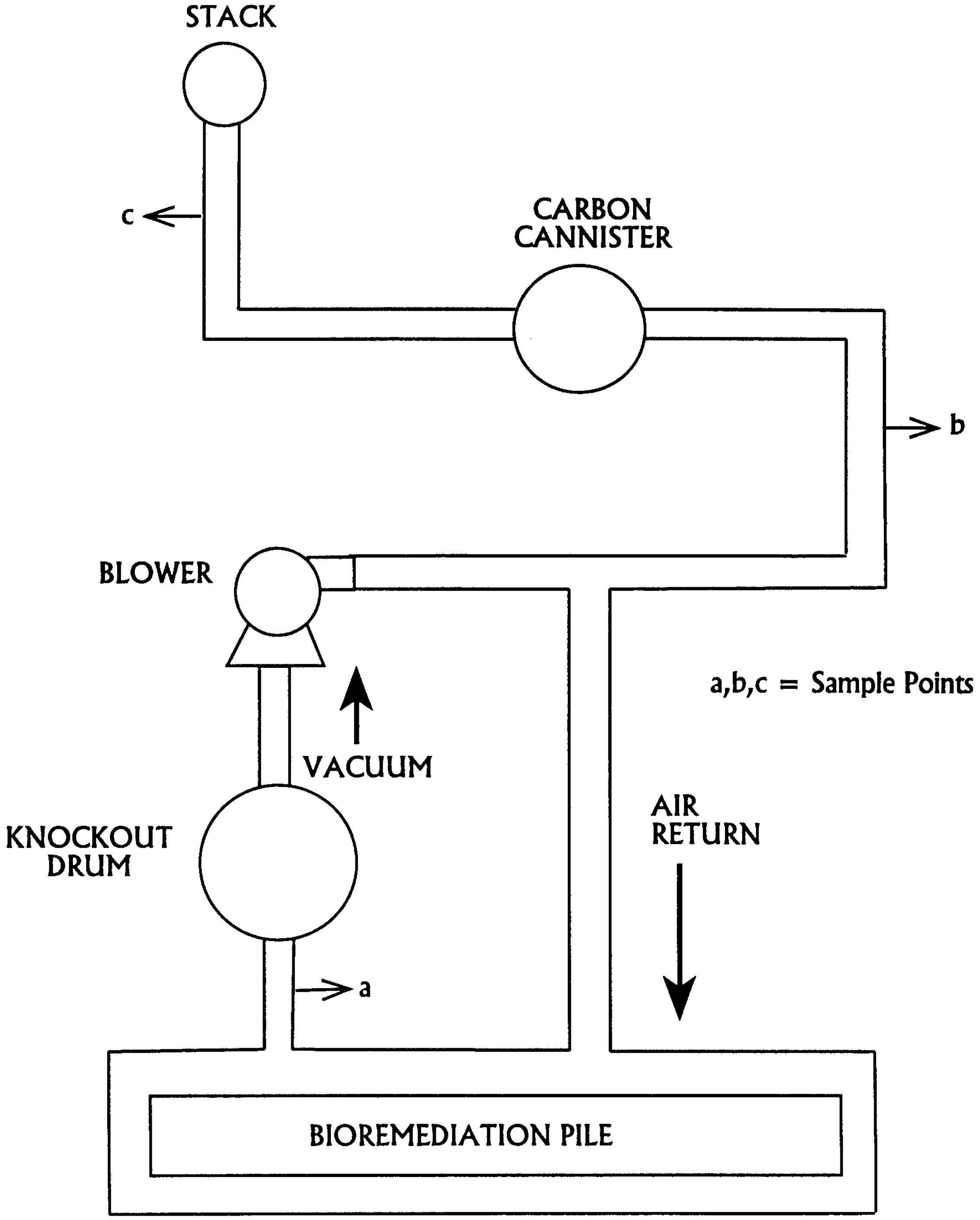


FIGURE 2
Emission Control System

TABLE 1
Stack Emission Measurements - ELDA
w/o use of Return Air Line (Sample Point "c" in Figure 2)

Sampling		Air Flow (dscfm)	Total Load (lb/hr)					
Date	Time		Benzene	Toluene	Ethyl Benzeze	Xylene	CH_4	ΔVOC
10/06/92	0905	223	<0.013	<0.015	<0.017	<0.017	0.021	<0.0033
10/06/92	1422	209	<0.012	<0.014	<0.014	<0.016	0.010	0.0062
10/06/92	1005	223	<0.013	<0.015	<0.017	<0.017	0.010	<0.0033
10/07/92	0435	218	<0.073	<0.014	<0.065	<0.065	0.025	0.0065
10/07/92	0855	223	<0.075	<0.015	<0.067	<0.067	0.0071	0.0067
10/07/92	1240	232	<0.078	<0.015	<0.069	<0.069	0.0078	<0.0035
10/07/92	1710	218	<0.073	<0.014	<0.065	<0.065	0.0057	<0.0033
10/07/92	2000	213	<0.072	<0.014	<0.064	<0.064	0.0048	<0.0032
10/08/92	0000	217	<0.073	<0.014	<0.065	<0.065	0.0024	<0.0032
10/08/92	0411	193	<0.065	<0.013	<0.058	<0.058	0.018	<0.0029
10/08/92	0815	190	<0.064	<0.012	<0.057	<0.057	0.0085	<0.0028
10/08/92	1628	180	<0.061	<0.012	<0.054	<0.054	0.0034	<0.0027
10/09/92	0914	204	<0.069	<0.013	<0.061	<0.061	0.046	<0.0030
10/09/92	2000	185	<0.062	<0.012	<0.055	<0.055	0.013	<0.0028
10/10/92	0900	191	<0.064	<0.012	<0.057	<0.057	0.0068	0.0057
10/10/92	2000	220	<0.074	<0.014	<0.065	<0.065	0.0049	<0.0033
10/11/92	0800	218	<0.073	<0.014	<0.065	<0.065	0.0041	0.0033

gasoline range organic (GRO) concentration is less than 200 ppm. Processed soils can also be reused in exterior slopes of the landfill if the combined DRO and GRO concentration is less than 10 ppm and concentrations of petroleum volatile organic compounds (PVOC) are below detection limits. After the pile is broken down and the soil is beneficially reused, the piping network can be reused for the next pile and the process can begin again.

WINTER OPERATION

To continue operation throughout the winter, the soil temperature needs to be maintained above 45°F. Reduced soil temperatures can increase treatment times by as much as 200% in the winter. Soil temperatures are maintained at an acceptable level in two ways. First, the periphery of the pile is insulated. Secondly, the off gas from the pile exiting the blower is recycled. The blower can generate as much as 50°F temperature increase between the inlet and outlet air stream. Recycling the offgas back to the pile will reuse this heat to maintain the required soil pile temperature. If necessary, an inline heater can also be used on the offgas before it is recycled back to the pile.

RESULTS FROM ELDA SOIL CENTER

Results from the second soil pile treated at the ELDA Soil Center have been well documented[1] and are representative of results to date from various operations. The pile was constructed from 6806 tons of soil. The TPH contents of the soil used to create the pile ranged from 45 to 61,820 ppm and averaged 117 ppm. The range and average concentrations of the BTEX constituents are presented in Table 2. Remediation began on October 6, 1992 and was stopped on November 16, 1992. Sampling conducted for pile closure produced results listed in Table 3. Table 3 also lists the maximum concentrations allowed by the Ohio Environmental Protection Agency (OEPA) for the soil to be considered non-regulated material.

A stack test was conducted in accordance with the OEPA Permit To Install (PTI) for the ELDA Soil Center when remediation began on the second pile. Data were collected on VOC and carbon dioxide (CO_2) emissions from the pile.

Over the 41 days of treatment the TPH content of the soil decreased to an average of 48 ppm, with all BTEX constituents with below the 0.005 ppm detection limits. On a mass balance basis this represents the removal of 15,500 pounds of TPH and 598 pounds of BTEX constituents. The total TPH and BTEX contents of the pile were determined from samples collected at the site where the contamination occurred.

TABLE 2
Range and Average of TPH and BTEX Concentrations of Soil in Second Soil Pile at ELDA

	TPH (ppm)	BENZENE (ppm)	TOLUENE (ppm)	ETHYL BENZENE (ppm)	XYLENE (ppm)
Range	45-61,800	<0.005-4.1	<0.005-37	<0.005-18	<0.005-150
Mean	1187	0.420	8.43	0.548	34.54

TABLE 3
Soil TPH and BTEX Concentrations of Remediated Soil and Criteria Used by Ohio Environmental Protection Agency (OEPA) to Establish Non-Regulated Soil

Parameter	Remediated Soil	OEPA Criteria
TPH	48 ppm	105 ppm
Benzene	<0.005 ppm	.006 ppm
Toluene	<0.005 ppm	4.0 ppm
Ethyl Benzene	<0.005 ppm	6.0 ppm
Xylene	<0.005 ppm	28.0 ppm

VOC emissions into the active vapor phase activated carbon unit were measured daily. The maximum amount of VOCs pulled through the pile was 0.066 pounds/hour. By the third day of treatment the VOCs pulled from the pile had decreased to <0.026 pounds/hour, and VOC emissions averaged <0.020 pounds/hour over the remaining 39 days. The analysis did not distinguish between BTEX- and TPH- related constituents, but the organics volatilized from the soil pile would predominantly be the more volatile BTEX fractions. The total VOC emissions were 15.7 pounds over the 41 day treatment period which accounts for approximately 0.1% of the reduction in TPH and 2.6% of the reduction in BTEX during the remediation process. The above values represent emissions from the pile and not emissions from the stack. Once the gas was passed through the vapor phase activated carbon, VOC emission rates from the stack decreased to <0.005 pounds/hour. The 0.005 pounds/hour represents <0.5% of the maximum emissions allowed by the Ohio Environmental Protection Agency permit for the facility.

MEASUREMENT OF BIOREMEDIATION RATES

In an effort to minimize soil sampling cost by optimizing the sampling events, carbon dioxide (CO_2), oxygen (O_2), and volatile organic compounds (VOCs) have been monitored during the course of operation of three of the facilities (4). One site was in Ohio (Northwood); the other two were in Wisconsin (Milwaukee and Whitelaw). It was anticipated that changes in O_2 use and CO_2 production would predict when soil sampling would be appropriate.

A weighted mean initial concentration of total petroleum hydrocarbons (TPH) for each pile was determined from analytical results submitted by customers during the profiling process. Samples from the Ohio site were analyzed for total petroleum hydrocarbons by EPA methods 418.1 and 8015 modified. Samples from the two Wisconsin sites were analyzed using Wisconsin diesel range organics (DRO) and gasoline range organics (GRO) methods. Soil gas samples were taken from the air distribution piping header connected to the blower. Samples were analyzed for carbon dioxide, volatile organics and non-methane hydrocarbons.

Treatment time required to reach regulatory limits for petroleum hydrocarbons at the three sites ranged from 27 to 56 days. Initial and final petroleum hydrocarbon levels for each site are listed in Table 4. The TPH value listed for the sites in Wisconsin are at the sums of measured DRO and GRO values.

TABLE 4
Biodegradation Rates

	Milwaukee, WI	Whitelaw, WI	Northwood, Oh
Initial Petroleum Hydrocarbons (mg/kg)	1910.0	994.2	4580.6
Final Petroleum Hydrocarbons (mg/kg)	197.0	108.4	65.8
Biodegradation Rate from Soil (mg/kg/d)	38.1	32.8	112.9
Biodegradation Rate from O_2 (mg/kg/d)	8.5	1.9	5.9
Biodegradation Rate from CO_2 (mg/kg/d)	12.5	3.9	7.4
Contaminants	diesel, gasoline, oil	diesel, gasoline	diesel, gasoline, oil

Carbon dioxide production and oxygen utilization for each site showed a decreasing trend, with final rates generally 30% or less of the initial rates (Figure 3). Carbon dioxide production and oxygen use were the highest within the first few days after the start of aeration and then tailed off. The large initial rates may be partially attributed to the accumulation of CO_2 and depletion of O_2 in the pile before aeration.

To relate oxygen utilization and carbon dioxide production to soil hydrocarbon reductions, a stoichiometric relationship for fuel biodegradation is required. Goldsmith and Balderson[5] used the following equation to describe the biological oxidation of diesel fuel:

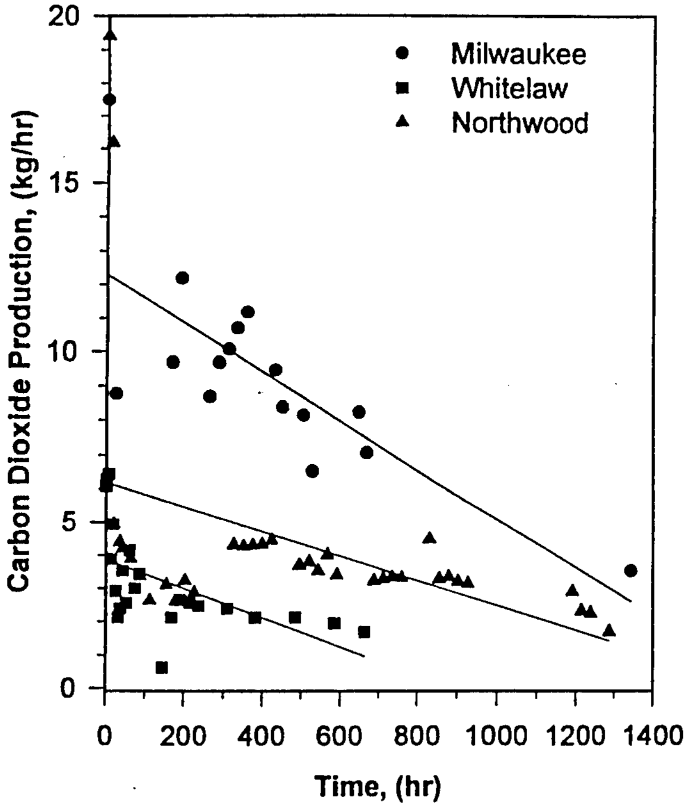
$$C_{13}H_{28} + 8.6\ O_2 + 2.4\ NH_4 \rightarrow 2.4\ C_5H_7O_2N + CO_2 + 10.4\ H_2O$$

$C_{13}H_{28}$ is a weighted average of hydrocarbons in diesel fuel and $C_5H_7O_2N$ represents a typical cell. Assuming that the stoichiometric cell yield is 71% and carbon not incorporated into biomass goes to CO_2, equation 1 becomes:

$$C_{13}H_{28} + 11.23\ O_2 + 1.846\ NH_4 \rightarrow 1.846\ C_5H_7O_2N + 3.77\ CO_2 + 11.231\ H_2O$$

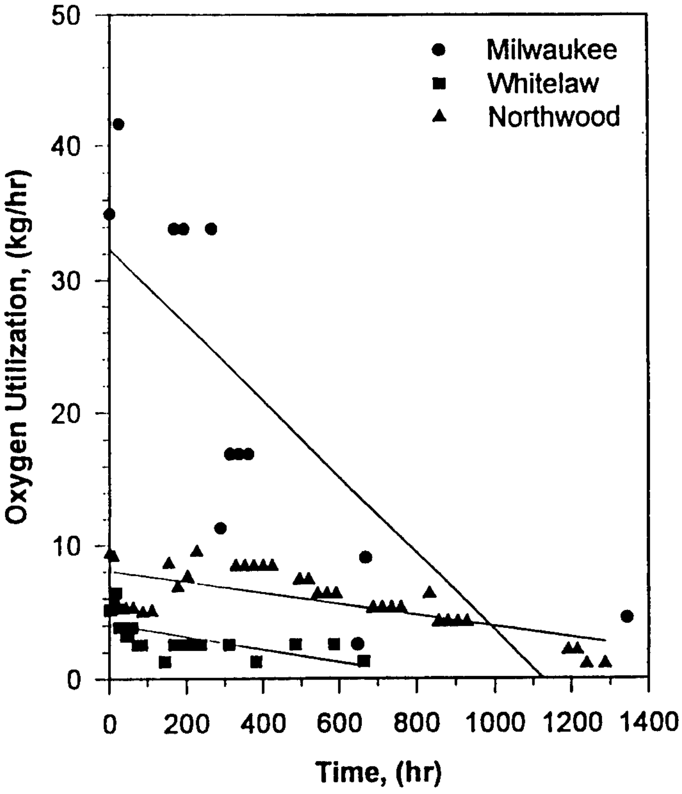
Biodegradation rates calculated using this equation are listed in Table 4. Rates based on petroleum hydrocarbon reductions ranged from 30 to 112mg/kg/day. Larger initial soil concentrations appear to have resulted in higher removal rates. In contrast, rates based on cumulative oxygen use and carbon dioxide production ranged from 1.85 to 10.0mg/kg/day. For each site, estimates based on carbon dioxide production yielded a higher rate than estimates based on oxygen utilization. The discrepancy between rates derived from soil samples and rates derived frm air samples may be attributed to the variability of petroleum hydrocarbon analytical methods and/or the partial degradation of petroleum hydrocarbons or incorporation into soil organic matter as opposed to total mineralization. Third, air flux into and out of the soil pile would reduce the apparent rate of oxygen use and carbon dioxide production. However, results of a helium tracer gas test[4] suggest that this last consideration may not be significant.

The study showed that the removal rate of TPH in three vacuum heaps appeared to be proportional to the initial TPH concentration. Oxygen and carbon dioxide monitoring significantly underestimated the mass of hydrocarbon removal indicated by soil analysis for three soil piles. This suggests O_2 use and CO_2 production may not be suitable surrogates for soil testing. However, oxygen utilization and carbon dioxide production rates decreased by more than 70% from the start of aeration to the time of closure sampling. Therefore,



Carbon Dioxide Production, (kg/hr)
0
5
10
15
20
0
200
400
600
800
1000
1200
1400
Time, (hr)
● Milwaukee
■ Whitelaw
▲ Northwood

Figure 3



Oxygen Utilization, (kg/hr)
0
10
20
30
40
50
0
200
400
600
800
1000
1200
1400
Time, (hr)
● Milwaukee
■ Whitelaw
▲ Northwood

oxygen and carbon dioxide monitoring can be used as a simple and inexpensive way to track treatment progress in aerated soil piles.

EXTENSION TO MORE BIOLOGICALLY REFRACTORY CONTAMINANTS

Efforts are underway to extend the technology to more difficult-to-treat organic contaminants. These include long chain hydrocarbons and polynuclear aromatic hydrocarbons with more than three rings. The approaches which are being explored use chemical pretreatment to convert the compounds of interest to shorter and simpler molecules which are more amenable to biological attack. Initial efforts have shown very promising results.

APPLICABILITY TO ON-SITE REMEDIATION

Where quantities justify, the soil pile biotreatment technique can be used to treat contaminated soil at a remediation site. The only modification required would be to design an aqueous runoff collection system that prevents contamination of soil and groundwater under and near the pile.

COST

Prices to the customer for treatment of soil delivered to the treatment site are typically in the $20-28 range.

CONCLUSIONS

1) Soil pile bioremediation can effectively remediate petroleum-contaminated soils, and the treated soil can be beneficially used within a municipal solid waste landfill or returned to the customer.

2) Aqueous runoff from the treatment system located on a municipal solid waste landfill is effectively captured by the landfill's leachate collection system.

3) The use of naturally occurring, custom adapted microorganisms in an aerobic environment effectively destroys petroleum hydrocarbons. A blower can be used to pull air through the pile, with the bulk of air recirculated to the pile. This is an effective means for controlling temperature, and hence biological activity, in winter months.

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CHARACTERIZATION, TREATMENT, AND DISPOSAL OPTIONS FOR EXPLOSIVES-CONTAMINATED SOIL

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INTRODUCTION

The results of a Remedial Investigation (RI) performed at an ammunition plant located in western Tennessee indicate that explosives compounds are present in soil near the load line sumps, buildings, and drainage ditches. The explosives compounds handled during the industrial operations at this ammunition plant include 2,4,6-trinitrotoluene (2,4,6-TNT), cyclotrimethylene trinitramine (RDX), and N-methyl-N,2,4,6-tetranitroanaline (tetryl) (1). In addition to the primary explosives compounds detected in the soil, the degradation products associated with 2,4,6-TNT, which include 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3-dinitrobenzene (1,3-DNB), nitrobenzene, 2,4-dinitrotoluene (2,4-DNT), and 2,6-dinitrotoluene (2,4-DNT), have also been detected in the soil. Cyclotetramethylene tetranitramine (HMX), an explosives compound and a degradation product of RDX, has also been detected in the soil. Chemical data from the RI indicate that explosives degradation products have been detected at concentrations ranging from non-detectable to a maximum of 5% of the concentration of the primary explosives compounds.

In the past, buildings in which large amounts of explosives compounds were handled were cleaned through the use of a high-pressure water spray. This water was allowed to run out the doors and onto the ground. In addition, industrial wastewater from these buildings has been directed to sumps where the bulk of the explosives compounds settled out. The water from the sumps would continue to flow through ditches and unlined drainageways before discharging to the river. In some cases the sumps may have leaked or overflowed during rain events and the wastewater entered the environment. Through these mechanisms, surface soil in some areas has become contaminated with explosives compounds. Chemical data collected during the RI indicated that the concentration of total explosives compounds decreases at approximately the rate of one order of magnitude for every five feet of depth (1). ICF Kaiser has performed a Feasibility Study (FS) to identify and evaluate applicable remedial technologies for treatment of the contaminated soil.

Two alternatives were developed to remove contaminated soil to below risk-based levels, treat the excavated soil (using thermal or biological processes), and dispose of the treated soil on-site. Selection of the treatment processes was based on the results of previous bench- and field-scale studies as well as full-scale operation at other sites. Under the thermal treatment alternative, the excavated soil would be treated using a mobile rotary kiln incinerator and the decontaminated soil would be backfilled into the original excavations. Under the second alternative, biological treatment, utilizing either composting or a bioslurry, would treat the soil until it passes both the Toxicity Characteristic Leaching Procedure (TCLP) test and the Paint Filter Liquid Test. The biologically-treated soil would be disposed in a solid waste landfill in order to contain the non-biodegradable explosives compounds and biodegradation products which would remain in the soil.

A detailed evaluation of biological treatment was performed using recently-collected data. Windrow composting biotransforms explosives compounds, creating intermediates which are bound to the soil matrix, and therefore, do not readily leach. Tests indicate that leachate from soil treated with composting is less toxic than leachate from untreated soil. Limited information on bioslurry treatment processes indicates toxicity reduction of explosives-contaminated soil occurs in a similar manner to windrow composting.

RISK-BASED REMEDIATION GOAL DEVELOPMENT

Federal and State regulations have not established chemical-specific "applicable" or "relevant and appropriate" requirements (ARARs) for explosives compounds in soil. However, the soil may be considered a hazardous waste if it fails the TCLP test due to high concentrations of nitrobenzene and 2,4-DNT in the soil. Therefore, risk-based remediation goals were developed for the site. The remedial objective for this project was to remove and treat soil which contains explosives compounds above risk-based levels. Soil remediation levels were developed based on both worker exposure to explosives-contaminated soil and the potential for leaching of contaminants to groundwater with subsequent ingestion by hypothetical residents. A simple leaching model was developed to evaluate the concentration of an explosives compound in groundwater that corresponds to a maximum concentration remaining in the soil after remediation. The remediation goals were based on a residual risk level of $1x10^{-5}$ for both worker exposure and hypothetical residential ingestion of groundwater.

Worker exposure was chosen because the future land use of these areas is expected to be industrial. Carcinogenic and non-carcinogenic remediation goals were developed for both 2,4,6-TNT and RDX. Remediation goals for carcinogenic risks were based on a target risk of $1x10^{-5}$ while the remediation goal for non-carcinogenic risks was based on a hazard quotient of one. The remediation goals for worker exposure were 520 mg/kg and 1,022 mg/kg for RDX and 2,4,6-TNT respectively. Parameters used to calculate remediation goals based on worker exposure are presented in Table 1.

Table 1 - Worker Exposure Risk Parameters

Duration	250 days/yr, 25 yrs
Avg. Wt.	70 kg Adult
Ingestion Rate	50 mg/day

Remediation Levels

RDX	520 mg/kg (carcinogenic)
	6,132 mg/kg (noncarcinogenic)
2,4,6-TNT	1,908 mg/kg (carcinogenic)
	1,022 mg/kg (noncarcinogenic)

The maximum concentration of explosives compounds which can remain in the soil after remediation was determined using a leaching model. The concentration remaining in the soil would be such that the risk due to ingestion of groundwater containing explosives compounds would be within the USEPA's target risk range. The leaching model used to estimate the mass flux of explosives compounds entering the groundwater is based on the following assumptions: the soil contained explosives compounds at or below the remediation level; the concentration of explosives compounds in the contaminated soil was based on the average concentration for all contaminated areas; leaching of the contaminants would occur for 30 years; and the groundwater volume was based on the average groundwater velocity and a mixing depth based on the average domestic well depth for the area. Carcinogenic risks were compared to the USEPA's target risk range, while the non-carcinogenic risk was presented as a hazard index. Parameters used to calculate the remediation goals based on groundwater consumption are presented in Table 2. Based on the results of the leaching model, for a residual soil concentration of 10 $\mu g/g$ (separately for 2,4,6-TNT-related compounds and RDX-related compounds), the corresponding downgradient water concentration would be 16 $\mu g/L$, which would pose a carcinogenic risk within the USEPA's target risk range. Although the hazard indices are generally added for non-carcinogenic risks to arrive at a total hazard index, the most sensitive organs for these two compounds are different (liver for 2,4,6-TNT and prostate for RDX); therefore, it was considered to be overly conservative to add the hazard indices.

Table 2 - Groundwater Exposure Risk Parameters

Duration	350 days/yr, 30 yrs
Avg. Wt.	48 kg Young Adult
Ingestion Rate	1.9 L/day

RDX Carcinogenic Risk	$7x10^{-5}$
RDX Hazard Index	0.2
2,4,6-TNT Carcinogenic Risk	$7x10^{-5}$
2,4,6-TNT Hazard Index	1.0

REMEDIATION METHODS

A variety of in-situ and ex-situ on-site treatment methods, as well as off-site treatment methods, are available to remediate explosives-contaminated soil. Treatment methods include thermal, biological, and physical/chemical processes. Based on the estimated 38,000 tons of soil to be remediated at this ammunition plant, two ex-situ treatment technologies were chosen; rotary kiln incineration and biological treatment (windrow composting and bioslurry treatment.) In each case, the soil would be excavated and treated. The incinerated soil would be backfilled into the areas of excavation, whereas the biologically treated soil containing non-biodegradable explosives compounds and biodegradation products would be disposed in a solid waste landfill.

INCINERATION

Incineration has been used in the remediation of explosives-contaminated soil at several Army

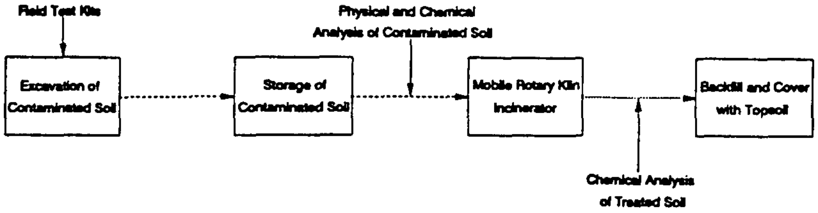

Figure 1 - Process Flow Diagram for the Incineration Alternative

ammunition plants, including Savanna Army Depot Activity (SADA), Savanna, Illinois; Cornhusker Army Ammunition Plant, Grand Island, Nebraska; and Louisiana Army Ammunition Plant (LAAP.) Incineration is underway at Alabama Army Ammunition Plant. In a pilot-scale treatability study performed with soil from SADA and LAAP, the minimum destruction removal efficiency (DRE) for the SADA soil was 99.999% while the DRE for the LAAP soil was 99.979% (2). The primary kiln ash and fly ash, collected from the air quality control system generated during the incineration of the SADA and LAAP soil, did not fail EPA's characteristic tests for ignitability, corrosivity, or reactivity. Furthermore, the metals concentrations were not elevated enough to cause the ash to fail the Extraction Procedure (EP) toxicity test. Therefore, in accordance with 40 CFR Section 261, the kiln ash and fly ash did not exhibit the characteristics of a hazardous waste.

The results of the studies performed at SADA and LAAP indicated that a mobile rotary kiln incinerator was a feasible alternative for treating explosives-contaminated soil at this ammunition plant. A process flow diagram of the incineration alternative proposed to remediate the soil at this ammunition plant is presented in Figure 1. The basic components of the rotary kiln incineration system are the soil feed system, the primary kiln, the secondary combustion chamber, the air quality control system, and the ash removal system. Explosives-contaminated soil and auxiliary fuel would enter the incinerator and be combusted with excess oxygen. The explosives compounds within the soil would be destroyed during incineration. Ash from incineration of the explosives-contaminated soil along with combustion gases, including carbon dioxide and water, would be the end products of incineration. A secondary combustion chamber would be used following incineration to ensure complete combustion of the gases followed by treatment to remove acid gases and particulates. A TCLP test and chemical analysis would be performed on the incinerated soil to confirm that the treated soil is non-hazardous. Concentrations of explosives compounds in the incinerated soil are not expected to be present above analytical detection limits; therefore, the decontaminated soil would be suitable for backfill material. The treated soil would then be placed into the areas where the explosives-contaminated soil was excavated, and covered with a layer of topsoil. The topsoil would be seeded with grasses and other durable vegetation.

BIOLOGICAL TREATMENT

Biological treatment was investigated as a treatment alternative for the excavated explosives-contaminated soil at this ammunition plant. Windrow composting and aerobic bioslurry treatment are expected to reduce the levels of explosives compounds in the soil to below 20 μg/g (separately for 2,4,6-TNT-related compounds and RDX-related compounds.) This treatment goal is based on the effective limit of the biological treatment technologies, as demonstrated in previous pilot-scale studies performed at Umatilla Army Depot Activity (UMDA) and LAAP. Bioremediation is expected to reduce the concentration of nitrobenzene and 2,4-DNT to ensure that the soil would pass the TCLP test; therefore, the soil could be disposed as a solid waste. The soil must also pass the Paint Filter Liquid Test in order to be placed in a solid waste landfill. A groundwater monitoring program would be implemented in conjunction with the solid waste landfill to monitor the integrity of the landfill system.

Windrow Composting

Windrow composting is a static pile method of reducing both the concentration of explosives compounds and the leachable toxicity of explosives-contaminated soil. In the composting system, explosives-contaminated soil is mixed with sources of organic carbon and bulk such as wood chips, straw, and manure. Once mixed, the compost is formed into long static piles called windrows. The windrows are turned over periodically with a windrow turner to provide adequate mixing of the compost. Bench- and field-scale studies using windrow composting have been performed at UMDA and LAAP. Data from these studies were used as a model for the FS for this ammunition plant.

The results of these studies indicate that composting is effective in reducing both the levels of explosives compounds and the toxicity of the explosives-contaminated soil (3;4). Extensive reductions in 2,4,6-TNT, RDX, and HMX were observed during studies performed at LAAP under both mesophilic (35°C) and thermophilic (55°C) conditions. The results of these studies indicated that higher explosives degradation rates occur under thermophilic conditions (3). During compost sampling, it was noted that there were areas of high explosives contamination within the static pile after composting. The reason for the hot spots may have been due to the lack of mixing during the studies. Mixing of the compost is required to achieve maximum reductions in explosives compounds within the compost (3).

Field-scale studies were performed using mechanically agitated in-vessel (MAIV) and static pile composting at UMDA (4) based on the work performed at LAAP. Three amendment configurations selected for the field-scale studies included: sawdust, apple pomace, potato waste, and chicken manure; alfalfa, horse feed, and horse and buffalo manure; and sawdust, apple pomace, potato waste, alfalfa, and cow manure. The soil loading which obtained the highest explosives degradation rate was approximately 30 percent soil by weight (4). Generally, MAIV composting removed a higher percentage of explosives than the static pile. The superior performance of the MAIV tests illustrates the importance of mixing during composting. Another finding in these studies was the importance of amendment composition. The amendment mixture of alfalfa, horse feed, and horse and buffalo manure did not perform as well as the other composting mixtures. Proper selection and combination of amendment materials used in composting is essential to ensure proper explosives removal during composting. In addition to explosives reductions during composting, preliminary toxicity tests performed on compost samples taken throughout the studies indicated a significant reduction in leachable toxicity by the tenth day.

Recently, field studies were performed at UMDA to optimize composting using windrows (5). Windrow composting was selected over other treatment methods because it was the most simplistic composting method in terms of equipment and operation. Compost mixing could be performed using a windrow turner as opposed to the more elaborate mixing system used in MAIV batch reactors. Studies were performed using uncontaminated soil loadings of 10, 20, and 30 percent by volume to determine whether thermophilic composting of soil matrices could be achieved. An amendment mixture of saw dust, wood chips, alfalfa, potato waste, and cow and chicken manure was chosen based on previous composting studies. Parameters such as temperature, pH, moisture content, and the percent oxygen were measured to determine the performance of the composting study. The temperature of the windrows was maintained under thermophilic conditions (between 50°C and 70°C.) Thermophilic composting was achieved in composts with soil loadings up to 30 percent by volume. The pH of the windrow increased over time, which is similar to the results of previous studies (4). An interesting observation of this study was that approximately one hour after turning the windrow, the oxygen level within the windrow fell far below ambient levels of 20.9 percent by volume.

Aeration studies were performed on windrows with 30 percent soil by volume to evaluate the effects of aeration on thermophilic composting. Aeration was performed by placing slotted pipe under the windrow and applying a vacuum to the pipes which pulled air through the windrow. Over the 40-day test, the number of aerobic, anaerobic, and thermophilic bacteria decreased over time in both the aerated and unaerated windrows. Oxygen levels in the aerated windrow were maintained at approximately 15 percent. During the initial 5 days of the test, the aerated windrow overheated due to increased microbial activity but reached approximately the same temperature as the unaerated windrow after 5 days. Studies performed on aerated and unaerated windrows using explosives-contaminated soil indicated that the unaerated windrow had a higher percent removal of HMX as compared to the aerated windrow. 2,4,6-TNT and RDX removals were similar for both studies. The results of these studies also indicated that windrow composting destroys both target explosives compounds and extractable explosives intermediates.

Toxicity and mutagenicity tests were performed on leachate extracted from samples collected over the 40-day compost studies. The extraction method used in this study was the Clean Closure Leaching Test (CCLT) method. Analytical results of the leachate indicate a significant reduction in explosives compounds and degradation intermediates in the compost leachate as presented in Table 3. It should be noted that leachate samples from the unaerated windrow contained lower levels of explosives compounds and intermediates than the aerated windrow. Preliminary results of the toxicity tests indicated complete detoxification by day 15 of windrow composting in both the aerated and unaerated windrows (5).

Table 3 - CCLT Leachate Data for UMDA Windrow Composting Study

Windrow Study	Day	TNT (mg/L)	RDX (mg/L)	HMX (mg/L)	2,6-DNT (mg/L)	2,4-DNT (mg/L)	2-A-4,6-DNT (mg/L)	4-A-2,6-DNT (mg/L)
Aerated Windrow	1	22.4	19.0	6.96	<1.10	<1.10	3.91	8.25
	40	<0.10	0.44	3.32	<0.11	0.19	<0.13	<0.10
Unaerated Windrow	1	26.5	20.2	7.52	<0.10	<1.10	5.41	11.4
	40	<0.10	<0.24	<0.19	<0.11	<0.11	<0.13	<0.10

(Source: USAEC, 1991b)

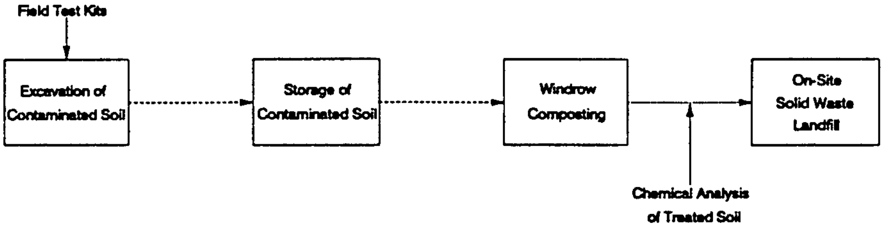

Figure 2 - Process Flow Diagram for the Windrow Composting Alternative

In addition to the studies performed at UMDA and LAAP, studies have been performed at Oak Ridge National Laboratory (ORNL) to investigate the use of composting to remediate explosives-contaminated soil (6). The preliminary results of these studies include several very interesting findings. Studies indicate that the concentrations of aminonitroaromatic intermediates were significantly reduced after 15-40 days of composting. Non-degraded explosives compounds, amino derivatives, azo compounds, carbon dioxide, and other identifiable species accounted for only a small fraction of the original loading of nitrogen compounds, whereas most products were not identified. Solvent extracts of aerated and non-aerated composts indicated a reduction in mutagenicity (as determined by the Ames Test) of greater than 99 percent after 40 days of composting. Weakly acidic extracts showed marked decreases in toxicity (lethality and reproduction effects using *Ceriodaphnia dubia*); most of the initial leachable toxicity was removed after 40 days of composting. A simulated 1000-year acid rain leaching test (modified USEPA Synthetic Precipitation Leaching Test), conducted before and after irradiation of the composted material by ultraviolet light, indicated that less than 10 percent of the 2,4,6-TNT transformation products were leachable. Bacteria isolated from composted materials were shown to effectively degrade 2,4,6-TNT in laboratory tests; most of the transformation products were not identified. The preliminary results also suggested formation of high-molecular weight species of very limited solubility during biotransformation. Additionally, preliminary experiments to evaluate the suitability of composted materials for land application suggested that the soil composts may adversely affect germination of certain plants, but earthworms and isopods both appeared to thrive in the medium.

The results of the studies conducted at UMDA, LAAP, and ORNL indicated that windrow composting is a feasible alternative for treating explosives-contaminated soil at this ammunition plant. A process flow diagram of the windrow composting system proposed to remediate the soil at this ammunition plant is presented in Figure 2. Soil containing explosives compounds above the risk-based remediation level would be excavated, mixed with amendments, and composted for approximately 30 to 45 days. The treated soil would be disposed in a solid waste landfill to contain the non-biodegradable explosives compounds and biodegradation products which would remain in the treated soil.

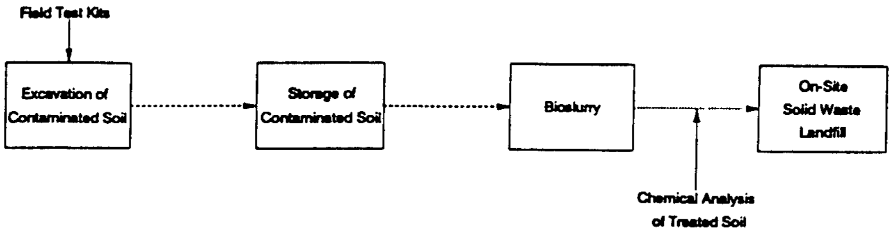

Figure 3 - Process Flow Diagram for the Bioslurry Treatment Alternative

Aerobic Bioslurry

Aerobic bioslurry treatment is an in-vessel method used to reduce the levels of explosives compounds and the leachable toxicity of explosives-contaminated soil by mixing the soil in a slurry of microorganisms, nutrients, and other additives. In the reactor, explosives-contaminated soil is mixed with amendments to aid in explosives degradation. Aerobic bioslurry systems have been used for the remediation of soil contaminated with simple aromatics, PAHs, petroleum hydrocarbons, and pentachlorophenol in bench-, pilot-, and full-scale systems (7). Full-scale treatment systems have demonstrated the capability to handle soil to water ratios as high as 50 percent (wt/wt), although 40 percent (wt/wt) is recommended. Recently, bench-scale studies have been performed to evaluate the biodegradation/biotransformation of explosives compounds in soil collected from the former Hastings Naval Ammunition Depot (NAD) in Nebraska. The data from the studies were used to evaluate bioslurry treatment in the FS for this ammunition plant.

The primary objective of the studies performed at Hastings NAD was to evaluate the feasibility of bioslurry systems for the treatment of explosives-contaminated soil. The first phase of the study involved determining the type of indigenous microorganisms within the soil. The most common microorganism was *pseudomonas aeruginosa*. In this study, the microorganisms were placed in a reactor with radiolabeled 2,4,6-TNT, a 2,4,6-TNT cometabolite (acetate or succinate), and nutrients (ammonia and phosphorus.) The indigenous microorganisms were capable of mineralizing 15 percent of the radiolabeled 2,4,6-TNT into carbon dioxide. Unfortunately, when the study was performed using the exotic microorganisms, no 2,4,6-TNT removal occurred due to ammonia toxicity resulting from excessive nutrient addition.

Several surfactants were evaluated to determine if they could improve the solubilization of explosives compounds from the soil particles into the aqueous phase of the reactors. In addition, further tests were performed to evaluate the effectiveness of the surfactants in extracting explosives compounds by sequential desorption. In this process, the soil was contacted four times with a fresh solution of surfactant. In addition to solubilizing 2,4,6-TNT, a number of transformation products were also solubilized using the sequential desorption technique.

Four bench-scale bioslurry studies were performed evaluating the removal of explosives compounds from soil. The following treatment conditions were evaluated: acetate-amended; acetate- and nutrient-amended; acetate- and surfactant-amended; and acetate-, nutrient-, and surfactant-amended. The results of the studies indicated that both the acetate- and surfactant-amended reactor and the acetate-, surfactant-, and nutrient-amended reactor had the most rapid rate of 2,4,6-TNT degradation and build-up of intermediates. The addition of nutrients to the acetate- and surfactant-amended reactor increased 2,4,6-TNT and intermediate degradation. Low levels of 2,4,6-TNT were detected in both the acetate- and surfactant-amended reactor and the acetate-, surfactant-, and nutrient-amended reactor after 7 weeks and 2,4,6-TNT was not detected in the acetate- and surfactant-amended reactor after 9 weeks (7).

The results of these studies indicated that bioslurry treatment was a feasible alternative for treating explosives-contaminated soil at this ammunition plant. A process flow diagram of the bioslurry treatment system proposed to remediate the soil at this ammunition plant is presented in Figure 3. Soil containing concentrations of explosives compounds above the risk-based remediation level would be excavated, mixed with amendments in the bioslurry reactor, and treated for 30 to 45 days. The treated soil would be disposed in a solid waste landfill to contain the non-biodegradable explosives compounds and biodegradation products which would remain in the treated soil.

Table 4 - Comparison of Costs for Soil Remediation Alternatives

Treatment Alternative*	Costs in 1994 Dollars		
	Capital Cost	Annual O&M Cost	Present Worth (30 yr, 5%)
Incineration	$24,100,000	$40,000	$24,700,000
Windrow Composting	$15,800,000	$44,000	$16,500,000
Bioslurry Treatment	$18,100,000	$44,000	$18,800,000

* Treatment of 38,000 tons of soil.

Summary of Mechanisms Which Affect Biological Treatment Performance

Available data from prior studies strongly suggest that explosives compounds normally act as *electron acceptors* to the microorganisms during biological treatment of soil, and are transformed into reduced intermediate species such as amines or azo compounds in the process. The reaction requires proper conditions of temperature and moisture content, as well as close proximity of three components: a source of energy (electron source) in the form of oxidizable substances that can be metabolized; a sufficient supply of appropriate organisms; and a sufficient supply of the electron acceptor (electron sink) molecules. The presence of essential nutrients such as phosphorus and trace metals is also important. Metabolism results in growth and reproduction of the organisms, formation of metabolic and biotransformation products, and corresponding depletion of the energy source and the electron acceptor materials. This requirement to aggregate separate materials accounts for the observations that thorough mixing is important if biological treatment is to be effective. Mixing may be even more important for treatment of soil containing low concentrations of explosives compounds, because depletion could easily occur on a local scale.

Mixing and aeration also may play an important role in the temperature control that is necessary for optimizing microbial growth rate. However, optimal conditions for the nitro-compounds to participate also require the absence or depletion of more aggressive oxidizers (i.e., materials with a higher oxidation-reduction potential) such as free oxygen and nitrate ions. Moderate to high concentrations of less aggressive oxidizers such as sulfate, iron(III), and manganese(IV) compounds also may compete unfavorably with the nitro-compounds during the composting process.

It is not known whether aerobic processes play a role in the ultimate degradation or fixation of reduced species formed from the nitro- compounds. It is possible that the intermediate degradation products such as aminonitrotoluenes are degraded further or fixed to the soil matrix if a change occurs from anaerobic to aerobic conditions. Although mineralization of the nitro- compounds does not appear to occur readily, aerobic conditions would favor those biotransformations that oxidize the methyl group or ring portions of the explosives compounds.

The probable mechanism for the initial biotransformation of explosives compounds in the soil favors selection of mixing equipment that minimizes the introduction of air. This analysis also favors use of water for temperature control and to encourage mixing or dispersion on the molecular level.

COMPARISON OF WINDROW COMPOSTING AND BIOSLURRY TREATMENT

Biological treatment with subsequent disposal in a solid waste landfill would comply with all State and Federal regulations. The non-biodegradable explosives compounds and degradation products which would remain in the soil would be contained within the solid waste landfill. Windrow composting would be easily implemented because all equipment required for treatment is commercially available and the technology has been implemented at other ammunition plants to remediate soil contaminated with explosives compounds. On the other hand, bioslurry treatment reactors, although commercially available, have only demonstrated successful treatment of soil contaminated with explosives compounds in bench- and pilot-scale studies. Full-scale treatment of soil contaminated with explosives compounds has not been performed; therefore, bioslurry treatment would not be as implementable as windrow composting. Based on a cost comparison (8), windrow composting is more cost effective than bioslurry treatment. A list of capital and operating and maintenance (O&M) costs is presented in Table 4.

COMPARISON OF WINDROW COMPOSTING AND INCINERATION

In comparing the two treatment technologies, incineration completely destroys the explosives compounds within the soil while windrow composting transforms the explosives compounds into biodegradation byproducts. The incinerated soil can be used as backfill as long as it does not exhibit the characteristics of a hazardous waste (i.e., ignitability, corrosivity, reactivity, or leachable toxicity.) Although the biologically treated soil is not expected to exhibit any of the characteristics of a hazardous waste, it contains non-biodegradable explosives compounds and biodegradation products; therefore, the biologically treated soil should be isolated from the outside environment using a solid waste landfill. Although windrow composting requires a solid waste landfill for proper disposal, the treatment cost of windrow composting is much less than that of incineration, making composting the most cost effective option for this site. A list of capital and O&M costs is presented in Table 4.

CONCLUSIONS

The results of the FS performed at this ammunition plant indicate that both workers and groundwater quality would be protected by excavating the soil containing explosives compounds above the risk-based cleanup level of 10 $\mu g/g$ (separately of 2,4,6-TNT related compounds and RDX-related compounds.) Once excavated, the soil would be treated prior to disposal in order to reduce the concentration of explosives compounds and the leachable toxicity of the soil. Biological treatment, specifically windrow composting, would be preferred over incineration because of its reduced cost and public acceptance. Biological treatment is more cost effective than incineration even though the biologically treated soil would be disposed in a solid waste landfill to contain the biotransformed and non-biodegradable explosives compounds which would remain in the soil. Although there is a general understanding of the mechanisms which are involved in explosives biodegradation, additional research should be performed to provide a better understanding of these mechanisms, to identify the biotransformed and non-biodegradable explosives compounds which remain in the soil after biological treatment, and to determine if complete mineralization of explosives compounds is possible.

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INNOVATIVE SOIL TREATMENT FOR METALS CONTAMINATION

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Introduction

Until now, remediation of metals-contaminated soil has been restricted to landfilling the soil or immobilizing it on-site. This limitation has costly long-term impacts for public and private sites around the country contaminated by metals like lead, mercury, and cadmium. The EPA has named lead a top-priority pollutant at Superfund sites.

Instead of relying on traditional approaches, the Twin Cities Army Ammunition Plant, in a risk-sharing arrangement with the Minnesota Pollution Control Agency, selected a pioneering soil treatment technology that combines soil washing with soil leaching. Started in 1993 with completion in the summer of 1995, the project will treat an estimated 15,000 tons of soil to significantly limit human and environmental health threats, long-term liability, and restrictions to real estate. In August 1994, this project was selected for an EPA-sponsored demonstration under their Superfund Innovative Technologies Evaluation (SITE) Program.

The Problem

The Twin Cities Army Ammunition Plant (TCAAP) is a Government-Owned/Contractor-Operated (GOCO) facility built during World War II and operated by Federal Cartridge Company. TCAAP lies at the heart of Minnesota's #1-ranked Superfund site, and is listed 43rd out of approximately 1,200 sites on EPA's National Priority list. Now on Modified Caretaker Status, TCAAP no longer has a mission to produce ammunition, and activities are concentrating on the cleanup and restoration of contaminated soils and groundwater under an estimated $370 million Installation Restoration Program. The 2,400-acre installation lies among densely populated Twin Cities suburbs, and the largely undeveloped land is a wildlife sanctuary targeted for popular nature walks and tours. With eventual redevelopment probable, cleanup is vital.

One of the most contaminated areas at TCAAP is a former open burning area called Site F. From 1942 to 1985, the Army used commonly accepted disposal practices there to burn scrap ammunition and powder. The ash and residue were dumped on the surface, and cartridge casings were buried in trenches.

Over the years, the soil at Site F was contaminated by heavy metals that included lead, antimony, cadmium, chromium, copper, mercury, nickel, and silver. Lead was the most prevalent, averaging 1,600 parts per million (ppm) and reaching 86,000 ppm. Metals contaminated the upper 1-2 feet of soil over 3 acres, and soil to depths of 10 feet in sixteen disposal trenches, totalling 15,000 tons of soil to remediate. In addition, the soil contained extensive amounts of cartridge casings. Groundwater is 120 feet down and was not impacted.

Site F had to be cleaned up to satisfy both a Federal Facility Agreement (under Superfund) between the Army, EPA, and Minnesota Pollution Control Agency, plus TCAAP's permit under the Resource Conservation and Recovery Act (RCRA). The MPCA initially pursued a lead cleanup level of less than 40 ppm (the background level). Negotiation resulted in a cleanup target of 175 ppm for lead, with an enforceable standard of 300 ppm based on the health-based Soil Exposure Guideline set by the Minnesota Department of Health. Other metals are to be reduced to negotiated background levels (see below). These guidelines are challenging--to give perspective, EPA health-based cleanup levels for lead are typically 500 to 1,000 ppm.

TCAAP Site F Cleanup Levels (ppm)

Antimony	4
Cadmium	4
Chromium	100
Copper	80
Lead	300
Mercury	0.3
Nickel	45
Silver	5

The Alternatives

The main dilemma concerning Site F was that no methods had been established to *remove* metals from soil. There have been three traditional options:

1. Cap the site so that rainwater does not leach contaminants to greater depths
2. Immobilize contaminants by injecting a binding material such as cement into the soil
3. Excavate the soil for disposal in a landfill

Contamination would remain on-site with capping and immobilization, which would severely limit site reuse, require long-term monitoring, and interfere with the Army's plans to eventually transfer or redevelop the land. Although excavating the soil for landfilling would clean the site and avoid restrictions to site reuse, the contaminants themselves would still not be destroyed or reclaimed. A major area of liability is contamination from hazardous materials after landfilling, so disposing of the Site F soils would sustain the Army's long-term liability.

With residential neighborhoods not far from a site contaminated by an EPA priority pollutant, both the Army and regulators wanted a better solution, and the Army was particularly interested in achieving "clean closure" of the site.

In response, TCAAP selected an untried technology called "soil washing/soil leaching." Soil washing reduces the volume of contaminated material by removing larger clean soil fractions, but much of the soil still requires landfilling because the metals content remains high in smaller soil particles. The addition of soil leaching solves this problem by dissolving the smaller metallic particles and ionic metals that otherwise remain bound to the soil. The recovered metals are recycled at a smelter, thereby eliminating their long-term risk. Ideally, the only outputs from soil washing/soil leaching are:

- Treated soil for return to the site
- Recovered metals for off-site recycling
- Ordnance drummed for proper disposal
- Neutralized leachant and process water sent to the sanitary sewer

Bench-scale testing confirmed that the Site F soil (mainly silty sand) would be amenable to treatment, but that soil washing alone would not remove enough metals. Leachant contact times were evaluated, including the impact of prior soil washing processes. The testing generated the optimum combination of soil washing (including density separation of lead particles) and soil leaching (the type of leachant and its contact time with the soil). The washing and leaching processes were then integrated into one treatment operation.

Based on these results, we proceeded with final design and implementation. The treatment project was a collaborative effort among:

- The U.S. Army
- TCAAP operating contractor Federal Cartridge Company
- The environmental engineering consulting firm of Wenck Associates, Inc.
- The California vendor COGNIS for soil leaching
- The Alaskan vendor Bescorp for excavation and soil washing

Soil Washing

Soil washing comes from the mining industry, mainly as a sorting technique. Some cleanup projects have adopted soil washing to reduce the volume of soil that must be landfilled because the larger, clean soil particles can be segregated from the more heavily contaminated fines. Soil washing can also remove larger, loose metallic fragments, especially when they are sand-size or greater. Soil washing as a remediation technique has been practiced in the Netherlands and Germany for nearly 10 years. In the U.S., Bescorp of Fairbanks, Alaska, recently used soil washing in the EPA-sponsored SITE Demonstration Program at an Alaska battery site. Bescorp is the contractor selected for the Site F project.

At Site F, the soil is excavated, stockpiled, and fed into a hopper to accommodate a processing rate of 6 to 15 tons per hour. The soil first goes through a trommel which breaks up soil clumps and screens out material greater than 1/4-inch in diameter for a high-pressure water rinse. From there, oversize material is sent to a conveyor where inspectors remove ordnance materials for storage and disposal; the rinsed stones and gravel are tested and returned to the site.

From the trommel, materials smaller than 1/4-inch in diameter are sent on to a chamber that separates the sand from the fine silts and clays. From there, the sand runs separately through a spiral classifier and a mining industry "jig" for removal of heavy metallic fragments by density separation. The recovered metals are dewatered and stored in drums for recycling while the sand is then sent on for chemical soil leaching.

The fines fraction contains most of the contamination that remains after soil washing, which consists of metallic-form metals smaller than sand-size and ionic metals bound to the fines. Therefore, the fines fraction is sent on from the separation chamber through its own series of clarifiers for soil leaching as well.

Soil Leaching

Soil leaching uses chemical processes to remove the metals remaining in the sand and the fine silts and clays. The physical and chemical properties of sand and fines differ so that they require different equipment to mix and convey each stream; therefore, the sand and fines are leached in separate, parallel circuits.

In each of the two treatment circuits, the soil undergoes an acid wash that dissolves fine metallic fragments and ionic metals into a solution. This occurs in a series of mixers and clarifiers where the leachant flows against the incoming soil current; the leachant is progressively stronger as the soil proceeds through the series.

The clean sand and fines are dewatered, neutralized, tested, and added to the clean oversize material for ultimate return to the site. The metals-containing leachant is sent to a recovery unit where the leachant flows through an electrochemical reduction system so that the metals precipitate out into a cake. The leachant itself is then recycled internally.

The soil leaching portion of the project is a proprietary process called Terramet™ that was developed by COGNIS.

Metals Reclamation

Metals reclamation is accomplished by collecting discrete metal particles from the physical soil washing process, as well as the precipitated metal from the chemical soil leaching process. The metals are drummed and shipped via a licensed hazardous waste transporter to a smelter in Minnesota. Metals reclamation removes the metals from the hazardous material cycle, thereby eliminating long-term liability and allows for future beneficial use of the metal.

Implementation

Beginning in Summer 1993, the site was cleared by burning the vegetation and removing trees, small buildings, and underground utilities; all materials were decontaminated before leaving the site. With much of the contamination in surficial soils, excavation proceeded in 6-inch layers. Sixteen disposal trenches approximately 10 feet deep were also addressed. The extent of excavation was directed using X-ray fluorescence analysis that detects metals while in the field, with confirmation in the laboratory. This greater precision in defining excavation limits helped to contain soil treatment cost while ensuring contaminant removal.

Since a nearby concrete pad had already been constructed for a PCB soil incineration project (1989), the equipment was set up there and the soil transported the short distance in covered trucks. Six flatbed trucks brought the treatment equipment on-site where both the soil washing and soil leaching processes were integrated into one operation.

Start-up began in September 1993. We were able to bypass pilot testing since the bench-scale studies had provided such convincing results; instead, the MPCA required simply an acceptance period consisting of the first six days of treatment. Start-up was successful, and full-scale treatment proceeded to treat 60 to 120 tons of soil daily, six days a week. After shutdown for the winter months, treatment resumed from May through October 1994, began again in May 1995, and is expected to be completed in July 1995. At that point the equipment will be decontaminated and removed, and remaining process water and leachant will be neutralized and sent to the sanitary sewer. Throughout the project, treated soil is dewatered, neutralized, and laboratory tested before return to the site, and the site will eventually be graded, covered with topsoil, and revegetated with prairie grasses.

Conclusions

The project has generally been successful, but in contrast to the ideal situation where all soil can be returned to the site, it will be necessary to landfill some soil that could not be treated to the project cleanup goals.

The COGNIS/Bescorp process works best for lead removal, which is the primary contaminant at Site F. By project completion, approximately 95% of the soil is expected to pass the enforceable lead standard of 300 ppm.

However, this process is less effective for the other metals of concern (especially copper and mercury), either because they are more difficult to leach or more difficult to recover from the leachant. These results suggest that the treatment technology has difficulty achieving stringent *background-based* cleanup goals for these metals, but would be more successful for cleanup levels based on *health risk*. As an example, 95% of the treated soil that failed the copper and/or mercury background-based goals would pass typical health-risk-based cleanup goals that are 10 to 100 times higher. TCAAP is currently attempting to renegotiate cleanup goals for metals since disposing of soil that poses little or no risk to human health and the environment is a questionable use of economic resources and limited landfill space.

We are hopeful that most of the soils can be returned to the site, thereby minimizing landfilling while providing unrestricted future land use. However, we face continuing challenges related to the Site F disposal trenches, which contain higher contaminant concentrations and greater clay content.

Also of note is that the processing rate has not been as high as expected, with a typical rate of 6 to 12 tons per hour compared to the design rate of 20 tons per hour. The moisture content of the treated soil, especially the fines, was a problem at first, but the addition of a centrifuge for dewatering was sufficient.

As with any new technology, it is inevitable that there will be improvements to the process in the years ahead, but we believe great progress has been made thus far. It is a big accomplishment to *treat* metals-contaminated soil rather than landfilling, with removal of metals from the waste stream for recycling and beneficial use. With metals-contaminated sites throughout the country, this project is a vital demonstration of the emerging treatment technology of soil washing/soil leaching.

APPLICATION OF THE TECHXTRACT™ PROCESS FOR EFFECTIVE DECONTAMINATION, WASTE MINIMIZATION, AND FACILITY REUSE

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INTRODUCTION

A substantial need exists for innovative, effective, and economical decontamination technologies which can be applied to contaminated buildings, equipment and other structures. Decontamination and decommissioning (D&D) programs in the U.S. Department of Energy (DOE), nuclear utility industry, and international markets are growing rapidly. Within the Department of Defense (DOD), Installation Restoration (IR) and Base Realignment and Closure (BRAC) are becoming major programmatic drivers for D&D activities. With this growth, the acceptability and costs of traditional D&D approaches, which rely largely on demolition and disposal, are being increasingly called into question. Disposal is a high cost option which often has low public acceptance. Furthermore, tight construction budgets and economic redevelopment goals encourage reuse of facilities whenever possible.

Thus, the stage is set for innovative technologies which can decontaminate structures and equipment to below regulatory levels, thereby avoiding large-scale bulk disposal. Such technologies must be effective in the removal of a variety of contaminants from different types of materials and substrates. They must also offer total economics - considering process costs, disposal, reuse, future liabilities, and other factors - which are attractive versus demolition and disposal.

The TECHXTRACT™ process is a chemical technology for the extraction of PCBs heavy metals, hazardous organics, and radionuclides from solid materials such as concrete and metal. TECHXTRACT™ uses specifically designed chemical formulas to penetrate below the surface and remove contaminants which have leached into the substrate. The technology has very high decontamination rates (e.g., 90-99% per cycle) and has been effective in cases where contaminants are as much as 1 to 3 inches below the surface. In addition to decontamination performance, economic analysis indicates that TECHXTRACT™ can save 25-75% of total project cost versus traditional methods. TECHXTRACT™ is a full-scale, commercialized technology which has been used in the DOD, DOE, electric utility, and private industry. This paper discusses the TECHXTRACT™ process in more detail and presents several actual applications within the DOD.

DECONTAMINATION TECHNOLOGIES: CURRENT PRACTICES AND NEEDS

Decontamination is one of the fastest growing segments of the environmental industry. BRAC, the Federal Facilities Compliance Act (FFCA), and the change in mission for the DOE are all significant drivers. Initial investigations of these contaminated facilities have shown that problems are widespread and quite significant.

The clean-up challenge is exacerbated by several additional factors. First, regulatorily required clean-up levels are typically very low due to the health risks associated with contaminants such as radionuclides, PCBs, and heavy metals. For example, the PCB clean-up standard is 10 micrograms (μg) per 100 cm^2. For radioactive contamination, readings below 5000 dpm per 100 cm^2 (total) or lower are typically required. Standards are often not even defined for other contaminants in buildings and structures. Furthermore, contaminants tend to become electrostatically bonded to the substrate material. Successful removal, therefore, requires some type of reaction to break these bonds.

In the best circumstances, this clean-up is difficult to achieve, but the passage of time complicates the problem. Over the years, contaminants will migrate deeper into the substrate through the pores in any material. This migration occurs naturally (due to gravity and specific gravity differentials), with water from routine cleaning, or with pressure. The depth to which this migration will occur is dependent on many factors, including the porosity of the material, the mobility and solubility of the contaminants, the presence of coatings, and the existence of other drivers. Migration of one-half inch or more is common, and can exceed four inches in some cases. Since many of the issues now being addressed are the result of incidents which occurred twenty or more years ago, deep penetration of contaminants is a widespread concern.

Despite these challenges, most current decontamination techniques lack the sophistication needed in this market. Standard approaches include physical (destructive) methods and chemical cleaning with surfactants, solvents, or acids. Physical mechanisms can be effective if the contamination is not deep and if damage to the surface is allowable. Their primary limitations are the large volume of waste that is generated, the risk for workers (primarily from airborne contaminants) during the clean-up, potential need to shut down plant operations, and ongoing liability for landfill disposal. Destructive methods can also be very expensive in cases of deep contamination, especially for radionuclides, due to the high cost of disposal. Off-the-shelf chemicals address surface contamination, but are usually ineffective when subsurface migration has occurred. In addition, many of these solutions (i.e., strong acids, solvents) pose significant health and safety risks for remediation workers.

Many projects where significant contamination is encountered end in one of two ways. Either the owner appeals to the EPA and other environmental authorities for a variance due to their inability to meet regulatory clean-up standards. Or total demolition is selected as the "only known technology" for solving the problem. The TECHXTRACT™ technology from EET is one solution to bridge the gap between current problems and ultimate clean-up.

DESCRIPTION OF THE TECHXTRACT™ TECHNOLOGY

The TECHXTRACT™ technology is a sequential chemical extraction process for the removal of PCBs, other hazardous organic and inorganic substances, and radionuclides from solid materials such as concrete, brick, and steel. The technology uses advanced chemical formulations and carefully engineered applications to achieve significant penetration and removal of these contaminants from below the surface of these materials.

The TECHXTRACT™ chemistry is based on several hypotheses relating to contaminant migration and removal. The first hypothesis is that contaminants migrate into the pores and microscopic voids of a material, even for seemingly non-porous media. Mobility of the contaminants, time, and secondary forces often drive these contaminants to deeper levels in the substrate. Furthermore, the contaminants tend to become chemically or electrostatically bonded to the substrate. In many cases, the time between the contamination event and decontamination efforts will allow the contaminant migration pathways to become partially closed.

All of these factors point to the need for a sophisticated chemical system which:

- Reopens the pores and capillary pathways to the maximum possible extent,
- Penetrates into the pores as deeply as possible,
- Breaks the substrate and contaminant bonds which may be holding the contaminants in place,
- And binds or encapsulates the contaminants to prevent recontamination.

The TECHXTRACT™ chemical formulas are designed to address each of these complex needs, using components which incorporate dissolution, oxidation, reduction, hydrolysis, wetting, complexation, microencapsulation, and flotation chemistry principles. The chemistry further compensates for situations in which the contamination is a mixture of pure elements, oxides, and related compounds with varying solubility indices. The spent chemical solutions do not contain any TCLP constituents (except for extracted contaminants) and have been disposed of by incineration, solidification (and land disposal), and discharge to liquid effluent treatment systems.

The TECHXTRACT™ process is a tailored sequence for applying and removing each of the chemicals. In most projects, three different chemical formulas are used. Chemicals are applied in low volumes, usually as a spray, to minimize consumption and secondary waste volume. After being applied, the chemicals are scrubbed into the contaminated surfaces, left to dwell for a defined time, and rinsed and removed. The application and removal of all three formulas constitutes one cycle of the TECHXTRACT™ process, and typically requires one day

(24 hours). Sampling and/or surveys can be performed at the end of any cycle, and often shows reductions of 90% or more per cycle.

The TECHXTRACT™ process has been found to be most applicable in remediation or decontamination projects when one or more of the following conditions apply:

- The acceptable level for any residual contaminant is very low.
- Simple surface cleaning is ineffective, due to the leaching of subsurface contaminants back to the surface,
- The removal and disposal of the entire contaminated surface (and subsurface) is undesirable, either because the volume and resulting disposal and replacement costs are too high or due to waste minimization objectives,
- Significant safety concerns - such as flammability, corrosivity, creation of airborne contaminant particles, fugitive emissions or generation of toxic fumes and/or explosive gases - are raised,
- Decontamination is to be performed on surfaces that are not flat and horizontal, such as equipment, walls, ceilings, structural beams, and internal piping,
- If very low residual contaminant levels are achieved, substantial economic benefits can be realized (i.e., resale of equipment, reclassification as nonhazardous, avoidance of disposal as hazardous, LLRW, or transuranic waste),
- All other options have failed to achieve the desired objectives.

DOD APPLICATIONS FOR TECHXTRACT™

Case History - Defense Construction Supply Center: TECHXTRACT™ has been used on several DOD remediation projects. One case which shows the capabilities and benefits of the technology was the PCB decontamination of a pit at the Defense Construction Supply Center (operated by McDonnell Douglas) in Columbus, Ohio. The pit was concrete construction and had housed the base of a piece of heavy machinery which had been used in the facility's manufacturing operation. The surface cross section of the pit was 10 ft by 10 ft, and the depth was 12 ft. As is the case with many older manufacturing plants, PCB-based oil had been used in the process and had contaminated the concrete. Even though this was considered an "old spill" under the EPA's PCB spill policy (40 CFR 761, Subpart G), it had been identified as a priority clean-up project. RMT, the site's prime environmental contractor, was charged with developing and implementing a solution for this project.

Initial PCB levels, as measured by standard surface wipes, were as high as 7,300 μg/100 cm^2. A prior contractor had used typical surfactant or solvent cleaning methods to reduce the PCBs to 2,270 μg/100 cm^2, but had been unable to achieve further reductions. Since this was well above the clean-up criteria of 10 μg/100 cm^2, RMT began looking for another solution.

Because the project had a tight completion deadline, RMT determined that the contaminated concrete wall, column and floor of the pit would be removed (demolished) if the clean-up standard could not be met by the end of August, 1994.

On August 11, 1994, EET provided a proposal to Chemical Waste Management, RMT's subcontractor, to complete the PCB decontamination of the pit. This proposal was accepted the next day, and EET had a two-person crew on-site to begin work on August 15, 1994. Personnel applied the TECHXTRACT™ chemicals using the process as described above. Except for one section of the floor, all sample locations were reduced to less than 10 μg/100 cm^2 in less than one week. The final locations were reduced to below the 10 μg standard on August 24, 1994, and EET's crew demobilized.

The project was successfully completed at a much lower cost than the planned "last resort" method of demolition and disposal. EET's customers were all satisfied with the performance of the TECHXTRACT™ technology and with the ability to meet the project deadline. The technology is being considered for future work at the site as dictated by clean-up needs.

Other Applications: The TECHXTRACT™ process has also been used (or is scheduled for use) on several other DOE demonstration or clean-up projects. These illustrate some of the other applications and benefits of an effective, non-destructive decontamination technology.

Rocky Mountain Arsenal - Demonstration for heavy metal and pesticide extraction from abandoned building foundations. The final report for this project is not complete, but initial results indicate significant reductions. Technical success and regulatory acceptance could result in much lower disposal costs as the buildings on the site are torn down.

Naval Air Station North Island (NASNI) - Demonstration and remediation under the Navy Environmental Leadership Program (NELP). This is an innovative technology contract, awarded through Naval Facilities Engineering Command (NAVFAC), Southwest Division. The initial application under this contract is the decontamination of a former plating shop (heavy metals and solvents) for conversion into storage or office space. A second application for oil stain removal on the flight line is also scheduled.

Ft. Hood - Successful clean-up project to achieve regulatory compliance for a PCB-contaminated bunker where transformers had been stored.

Puget Sound Naval Shipyard - Planned demonstration for decontamination of radioactive spill areas on board nuclear vessels, to assess potential cost and performance improvements versus baseline methods.

Y-12 Plant, Oak Ridge, Tennessee - This DOE-owned facility is operated by Martin Marietta Energy Systems and manufactures components for various nuclear and non-nuclear weapon systems. A major PCB decontamination project using the TECHXTRACT™ process was performed at this plant to achieve regulatory compliance and to allow a critical construction and manufacturing project to proceed.

CONCLUSIONS

The power of the TECHXTRACT™ process is its ability to penetrate into the substrate through the pores in the material so that PCBs, heavy metals, radionuclides and other contaminants can be pulled into and held in solution and ultimately extracted. This technology offers significant benefits in reuse of previously contaminated buildings and equipment, waste reduction, and avoided disposal costs. As such, it has a variety of high benefit applications within the DOD and other restoration markets.

TWO-STAGE BIOREACTOR TO DESTROY CHLORINATED AND NONCHLORINATED ORGANIC GROUNDWATER CONTAMINANTS

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ABSTRACT

Both chlorinated and nonchlorinated volatile organic compounds are found as common contaminants of groundwater across the nation. Two field-pilot bioreactors successfully treated contaminated groundwater at Robins Air Force Base (AFB). The ENVIROGEN fluidized bed bioreactor (FBR) effectively removed >97% of the 1,2-dichlorobenzene (DCB) and >95% of the benzene, toluene, xylene(s), and ethylbenzene (BTEX) from over 210,000 gal of contaminated groundwater. The ENVIROGEN FBR removed 84% of the TCE, also found in this groundwater, based on a total mass balance beyond carbon adsorption. Enhanced operational stability was demonstrated for the ENVIROGEN gas phase reactor (GPR) with 10 months of continuous operation in the laboratory and 2 months in the field. TCE concentrations in contaminated air entering the pilot GPR were reduced by 75% on average. Capital and operating costs for the ENVIROGEN FBR system were compared to other treatment options including UV-peroxidation, air stripping with carbon adsorption, and wet carbon adsorption. GPR economics were compared to carbon adsorption at two TCE concentrations. These bioreactor systems provide economical, destructive technologies for treating either contaminated water or contaminated air originating from air stripping, air sparging, or soil vapor extraction operations and will be effective remedial options at many sites.

INTRODUCTION

Through a combination of accidental discharges and previously accepted disposal practices, chemical contaminants have been introduced to soils and surface water at sites across the United States. Benzene, a constituent of jet aviation fuel, is one contaminant commonly found at defense sites. Benzene and related aromatic hydrocarbons tend to be readily biodegradable. TCE is one of the most prevalent organic chemical contaminants found in soil and groundwater. At many sites, these and other chemicals threaten groundwater supplies.

TCE contamination is aggravated by its relatively high solubility, high density, and recalcitrance. Characterization of anaerobic and aerobic biotransformation of TCE and related volatile organic compounds (VOCs) has been ongoing for more than a decade.[1] Under anoxic conditions, TCE undergoes reductive dehalogenation to dichloroethylene, vinyl chloride, and finally to ethylene. Under aerobic conditions, a broad variety of microorganisms cometabolize TCE following growth with methane, propane, ammonia, phenol, or toluene. Though these bacteria apparently cannot grow with, or derive energy from, the transformation of TCE, they can oxidize it to innocuous products. TCE represents a class of recalcitrant chemicals that often require a unique set of conditions for biodegradation to occur.

A variety of bioreactor configurations has been studied to establish feasibility and to overcome limitations associated with cometabolic degradation of TCE and related VOCs.[2,3,4,5] Envirogen has developed a GPR system for destroying TCE, overcoming a variety microbial and engineering limitations. Both laboratory-scale and pilot-scale systems were designed to balance the mass transfer of TCE from air to water with biodegradative capacity.

The major objective of this project was to demonstrate the efficacy of a bioreactor system for treating groundwater contaminated with hydrocarbon-based fuels and solvents commonly found at Air Force installations. Initial screening experiments demonstrated that (1) TCE-degradative microorganisms were not capable of degrading benzene unless they had been induced following growth with toluene and/or phenol, (2) TCE did not inhibit benzene degradation over the range of concentrations tested and, (3) benzene-degradative organisms did not degrade TCE (Folsom 1993). The number of chemicals to be treated during the field demonstration was expanded to include benzene, toluene, ethylbenzene, xylenes (BTEX), and dichlorobenzenes (DCB), and TCE.[6]

METHODOLOGY

The base industrial area (OT20 site) at Robins AFB was selected as the demonstration site. The test site was next to a fuel tank storage facility and the base industrial area. Principal contaminants in the groundwater included benzene (46 µg/L), TCE (1,445 µg/L), toluene (40 µg/L), ethylbenzene (23 µg/L), xylene(s) (50 µg/L), and dichlorobenzene(s) (2,014 µg/L), primarily the 1,2-DCB isomer, though all isomers were present.

The laboratory-scale FBR systems was constructed of glass with Teflon® tubing and polypropylene fittings and had a total liquid volume of 4 liters and an empty bed volume of 800 mL. Contaminated water was fed at 15 to 20 mL/min which resulted in an empty bed hydraulic retention time (HRT) of approximately 40 to 50 minutes. Dissolved oxygen (DO) levels were maintained above 2 ppm, pH was automatically controlled between 6.8 and 7.0, and temperature was maintained between 22 and 30°C. Liquid samples were analyzed using GC/FID purge and trap methods.

The laboratory GPR system, liquid volume of 2 liters, was constructed from glass, Teflon® and stainless steel. A proprietary nutrients mixture was added at a rate of about 0.7 mL/min which gave a hydraulic retention time of about 10 days. Liquid pH was automatically controlled between 6.8 and 7.0 and temperature was maintained at 28°C. Air contaminated with TCE entered through a 1/8-inch tube at the bottom of the vessel and exited after passing through the liquid column with suspended bacteria. An automated gas sampling system was connected to both inlet and outlet gas streams and TCE concentrations were monitored by an automated GC/ECD.

The field pilot Fluidized-Bed Reactor system was constructed of stainless steel, had approximate dimensions of 12.5-feet long by 5.5-feet wide by 15-feet high, with an empty bed volume of about 66 gallons. All process controls and equipment are weatherproof, and used a computer control and data logging system. DO levels were maintained above 2 ppm and pH was maintained between 6.8 and 7.0. Approximately 210 pounds of GAC was used as the bed support. Bed height level was monitored and logged. The system was operated with a 2 gpm feed flow with a 4.5 gpm upflow through the reactor yielding a 25% bed expansion. An automated purge and trap GC system was used to automatically monitor feed and effluent water streams.

A stirred-tank field-pilot Gas-Phase Reactor system had approximate dimensions of 8-feet long by 8-feet wide by 11-feet high and held approximately 750 gallons of liquid. System pH was automatically controlled and water temperature was controlled at 88°F and operated with a hydraulic retention time of about 10 days. . Average air flow to the reactor was 7 cfm with contamination levels in feed and effluent air streams automatically monitored using a GC/ECD system.

Standard methods for water analysis were used to monitor a variety of operating parameters including, pH, biomass density, and nutrient concentrations. VOC concentrations were automatically monitored using gas chromatography (GC) systems. Two GC systems were employed, one for monitoring VOC concentrations in water and one for monitoring TCE concentrations in air. Both systems were routinely calibrated. Concentrations were determined by an external standard method.[7]

RESULTS

Laboratory Study

Results from operation of a laboratory FBR system using both site water and a surrogate water at the concentrations listed above demonstrated efficient removal of BTEX, DCB, and TCE. The granular-activated carbon (GAC) used as a biofilm support in the FBR was saturated with chemicals before inoculation with degradative bacteria. Following inoculation and adaptation, effluent concentrations for all of the chemicals decreased. Once steady-state operation was achieved after three weeks of operation, greater than 90% of all chemicals and 80 to 90% of the TCE were degraded in the FBR (Folsom 1995). Three major points were concluded from this test. First, chemical removal was biologically mediated and not merely a physical process. Second, there was an apparent adaptation of bacteria responsible of degrading toluene, ethylbenzene, and TCE. Third, no apparent toxic or inhibitory effects were detected following long-term operation.

Laboratory efforts focused on GPR operational stability, which was enhanced following a change to continuous operation. Typically, between 200 and 600 µg TCE/L air entered the reactor at an air flow rate of 70 mL/min with effluent concentrations close to, or below detection limits (Folsom 1995). Performance was extended to beyond 10 months of continuous operation using laboratory systems. Overall TCE removal efficiencies exceeded 95% though there were several minor operational upsets which included plugged feed lines and interruptions in electrical service. Following each event, biological activity in the reactor recovered without amendments to, or replacement of, the bacteria. The bacterial composition of the reactor became a mixed culture after the first week of operation. Modifications made in gas-phase bioreactor operation led to stable and reliable performance for extended time periods.

Pilot Demonstration

The field demonstration system included an FBR for primary treatment of groundwater, an air stripper for transferring residual volatile organic compounds (VOCs) to an air stream, and a GPR for final treatment of those residual VOCs, primarily TCE. Due to the enhanced performance of the FBR towards TCE, the demonstration essentially became a test of two independent pilot systems, one for treating contaminated water in the FBR and the second for treating contaminated air in the GPR.

The FBR pilot was assembled and filled with GAC. Contaminated groundwater was pumped through the reactor for 4 weeks prior to adding the bacterial inoculum. The system was operated at a flowrate of 2 gal per min (gpm) with an empty bed hydraulic retention time (HRT) of about 30 min, pH 6.7, 24°C, and 4.6 mg/L dissolved oxygen. The FBR demonstrated greater than 95% removal of most targeted contaminants and greater than 85% removal of TCE from groundwater (Table 1). Over 210,000 gal of contaminated groundwater were treated in the pilot FBR with effluent quality close to drinking water standards (Folsom 1995). Pilot FBR performance was fully consistent with the laboratory studies.

The bed material removed from the FBR was also subjected to methanol extraction to quantify the amount of key organic chemicals bound to the GAC. A methanol extraction method was able extract >95% of the bound organic chemicals from virgin GAC. Chemical recoveries from the GAC were consistent with the isotherms generated using virgin carbon. The amount of chemicals bound to the carbon were greatest at the bottom of the reactor (Table 2). This was consistent with the pseudo-plug flow operation of the FBR system in which the highest concentration of chemicals in the water was greatest at the bottom of the reactor. The total organic load to the carbon was less that the maximal holding capacity due to isotherm effects at the chemical concentrations in the feed and effluent streams. Maximal loading capacities are only achieved when the carbon can be saturated which clearly was not achievable under these operating conditions. A total mass balance was determined for operation of the pilot FBR system (Table 3). Overall, 83% of the TCE, 93% of the 1,2-DCB, and 67% of the BTEX were destroyed during FBR operation using the conservative estimate of bound chemicals. These results clearly demonstrated a significant loss of chemical as a result of biodegradative activity beyond the binding capacity of the GAC in the reactor.

The GPR was then prepared for normal operation using an inoculum of TCE degradative bacteria grown with phenol as the sole carbon source. The system was operated at a 10 day HRT once biomass concentrations reached 0.35 mg/mL. A chemical addition system was installed to deliver TCE into the air entering the GPR. Over the course of steady-state operation, average feed and effluent concentrations for TCE were 371, and 80 μg/L air respectively. A pH excursion during the sixth week of operation resulted in a 75% loss of biomass which significantly lowered the volumetric performance of the reactor. The pH control issue was rectified and the reactor was temporarily switched to batch operation and within 24 hours, biomass levels doubled from 0.4 to 0.8 mg/mL protein at which time the TCE feed was re-initiated and normal operation resumed. This system demonstrated stable operation for 2 months before it was shut down. TCE was reduced by an average of 75% in the GPR. This removal rate can easily be increased to over 90% by increasing biomass concentrations in the reactor. Pilot operation and stability were consistent with laboratory studies, although overall performance was lower than normal during the demonstration.

DISCUSSION

An economic evaluation was performed based on key parameters expected to represent those typically found at contaminated sites. The standard contaminated groundwater characteristics used for analysis were a feed flow rate of 100 gpm, containing 15 ppm BTEX (ratio of 7.5:4:1.5:2) with 1 ppm TCE. Capital and operating costs were developed for an FBR system, wet carbon adsorption, air stripping/dry carbon adsorption, and UV/peroxidation using this set of flow rates and concentrations (Figure 1). All cost estimates include installation of the complete system on customer supplied foundations and exclude: (1) routing of groundwater to the system; (2) routing treated effluent from the system; (3) start-up; (4) field supervision; (5) equipment freight; (6) taxes and; (7) additional, site specific pre- or post-treatment equipment requirements. Power calculations were based on a rate of \$0.07/kwh and a labor rate of \$50/hr was used. Carbon replacement costs were set at \$2.00/pound which included replacement carbon and extras such as vacuuming, shipping, removal and disposal of spent carbon. FBR carbon attrition rate was assumed to be 5% (approximately 320 pounds/year). Estimates of carbon usage for the air stripping with carbon adsorption, obtained from two vendors, were 112 and 136 pounds/day . For the FBR system, the desired effluent quality can be met using a 5 ft diameter by 11 ft tall fluidized bed bioreactor with a system capital cost of \$200,000 and an operating cost of \$17,520/year including power, nutrients, carbon replacement due to attrition, manpower and maintenance costs. As shown in Figure 1, the break even point for the FBR is 1.6 years as compared to the best alternative technology, air stripping/carbon adsorption. This payback reflects an \$82,000 savings in yearly operating and maintenance costs for the FBR system compared to air stripping/carbon adsorption. The cumulative total cost savings (operating, maintenance and capital) for a 10-year project would be \$690,000.

An economic evaluation was also performed for the GPR system based on key parameters expected to represent those typically found at contaminated sites during soil vapor extraction (SVE) operations. Assuming an air flow rate of 300 cfm and TCE concentrations in the air of either 100 or 300 ppmv, an 11 ft diameter, 7,500 gal GPR is required to achieve the desired treatment level (Figure 15). System costs were estimated at \$125,000 ± 15% installed on customer supplied foundations. Operating costs were estimated at \$25,000/year including power (@ \$0.07/kwh), nutrients, manpower and maintenance costs. Comparable capital and operating costs were developed for carbon adsorption using the same set of flow rates and concentrations. Carbon consumption was based on theoretical isotherm data and changed significantly for the two concentrations of TCE used (Figure 2). Capital costs were estimated at \$10,000 ± 15%. System costs included complete carbon adsorption system installed on customer supplied foundations. Costs excluded installation of SVE system, routing air to and from the carbon adsorbers and any start-up and field supervision services. The annual operating costs were estimated to range from \$50,000 to \$250,000 depending on TCE concentrations. Carbon replacement service costs may vary depending on site location.

Due to the high performance of the FBR, the vapor entering the GPR for treatment had to be spiked with TCE. Operational stability was successfully demonstrated with 10 months of continuous operation using the laboratory system and 2 months using the field-pilot system. Commercial GPR systems have been designed to treat 50 to 300 cfm of contaminated air, typical for soil vapor extraction operations. The economic analysis generated as part of these projects indicate typical savings in operating costs of 70 to 80% using the biological treatment system as compared to carbon adsorption (Figure 2).

In essence, two independent field demonstrations were successfully performed. Due to the high performance of the FBR, the vapor entering the GPR for treatment had to be spiked with TCE. All hazardous chemicals were treated to concentrations near or below drinking water standards. An economic evaluation of these innovative technologies to conventional carbon adsorption suggests a significant cost savings. If chemical concentrations were higher than the assumptions used in the cost estimates, operating costs for carbon adsorption would increase, whereas FBR and GPR operating costs would not change significantly. Biological treatment provides an economical, destructive technology for remediating contaminated air or water.

ACKNOWLEDGMENTS

The project was performed under a contract (FO8635-91-C-0198) sponsored and administered through HQ AFCESA/RAVW Tyndall Air Force Base, Florida, 32542-5000. The authors wish to acknowledge the support provided by the Environmental Restoration Division at Robins AFB, Georgia.

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Figure 1Life-cycle cost comparison for FBR vers wet carbon adsorption, UV/peroxidation, or air stripping followed by carbon adsorption.
Figure 2. Life-cycle cost comparison for GPR vers carbon adsorption.

TABLE 1: Feed and Effluent Chemical Concentrations During Steady-State Operation of the Pilot FBR.

chemical	Feed (μg/L)	Effluent (μg/L)	% Degraded
benzene	46 ± 30	<10 ± 4	>78*
TCE	1,445 ± 173	206 ± 142	86
toluene	40 ± 46	<11 ± 5	>73*
ethylbenzene	23 ± 17	<12 ± 8	>46*
xylenes	50 ± 29	<20 ± 7	>40*
1,3-DCB	123 ± 10	10 ± 2	92
1,4-DCB	227 ± 20	9 ± 2	96
1,2-DCB	1,664 ± 134	13 ± 5	99

* - Degradation based on detection limit for compounds giving a conservative estimate of performance.

TABLE 2: Methanol Extractable Organic Chemicals Removed From Pilot FBR.

Chemical	bottom sample (mg/g GAC)	middle sample (mg/g GAC)	top sample (mg/g GAC)
TCE	9.61	<0.01	<0.01
1,2-DCB	1.95	0.20	0.31
BTEX	5.16	0.84	0.69

A 1 g GAC sample was extracted with 9 mL of methanol. The methanol phase was injected onto a GC and the amount of chemical quantified using an external standard. The bottom sample represents the average of 4 separate extractions and analysis.

TABLE 3: Chemical Mass Balance for Key Contaminants During Operation of the Pilot FBR.

Chemical	total input in feed (g)	total output in effluent (g)	net load to reactor (g)	total bound to GAC (g)	net destroyed (g)
TCE	6041	518	5523	912	4611
1,2-DCB	2830	92	2738	185	2553
BTEX	1536	65	1471	490	981

Loading calculations were based on weekly averages for feed and effluent chemical concentration and totaled liquid flow to system. The loading calculations also included the chemicals added to enhance breakthrough adjusted for losses to the effluent. GAC loading was based on 95 kg of activated carbon in reactor and the amount of organic sorbed to carbon at the bottom of the reactor from Table 2.

FIGURE 1

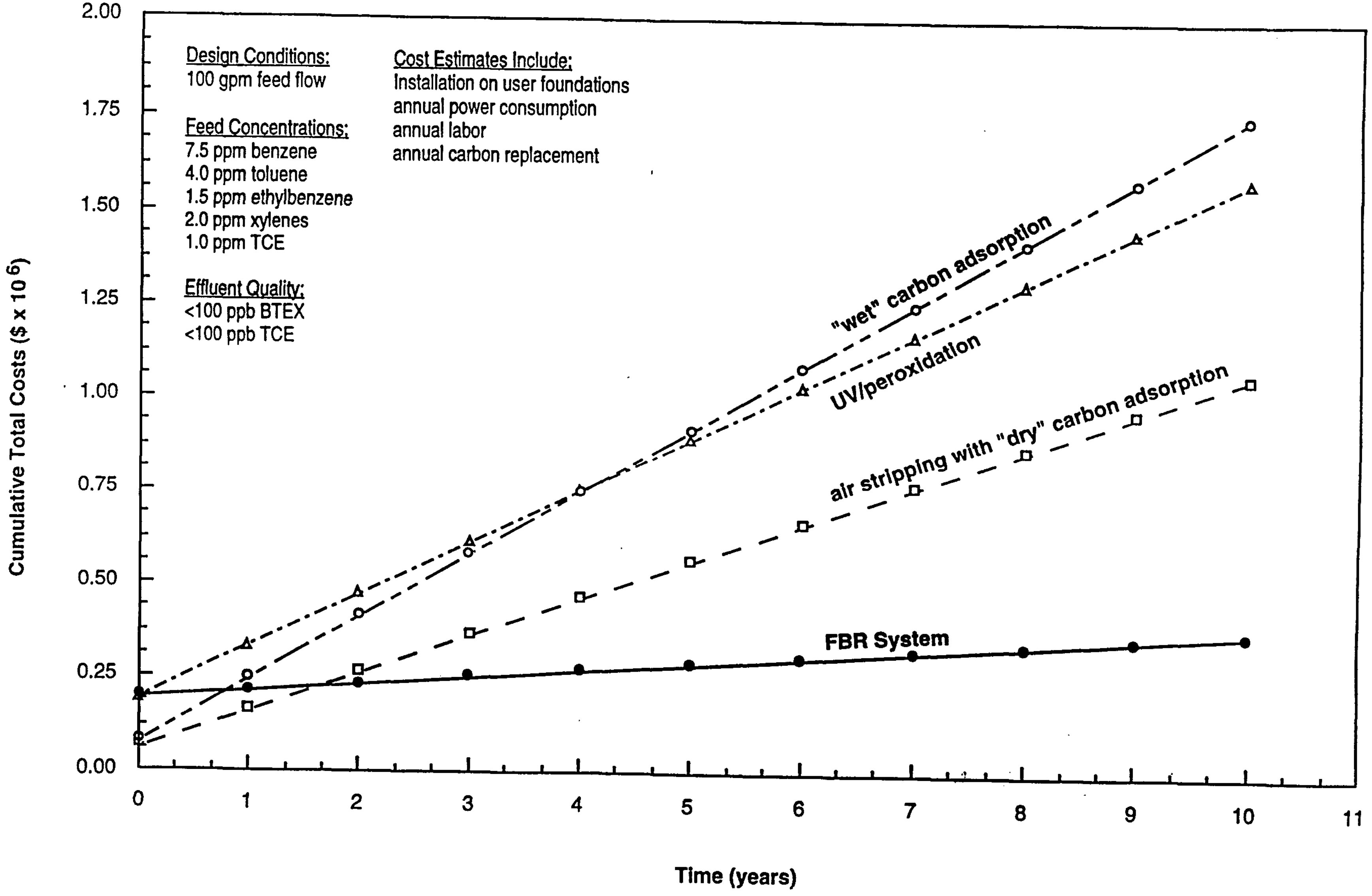
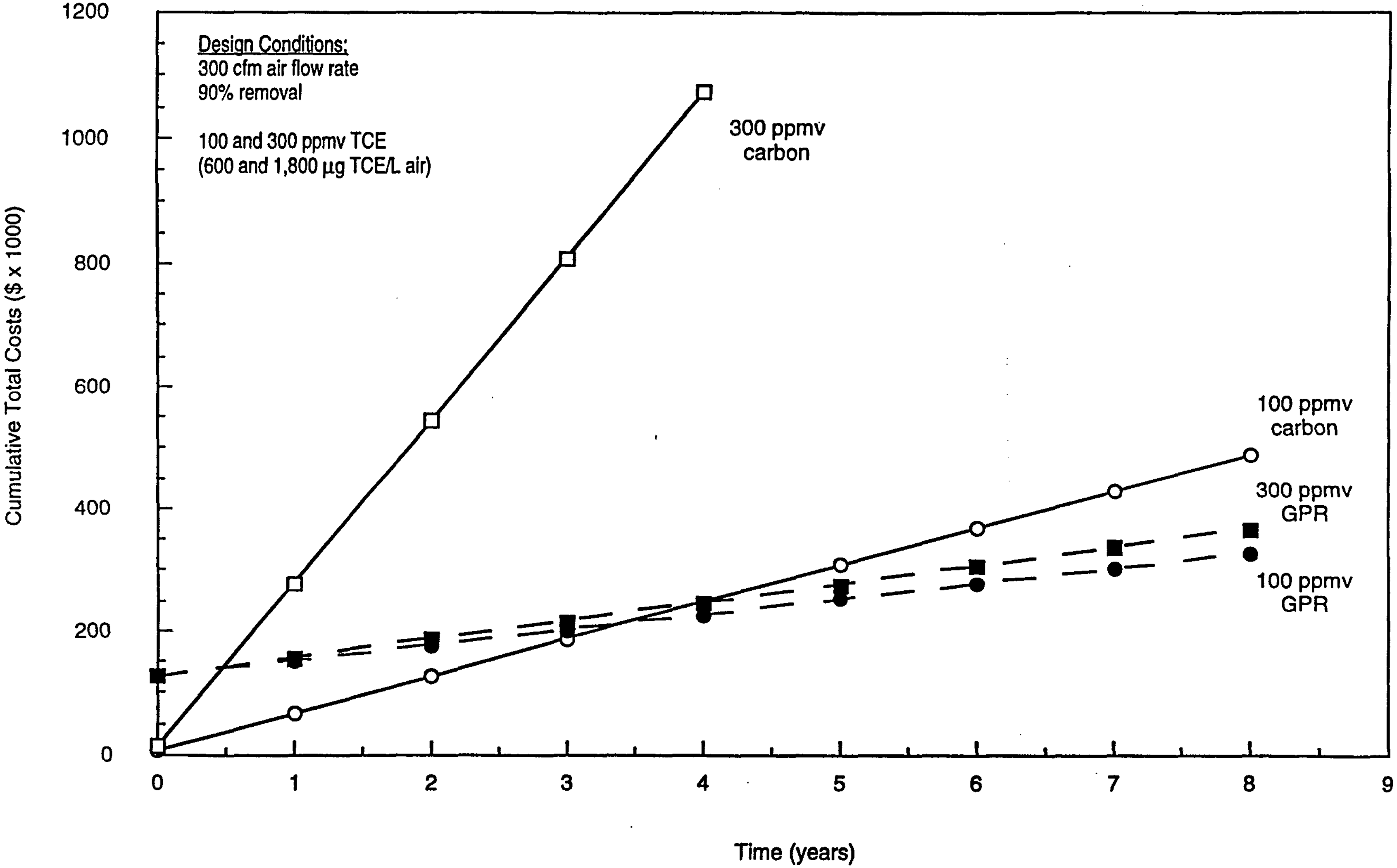

Design Conditions:
100 gpm feed flow
Feed Concentrations:
7.5 ppm benzene
4.0 ppm toluene
1.5 ppm ethylbenzene
2.0 ppm xylenes
1.0 ppm TCE
Effluent Quality:
<100 ppb BTEX
<100 ppb TCE
Cost Estimates Include:
Installation on user foundations
annual power consumption
annual labor
annual carbon replacement
"wet" carbon adsorption
UV/peroxidation
air stripping with "dry" carbon adsorption
FBR System
Cumulative Total Costs ($ x 10^6)
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
0
1
2
3
4
5
6
7
8
9
10
11
Time (years)

Figure 2


Design Conditions:
300 cfm air flow rate
90% removal
100 and 300 ppmv TCE
(600 and 1,800 µg TCE/L air)
300 ppmv carbon
100 ppmv carbon
300 ppmv GPR
100 ppmv GPR
Cumulative Total Costs ($ x 1000)
0
200
400
600
800
1000
1200
Time (years)
0
1
2
3
4
5
6
7
8
9

ASSESSING ADVANCED OXIDATION PROCESSES FOR THE TREATMENT OF TRINITROTOLUENE CONTAMINATED GROUNDWATER

by

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Environmental Engineering Division
USAE Waterways Experiment Station
Vicksburg, MS

ABSTRACT

Advanced oxidation processes (AOPs) are groundwater remediation techniques that use powerful chemical oxidizers under catalyzing conditions to produce hydroxyl radicals which in turn can destroy a wide variety of organic compounds. The USAE Waterways Experiment Station (WES) has been investigating AOPs, traditional and non-traditional, for treatment of trinitrotoluene (TNT) contaminated groundwaters. Processes evaluated include ultraviolet (UV) catalyzed ozone/hydrogen peroxide based AOPs which have been traditionally used for treatment of contaminated wastewaters. WES studies indicate that these processes also show promise for treatment of explosives contaminated groundwaters. Non-traditional AOPs are also currently being evaluated by WES for treatment of TNT contaminated groundwaters. These processes include peroxone and ultrasonically (sonolysis) catalyzed oxidation.

The test influent used in this study was a 1,000 ug/l TNT solution made of partially hydrated TNT and distilled, ionized water. The UV based AOPs had the highest TNT degradation kinetics, while the non-UV based systems proved to be more economical for the same level of treatment. The results of these studies indicate much promise for treating TNT contaminated groundwaters with the non-traditional AOPs at a potential cost savings as high as an order of magnitude over the more traditional AOPs. The addition of sonolytic catalyzation generally increased TNT degradation kinetics.

INTRODUCTION

The US Department of the Army has numerous sites that are contaminated with explosive compounds. These chemicals threaten the overall integrity of one of the country's most valuable resources; groundwater. Unfortunately, extensive groundwater contamination has already occurred at many of these sites, requiring that some form of groundwater remediation be initiated. Existing state-of-the-art technology, activated carbon adsorption, can be cost prohibitive and does not result in the on-site destruction of the contaminants. Activated carbon simply results in the transfer of contaminants from the liquid phase onto the solid phase. Also, some difficulty in the disposal of explosives laden spent carbon has been encountered.

Although activated carbon is a valid option for treating contaminated groundwaters, innovative treatment techniques such as chemical oxidation processes may offer both a cost effective and technically sound alternative. Selected data for 2,4,6-trinitrotoluene (TNT) oxidation in distilled water solutions using both traditional and non-traditional AOPs are presented. These research efforts were performed by the US Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, within the WES Hazardous Waste Research Center.

ADVANCED OXIDATION PROCESSES

Chemical oxidation processes are a group of treatment technologies that use powerful chemical oxidizers and/or ultraviolet light to destroy organic solutes and pathogenic organisms in water. These processes have traditionally been used by United States municipalities for treatment of drinking water. Over the last twenty years, oxidation processes have been successfully used for cleanup of contaminated groundwaters and wastewaters.

Chemical oxidizers commonly used in oxidation processes for treating contaminated groundwater include ultraviolet photolysis in conjunction with ozone, hydrogen peroxide, and/or potassium permanganate addition. Since the mid-1970's, the WES has been developing and evaluating chemical oxidation processes for treatment of groundwaters contaminated with a wide variety of organic contaminants. The early research efforts at the WES indicated that chemical oxidation processes were technically attractive; however, the economics of the process versus alternative treatment options during that period were not conducive toward widespread application. Today, recent technology developments and stricter environmental regulations have made chemical oxidation processes much more cost competitive. The WES, under the Army's Environmental Quality and Technology Program, is currently performing research in the development and refinement of chemical oxidation processes for use in the remediation of explosives contaminated groundwaters.

Of primary research interest by WES are those chemical oxidation processes that result in the generation of the hydroxyl radical, ($OH^{\cdot}$). These processes are by definition referred to as advanced oxidation processes (AOPs). The hydroxyl radical is an oxidizer species that is much more powerful than traditional oxidizer species such as ozone (O_3) and hydrogen peroxide (H_2O_2). Due to its high reactivity, the hydroxyl radical is very unstable requiring that it be produced on-site. There are a variety of chemical oxidation processes that may be used for production of hydroxyl radicals. Examples of such processes include combinations of ultraviolet (UV) light, hydrogen peroxide, and/or ozone.

Degradation of TNT during AOP treatment is accomplished through one or more of the following oxidation mechanisms:

a. Oxidation by the parent oxidizer (ozone or hydrogen peroxide),

b. Oxidation by secondary oxidizer species (hydroxyl radicals),

c. Direct photolysis by UV light,

d. The synergistic effect of all of the above mechanisms.

The final products of TNT chemical oxidation reactions are usually simple organic acids, carbon dioxide, water, residual levels of oxidizers, and nitrate. None of these compounds pose a threat toward human or environmental health. However, in some cases, chemical oxidation may not be effective in completely oxidizing the TNT into environmentally benign chemical species. Trinitrobenzene (TNB) is a commonly detected oxidation intermediate of incomplete TNT oxidation. Understanding treatment kinetics is crucial to the safe application of oxidation processes for TNT contaminated groundwater remediation. Figure 1 presents a proposed oxidation pathway for TNT. This pathway is currently being validated by WES researchers. A properly designed oxidation process will completely cleave the aromatic ring into the above listed "safe" oxidation products.

TRADITIONAL AOPs

In terms of groundwater remediation, most applications of AOPs involve the addition of ultraviolet (UV) light into ozone or hydrogen peroxide dosed reactors. Ultraviolet light is a relatively short wave radiation that is capable of exciting a wide variety of chemicals including organic compounds and chemical oxidizers. The two most common types of UV sources (lamps) in groundwater treatment are low and medium pressure mercury (Hg) vapor UV lamps. Low pressure mercury vapor lamps emit the majority of its spectra at or near the 254 nm wavelength. Medium pressure mercury vapor UV lamps emit a spectra that is extremely wide in comparison to low pressure UV lamps. Unlike low pressure Hg vapor UV lamps, medium pressure Hg vapor UV lamps produce a significant amount of photons within the 200 nm to 250 nm range which is the band where explosive compounds and hydrogen peroxide absorb UV light. Low pressure Hg vapor UV lamps have a lower energy consumption and are more energy efficient than medium pressure lamps. Improved energy efficiency results in less heat generation which is an inefficient use of expensive electrical power. Although more energy intensive, medium pressure Hg vapor UV lamps produce more UV photons available for contaminant destruction and hydrogen peroxide excitation (i.e. radical production if using hydrogen peroxide). Increased photon production at key wavelengths usually equates to more rapid degradation kinetics through improved quantum yield (the amount of photons within a given wavelength involved in beneficial reactions over the total amount emitted by the lamp).

Ozone based AOPs have traditionally almost exclusively used low pressure Hg vapor UV lamps (LPUV). WES has successfully used UV/ozone systems for treatment of a wide variety of contaminated groundwaters. The major drawback to UV/ozone based systems is the relatively high capital costs associated with the ozone generation equipment. Positive aspects of UV/ozone based systems includes relatively lower operational and maintenance (O&M) costs, little or no heat generation, and a lower potential for fouling of the quartz sleeves housing the UV lamps.

On the other hand, hydrogen peroxide based AOPs have traditionally used medium pressure Hg vapor UV lamps (MPUV). Compounds successfully treated using this technology generally include the same compounds treated by the UV/ozone based systems. UV/hydrogen peroxide based systems usually have higher O&M costs and a higher fouling potential for the quartz lamp housing sleeves. Advantages of UV/hydrogen peroxide processes include increased degradation kinetics, little or no process off-gasses, reduced potential for oxidation intermediates, and lower capital costs.

Costs associated with treatment of TNT contaminated groundwater using traditional UV based AOPs range from approximately $1.00 to $5.00 per thousand gallons treated. Commercial vendors of these processes are currently available. WES has experience with most of these vendors and, in general, they all market well designed process equipment that are quite effective for treating organics contaminated groundwaters.

Figure 2 presents treatment data for a 1,000 ug/l TNT dosed distilled water solution using traditional UV based AOPs. These results were generated by WES using one liter, bench scale reactors. As shown in Figure 2, both traditional AOPs, MPUV/hydrogen peroxide and LPUV/ozone sparging, achieved extremely rapid TNT removals. The MPUV/hydrogen peroxide does appear to be more aggressive than the LPUV/ozone sparged system based on complete TNT removal with five minutes of treatment as compared to complete TNT removal achieved by the ozone based system within ten minutes. TNB, the predominant intermediate of TNT oxidation, was not detected in any of the post five minute study effluents.

NON-TRADITIONAL AOPs

Peroxone is one of the most innovative AOPs for treatment of organics contaminated groundwaters. Until recently, application of this process has been limited to drinking water treatment. Bench and pilot studies performed by the WES and other research organizations indicate a high potential for utilization of peroxone for treatment of contaminated groundwaters. Peroxone involves the generation of hydroxyl radicals through reaction of ozone with hydrogen peroxide. Optimal stoichiometric ratios of hydrogen peroxide to ozone are in the 0.25 to 1.5 range. Estimated treatment costs range from $0.10 to $1.00 per thousand gallons treated. This represents a potential cost savings of an order of magnitude over the costs of traditional UV based AOPs. Discussions with French researchers indicate that some French municipalities are removing low levels of pesticides from drinking water at a cost of only $0.02 per thousand gallons at flowrates within the hundreds of millions of gallons per day range. The City of Los Angeles, California, has recently installed a pilot scale peroxone water treatment plant with a few million gallon per day flow capacity. Preliminary results are encouraging and process economics attractive.

Ultrasound are soundwaves produced from 20 khz to 100 khz frequency range by electrical devices. Ultrasound is commonly used for cleaning small objects where extremely clean conditions are required in hard to reach areas. Ultrasound has also been used to catalyze slow chemical reactions. Using a directional 40 watt ultrasonic probe along with one liter, glass reactors, WES has evaluated the feasibility of using ultrasound to increase the reaction rate of TNT during ozonation and peroxone oxidation. Mechanisms responsible for increasing reaction rate are improved mass transfer, production of hydroxyl radicals, and localized pockets of high pressure and temperatures. Unfortunately, there are little or no cost information of ultrasonic reactors. Furthermore, there are no large scale ultrasonic chemical reactors available at this time for evaluation of ultrasonic catalyzed oxidation on the pilot scale.

Figure 3 presents the results of both peroxone and ultrasound catalyzed oxidation. Comparing this figure to Figure 2, it can be seen that the non-traditional AOPs have slower TNT removal kinetics than the more traditional UV based AOPs (approximately four times slower). However, peroxone, a non-traditional AOP, can be implemented at a potentially much lower cost. A 10 mg/l hydrogen peroxide dose in the peroxone system indicates potential to remove all of the TNT within 30 minutes of treatment. Subsequent studies (not shown) indicates that a 100 mg/l dose was able to achieve similar treatment within less than 20 minutes of batch treatment.

The beneficial impact of ultrasound on ozonation and peroxone treatment is evident in Figure 3. The addition of ultrasound to the 10 mg/l hydrogen peroxide dosed peroxone system substantially enhances the rate of TNT removal at both the 20 and 40 watt dose. With increasing ultrasound intensity, from 20 watts to 40 watts, an overall increase in reaction kinetics is achieved. Ozonation in an ultrasonic field appears promising as illustrated in Figure 3. Much like the peroxone data, as the level of ultrasonic power into the ozonation system is increased, so does the overall TNT oxidation rate.

The formation of TNB in the non-traditional AOP systems was noted as presented in Figure 4. The additional 40 watts of ultrasound to the 10 mg/l dosed hydrogen peroxide peroxone system was able to completely remove all of the TNB that was formed during TNT oxidation. The 20 watt peroxone and 40 watt ozonated sonic systems indicated potential for removing the TNB within 30 minutes of treatment. The peroxone system requires treatment times longer than 25 minutes to completely remove TNB from the test solution. Data recently generated by WES indicates that higher hydrogen peroxide to ozone dosing ratios does significantly improve TNB removal. The 20 watt ozonated sonic system did not indicate a downward trend in TNB removal indicating longer treatment times are probably required to remove the TNB to below detection levels.

ON-GOING WES RESEARCH ACTIVITIES

As knowledge of the mechanisms involved in contaminant destruction improves, it is expected that treatment costs associated with UV based systems will decrease and the range of application will increase. Of significant note, is the definition of oxidation pathways of explosives compounds (TNT, RDX, and HMX) during AOP treatment currently under investigation by the WES under collaboration with Howard University and the University of North Carolina, Chapel Hill.

The WES has performed three pilot studies at Rocky Mountain Arsenal, Commerce City, Colorado during the Fall of 1994, for treatment of three contaminated groundwaters using peroxone. The focal point of these studies was the WES designed and constructed Peroxone Oxidation Pilot System (POPS). This unit has a 0.5 to 15 gpm flowrate and is completely mobile. WES is also developing other UV based AOPs that are non-traditional in nature. The primary system under development are semi-conductor catalyzed photolysis and second generation hydrogen peroxide/UV based AOPs.

CONCLUSIONS

Recent advances in AOP technologies have made these processes cost competitive as compared to traditional groundwater treatment processes such as carbon adsorption. Design engineers currently have a wide variety of AOP configurations at their disposal for use in remediating contaminated aquifers. Traditional AOPs that utilize UV irradiation had the most rapid TNT removal kinetics of all the AOPs studied. Non-traditional AOPs, such as peroxone and ultrasonically enhanced oxidation also had appreciable removal kinetics.

Traditional UV based AOPs costs typically range from $1.00 to $5.00 per thousand gallons treated. Peroxone oxidation costs are estimated to range from $0.10 to $1.00 per thousand gallons treated. Ultrasonically catalyzed oxidation is still in a state of process conceptualization and development and as such process costs are not yet available. Ongoing research at the WES should further reduce AOP treatment costs and increase the range of applicability of AOPs toward remediation of DoD sites.

ACKNOWLEDGEMENTS

The authors would like to thank the various project sponsors throughout the years for their support; thereby, allowing for the development of AOPs to continue. Special acknowledgement is felt to WES management for continual support both technically and economically. The authors would also like to thank the able staff of the Hazardous Waste Research Center, WES, for their valuable contributions and diligent efforts during performance of experiments and chemical analyses. Permission to publish this information was granted by the Chief of Engineers.

Figure 1.

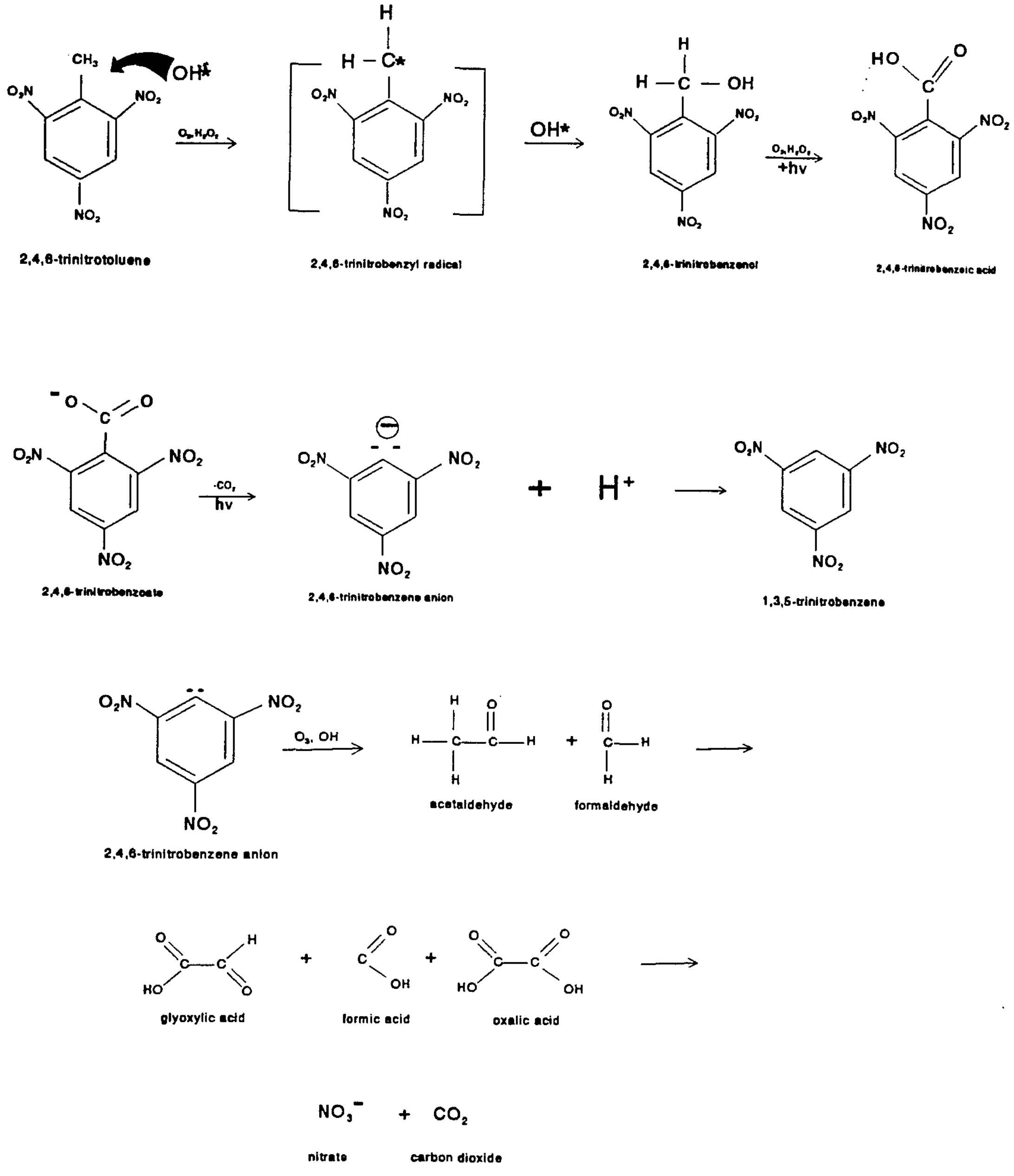

CH3
OH*
O2N
NO2
O2, H2O2
2,4,6-trinitrotoluene
H
H – C*
2,4,6-trinitrobenzyl radical
OH*
H – C – OH
2,4,6-trinitrobenzenol
O2, H2O2, +hv
HO
O
C
2,4,6-trinitrobenzoic acid
-CO2
hv
2,4,6-trinitrobenzoate
2,4,6-trinitrobenzene anion
+
H+
1,3,5-trinitrobenzene
O3, OH
acetaldehyde
formaldehyde
glyoxylic acid
formic acid
oxalic acid
NO3-
CO2
nitrate
carbon dioxide

Figure 2. Evaluation of Traditional UV Based AOPs
TNT Oxidation

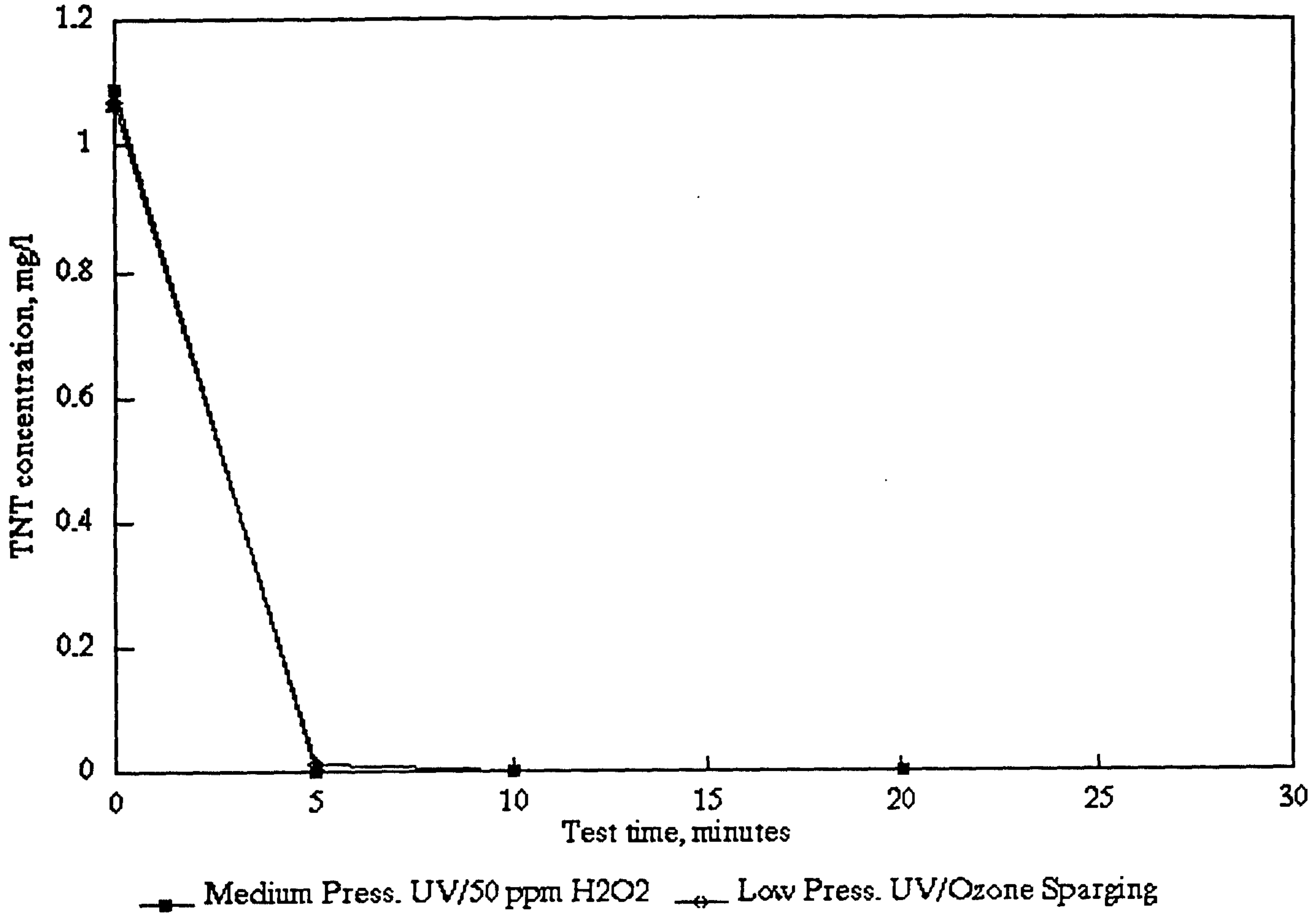


Figure 3. Comparison of Non–Traditional AOPs

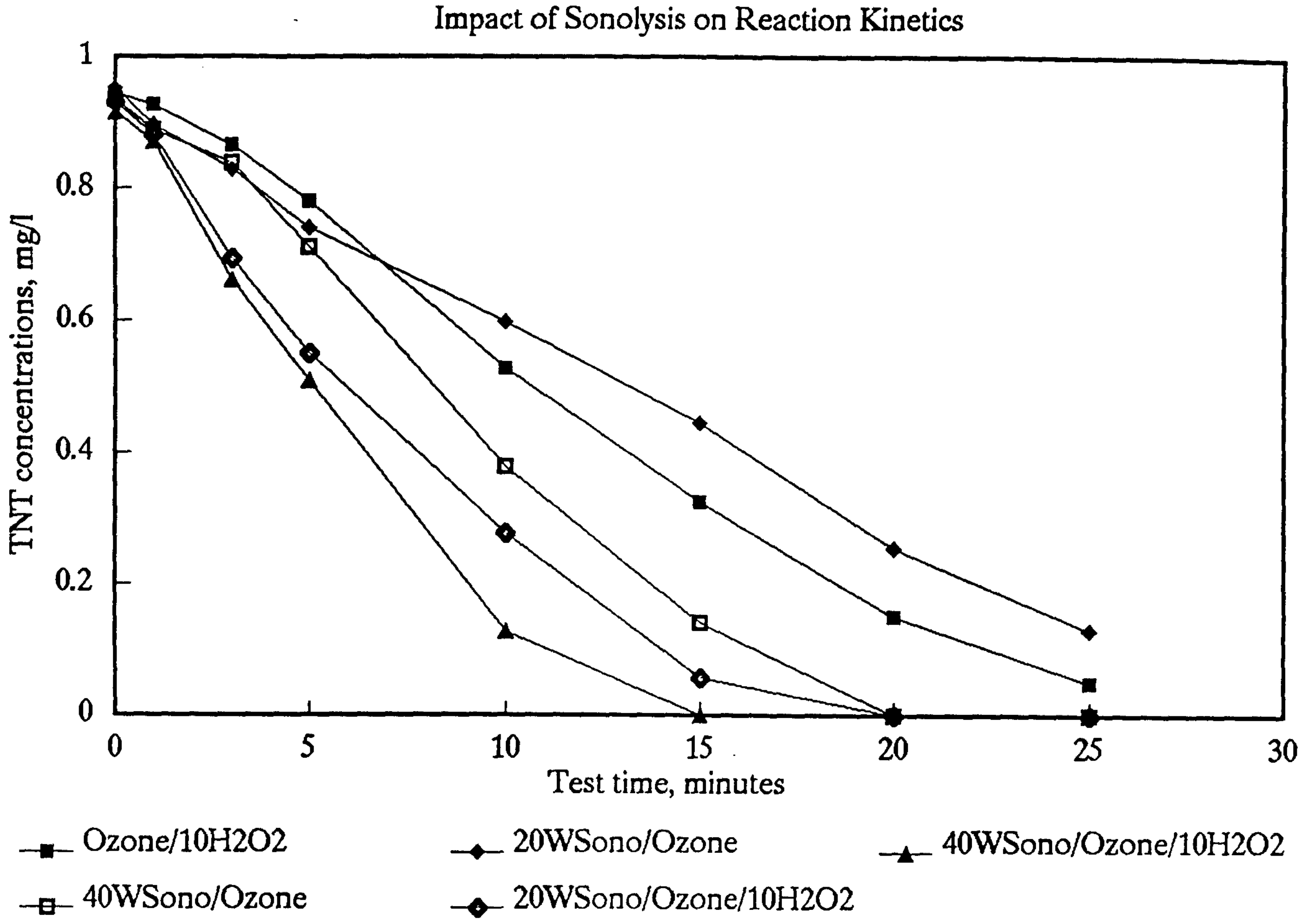
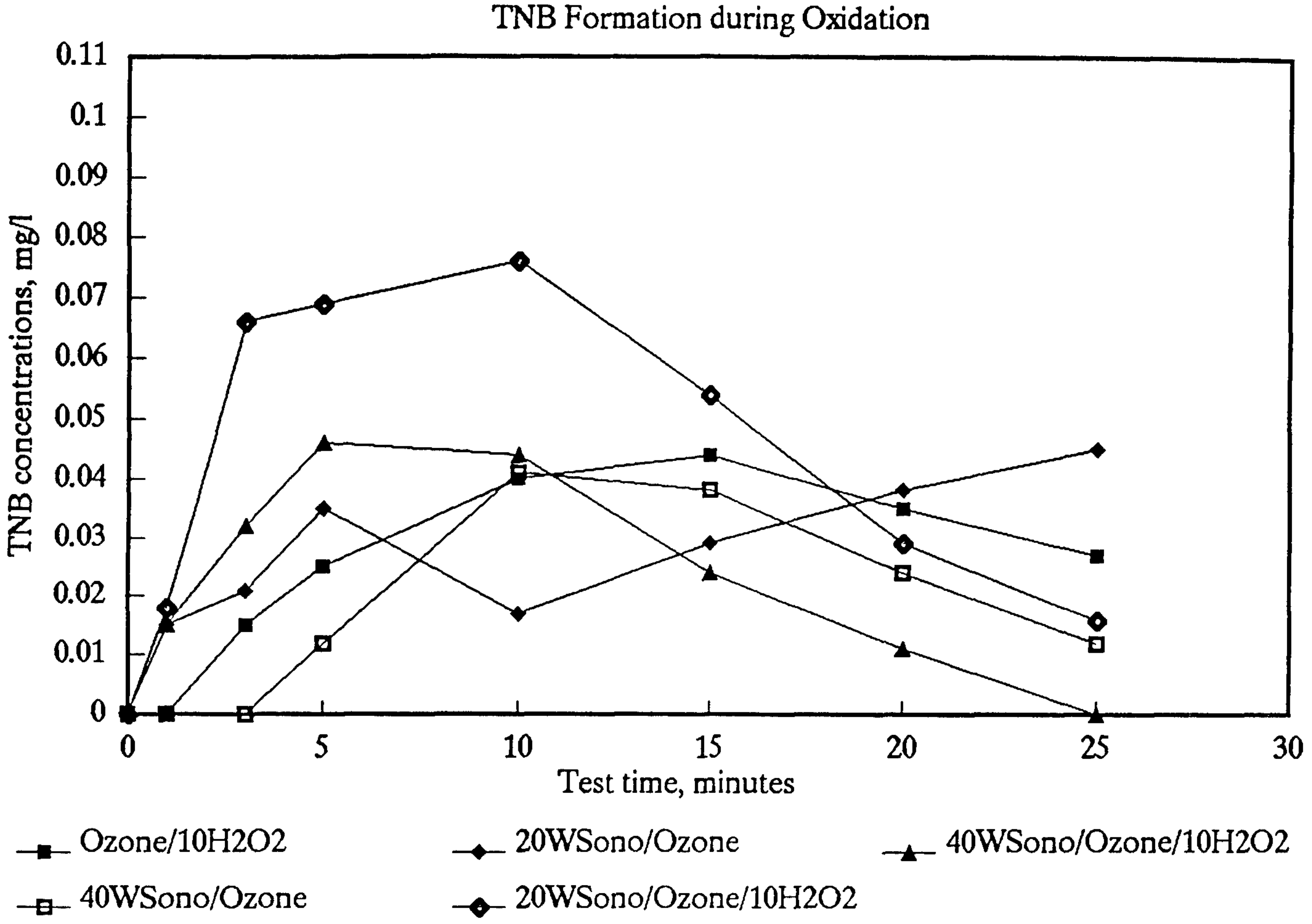


Figure 4. Comparison of Non–Traditional AOPs



INNOVATIVE TECHNOLOGIES

THE USE OF INNOVATIVE TECHNOLOGIES FOR ENVIRONMENTAL RESTORATION BY THE U.S. ARMY CORPS OF ENGINEERS - April 1995

Donna R. Kuroda, Headquarters, U.S. Army Corps of Engineers*
David Nusz, Missouri River Division, U.S. Army Corps of Engineers
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(U.S. Geological Survey)

INTRODUCTION:

The U.S. Army Corps of Engineers (Corps) plays a significant role in the restoration of the Nation's hazardous, toxic and radioactive waste (HTRW) sites. In addition to addressing U.S. Army needs, the Corps environmental restoration activities include support of the U.S. Environmental Protection Agency Superfund program and provision of remediation assistance to other Federal Agencies such as the Air Force and Department of Energy. The Corps is also responsible for restoration of property formerly owned or used by the U.S. Department of Defense. Contaminants commonly found on HTRW sites include explosive wastes, solvents, petroleum products, heavy metals, and mixtures. To achieve more effective HTRW cleanups, the Corps is turning to innovative technologies. Innovative technologies may be generally defined as lacking full scale cost and performance data. The Corps is moving forward with innovative technologies on four fronts: first, the Innovative Technology Advocate (ITA) Program was initiated to foster the use of innovative technologies; second, the research, development, and demonstration program is making new technologies available for environmental remediation; third, the Corps is developing guidance documents on the application and design requirements for innovative technologies; and fourth, Corps districts are using innovative technologies to remediate sites.

INNOVATIVE TECHNOLOGY ADVOCATE PROGRAM:

In 1989, the Corps established ITA positions at Headquarters, the Missouri River Division, and the Kansas City and Omaha Districts. Earlier in 1994 an ITA position was established at the Tulsa District. Very recently additional ITA positions were established at the New England Division, Baltimore District, Sacramento District, and Alaska District. The mission of the ITAs is to inform, encourage, and support the use of HTRW innovative technologies for restoration of sites administered by the Corps. They gather and disseminate information regarding innovative technologies to HTRW personnel and are in the process of setting up their own Home Page on the World Wide Web. The ITAs hold workshops, seminars, and site visits to review significant topics such as remediation and site characterization technologies, treatability studies, and contracting barriers. They are leading the Corps' effort to gather cost and performance data on innovative and proven technologies so that accurate comparisons can be made the various technologies. The ITAs work both separately within their own organization and together within USACE to accomplish their goals.

To formalize many of the ITA activies, an HTRW Innovative Technology Action Plan has been developed to cover critical areas such as formal process for innovative technology selection; training, education, and sharing lessons learned; standard format for collecting cost and performance data; appropriate contracting tools; regulator flexibility through partnering; risk sharing and indemnification; and incentives to accelerate commercialization of R&D efforts. This strategy will give the Corps a cohesive and proactive plan for using innovative technologies to do HTRW cleanups.

RESEARCH, DEVELOPMENT, AND DEMONSTRATION:

Research, development, and demonstration efforts associated with newly developed technologies is a joint effort between the Corps research and development laboratories (such as U.S. Army Engineer Waterways Experiment Station and U.S. Army Cold Regions Research and Engineering Laboratory) and the U.S. Army Environmental Center. The Corps laboratories are responsible for technology development from concept through large scale pilot testing. The Army Environmental Center then typically takes responsibility for large scale field demonstration and eventual fielding of the technology.

Several examples of technology development for HTRW applications follow. In the field of bioremediation, the laboratories are investigating variations such as bioslurry, composting, landfarming and in situ techniques for treatment of explosive wastes. Additional cold climate techniques for bioremediation are also under evaluation. Natural restoration is also an important area worthy of attention. Another kind of technology, the frozen wall barrier, which is a containment technology, is being studied for its application to HTRW sites.

In the area of site characterization, the Site Characterization and Analysis Penetrometer System (SCAPS) is being developed as a joint effort with several other Federal agencies. There are SCAPS units at the Kansas City, Tulsa, and Savannah Districts. Microwells are also being developed as an alternative to conventional drilling techniques for environmental investigations. Other site characterization techniques developed include a field testing kit for explosives.

HTRW GUIDANCE DEVELOPMENT DOCUMENT PROGRAM:

This program develops and maintains Corps technical guidance needs of the many programs related to HTRW, e.g., Installation Restoration Program and Formerly Used Defense Sites. The objectives are to provide consistency in the investigation of HTRW sites and design of remedial actions, to minimize overall time and costs required for the design and construction process, and to ensure that these efforts are completed at an established, uniform level of quality. Moreover, repetitive application of the economical and efficient investigation procedures and construction materials and methods established under this program reduces lost design effort, change orders during construction, and long term maintenance costs over the life of projects. The Corps produces several types of Guidance Documents which are available to the public. Information on how to obtain Guidance Documents is attached. Only those Guidance Documents that apply to innovative technologies are discussed below.

- Guide Specifications are used to assist bidders on remedial action projects by assuring uniformity to the description of work to be performed. Guide Specs under development are Landfarming and Soil Washing. In outyears Insitu Vapor Extraction Off-gas System Design Criteria and Chemical Oxidation will be prepared.

- Engineer Technical Letters (ETL) contain "advance" information on design, engineering and construction projects. They are considered intermediary publications that will eventually be republished in the more permanent media such as Engineering Regulations or Engineering Manuals. ETLs for Landfarming and Chemical (UV) Oxidation have begun. In the outyears Insitu Vapor Extraction Systems Off-gas Sytems is planned.

- Engineering Manuals (EM) contain technical guidance of a continuing nature concerned primarily with Engineering and Design Projects. EM on Soil Vapor Extraction has begun and in outyears one on Soil Washing is planned.

REMEDIATION OF HTRW SITES:

The major thrust of this paper is the use of innovative treatment technologies for remediation of HTRW sites by Corps districts. In functional terms, all technologies exclusive of incineration and solidification/stabilization for source control and pumping with conventional treatment for goundwater are considered innovative. Modifications to proven technologies can be considered innovative. The "Results" section of this paper present a more detailed overview of the Corps projects for which innovative technologies were used, are underway, have been selected, or being considered.

Methodology:

Data calls were made within the Corps to obtain information about specific HTRW sites involving innovative technologies. As such, the information obtained should not be considered to be totally comprehensive. However, data obtained do provide significant information from which conclusions and trends can be discerned. Additionally, the knowledge base associated with historical information is useful for future applications.

Results:

The most commonly used innovative technologies for soils include bioremediation, soil vapor extraction, low temperature thermal desorption, and soil washing. Other technologies used to a lesser degree are macroencapsulation, dechlorination, soil flushing, and solvent extraction. For groundwater, the most common innovative technologies are UV oxidation, bioremediation, and air sparging. Horizontal well applications reflect an innovative method of injection or extraction. Moreover technologies may be combined together in a treatment train for a more effective means to perform a restoration.

Bioremediation:

Bioremediation technologies involve degration of contaminants by microbial organisms. Nutrients, oxygen, or other amendments may be used to enchance the biodegration process. Bioremediation is effective for organic contaminants, especially simple hydrocarbons. However, bioremediation of chlorinated chemicals is more difficult to perform and can require special techniques. There are several approaches to bioremediation, but all fall under two categories, ex situ or in situ. Exsitu processes require the excavation or removal of contaminated media and transportion to treatment facilities. Insitu processes involve treatment in place.

Ex situ Bioremediation

Ex situ bioremediation is the most common category of bioremediation.

- **Landfarming** is a relatively simple technique in which contaminated soil is spread over a given area and periodically tilled to aerate. Usually indigenous bacteria are used. Collection of leachate and/or volatiles may be required. This versatile technique is used widely in warmer climates and is being tested and tried in colder climates.

o The Corps provided technical assistance to Ft. Polk, LA to develop a plot of eight acres for remediating soils from petroleum product spills on the installation. Once the soil is remediated, it is removed to allow more contaminated soil to be treated. This technique has saved Ft. Polk more than $1 M as an alternative to off site dumping.

o Ft. Ord, CA is developing a similar type of facility to be known as the Fort Ord Soil Treatment Area.

o Landfarming projects have been completed at Ft. Jackson, SC; Matagorda Island, TX; Davis Monthan Air Force Base, AZ; and Ft. Ord, CA. Landfarming projects are underway at Ft. Ord, CA (groundwater treatment train); Ft. Bragg, NC; and former Stead Air Force Base, NV. Landfarming projects are being designed at Bethel Bank Project, AK and former Glasgow Air Force Base, MT. Landfarming is an option at a site at Ft. Richardson, AK. Landfarming is planned for the former Chennault Air Force Base, LA.

o Cold climate techniques for landfarming are being studied in Farmers Loop, Fairbanks, AK and Fairbanks Airport, AK.

- **Composting** is a technique that involves combining contaminated soil with amendments such as horse manure or potato waste. The mixture is turned or aerated periodically until remediation is complete.

o Composting is underway at the Umatilla Army Depot Activity, OR which is on the National Priorities List. The contaminants are explosive wastes (TNT, RDX, & DNT).

- **Soil pile** is a general technique similar to composting in which contaminanted soil and bacteria are heaped in a pile that is turned occasionally until the remediation has been completed.

o This technique has been used successfully at Sheppard Air Force Base, TX and Williams Air Force Base, AZ. It is in the design stage at Ft. Wainwright, AL

- **Bioslurry/bioreactor systems** involve reactor vessels in which an aqueous slurry is created by combining soil or sludge with water and other additives (bioslurry) or contaminats in extracted groundwater are put in contact with microorganisms through attached or suspended biological systems (bioreactor). This process can be aerobic or anaerobic depending on the conditions needed to meet the cleanup endpoint.

o This technique is being used at Schilling Landfill, OH at a Superfund project as part of a treatment train. Data from a demonstration project at Joliet Army Ammunition Plant, IL showd that this approach will meet cleanup goals for TNT contaminated soil. Further studies are planned to extend this process for other contaminats and to optimize results.

o Anerobic bioslurry treatment of TNT contaminated soil was the subject of a demonstration effort at Weldon Spring, MO. Another anerobic bioslurry study is being planned for the Iowa Army Ammunition Plant.

In situ Bioremediation

These bioremediation techniques offer the advantage of providing "in place" treatment thereby avoiding soil excavation and groundwater extraction.

-**Bioventing** is the most common in situ bioremediation technique and involves supplying air through wells into the contaminated soil so that the bacteria are stimulated by the oxygen. It works especially well for simple hydrocarbons and can be used where is contamination is deep.

o Bioventing is underway at Ft. Carson, CO. This technique is being planned for Davis Monthan Air Force Base, AZ; Ft. Greeley, AK, and Kincheloe Air Force Base, MI. At Kelly Air Force Base, TX the Corps set up a soil vapor extraction system that will later be used for bioventing to remove remaining contamination.

- **In situ biodegradation** involves supplying oxygen and nutrients to stimulate naturally occuring bacteria. It can be used for soils and groundwater. Generally, this process includes conditioning of infiltration water with nutrients and an oxygen or other electron acceptor source.

o This technique is being used to treat soils and groundwater at the Aua Fuel Farm in American Samoa for diesel fuel contamination.

- **Natural restoration** is an alternative which should be considered if immediate risk is low and off-site migration is a minimal concern. Natural subsurface processes are known to reduce soil or groundwater contaminant concentration to acceptable levels without external stimulation.

o After collecting more than a year of data at a U.S. Army Reserve site at State College in PA, the results indicate that the contamination is being remediated by naturally present bacteria.

o A Record of Decision was signed for a groundwater site contaminated with TCE at Hanford, WA. The Corps is placing monitoring wells to demonstrate that contamination is being remediated by naturally occurring organisms.

Soil Vapor Extraction (SVE)

This technology involves applying a vacuum through the use of extraction well to remove the more volatile contaminants from soil. The process typically includes a system for handling off gases. It can be followed up by bioventing.

o SVE remediations have been completed at the Rocky Mountain Arsenal, CO (Motor Pool Area) and Sacramento Army Depot, CA (Tank 2 OU)

o SVE remediations are underway at sites on Commencement Bay (Superfund) South Tacoma Channel, Tacoma, WA; Langley Air Force Base, VA; Luke Air Force Base, Glendale, AZ; and Reese Air Force Base, Lubbock, TX.

o SVE remediations are planned for Sacramento Army Depot, CA (Burn Pits); ThermoChem Superfund, MI; Garden State Cleaners, Minotola, NJ; Holloman Air Force Base, NM (Bx Gas Station); and Marsh Run Park, New Cumberland, PA.

o SVE is under consideration at Silresim Superfund, Lowell, MA; Union Chemical Company (Superfund), South Hope, MA; Vance Air Force Base (Site 12), Enid OK; and George Air Force Base (Flightline Fuel Spill), Victorville, CA

Low Temperature Thermal Desorption (LTTD)

This technology involves heating contaminated soils at temperatures high enough (200 to 600 F) to drive off the volatile or semi-volatile contaminants, but well below those of incineration. The volatilized components must be collected and further treated. LTTD is a physical separation process not designed to destroy organics. This technology is often combined with other technologies.

o LTTD projects are underway at Ft. Wainwright (Stockpile of petroleum contaminated soil), AK; Savanna Army Depot Activity (Fire Training Area), Savanna, IL; Ft. Campbell (UST Removal & Cleanup), KY; and a site at the O'Hare International Airport, Chicago, IL.

o LTTD projects are planned for American Thermostat (Superfund), South Cairo, NY; Caldwell Trucking (Superfund), Fairfield Township, NJ; Claremont Polychemical (Superfund), Old Bethpage, Nassau County, NY; Metaltec/Aerosystems (Superfund), Franklin Borough, NJ; Waldick Aerospace (Superfund), Wall Township, NJ; Ft. Greeley (Texas Tower), AK; and Wright Patterson Air Force Base, Dayton, OH.

Soil Washing

Wash water separates small soil particles on which contaminants are sorbed from larger contaminant-free soil particles. The resultant reduction in contaminant volume reduces costs of further treatment. Soil washing is often used as part of a treatment train.

o Soil washing was used successfully at a Saginaw River, MI sediment project for concentrating PCBs to 10 ppm from 1-2 ppm. The contaminated soil was then treated using an experimental ex situ bioremediation technique.

o Soil washing is underway at Gould Battery (Superfund), Portland, OR; Sacramento Army Depot (Burn Pitts), CA; and Ft. Wainwright (petrolum contaminated soil stockpile), AK

o Soil washing is planned for Savanna Army Depot Activity (Old Burning Grounds), Savanna, IL and Sand Creek, Commerce City, CO.

UV Oxidation

This technology is the most widely used innovative technology for groundwater technology. Ultraviolet (UV) radiation, ozone, and/or hydrogen peroxide are used to destroy organic contaminants as part of a pump and treat system.

o UV oxidation is underway at Bofors Nobel (Superfund), Muskegon, MI; Sacramento Army Depot, CA; Rocky Mountain Arsenal (CERCLA water treatment plant), CO; New Bedford Harbor (Superfund), New Bedford, MA; and Hanscom Air Force Base (for sites 1, 2, & 3), MA.

o UV oxidation is planned at Milan Army Ammunition Plant, Milan, TN; Redstone Arsenal (three separate locations), Huntsville, AL; Groveland Wells 1 and 2 (Superfund), Groveland, MA; and Southern Maryland Wood Preservers (Superfund), Hollywood, MD o UV oxidation is under consideration at two sites on March Air Force Base, CA.

Air Sparging

This technology involves injecting air into the groundwater to release volatile contaminants which then can be captured by a soil vapor extraction (SVE) system.

o This approach is under consideration at Dover Air Force Base (WP-21), Dover, DE; Sacramento Army Depot (Parking lot 3), CA; Nellis Air Force Base, NV, and Hastings East Industrial Park Groundwater, Hastings, NE.

Other Technologies

The Corps has used, is planning to use, or considering other innovative technologies for soil and groundwater remediation but not as extensive as those covered above.

o **Dechlorination**, an ex situ technology, was used to treat soils containing PCBs at Wide Beach (Superfund), NY.

o **Soil flushing** is being used at the Lipari Landfill (Superfund), Glouster County, Pitman, NJ

o **Solvent extraction** is planned for the Norwood PCB Site (Superfund), Norwood, MA

o **Macro Encapsulation** has been complete for a project at the Naval Ordnance Plating Shop, KY

o **Modified Air Stripping** using sieve plates was conducted to remove TCE and diesel contaminants at the Cold Regions Research and Engineering Laboratory, Hanover, NH.

o **Funnel and Gate** reductive dechlorination is being planned at the Air Force Reserve site on the Duluth Air Force Base in MN.

o **Electro-osmosis** is under consideration at the Offut Air Force Base in Omaha, NE

CONCLUSIONS:

Because of inherent risks associated with innovative technologies, fear of failure promotes "defensive engineering" resulting in a natural bias toward tried and true technologies, i.e. proven technologies. Inadequate demonstration data/information is considered the largest source of risk associated with innovative technologies. Available information is often based only on bench scale efforts. As a result, full scale cost and performance data has not been available to support increased application of innovative technologies.

As more HTRW remediations involving innovative technologies are completed, availability of full scale cost and performance data will increase. As a result, there will be less reluctance associated with consideration and selection of innovative technologies. In particular, increased numbers of bioremediation applications are anticipated as understanding of potential applications grows. In situ techniques will likely receive greater consideration as the knowledge base increases. Enchanced research and development efforts for in situ treatment of contaminated groundwater (especially for metals contaminated) will be reflected in future innovative technology applications. The authors conclude that within the Corps, the use of innovative technologies for HTRW remediation is expected to increase.

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BENCH- AND PILOT-SCALE STUDY FOR THE BIOLOGICAL TREATMENT OF TCE IN GROUND WATER AT SITE 44, NELLIS AFB, NEVADA

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INTRODUCTION

Previous research by U.S. Air Force, Southern BioProduct Technologies (SBP) and researchers at the University of West Florida have isolated two microorganisms (*Pseudomonas cepacia* 17616 pTOM31c (17616) and *Pseudomonas cepacia* G4PR1$_{23}$ (PR1$_{23}$)) from a trichloroethylene (TCE) impacted aquifer. These microorganisms produce a monooxygenase enzyme capable of breaking TCE down into readily biodegradable forms, ultimately leading to complete mineralization (end products of carbon dioxide and water). Recent research efforts have focused on optimizing environmental conditions (growth carbon source, pH, nutrients, oxygen demand, and enzyme activity) that will allow the organisms to grow and proliferate, ensuring sufficient monooxygenase enzyme to remediate TCE-impacted sites. The capability to degrade hazardous constituents to their basic components at the site of the pollution would offer considerable treatment value and an alternative treatment train for pump and treat technologies.

The Air Force elected to perform a pilot study of this technology at an existing TCE-impacted area. The site selected for this Pilot Study was Site 44 of Nellis AFB's Installation Restoration Program (IRP). Site 44 occupies a 900 foot by 1,200 foot area along the flightline of Nellis AFB.

A Remedial Investigation (RI) of Site 44 ("Remedial Investigation of Site 44 at Nellis Air Force Base, Las Vegas, Nevada," Final edition, dated May 1994, prepared by Engineering-Science for the Fighter Weapons Center, Environmental Management Office, Nellis Air Force Base and Armstrong Laboratory/OEBE) identified a plume of TCE-contaminated ground water along the flightline at Nellis AFB. The RI also identified a second plume, adjacent to the TCE plume, that has elevated levels of benzene, toluene, ethylbenzene, and xylenes (BTEX). The significance of the second plume is that it represents a potential additional fuel source to aid in maintaining the organism in addition to the real potential of remediating two plumes with one technology.

The well chosen for the bench- and pilot-scale demonstration is located in the heart of the chlorinated hydrocarbon-contaminated plume where TCE is the major constituent of concern. A second monitoring well was selected to provide BTEX-contaminated ground water for bench-scale testing to evaluate the use of BTEX as a primary carbon source for 17616 and $PR1_{23}$.

SUMMARY OF BENCH-SCALE TESTING

The objectives of the bench scale test were to

- establish the aquifer ground water quality;
- evaluate the effectiveness of the two organisms (17616 and $PR1_{23}$) in degrading TCE;
- evaluate the impact of BTEX on organism sustainability;
- operate vapor and liquid phase bench scale units to evaluate biological treatment of TCE; and
- optimize the environmental conditions that allow the organisms to grow and produce the enzyme monooxygenase.

Data collected from the bench tests were used to determine whether and how fast a biological system can degrade the waste stream in question and also be used to optimize the engineering design of a pilot scale system.

The first objective was to establish the aquifer ground water quality in terms of nutrient supply for the organism and/or potential toxic constituents. The results clearly indicated that no inhibitory constituents existed in the site water, but that the waters were low in the nutrients, nitrogen and phosphorus. Bases on this information these nutrients would need to be supplemented during the pilot scale test. In addition, tests were run to determine if hydrogen peroxide could be utilized as an oxygen source for the organisms during treatment since air or oxygen injection could result in air stripping which would compete with the biological treatment. It was found that hydrogen peroxide was toxic to both of the organisms at concentrations above 68 milligrams per liter (mg/L).

The second objective was to evaluate the effectiveness of both microorganisms in degrading TCE. Several batch tests were run to document whether the organism could attain complete degradation of the TCE. These tests resulted in complete removal of TCE, benzene, and toluene; and greater than 90% removal of xylenes which indicate that both microorganisms could degrade TCE and BTEX in the site waters.

The breakdown of TCE is energy consuming and provides no net growth for the organisms. Consequently, the organism requires the presence of a food source. Therefore, the third objective was to evaluate the impact of BTEX on organism sustainability. BTEX was chosen as a possible alternate source since there is an adjacent BTEX contaminant plume located adjacent to the Site 44 TCE area. If the organism could utilize the BTEX, potentially, both contaminant sources could be treated simultaneously. A bench test was performed using BTEX-containing water from Nellis AFB as the only source of carbon for the organism. The results indicated the use of BTEX contaminated ground water would offer specificity and thereby maintain the dominance of either microorganism.

The fourth objective was to operate both vapor and liquid phase bench scale units to evaluate biological treatment of TCE. Results of the vapor phase test indicated that TCE biodegradation approached 60% at a feed rate of 0.34 micrograms TCE per minute and a residence time in the reactor of 13 minutes. Results of the aqueous phase test indicated biodegradation approached 78% at a feed rate of 0.13 micrograms TCE per minute and a residence time of 60 minutes.

PILOT SYSTEM DEMONSTRATION

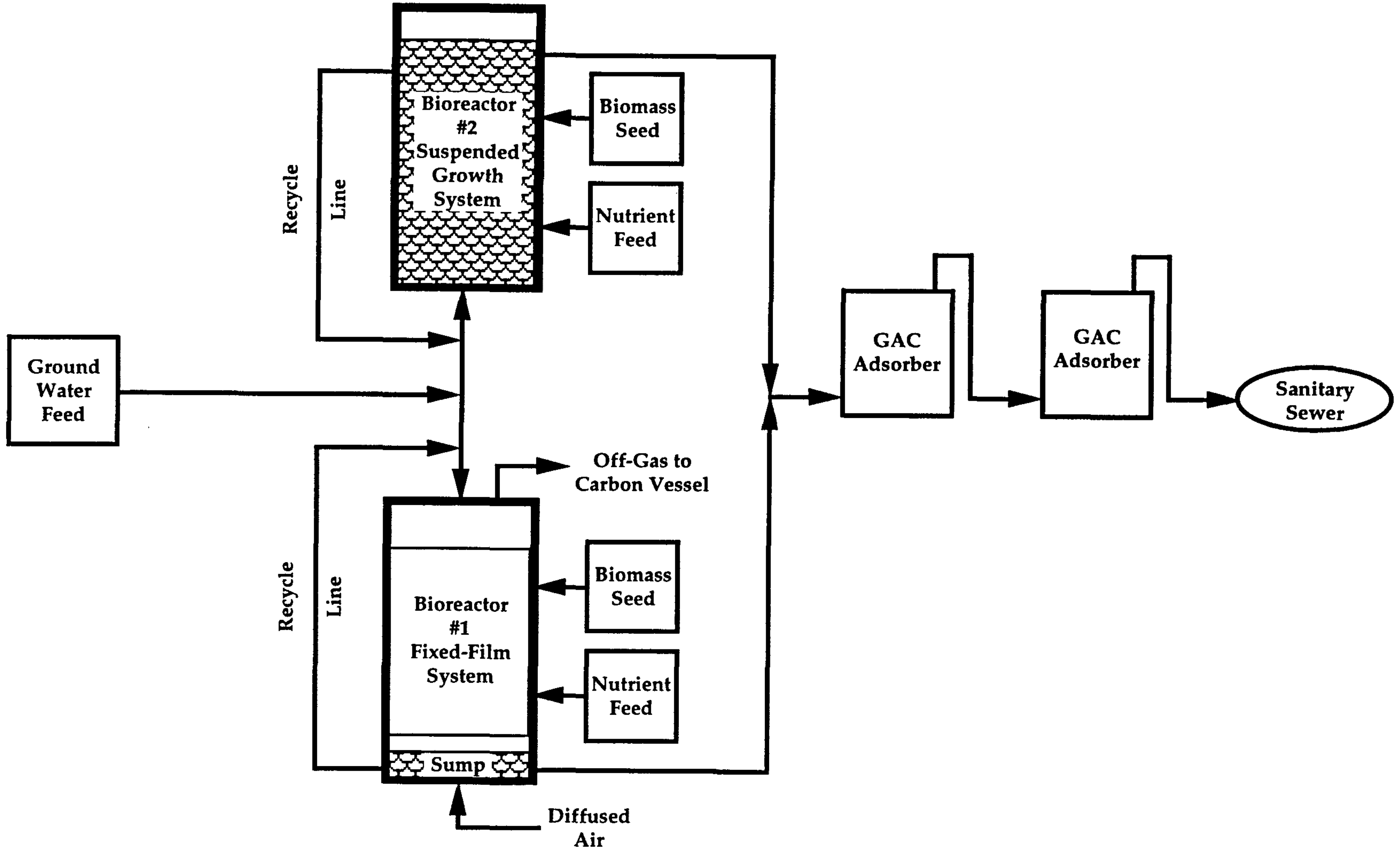
The primary objective of the pilot study was to demonstrate aerobic biological treatment of TCE-containing ground water using a microorganism specific for TCE degradation. Secondary objectives are the evaluation and optimization of two process alternatives (fixed-film and suspended growth). Based on the results of the bench-scale testing, it was decided to utilize microbial strain 17616 because it demonstrated better TCE biodegradation and better toxicity resistance than the other strain tested. Figure 1 shows a process flow diagram of the two systems utilized in the study.

Equipment Configuration

The fixed-film bioreactor was a 7.5 foot tall by 1 foot diameter stainless steel column with a working volume (empty) of 37 gallons. The column was packed with diatomaceous earth (DE) to a bed depth of approximately 4 feet as a support medium for biofilm development. Working volume of the packed column was approximately 28 gallons, with a void volume of approximately 18 gallons in the packed bed.

Figure 1

Nellis AFB Site 44 Pilot Demonstration
Process Flow Diagram



Initially, ground water feed was introduced into the top of the column and distributed across the cross section of the DE by a system of notched troughs. The system was also designed to allow ground water to be added to the center of the packed bed via two laterals. The water percolated through the DE packing to an aerated sump in the bottom of the column, where a portion was recycled to the top of the column (to maintain a moist biomass) and a portion pumped to a combined effluent sump. Biomass seed and nutrients were added to the recycle loop as necessary to establish and maintain the TCE-degrading biomass (strain 17616) on the DE packing.

The suspended growth reactor was also a 7.5 foot tall by 1 foot diameter stainless steel column with a working volume of 37 gallons. This reactor was designed to work as a conventional complete-mix activated sludge unit with supplemental dosing of TCE-degrading biomass (strain 17616). Ground water feed was introduced to the bottom of the column. The water was in contact with the biomass during the hydraulic retention time (HRT), after which a portion was recycled to the bottom of the column to aid in mixing and a portion overflowed to a clarifier tank. The clarifier was intended to remove settleable biomass for return to the column, while clarifier overflow would drain by gravity to the combined effluent sump. However, since no primary substrate was added to the suspended growth reactor, settleable biomass was negligible and the use of the clarifier was discontinued (reactor overflow sent directly to combined effluent sump). Additional biomass seed was added to the column as necessary to maintain an active TCE-degrading population within the reactor.

Ground water was recovered at a rate of between 0.1 and 0.2 gallons per minute (gpm) from well MW-7. To minimize TCE losses to volatilization, recovered ground water was pumped directly to each system. Bioreactor effluent was collected in a 55 gallon tank and pumped through two, 55 gallon granular activated carbon (GAC) absorbers in series to remove any remaining TCE. Treated water was then discharged to an existing Nellis AFB sewer manhole under a Clark County Sanitation District Permit.

Monitoring Requirements

A Photovac 10S50 portable gas chromatograph was used to analyze both gas and liquid samples for TCE on-site. During steady-state operation, 10 percent of the samples collected were sent to an off-site laboratory for verification of TCE analytical results. Other analyses to be performed on-site are shown in Table 1.

TABLE 1 - Analytical Parameters

COD (mg/L) - high/low range as necessary
TSS (mg/L) - filtration, dry at 105 °C and weigh
Volatile suspended solids (VSS) (mg/L) - similar to TSS except dry at 550 °C
Ammonia Nitrogen (mg/L) - calorimetric method (salicylate method)
Phosphate Phosphorus (mg/L) - calorimetric method
3-trifluoromethylphenol (TFMP) Activity Test - calorimetric method
BCA Protein Assay - calorimetric method
Plate Counts - following standard procedure for colony development and counting

Operational Parameters - Fixed Film Process

During start-up, the fixed-film system (R-1) was operated as a batch process and inoculated daily with batches of laboratory-grown microorganisms for a period of 6 days. The cells were added along with nutrients and sodium lactate as a primary carbon source. A lactate concentration of approximately 500 mg/L as COD (1.07 mg COD/mg lactate) was maintained during start-up, in order to rapidly establish the microorganisms on the packing. Growth of TCE-degrading biomass on the DE packing was evaluated based on protein and TFMP activity assays conducted on DE samples from the top and bottom of the packed bed. Once the biofilm had developed, continuous ground water flow was initiated and no further inoculation took place.

During continuous flow operation, nutrients and lactate feed were supplied daily. The nutrient feed for R-1 included nitrogen, phosphate, and the trace minerals necessary for aiding in the attachment of the biomass to the packing material and for assuring the growth and proliferation of the TCE-degrading microorganisms. In addition, lactate was added at a concentration of 50 mg/L as COD, supplementing the levels of organic carbon in the raw ground water to aid in the establishment and long-term maintenance of the TCE-degrading microorganisms on the packing material.

Optical density (A_{600}) and total suspended solids (TSS) of the reactor sump contents were measured periodically to monitor attachment of the microorganisms to the DE packing. DE samples from the top and bottom of the packed bed were analyzed for biomass protein and TFMP activity to assess the health of the TCE-degrading microorganisms and their distribution throughout the height of the packed bed.

The initial flow rate of ground water feed to the fixed-film reactor was just less than 0.2 gpm. The initial aeration rate was approximately 0.5 cubic feet per minute (CFM). On the basis of initial TCE concentration data obtained from on-site gas chromatography (GC), a TCE mass balance indicated that air stripping kinetics were out-competing the biodegradation kinetics. In an effort to favor biodegradation kinetics, the aeration rate was reduced, and the ground water feed was diverted to the center of the packed bed (recycle flow still went to the top of the bed). On the basis of continued high TCE values in the off-gas, the aeration rate was reduced several more times, in an attempt to reduce stripping while still maintaining an aerobic biomass.

Further testing was completed at reduced ground water flow rates down to approximately 0.1 gpm. Recycle rates ranged between 1.5 and 2 gpm. HRT in the sump ranged between 30 and 60 minutes. After it was discovered that the TCE-degrader was being overgrown by other organisms, it was decided to resume daily inoculation with 5 gallon batches of strain 17616 in an attempt to restore the activity of the TCE-degraders.

Operational Parameters - Suspended Growth Process

During start-up, the suspended growth reactor (R-2) was operated as a batch process and inoculated daily with a 5 gallon batch of TCE-degrading microorganisms, nutrients, and 5 gallons of ground water containing TCE for a period of 3 days, after which continuous ground water feed operations began.

Nutrients added to the suspended growth process consisted solely of nitrogen and phosphorus to meet biological growth requirements based on the TCE levels in the influent ground water. No co-substrate was utilized because activity was sustained by daily feeding of 17616 directly to the reactor. During the early part of the study, some COD carryover to R-2 from the 5 gallon cultures was noted.

Optical density (A_{600}) and TSS of the reactor contents were measured periodically to monitor the general health of the reactor. Liquid samples were analyzed for biomass protein and TFMP activity to assess the health of the TCE-degrading organisms.

The initial flow rate of ground water feed to the suspended growth system was approximately 0.5 gph (0.008 gpm), yielding an HRT of approximately 3 days. The initial aeration rate was approximately 0.25 CFM. On the basis of on initial TCE concentration data obtained from on-site GC, a TCE mass balance indicated that air stripping kinetics were out-competing biodegradation kinetics. As a result, forced aeration of R-2 was stopped. Since no lactate was added to the reactor, the biological oxygen demand was met by the DO in the ground water and recycle stream. Recycle rates ranged between approximately 0.07 and 0.2 gpm. The recycle rate was increased to improve reactor mixing when forced aeration was stopped.

The ground water feed rate was increased to approximately 0.8 gph (0.013 gpm), decreasing HRT to approximately 2 days to determine effect of HRT on treatment efficiency. Near the end of the demonstration, the ground water feed rate was increased to 1.5 gph (0.025 gpm), decreasing HRT to approximately 1 day in an attempt to wash out the system and provide an abiotic mass balance.

During continuous flow operation, R-2 was inoculated daily with 5 gallon batches containing strain 17616 and residual inorganic nutrients. Inoculation was reduced to 2.5 gallons per day, and then reduced further to approximately 0.25 gallons per day. As the daily inoculum volume decreased, the residual ammonia nitrogen carryover from the batch inoculum decreased. For this reason, a separate inorganic nutrient feed to R-2 was initiated.

CONCLUSIONS

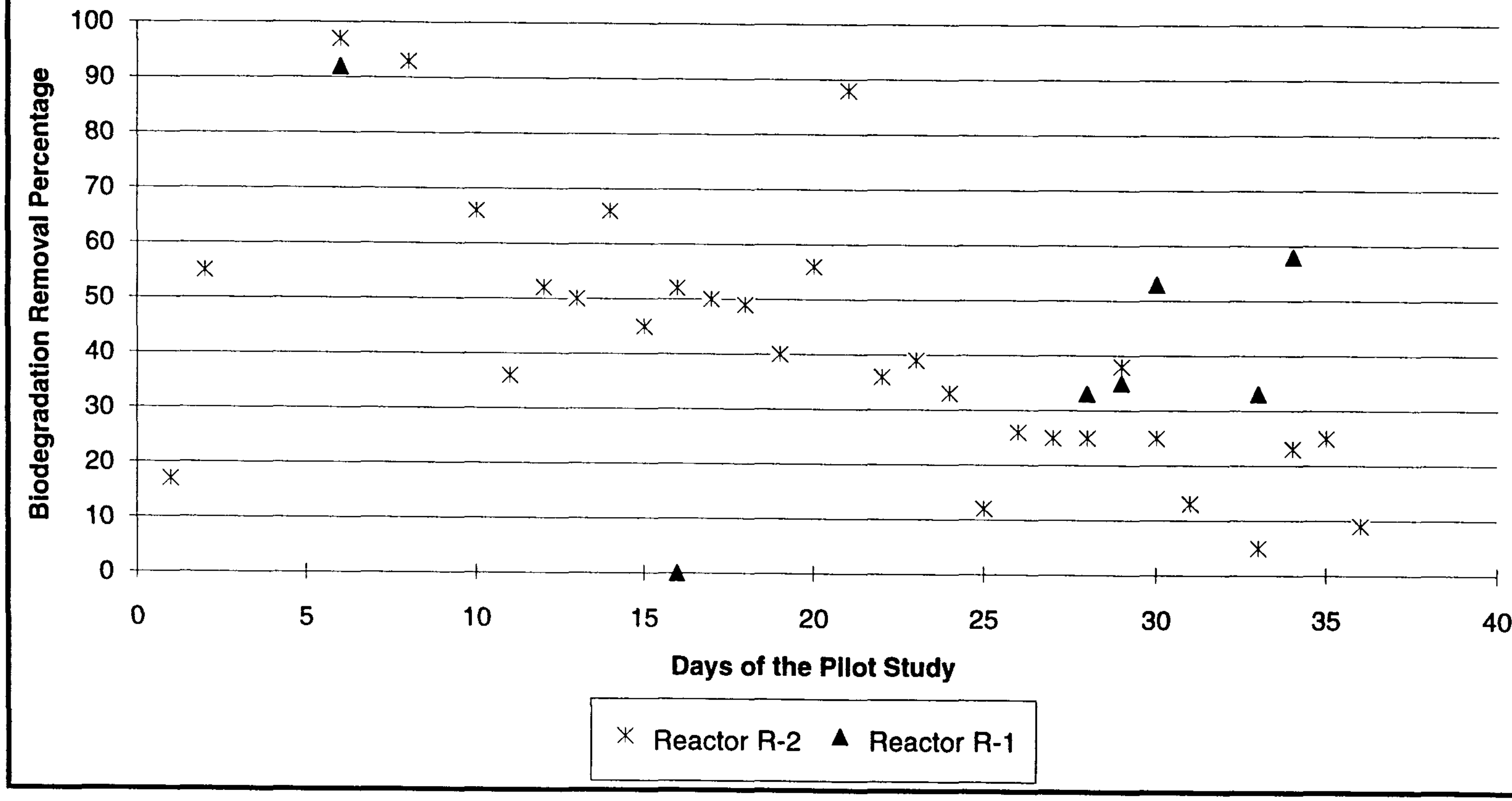
Based on this pilot-scale demonstration, it is concluded that bioremediation of TCE-contaminated ground water using the specialty microorganism *Pseudomonas cepacia* 17616 pTOM31c (17616) is feasible. The data and information collected during the study provided evidence that biodegradation did occur in both Reactors R-1 and R-2 (Figure 2). This data shows only the removal efficiencies calculated from off-site laboratory analysis. In-field analytical results coincided with the laboratory results in most cases but were not utilized in this figure to avoid confusion.

The limited time frame for completion and scope of the study did not allow for extensive testing to optimize the process. Although the results of the study allow for conclusions to be drawn about both types of reactor systems utilized in this study.

Application of 17616 in a fixed-film system is limited by requirements for a primary carbon source to establish and maintain the biofilm. With a high biological oxygen demand, an alternate source of oxygen is required. However, forced aeration will result in air stripping that would ultimately out compete biodegradation. Application of 17616 in a complete-mixed suspended growth reactor is limited by reactor sizing (based on required HRT) and incoming contaminant concentration to maintain biomass to achieve the required TCE removal efficiencies.

The study provided invaluable field data on the use of this microorganism. Future testing should be geared to providing a better understanding of the relationship among 17616 activity duration, TCE concentration, and primary substrate dosage. Optimization of the operating parameters and limitations can then

Figure 2 - Biodegradation Removal Percentage for Reactors R-1 and R-2



be completed and a full-scale design and operation of a system could be evaluated effectively against other technologies.

The site-specific conditions (low TCE concentrations, proximity of the plume to the flightline, limited definition of the plume, uncertain treated water discharge location, etc.) at Site 44 limit the potential usefulness of this technology.

One of the main factors that would need to be considered for use of this type of system is the existence of an economic carbon substrate on which the microorganism 17616 can flourish. During the breakdown of the TCE molecule, the microorganism uses more energy that it can then gain back from degrading the carbon portion of that molecule. Therefore, a carbon substrate is needed to maintain a healthy abundance of the microorganism. The location of a BTEX plume in such proximity to the TCE plume, such as at Site 44, offers an excellent opportunity to utilize a high-concentration carbon source (BTEX) that is readily available for the cost of running a pump. The bench-scale testing indicated that 17616 could survive on BTEX-contaminated ground water and would grow to accommodate the degradation of TCE. An added benefit is that this treatment could also be used to remediate the BTEX plume.

An additional factor that should be considered for potential further evaluation is determining the presence of any potential TCE-degrading microorganism in the ground water. Such an organism was found at Nellis, although the concentrations were low. This technology can be evaluated further. Testing should center on whether some type of stimulation to promote organism growth may yield a means of in-situ bioremediation via addition of oxygen and nutrients. Consideration could also be given to an in-situ bioaugmentation process, growing 17616 on-site using extracted contaminated ground water and introducing these organisms with additional nutrients and oxygen into the treatment area to decrease the time period for cleanup.

EVALUATION OF ULTRAVIOLET OXIDATION METHODS FOR THE REMEDIATION OF EXPLOSIVES-CONTAMINATED GROUNDWATER

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INTRODUCTION

The U.S. Army Environmental Center (USAEC) has performed an evaluation of commercially available ultraviolet oxidation (UV/OX) processes for the remediation of explosives-contaminated groundwater by conducting a pilot-scale demonstration at Savanna Army Depot Activity (SADA), located in Savanna, Illinois. This demonstration was performed to assess whether UV/OX methods offer a technically feasible and cost-effective alternative to granular activated carbon (GAC) for the treatment of explosives compounds including trinitrotoluene (TNT), trinitrobenzene (TNB), and other nitroaromatics found in groundwaters at Army installations nationwide. Roy F. Weston, Inc. (WESTON®), of West Chester, Pennsylvania, was contracted to coordinate the demonstration and evaluate the results.

Currently, GAC is the conventional technology for treating wastewaters and groundwaters containing explosives and nitroaromatics. Although the technique is simple and effective, the resulting spent carbon containing the explosives is listed as a K045 hazardous waste and requires additional treatment and/or disposal.[1] This spent explosives-laden carbon can either be regenerated at a single commercial facility in the United States or be incinerated at a permitted incinerator at a high cost. In contrast, the UV/OX methods are destructive processes in which the target organic compounds are fully oxidized to the relatively innocuous end products of carbon dioxide, water, and salts. The absence of a residual requiring additional treatment from these processes makes them an attractive solution, if their treatment effectiveness can be demonstrated for nitroaromatic compounds.

In addition to evaluating the treatment effectiveness of UV/OX methods, USAEC hoped to identify which of the commercially available process configurations offer the more economical treatment of explosives and nitroaromatics and to assess the adequacy of bench-scale testing data for predicting full-scale equipment requirements. Pilot-scale studies are an inherent, but expensive, component of UV/OX technology implementation. Significant savings could be realized by minimizing or eliminating the need for competitive, multiple vendor pilot-scale testing. Streamlining the evaluation and implementation of UV/OX systems for treating explosives-contaminated groundwater is feasible only if the treatment effectiveness and economics of the individual vendor processes can be accurately assessed on the basis of bench-scale testing results.

METHODS

Initial planning of this evaluation included the findings of a literature survey on the current state of UV/OX technologies and discussions with technical staff and plant walkthroughs at selected UV/OX vendors' facilities. In addition, analytical data contained in the Army's Installation Restoration Data Management Information System (IRDMIS) on the concentrations of explosives and selected treatability parameters in groundwater at several Army facilities were examined in selecting a suitable demonstration site. SADA was selected on the basis of these IRDMIS data and on operational aspects such as adequate hydraulic conductivity to allow withdrawal of sufficient groundwater for the testing and the proximity of shelter and utilities. The information gained from these planning activities and the site selection process was used (1) to finalize the approach for the technology evaluation, (2) to develop a comprehensive work plan for conducting the study, and (3) to issue a Request for Proposal (RFP) to seven commercial UV/OX system vendors for potential participation in the demonstration project.

The project work plan described the nature of contamination at the SADA test area, the design and materials of construction for the groundwater recovery and distribution system, monitoring instrumentation, post-UV/OX system GAC polishing system, and the final effluent conveyance and outfall. In addition, the work plan documented the sampling schedule and methods, the sample handling and shipping, the analytical methods, and the field and laboratory quality assurance and quality control procedures to be used during the demonstration and subsequent data evaluation.[2] The extensive planning and design effort was necessary to ensure the proper functioning of the groundwater supply/distribution and other ancillary systems during testing and to obtain all the data required to meet the project objectives.

Four commercial vendors were invited to operate their UV/OX processes at SADA. These vendors were selected based on their responses to an RFP issued for the demonstration. The technical merit of the proposals, followed by qualifications and experience, and cost were the evaluation criteria, in order of decreasing weight, in the decision matrix developed for vendor selection. Based on the evaluations of the proposals, the four vendors selected for participation in the demonstration were Purifics Environmental Technologies (Purifics), Solarchem Environmental Systems (Solarchem), Ultrox International (Ultrox), and Vulcan Peroxidation Systems Incorporated (VPSI). Each of the participants conducted bench-scale testing of their respective systems using groundwater samples collected from SADA. Although specific requirements for the economic data and cost estimates to be prepared on the basis of bench-scale testing were provided, the participants were free to determine the appropriate methods and materials to be used in the bench-scale tests. Once the bench-scale testing was complete, the vendors submitted bench-scale test reports and subsequently mobilized pilot-scale systems to SADA for the pilot-scale demonstration.

The pilot-scale demonstration program was conducted under the supervision of WESTON and USAEC personnel. Construction and oversight tasks included site preparation, implementation of health and safety protocols, systems monitoring, and sampling and analyses. The focus of this demonstration was on evaluating the performance of each UV/OX process based on common input conditions. A common groundwater distribution system was installed to ensure that all four vendors were receiving groundwater of identical quality. The participants were free to select an appropriate flow rate of up to 10 gallons per minute for their process. Each participant's flow rate and electrical energy usage were logged hourly. A common influent sample and individual effluent samples from each process were collected three times daily at random intervals and submitted for explosives analyses by EPA Method 8330. The primary target compounds in this demonstration, TNT and TNB, were the dominant nitroaromatics in the influent groundwater.

RESULTS

Daily average effluent concentrations of TNT, TNB, and the other nitroaromatic compounds were calculated by averaging the results of the three random effluent samples collected daily from each of the processes. Daily averages were compared with the daily average treatment criteria that were established by the Illinois Environmental Protection Agency. All four UV/OX process configurations achieved the treatment criteria for TNT and TNB on one or more days of the demonstration. There was considerable variation in the consistency with which the processes met these criteria. Only the Ultrox process (Figure 1) achieved the criteria for all 14 days of the demonstration. The Purifics process (Figure 2) achieved the criteria for TNT and TNB on four days during the last week of the demonstration and after an effective modification was made to its treatment process. However, the Purifics processes failed to meet the criteria for 1,3 DNB because the effluent contained 1,3 DNB slightly above the effluent criteria of 4 μg/L. The Solarchem process (Figure 3) met the criteria on three of the days because it encountered difficulties in meeting the TNT criterion. The VPSI process (Figure 4) met the criteria on one day of the demonstration. Although the TNT concentrations were typically below the criterion, the VPSI process had difficulty meeting the TNB criterion.[3]

The participants were required to prepare initial cost estimates after bench-scale testing for a full-scale system and to subsequently revise the cost estimates on the basis of the pilot-scale test data. Cost estimates were based on a hypothetical groundwater remediation with a design flow of 50 gallons per minute and a groundwater quality similar to that of the water treated during the demonstration at SADA. The discharge criteria were

FIGURE 1

Purifics Treatment Results

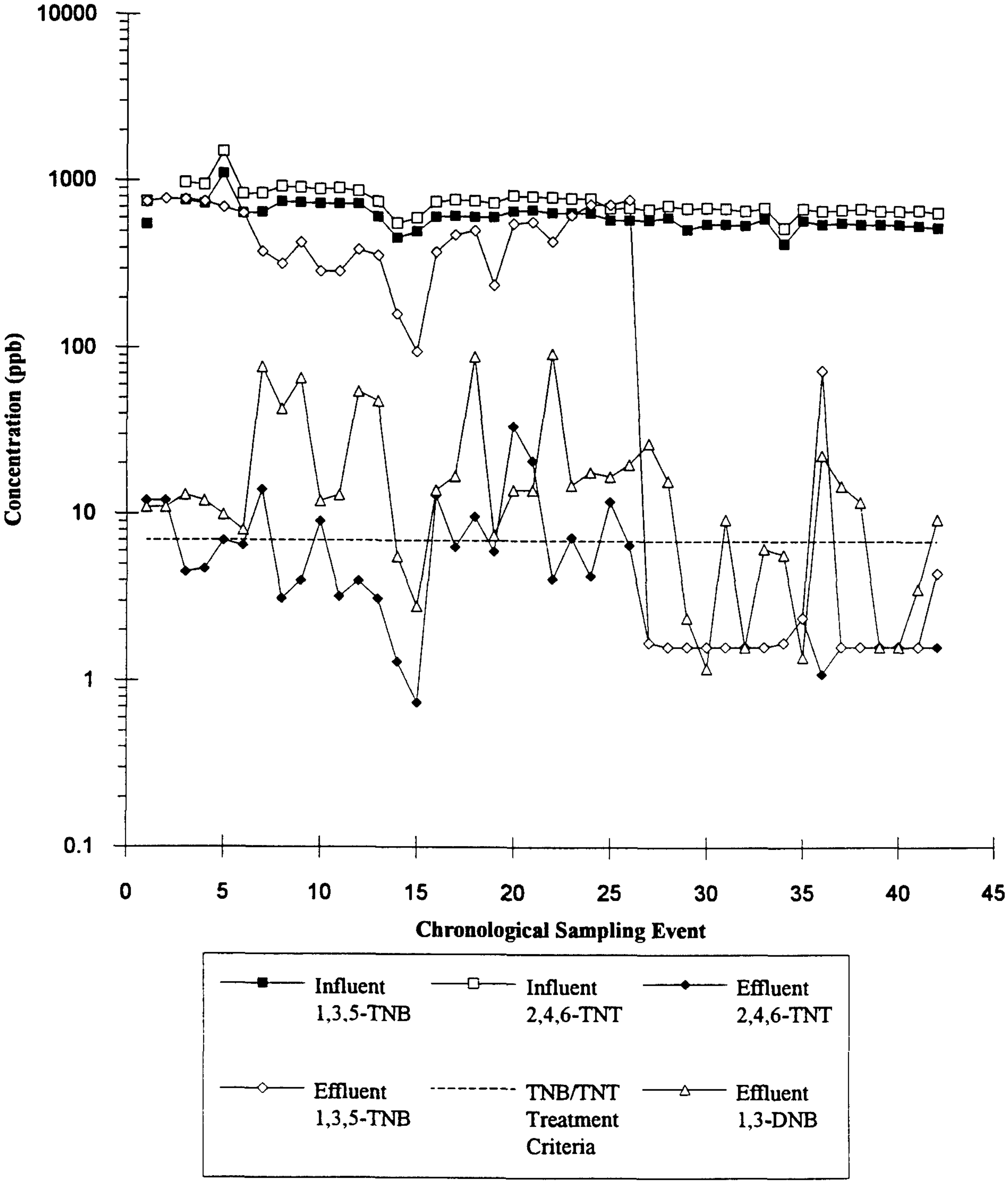


FIGURE 2
Solarchem Treatment Results

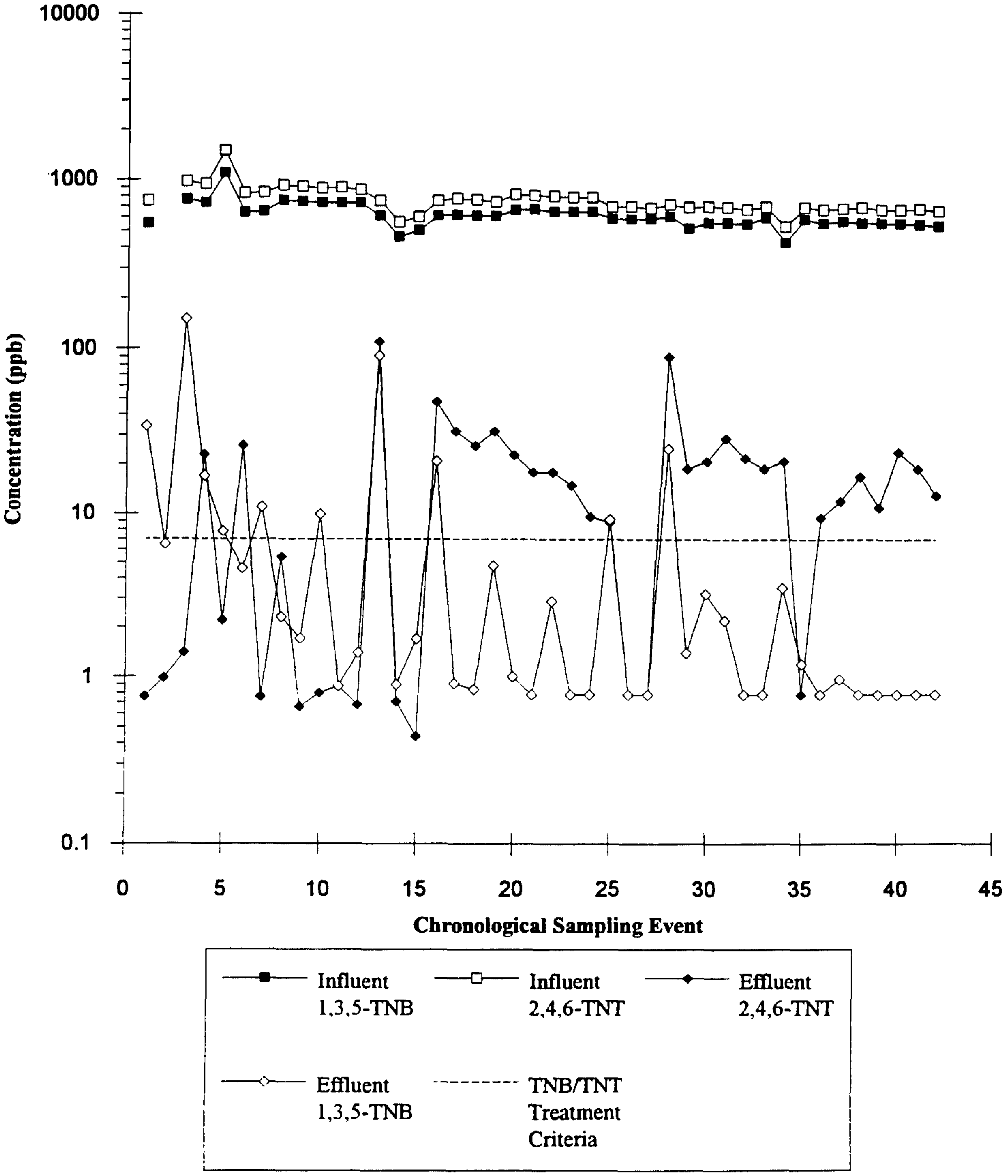


FIGURE 3

Ultrox Treatment Results

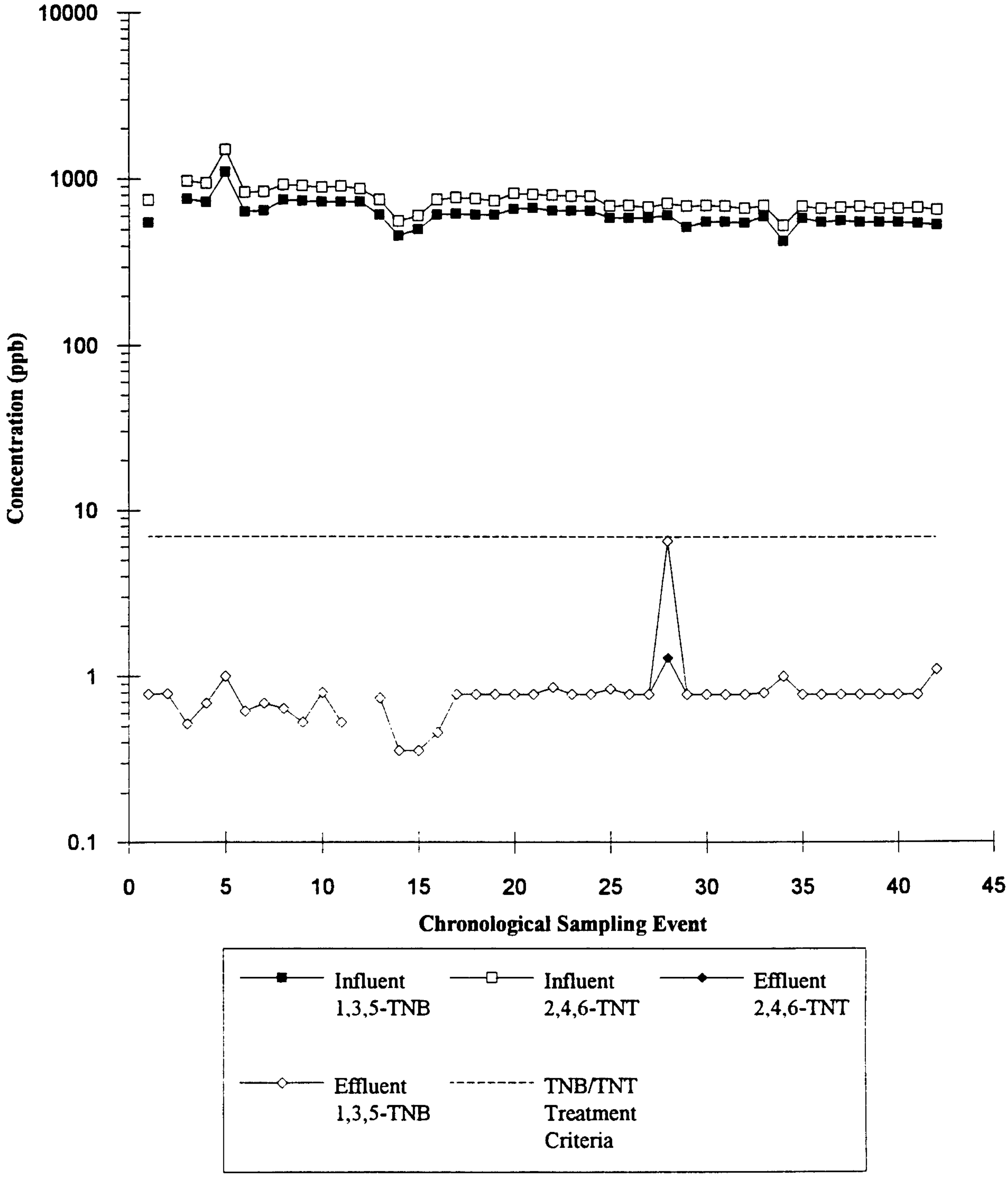
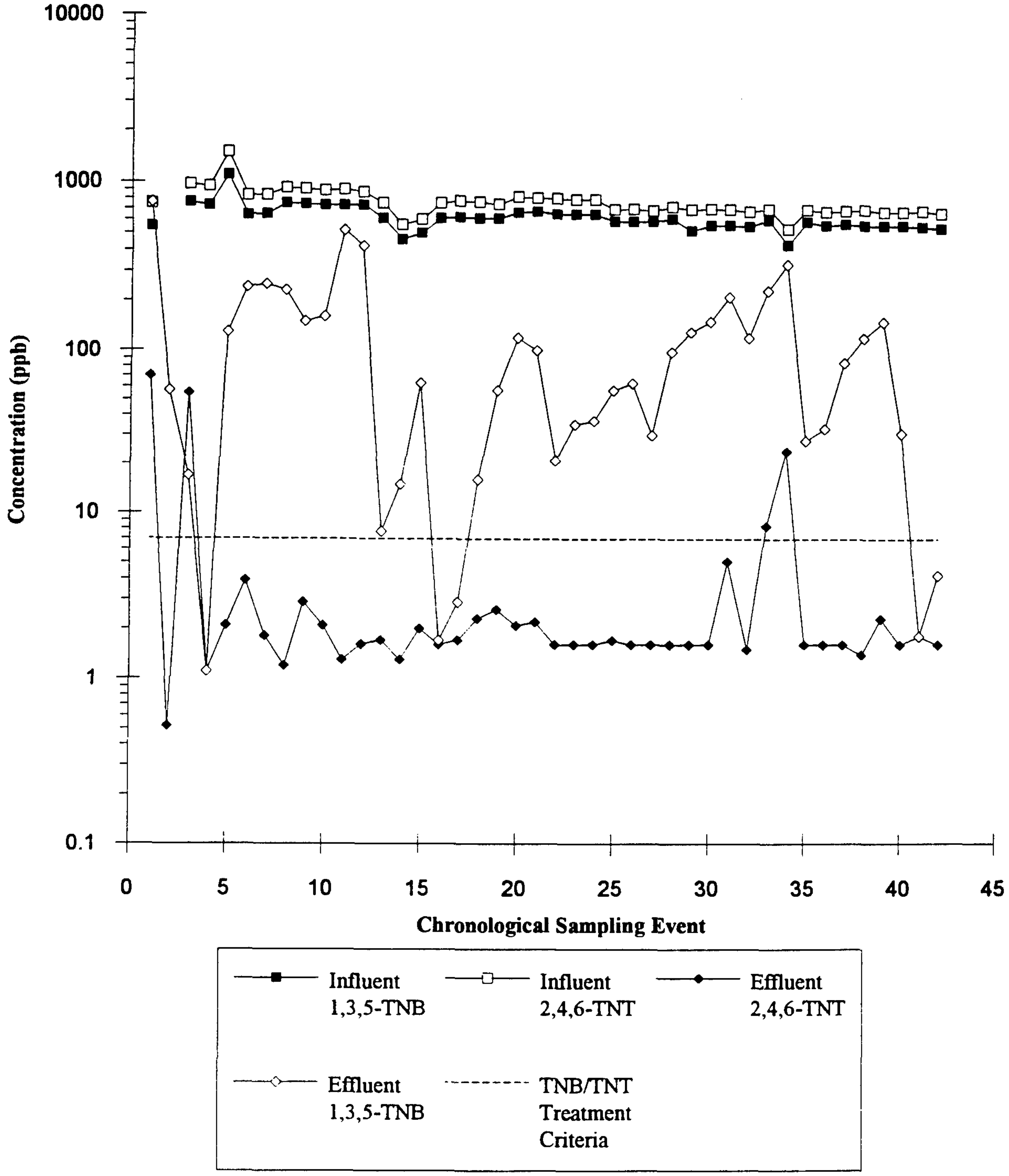


FIGURE 4
VPSI Treatment Results



identical to those imposed during the demonstration. This approach allowed the evaluation of whether the initial system sizing and cost estimates provided after bench-scale testing were accurate or whether the data collected during the pilot-scale demonstration resulted in significant modifications to the equipment and costs of the prescribed full-scale systems. Initial and revised capital and annual operation and maintenance (O&M) cost estimates provided by the participants for their full-scale systems are shown in the table.

Based on the initial full-scale system capital and annual O&M costs provided by each of the vendors following bench-scale testing, 30-year present worth values were calculated with a 5.25% interest rate and a 3.5% inflation rate and are as follows:

- Purifics: $3,388,355
- Solarchem: $5,009,758
- Ultrox: $2,629,528
- VPSI: $10,359,390

The revised present worth values calculated after the performance of the pilot-scale demonstration using the same interest and inflation rates are as follows:

- Purifics: $3,300,853
- Solarchem: $6,082,350
- Ultrox: $2,650,591
- VPSI: $11,102,291

The net present worth values were based on the treatment of groundwater only and do not include the costs for structures, well installation, conveyance piping, pumping, effluent monitoring, and other ancillary costs that would be incurred with any type of pump and treat groundwater remediation project.

CONCLUSIONS

Based on this demonstration, routine bench-scale testing is inadequate for providing sufficient data for accurate design, sizing, and costs for full-scale UV/OX systems for remediating explosives-contaminated groundwater. On the basis of bench-scale testing, only one of the four vendors was able to prescribe and operate a pilot-scale system that consistently achieved the discharge criteria for all 14 days of the demonstration. Furthermore, the full-scale system configurations and cost estimates made after bench-scale testing and after pilot-scale testing were significantly different, indicating that pilot-scale testing provides important data necessary for the accurate sizing of full-scale systems. Nonetheless, bench-scale testing appears adequate for evaluating the technical feasibility of UV/OX processes and for obtaining conceptual level costs for explosives remediation. More comprehensive and rigorous bench-scale testing and analysis, performed under oversight and in accordance with a formal test plan, could be adopted for use in competitive bench-scale testing. These procedures could either minimize or eliminate the need for competitive, multiple vendor pilot-scale testing. Refinements in the bench-scale testing protocols could be adopted as additional experience with UV/OX treatment of explosives compounds and their breakdown products at bench-, pilot-, and full-scale levels is gained by the Army and system vendors. These refined bench-scale testing protocols might provide sufficient information for full-scale design decisions and allow for the more accurate assessment of the economics of these systems.

Bench-Scale vs. Pilot-Scale Cost Comparison

Vendor	Bench-Scale Estimate		Pilot-Scale Revised Estimate	
	Capital Cost ($)	Annual O&M Cost ($)	Capital Cost ($)	Annual O&M Cost ($)
Purifics	695,230	115,632	687,500	112,216
Solarchem	600,000	189,000	480,000	239,936
Ultrox	583,000	87,904	393,000	96,813
VPSI	650,000	415,719	650,000	447,496

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[2] WESTON. September 1994. *Evaluation of Ultraviolet Oxidation (UV/OX) Methods for the Remediation of Explosives-Contaminated Groundwater,* Work Plan Prepared for USAEC.

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MANGANESE AND TRACE METAL REMOVAL IN SUCCESSIVE ANAEROBIC AND AEROBIC WETLAND ENVIRONMENTS

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ABSTRACT

Constructed wetlands designed for removal of Fe from acid mine drainage can be an effective technology with removal rates ranging from 10 to 20 g/m^2/d. Removal of Mn is less effective, especially in the presence of Fe^{2+} which readily reduces any oxidized Mn formed. Although not a widespread concern now, removal of trace metals will become increasingly more important in metal-laden wastewater with imposed discharge limits. A microcosm study was conducted to evaluate the use of anaerobic wetland systems preceding aerobic wetland systems for removal of Mn, Cu, Ni, Zn, and Pb in wastewater. Initial concentrations for Mn, Cu, Ni, Pb, and Zn were 20, 2.1, 1.5, 1.9, and 2.1 mg/L, respectively. Each experimental unit consisted of three troughs set in series. The first trough was anaerobic and the last two were aerobic. The anaerobic troughs with organic matter were effective in reducing SO_4^{2-} to S^{2-} and producing alkalinity in the range from 80-300 mg/L. Production of alkalinity decreased with time and coincided with seasonal decline in water temperature. Manganese removal in the anaerobic systems decreased with time which may have been due to decreased $MnCO_3$ precipitation with decreased alkalinity. Manganese removal in the reciprocating aerobic cells was quicker than in the nonreciprocating aerobic cells. Removal in the aerated systems appeared to be due to precipitation of Mn oxides. Removal of Cu, Ni, Zn, and Pb was very effective in the anaerobic cells with organic matter and was presumed to be due to precipitation of metal sulfides.

INTRODUCTION

Due to federal limits placed on Fe and Mn concentrations in acid mine drainage effluent, considerable research has been conducted on the use of wetlands for removal of these metals. Monthly averages for Fe and Mn concentrations must be below 3 and 2 mg/L, respectively (1). Both aerobic and anaerobic surface-flow wetlands have been used. Aerobic wetlands consist of a layer of water over soil with O_2 supplied via diffusion. Iron and Mn removal occurs via precipitation of metal oxides. Anaerobic wetlands consist of a layer of organic matter placed on top of soil material. Anaerobic conditions are imposed with high C in the organic layer and rapid depletion of available O_2. Anaerobic conditions promote SO_4^{2-} reduction to S^{2-} and subsequent precipitation of metal sulfides.

Removal rates for Fe and Mn in surface flow wetlands range from 10 to 20 and 0.5 to 1 $g/m^2/d$, respectively (1). The reason for less efficient removal of Mn is due to slower kinetic processes in the oxidation of Mn(II) (2). Ferrous Fe readily oxidizes to ferric Fe at pH above 3.5 with rapid precipitation of ferric Fe oxyhydroxides. Uncatalyzed manganese (II) oxidation does not occur readily until pH >10 (3). Mn (II) oxidation can be catalyzed by sorbing solids (4) or microorganisms (5, 6) from pH 6 to 9. Another process that limits Mn removal is the reduction of oxidized Mn in the presence of ferrous Fe. Ferrous Fe will readily reduce oxidized Mn precipitated as oxides, keeping Mn in solution (1). Due to the disadvantageous interaction between Fe and Mn, Mn removal in acid mine drainage does not occur significantly until Fe is reduced to low concentrations.

Passive Mn removal has been studied in a number of systems. Gordon (7) and Gordon and Burr (8) found Mn oxidation to be related to a black microbial coating found on rock surfaces. Adequate Mn removal occurred in rock bed filters with a similar black coating observed on rock surfaces (9) and with gravel beds supporting a green algae-microbial mat consortium (10). Manganese removal in both systems was purported to be biotically controlled. Biotic mediation in the algae mat may have been due to O_2 release and CO_2 uptake from the algae, maximizing Mn oxide precipitation in aerobic alkaline microenvironments (6). McMillen et al. (11) studied the use of unsaturated vertical flow wetlands to provide enough O_2 for Mn oxidation and precipitation and found effective Mn removal at initial Mn concentrations ranging from 60 mg/L to 0.5 mg/L. When a biocide was added, Mn removal remained high which indicated that abiotic catalysis of Mn oxidation and precipitation was the controlling factor for Mn removal.

Iron and Mn have been the focus for metals removal in acid mine drainage. However, removal of trace metals in acid-mine drainage and other metal-laden wastewater will receive more attention in the future due to impending limits on effluent concentrations. Concentrations of Fe and Mn in acid mine drainage can range from 2 to 150 mg/L, while concentrations of trace metals such as Cu, Ni, Pb, and Zn are usually less than 2 mg/L. An appropriate passive technology for trace metal removal is anaerobic wetlands since many of the trace metals of concern form metal sulfides with very low solubility. The disadvantage with surface-flow anaerobic wetlands is the anaerobic conditions are limited to the water-sediment interface with not all of the water being exposed to the reducing conditions. Improvement of treatment efficiency can occur by forcing water downward through an organic layer as done with successive alkalinity producing systems (SAPS) (12). A typical SAP design consists of a surface layer of 1.6 to 1.9 m of water, 45 cm of compost below the water, and a 45 to 60 cm layer of limestone rock below the compost. The system provides reducing conditions and adds alkalinity to the water from SO_4^{2-} reduction and limestone dissolution.

The objectives of the current study were to evaluate the use of anaerobic and aerobic wetland cells to remove Mn, Cu, Ni, Pb, and Zn in simulated acid mine drainage pretreated by an anoxic limestone drain and surface-flow aerobic wetlands. The anaerobic cells were hypothesized to remove the trace metals via sulfide precipitation. The aerobic cells were hypothesized to remove Mn via oxide formation.

MATERIALS AND METHODS

The study was conducted inside a greenhouse at the TVA Environmental Research Center in Muscle Shoals, AL. The cells used to simulate anaerobic and aerobic wetlands were insulated cattle feeding troughs that measured 1.1 x 0.6 x 0.6 m^3. The troughs were lined with a 40 mil plastic liner to prevent metal leakage from the galvanized steel. Each experimental unit consisted of 3 troughs placed in series with the first trough being the anaerobic cell and the second two troughs being the aerobic cells (Fig. 1). The troughs were plumbed with PVC pipe so water entered the surface of the first cell, exited at the bottom of the first cell, entered the second cell at the bottom, exited the surface of the second cell, entered the surface of the third cell, and exited on the bottom of the third cell. Surface area of one experimental unit was 1.9 m^2.

The experiment included 6 experimental units with 3 anaerobic treatments and 2 aerobic treatments. The anaerobic treatments consisted of canarygrass (CG) (*Phalaris arundinacea)*, SAPS (S) (12), and a SAPS+canarygrass combination (CG&S). The S treatment had a bottom 10 cm layer of crushed limestone gravel, a 30 cm layer of composted chicken litter, and an 18 cm surface layer of water. The CG treatment consisted of canarygrass planted in 58 cm of river gravel. The CG&S treatment consisted of river gravel on top of compost as in the S system and canarygrass planted in the gravel.

The anaerobic treatments were replicated 2 times. Three replications of each aerobic treatment were placed after a complete set of anaerobic treatments. The two aerobic treatments consisted of reciprocating the top 20 cm of water from one cell to another (w/recip) or not reciprocating (wo/recip) (18). The water was air-lifted by placing airstones at the bottom of each of 2 paired aerobic cells. The airstones were placed within a 5 cm diameter pipe. Air was intermittently pumped to each airstone at 15 minute intervals. The air pumped through the air stone moved the top 20 cm of water from one cell to another which exposed rock surface biofilms to air and provided aeration of the water.

After putting the appropriate media in the cells, 2 L of septic tank effluent were added to the composted chicken litter and on the surface of the planted gravel in order to inoculate the system with sulfate reducing bacteria. Nutrient solution was flowed through the anaerobic cells at 20 ml/min for a period of 1 month to nourish the canarygrass and sulfate-reducing bacteria. The nutrient solution contained 112, 137, 55, 12, 46, 2.3, 3.6, and 186 mg/L NH_4-N, Ca, K, P, Mg, Na, Cl, and S, respectively. Micronutrients in the solution consisted of 11, 59, 55, 17, 13, 3.2 and 296 µg/L B, Co, Mn, Mo, Zn, Cu, and Fe, respectively.

Acid mine drainage that simulated water pretreated with an aerobic wetland was passed through the experimental cells on August 24, 1994 after the cells were acclimated with nutrients. The salts $MnSO_4.H_2O$, $FeSO_4$.7H2O, $NiSO_4$, $CuSO_4.5H_2O$, $PbSO_4$, $ZnSO_4.7H_2O$, $CaSO_4$, and $MgSO_4.7H_2O$ were added to 1135 L resulting in expected concentrations of 20, 1.5, 2, 2, 2, 2, 90, 90, and 209 mg/L of Mn, Fe(II), Ni, Cu, Pb, Zn, Ca, Mg, and S, respectively. The solution was added to the first trough in each experimental unit at 20 ml/min. This flow rate results in loading rates of 0.82 and 0.12 g/m^2/d for Mn and Fe, respectively, and a loading rate of 0.08 g/m^2/d for the trace metals Cu, Ni, Pb, and Zn. Assuming the effluent water from TVA aerobic wetlands (13) were treated by an equivalently sized wetland system for Mn removal, the Mn loading rates would range from 0.03 to 1.73 g/m^2/d with an average of 0.34 g/m^2/d.

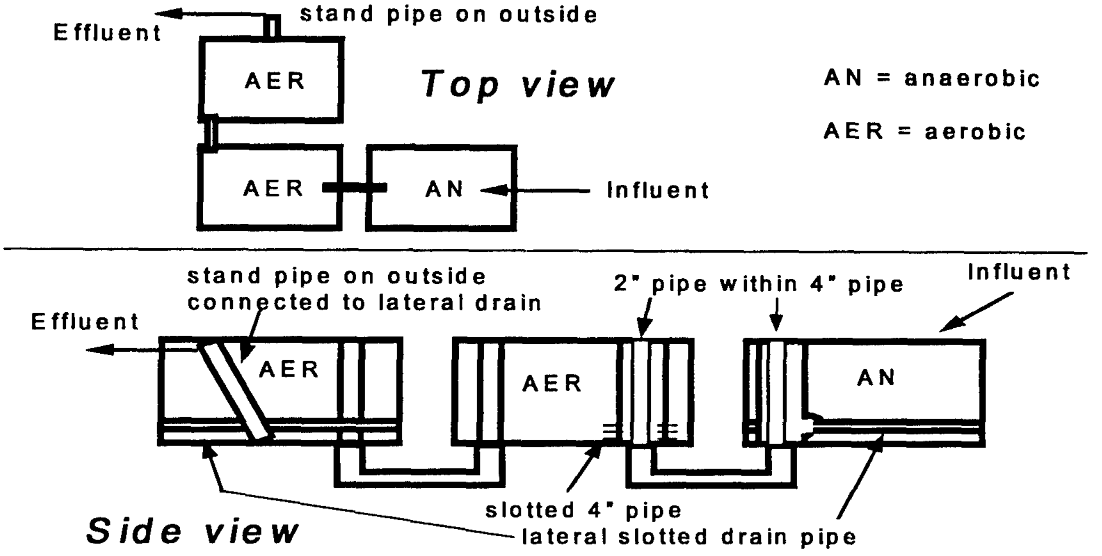

Figure 1. Diagram of one experimental unit used in the study.

Based on rock and compost porosity, the average pore volume in the cells was 35%, the retention time through each trough was 4.6 days and the retention time through the experimental unit was 13.8 d. Retention time through the organic layer in the anaerobic cells was approx. 2.3 d. This retention time is less than the retention times of 5-10 d reported to be maximum required for adequate SO_4^{2-} reduction (14). The retention time through the limestone layer in the SAPS is approx. 0.9 d which is greater than the retention time of 0.5 d required for maximum alkalinity production (1). The hydraulic load for the whole experimental unit is 1.6 cm/d and is within the range of hydraulic loads of 0.9 to 27 cm/d reported for wetland systems treating acid mine drainage (1, 13).

Approximately once a month for a total of 4 sampling periods, water samples were collected for chemical analysis. Samples were collected in 4 locations at the influent, effluent of anaerobic cells, a 10 cm well in the first aerobic cell, and final effluent from the aerobic cell. Samples were analyzed for Fe, Mn, Ni, Cu, Pb, Zn, Ca, and Mg by inductively coupled plasma spectrophotometry (ICP). Sulfate was determined by ion chromatography. Alkalinity was determined via titration with NaOH. Total organic C was determined by TOC analyzer. Sulfide was determined with a S^{2-} ion-selective electrode. pH was determined with a glass electrode. Carbon dioxide partial pressure was calculated from alkalinity, pH, and ionic strength.

Probes were placed into access wells to monitor dissolved oxygen (DO), temperature, electrical conductivity (EC), and redox. Two redox platinum electrodes were placed into the effluent pipe of each anaerobic cell and one redox probe was placed in each aerobic cell. The reference electrode used for redox was a saturated calomel electrode. Redox potentials were adjusted in reference to a standard H_2 reference electrode by adding 244 mV to the electrode readings (2).

Predicted alkalinity produced from calcite dissolution was calculated from the increase in Ca concentrations. For every mole of Ca dissolved from calcite dissolution, 2 moles of alkalinity are produced:

$2 H^+ + CaCO_3$ ---> $Ca + 2 HCO_3^-$

The alkalinity was calculated as Ca (mg/L) / 40.1 x 100. For SO_4^{2-} reduction, 2 moles of alkalinity are produced for every mole of S^{2-} produced:

$2 CH_2O + SO_4^{2-}$ ----> $S^{2-} + 2 HCO_3^-$

The alkalinity was calculated as S (mg/L) / 32.1 x 100.

Metal activities were calculated from concentrations for comparison to predicted solubility lines of solid phases. Two factors taken into account when calculating activities were metal hydrolysis and activity coefficients. From the hydrolysis of the metals, 100, 100, 62, 60, and 6% of the metal is expected to be free at pH 7.5 for Mn, Ni, Pb, Zn, and Cu, respectively. The fractional percentage was multiplied by concentration to obtain free concentration. In addition, electrical conductivity was used to estimate ionic strength so activity coefficients could be determined with the Davies equation (Lindsay, 1979). The activity coefficient was multiplied by free concentration to obtain metal activities.

RESULTS AND DISCUSSION

In the anaerobic effluent waters, pH and alkalinity were greater in the S and CG&S treatments compared to the CG treatment (Table 1). The organic matter in the S and CG&S treatments was effective in producing highly anaerobic conditions as evidenced by redox less than -200 mV, DO less than 6% saturation, and S concentrations of 12 to 14 mg/L in the effluent waters. The high alkalinity produced in these anaerobic waters resulted in CO_2 pressures that were supersaturated with respect to atmospheric CO_2 of $\log(CO_2) = -3.52$ (Table 1). As the water was treated by the aerobic cells, the CO_2 degassed from the water more effectively in the reciprocating treatment compared to the non-reciprocating treatment which resulted in lower alkalinity and CO_2 pressures in the effluent from the reciprocating treatment.

Calcium concentrations in the effluent of the anaerobic cells increased from the influent concentrations due to dissolution of calcite. Calcite was added to the S and CG&S treatments as limestone. Since river gravel was the only medium used in the CG treatment, an increase in Ca concentration in this treatment is indicative of some calcite present in the river gravel. Batch titrations with HCl has shown the river gravel to have a calcium carbonate equivalence of 0.35%. Since Ca concentrations do not decrease in the effluent of the aerobic cells, the Ca concentrations do not exceed the solubility limit of calcite which would result in precipitation of calcite and decreased Ca concentration. On the other hand, Mg concentrations are lower in the effluent from the aerobic cells compared to the anaerobic cells, which may be due to precipitation of dolomite at the higher pH levels of the aerobic cells.

Manganese concentration was decreased at least 75% in the anaerobic cells with further reduction to levels below 0.2 mg/L in the aerobic cells (Table 1). The S and CG&S treatments of the anaerobic cells were very effective in reducing concentrations of Cu, Ni, Pb, and Zn below the detection limits of the ICP. The CG anaerobic treatment was less effective with concentrations ranging from 0.02 to 0.5 mg/L for Cu, Ni, and Zn.

The alkalinity produced in the effluent waters from the anaerobic cells is derived from calcite dissolution or SO_4^{2-} reduction (Fig. 2). Alkalinity as predicted from calcite dissolution and SO_4^{2-} reduction both decreased with time. The decrease in alkalinity correlated well with decreased temperature. Decreased temperatures may decrease the activity of SO_4^{2-} reducing bacteria resulting in decreased alkalinity from SO_4^{2-} reduction. In addition, decreased available C may decrease SO_4^{2-} reduction. The decreased alkalinity from calcite dissolution with decreasing temperature may be due to decreasing concentration of organic acids produced in the S and CG&S treatments. Organic acids can chelate Ca and increase calcite dissolution due to

Table 1. Chemistry of water in the influent and effluent of anaerobic cells and effluent of aerobic cells.

		Anaerobic effluent			Aerobic effluent	
Parameter [†]	Influent	CG	S	CG&S	w/recip	wo/recip
pH	4.7(0.4)[‡]	6.8(0.1)	7.3(0.1)	7.1(0.1)	7.8(0.2)	7.7(0.5)
Alkalinity	0	88(24)	133(50)	201(78)	64(16)	122(50)
log(CO_2, atm)		-1.81(0.10)	-2.14(0.25)	-1.77(0.23)	-2.99(0.15)	-2.57(0.52)
Redox		441(151)	-204(135)	-229(33)	537(46)	469(142)
DO	93(13)	16(13)	5.3(6.1)	3.3(2.8)	91(10)	20(18)
Ca	89(4)	131(17)	131(7)	150(10)	136(11)	146(16)
Mg	93(4)	97(1)	98(2)	100(4)	80(16)	79(23)
Mn	20(1)	4.7(3.0)	4.3(2.5)	2.8(2.3)	.06(.06)	.12(.12)
Cu	2.1(0.2)	.02(.02)	< .004	< .004	< .004	.06(.06)
Ni	1.5(0.3)	0.57(0.42)	< .005	< .005	< .005	< .005
Pb	1.9(0.2)	< .03	< .03	< .03	< .03	< .03
Zn	2.1(0.1)	.38(.38)	< .003	< .003	.008(.008)	< .003
Fe	0.9(0.5)	.013(.013)	.13(.13)	.13(.02)	.004(.004)	.009(.009)
S	< .02	< .02	12(4)	14(5)	< .02	< .02
SO_4-S	208(10)	218(7)	197(15)	193(18)	197(23)	188(32)
org-C	0.8(0.4)	0.8(0.4)	5.9(2.3)	5.6(2.4)	3.5(2.2)	4.3(3.1)

[†] Units for all parameters are in mg/L except for pH and log (CO_2), which are unitless, redox is in mV, and DO is % saturation.

[‡] Data is averaged across sampling time and replications. Values in parenthesis represent standard deviations.

chelation. The Ca chelation hypothesis does not explain the decreased alkalinity in the CG treatment because very low levels of organic carbon were observed in this treatment (Table 1). Another possibility for decreased calcite-derived alkalinity in all the treatments is that calcite particles were being continually coated by organic matter and inorganic precipitates. Continued analysis of these systems when the

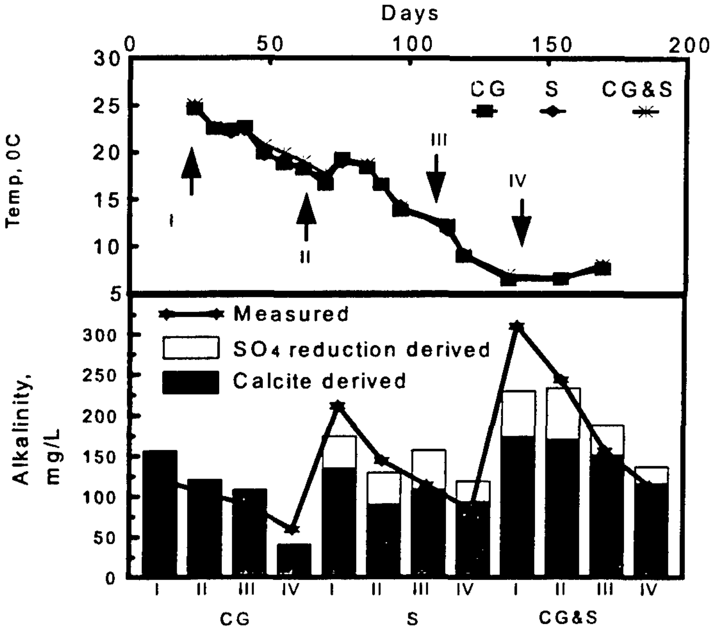

Figure 2. Alkalinity and water temperature changes in effluent from anaerobic cells. Roman numerals signify sampling periods.

temperature warms up will help determine if the decrease in calcite-derived alkalinity was due to coating of the calcite or temperature-related effects.

There was some discrepancy between measured alkalinity and total alkalinity predicted from calcite dissolution and SO_4^{2-} reduction. The overestimated alkalinity predicted from calcite dissolution and SO_4^{2-} reduction can be due to an increase in Ca concentration being due to exchangeable Ca or dissolution of non-carbonate Ca minerals. The large underestimation of alkalinity in the CG&S treatment at time I can be due to canarygrass roots releasing HCO_3^- (16), which would be an unaccounted for source of alkalinity.

Manganese concentration increased with time in the effluent water of the anaerobic cells (Fig. 3). The increase in Mn was correlated with a decrease in alkalinity as shown in Fig. 2. A plot of log Mn activity vs pe+pH was constructed (Fig. 4) for predicting what solid phases could be controlling Mn concentration in both anaerobic and aerobic systems. The lines are predictive solubility lines for MnS, $MnCO_3$, MnOOH, and MnO_2. The 4 lines for $MnCO_3$ show the increasing solubility of $MnCO_3$ as alkalinity decreases from time I to time IV. The redox axis on top of the graph is the redox level in mV at the average pH of 7.5. Both MnS and $MnCO_3$ solid phases are predicted to coexist at redox levels less than -200 mV. At redox levels between -200 and 380 mV, $MnCO_3$ is the controlling solid phase. Above 380 mV, Mn oxides

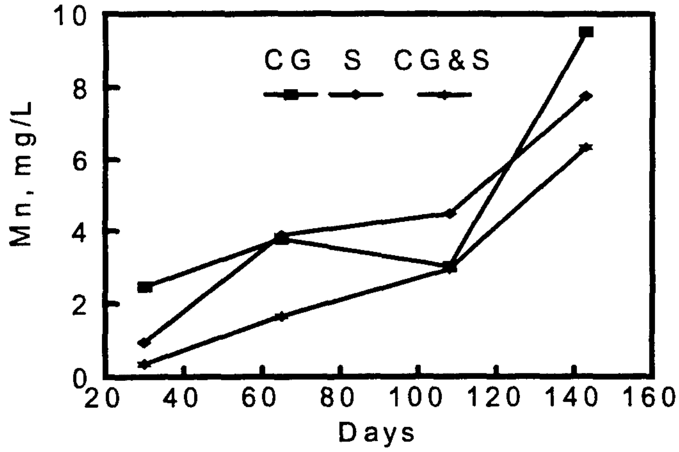

Figure 3. Manganese concentrations in effluent from anaerobic cells as affected by time.

become the solid phase controlling Mn in solution. The treatments from the anaerobic cells containing organic matter (S and CG&S) do attain redox levels below -200 mV which is an indication that MnS may be precipitating. In the anaerobic CG treatment, the redox level was fairly high but Mn concentrations remained supersaturated with Mn oxides and appeared to be controlled by $MnCO_3$. The arrows associated with the anaerobic treatments in Fig. 4 indicate the increase in Mn concentration with time in these systems. These increases are closely aligned with the increase in solubility of $MnCO_3$ due to observed decrease in alkalinity.

When redox reached levels greater than 380 mV in the aerobic treatments, Mn was effectively removed from solution and appeared controlled by Mn oxides. The reciprocating aerobic treatment was more effective in producing redox levels greater than 380 mV compared to the non-reciprocating treatment. Since Mn oxidation by itself is extremely slow at pH 7.5, some process was occurring to result in adequate oxidation of Mn^{2+} to thermodynamic limits imposed by Mn oxide solubility. There was some black slime on the rocks of the aerobic treatments. Whether the catalysis of Mn oxidation was biotic or abiotic is not known.

There was limited differences in pH, alkalinity, redox, DO, and Mn in the effluent waters from the aerobic cells comparing reciprocating treatment with non-reciprocating treatment. However, considerable differences were observed for these parameters in waters taken from the first aerobic cells (Table 2). The cells with reciprocation resulted in high DO, redox, and pH levels in the first aerobic cells. The high redox and pH levels most likely resulted in lower Mn concentrations in the first

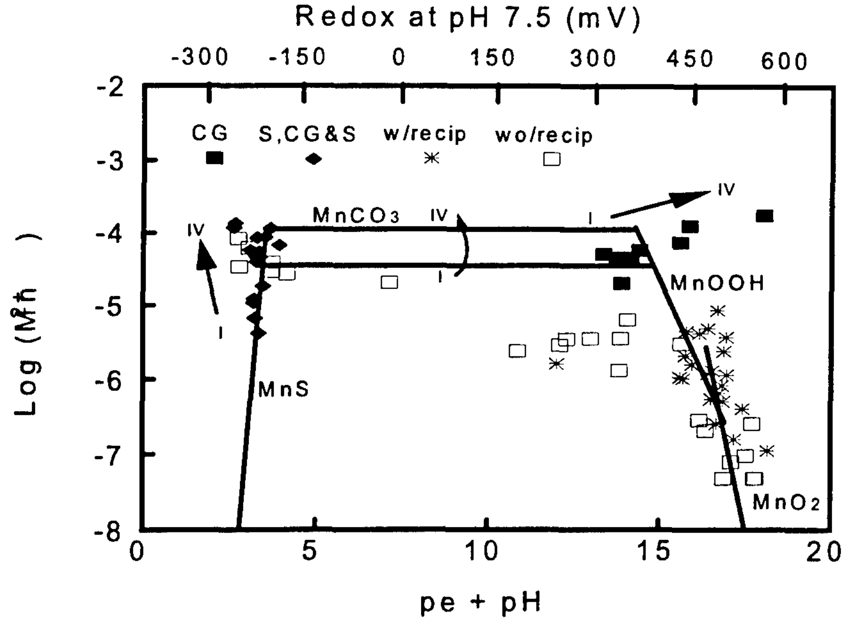

Figure 4. Mn activities as a function of pe + pH or redox at pH 7.5. Symbols represent experimental data. Lines represent solubility of known solids (15). Roman numerals signify sampling period.

Table 2. Water chemical parameters affected by reciprocation in aerobic treatment.

	First aerobic cell		Aerobic effluent	
Parameter	w/ recip	wo/ recip	w/ recip	wo/ recip
pH †	7.8	7.3	7.8	7.7
Alkalinity	65	144	64	122
$Log(CO_2)$	-2.97	-2.07	-2.99	-2.57
Redox	497	50	537	469
DO	94	9.4	92	20
Mn	0.16	1.8	0.06	0.12

† Units for pH and Log (CO_2,atm) are unitless, alkalinity is in mg/L, redox is in mV, DO is in % saturation, and Mn is in mg/L.

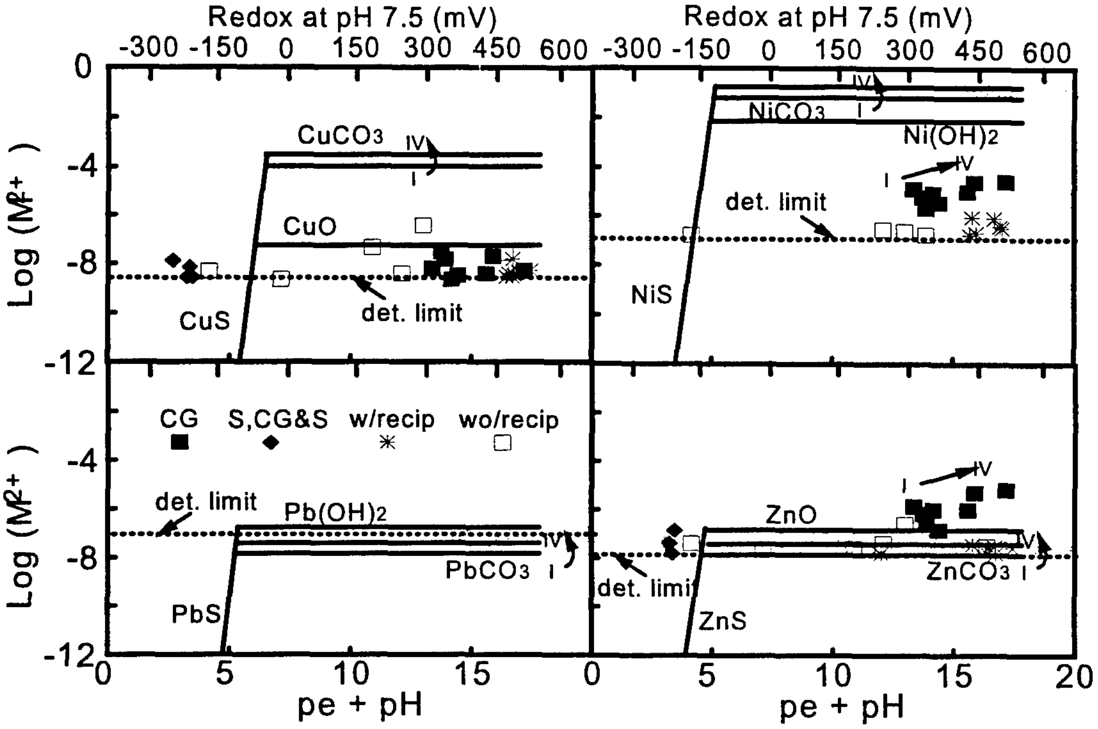

Figure 5. Metal activities as a function of pe + pH and redox at pH 7.5 for Cu, Ni, Pb, and Zn. Symbols represent experimental data. Lines represent solubility of known solids. Roman numerals signify sampling period.

aerobic cells due to greater likelihood of Mn oxide precipitation (Fig. 4). The retention time in the aerobic cells was long enough to result in adequate removal of Mn in the effluent whether the cells were reciprocating or not. The much lower concentration of Mn in the first aerobic cell where reciprocation occurred indicated the size of aerobic gravel beds may be greatly reduced with reciprocation.

The concentrations of Cu, Ni, Pb, and Zn were greatly reduced in the S and CG&S anaerobic treatments (Table 1). For predicting the solid phases controlling solubility of the trace metals, calculated concentrations of the metals as controlled by sulfide, carbonate, and oxide phases are shown in Fig. 5. The detected Cu activities were undersaturated with respect to $CuCO_3$ at high pe+pH and supersaturated with respect to CuS at low pe+pH. Most of the data at higher pe+pH indicate Cu may be controlled by a Cu oxide solid phase. Nickel activity levels were undersaturated with respect to $NiCO_3$ and $Ni(OH)_2$ indicating some other solid phase was controlling this metal in solution. All the Pb data were below the detection limit. The solubility of $Pb(OH)_2$ and $PbCO_3$ are similar with Pb solubilities near the limit of detection. For Zn, activities indicated supersaturation with respect to ZnS at low pe+pH and equilibrium to supersaturation with respect to ZnO and $ZnCO_3$ at high pe+pH. Figure 3 only predicts the solution activity of metals as predicted by solubility of the minerals. Sorption of the metals onto Fe and Mn oxides could also occur (17) and may be an additional process controlling metal solution concentrations.

Metal sulfides are believed to be the solid phase controlling the metals at low pe+pH. The limited data showing supersaturation with respect to CuS and ZnS may be spurious data at the limit of detection. The range of likelihood for metals to precipitate as metal sulfide follow the order Cu>Ni>Pb>Zn with required redox levels at pH 7.5 of -50, -120, -120, and -150, respectively. For comparison, MnS precipitation requires redox levels less than -200 mV (Fig. 4).

There was an observed increase in Ni and Zn concentrations in the anaerobic effluents from the CG treatment with time (Fig. 6). If the observed increase was due to increased solubilization of metal carbonates with decreased alkalinity, the calculated metal activities in Fig. 5 may be in error. Overestimated Zn activities could have been calculated without taking into account soluble complexes forming with SO_4^{2-} and organic C. In any case, whatever conditions were controlling Zn and Ni concentrations in the anaerobic effluent was dependent on time.

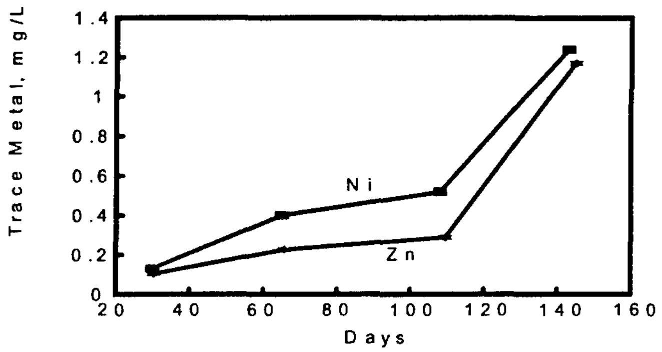

Figure 6. Concentrations of Ni and Zn in effluent of anaerobic CG treatment as affected by time.

CONCLUSIONS

The data collected thus far from this study has shown decreased alkalinity and Mn removal efficiencies in the anaerobic system with cooler temperatures. Mn removal was very effective with the consecutive anaerobic and aerobic treatment systems. Trace metal removal was very effective in the anaerobic treatments with organic matter. The conclusions reached in this study are for a system run for a short-term period of 4 months. The study is being conducted for longer time periods to determine seasonal and long-term effects on alkalinity production and metal removal.

ACKNOWLEDGMENTS

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The work of Jerry Berry, Danny Williams, and Eddie White in constructing and maintaining the system is greatly appreciated. The help of Steve Coonrod, Michael Bulls, and Earl Bailey in sampling and analyses is also greatly appreciated.

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FIELD DEMONSTRATION OF SOIL SLURRY BIOREACTOR TECHNOLOGY FOR THE REMEDIATION OF EXPLOSIVES-CONTAMINATED SOILS

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ABSTRACT

The past production and handling of conventional munitions has resulted in explosives contamination of the soils at various military facilities. The principal explosive contaminants are trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX). Depending on the concentrations present, these explosives-contaminated soils pose both a reactivity and toxicity hazard and the potential for groundwater contamination.

Bioremediation technologies are currently being developed by the U.S. Army Environmental Center as cost-effective alternatives to the current proven technology, high temperature incineration. A technology which is gaining popularity in the remediation industry is the use of soil slurry biodegradation systems in which an aqueous slurry is created by combining soils or sludge with water.

Previous studies using soils contaminated with explosives from Joliet Army Ammunition Plant (JAAP) demonstrated the feasibility of this technology. Using a microbial consortia isolated from JAAP, bench-scale studies showed the degradation of explosives-contaminated soils could be accomplished under aerobic and anoxic conditions with molasses as a co-substrate. Aerobic reactors reduced TNT concentrations from about 1,300 ppm to less than 10 ppm in 15 days. Anoxic reactors achieved the same kind of reduction but at a slower rate. The same study indicated a Soil Slurry Sequencing Batch Reactor (SS-SBR) was the most suitable reactor system for full-scale implementation.

A field demonstration to determine the feasibility of using SS-SBRs to treat explosives-contaminated soils is being conducted at JAAP. Key factors to be investigated include the percent reduction of explosives and the identification of degradation products. In addition, the efficiency of reactor operations using different soil replacement volumes will be examined.

The demonstration is being performed in three phases. Phase I determined optimal oxygen transfer capabilities and other operating characteristics of the system. Phase II enhanced the indigenous microbial population capable of degrading the explosives-contaminated soil. Phase III is ongoing and will provide extended operating data on the reliability of the system and preliminary biodegradation kinetic information.

Background on the bench-scale research, the process design, and the success of the field demonstration will be presented.

FIELD DEMONSTRATION OF SOIL SLURRY BIOREACTOR TECHNOLOGY FOR THE REMEDIATION OF EXPLOSIVES-CONTAMINATED SOILS

INTRODUCTION

The past production and handling of conventional munitions has resulted in explosives-contaminated soils at various military facilities. Energetics contamination of soils and groundwater has been determined to be the largest environmental pollution problem at Army sites. The principal explosive contaminants are trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX). Depending on the concentrations present, these explosive-contaminated soils pose both a reactivity and toxicity hazard. Because of the potential for migration of hazardous substances and groundwater contamination, treatment of the contaminated soils will be necessary. Although incineration is the current proven treatment technology, its capital and operating costs are high, and public acceptance has diminished.

A variety of biotechnologies are currently being developed by the U.S. Army Environmental Center to treat explosives-contaminated soils. Biotreatment by windrow composting was recently demonstrated to be a cost-effective alternative to incineration at Umatilla Military Depot Activity, Oregon. At some installations, due to the soil composition or availability of amendments, composting may not be appropriate. A technology which has the potential to provide a cost savings is the use of soil slurry biodegradation systems in which an aqueous slurry is created by combining soil or sludge with water.

In this treatment process, explosives-contaminated soils and water are biologically treated in a reactor. Contaminated soils are excavated and prescreened to remove large rocks and debris. In the reactors, conditions are optimized to promote the growth of microorganisms indigenous to the soil which are capable of degrading explosives. The soils are mixed with water to produce a water based slurry (typically 10-40% solids by weight) and pumped into the reactors. The operation of the reactors employs a replacement strategy in which a specified volume of material is removed at a defined interval. This reduces material handling costs and allows for adapted microorganisms to remain in the reactor to degrade the newly added contaminated soil. After addition of the soil and co-substrate the reactors are operated under aerobic/anoxic conditions. This operating strategy promotes a wide range of metabolic capabilities.

The reactors are designed and instrumented with various process controls. Co-substrate, nutrients, oxygen, and mixing can be altered to achieve desired treatment. After biological treatment, the treated soil is dewatered and then disposed. Process water is recycled to the reactors as much as possible.

The advantage of a reactor system is its process control and ability to optimize the microbial activity within. This offers the potential for greater rates of degradation than seen with solid phase biotreatment processes. Reactor process controls are also inherently flexible. By changing conditions in the reactor, a treatment train technique can be achieved. This treatment technology is best suited for sites polluted with small volumes of contaminated soil where incineration would be cost prohibitive.

Laboratory Studies

Laboratory studies conducted in support of pilot demonstration have indicated the ability of a soil-slurry reactor to biodegrade explosives-contaminated material. Soil replacement strategies have proven successful in removing TNT from soil with the generation of few, if any, of the traditional amino intermediates (2-amino-4,6 trinitrotoluene and 4 amino-,2,6-dinitrotoluene). Table 1 shows the results from operating the reactors for 100 days on replacement strategies of 1x, 2x, 3x per week

(1 time per week, 15% of the reactor volume is removed and replaced with contaminated soil slurry, 2 times per week, 15% of the reactor volume is removed and replaced with contaminated soil slurry, etc.). Long term operation of the system indicated initial soil slurry TNT concentration of 2500-3500 ppm were reduced to less than 20 ppm, and the formation of the amino intermediates depended on the replacement strategy.

The key to this reactor technology is the operation strategy of aerobic/anoxic periods. During a 8 hour cycle, air was supplied to the reactor for 15-30 minutes. The air was then shut off and the reactor was mixed with a magnetic-stirrer. During the next 7.5 hours the dissolved oxygen concentration in the reactor slowly decreased to values less than 0.1 mg/L. The cycle was repeated 3 times per day.

In addition, laboratory studies have demonstrated that molasses is an effective co-substrate. Table 2 shows that molasses can increase the rate of TNT biotransformation by an order of magnitude. These studies have demonstrated the ability of a soil slurry reactor at the laboratory scale to degrade TNT contaminated soil. This aerobic/anoxic operating strategy promotes a wide range of metabolic capabilities in the bioreactor.

Field Demonstration

A field demonstration to determine the feasibility of using Soil Slurry Sequencing Batch Reactor (SS-SBR) to treat explosives-contaminated soils is being conducted at Joliet Army Ammunition Plant (JAAP), IL. Figure 1 provides a layout of the various components of the pilot system. In this demonstration the soil is manually excavated and wet screened in a mechanical screening system. The slurry is prepared by weighing the correct amount of soil in predetermined amount of water and pumped to the reactor while the reactor is continuously mixed. As material is removed from the reactor it is placed on a drying bed to dewater the slurry, leaving behind moist soil and water which can be recycled.

The demonstration consists of three phases. Phase I determined the mechanical integrity of the 420 gal SS-SBRs constructed for this demonstration, assessed the oxygen transfer capabilities and identified the operating characteristics of the system. Phase II will enhance the microbial population capable of degrading the explosives-contaminated soil. Phase III will provide extended operating data on the reliability of the system and preliminary biodegradation kinetic information.

During Phase III reactors will be operated as follows: control with no co-substrate, 10% replacement volume per week, 20% replacement volume per week and 5% replacement volume per day. The last 3 reactors will have co-substrate added once per week and will be operated on the aerobic/anoxic operating strategy. To achieve aerobic/anoxic conditions short 1/2 hour periods of air addition will occur once per day and mixing will occur for the rest of the time. Mixing allows the microorganisms to remain in contact with the soil and co-substrate while promoting the environment for a diverse microbial population. The key variables to be investigated include daily soil replacement quantities, the percent reduction of explosives and identification of degradation/biotransformation products.

The goals of this demonstration are to prove the bioreactor is both an economical alternative to incineration and is effective in removing TNT and reducing toxicity. The ability of the system to biologically degrade explosives over an extended period of time will be validated during Phase 2 & 3. The information gained during this operation will provide the necessary data to transfer this technology to potential users.

The key technical issues that are being examined in the demonstration involve the following:

(1) Evaluating impeller mixer configurations to provide the optimal mixing regime.

(2) Determining the optimal oxygen transfer characteristics of the reactors.

(3) Monitoring development of the microbial consortium capable of degrading explosives.

(4) Testing the ability of the microbes to degrade explosives under aerobic conditions.

(5) Evaluating operation of the SS-SBR with a variety of replacement strategies.

(6) Investigating the effectiveness and degradation rates of explosives under various reactor operating conditions.

(7) The slurry will be analyzed for TNT. RDX, HMX, and degradation intermediates. In addition, process control parameters such as dissolved oxygen, pH, ammonia, nitrate, nitrite and phosphorus will be monitored. Multiple toxicity studies will document the reduction in toxicity and mutagenicity in the treated soil.

Preliminary data from the pilot demonstration (Table 3) indicate that these reactors are designed to acceptably mix TNT contaminated soil and provide sufficient dissolve oxygen. Phase 2 results have demonstrated that TNT contaminated soil can be biodegraded with generation of minimal amino intermediates. Phase 3 is being conducted at the present time.

SUMMARY

An innovative soil treatment system, the soil slurry reactor has been tested at the laboratory scale and is currently in field demonstration. Preliminary results from the field demonstration are encouraging that the system can be operated to remove TNT to anticipated regulatory limits.

Performance and cost information will be provided to the JAAP authorities so that the Technology can be considered as an option for the clean-up of explosives contaminated-sites at JAAP. The results of these studies will be applicable to other Department of Defense sites with explosives contaminated-soil. Technical, Economic and Engineering reports will be available to other potential users.

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Biodegradation of 2,4,6-Trinitrotoluene: A Laboratory Study to Support the Pilot Demonstration of a Biological Soil Slurry Reactor, November 1994 (SFIM-AEC-TS-CR-94038)

Table 1. Laboratory Soil Slurry Reactor Results

Replacement Strategy per week 15% volume	TNT (mg/kg)	2-amino-4,6-Dinitrotoluene (mg/kg)	4-amino-2,6-Dinitrotoluene (mg/kg)
1	<1	<2	<2
2	<10	<10	<10
3	<40	<100	<100

Table 2. Impact of Co-Substrate on TNT Biotransformation

Substrate (0.5%)	TNT Conc. (ppm) Initial	TNT Conc. (ppm) Final	% TNT Transformed	Specific Transformation Rate (ppm/hr)
Control	100	99	1.0	0.007
TNT Alone	100	98	2.0	0.014
Malic Acid	100	11	88.2	0.68
Acetate	100	14	85.8	0.66
Citrate	100	5	94.4	0.73
Sucrose	100	10	89.2	0.69
Glucose	100	7	92.6	0.71
Succinate	100	0	100.0	0.93
Molasses (0.3%)	100	0	100.0	8.3

Table 3. Preliminary Results

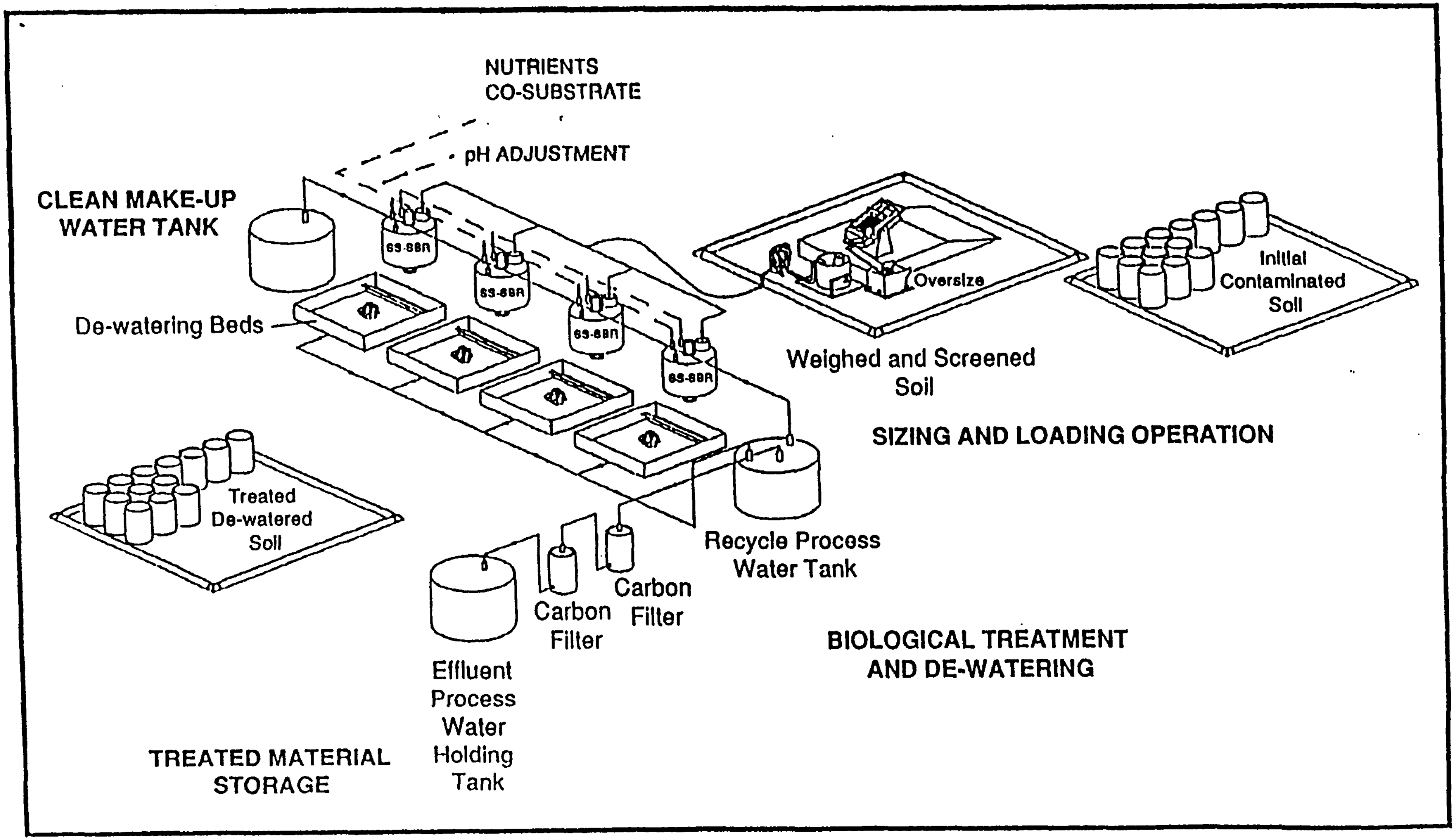
Phase 1

- Optimum Mixing Rate - 100 rpm with a 1 hp motor
- Oxygen Concentration Reaches 6-7 mg/L in 5-10 minutes with 5-6 cfm of air per reactor
- Impeller design is not critical at this size

Phase 2

- TNT removal is possible
- No nutrients other than what is in molasses are needed
- Natural pH control is sufficient

Figure 1. Bioremediation Flow Diagram



DENITRIFICATION OF LIQUID WASTES RESULTING FROM HYDROLYSIS OF NITROCELLULOSE AND NITROGLYCERIN CONTAINING ROCKET PROPELLANTS

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ABSTRACT

Alkaline hydrolysis of double base rocket propellants results in a liquor rich in nitrates, nitrites, and BOD. Bench-scale biological denitrification has been applied to a waste liquor produced from the alkaline hydrolysis of a double base rocket propellant, AHH. Nitrocellulose and nitroglycerin are the energetic components of the propellant which also contains other organic compounds such as triacetin and 2-nitrodiphenylamine. The liquid waste was generated by adding 1% solid propellant by weight to sodium hydroxide solutions of various strengths and reacting the mixture at temperatures as high as 95°C. The typical observed concentrations of nitrates and nitrites in the digested liquor were 260 and 540 mg/L as nitrogen respectively. Prior to denitrification lead, which is present in the propellant as a ballistic modifier and constitutes approximately 2% of the mixture by weight, was removed by chemical precipitation. The denitrification experiments were conducted in batch mode in a chemostat. It was found that the denitrification process was inhibited when the denitrifies were not properly acclimated to the high nitrite concentrations characterizing the feed stream. However, proper acclimation of the microorganisms resulted in high removal of nitrites and nitrates. Moreover, the post-digestion liquor contains sufficient amount of carbon for denitrification to occur without addition of external carbon sources. The effect of high nitrite concentrations on the activity of the microorganisms was studied and the rates of denitrification were computed. The technology developed for the destruction of the AHH may be applied for the safe disposal of propellants and munition wastes of similar formulation.

INTRODUCTION

Hazardous materials generated from demilitarization programs have to be disposed in accordance with state and federal environmental laws. Energetic materials are classified as reactive (40 CFR § 261.21) and are listed under the Resource Conservation & Recovery Act (RCRA). This RCRA classification designates energetic materials as a hazardous waste. A goal of the current US demilitarization disposal program is to develop and utilize new technologies that destroy the hazardous constituents rather than transferring them into another medium (air, soil or water).

AHH, a double-base propellant, which was manufactured at the Radford Army Ammunition Plant (RAAP) has been used as an energetic material in various weapon systems including the M753 8-Inch Projectile System. The nominal AHH propellant grain composition is given in Table 1.

Table 1: Nominal AHH propellant composition

Component	Composition, wt %
Nitrocellulose	53.9 min.
Nitroglycerin	31.6 nom.
Triacetin	8.8 nom.
2-Nitrodiphenylamine	0.9 min.
Lead Salicylate	1.2 nom.
Lead 2-Ethyl hexoate	2.0 nom.

The alkaline digestion of the intact ground AHH propellant results in a liquor containing high levels of nitrates, nitrites and organic compounds that was shown to be biodegradable using a combination of biological denitrification and BOD removal processes[1].

The digestion of the solid propellant was carried out in Erlenmeyer flasks. Approximately 0.5 grams of solids were added to fifty milliliters (50 ml) of aqueous sodium hydroxide solution in a 125 ml flask. This resulted in 1% by weight solids mixture. The flasks were immersed in a sonicator equipped with a water bath capable of maintaining a maximum temperature of 95°C. In a typical experiment at a given temperature and sodium hydroxide concentration, the alkaline hydrolysis was carried out for 30 to 60 minutes. After digestion the solution was cooled to room temperature and prepared for precipitation of lead by pH adjustments, and sodium sulfide addition. The pH of the decomposition mixture was adjusted with sulfuric acid. Upon removal of lead, the BOD and COD of the mixture was determined. The lead free supernatant solution, rich in carbon and nitrogen, were neutralized and passed through an acclimated denitrification reactor.

The nitrate and nitrite production were monitored during the course of the reaction for different NaOH concentrations. The total nitrogen produced in the forms of nitrate and nitrite is proportional to the amount of propellant digested and appears to be independent of NaOH concentration. The obtained ratio of nitrite to nitrate is approximately 2 to 1 regardless of the degree of digestion[2].

Since the digested propellant contains large amounts of nitrites and nitrates a denitrification step may be necessary for their removal. Biological denitrification is appealing because it converts the undesirable nitrates and nitrites to nitrogen gas and does not, contrary to other techniques such as ion exchange or reverse osmosis, concentrate these contaminants. In addition, ion exchange denitrification is severely limited because the regenerant disposal is a problem itself.

BIOLOGICAL DENITRIFICATION

Denitrification results from the metabolic activity of certain facultative heterotrophic bacteria that utilize organic carbon both as a carbon source and energy source. Nitrate is used by these organisms as an electron acceptor in energy metabolism. The main biological pathways involved are the same as those used in aerobic respiration. The major difference here is that nitrate replaces oxygen in the electron transport chain. Therefore, denitrification falls into the category of anoxic respiration, occurring in the presence of nitrate and absence of molecular oxygen, rather than aerobic respiration.

The denitrification pathway [3,4] is given by:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The above pathway indicates that nitrate and nitrite can be converted under appropriate conditions to nitrogen gas. The pathway indicates also that denitrification is a two-step process in which the first step converts nitrate to nitrite and the second step carries nitrite through two intermediates to nitrogen gas.

Although conversion of nitrate to nitrogen via nitrite is a fairly well establish process, the major challenge in the present work is that the digested liquor contains both nitrate and nitrite at high levels. The effects of high nitrite concentration on the activity of the microorganisms were studied, and the rate of denitrification was evaluated.

MATERIALS AND METHODS

The liquid waste was generated from the alkaline hydrolysis of a double base rocket propellant, AHH. Denitrification experiments were carried out in a chemostat equipped with temperature control and mixer (Omni-culture model, Virtis Co., NY). The experimental set-up is shown schematically in Figure 1. The reactor has been acclimated to gradual doses of digested lead-free propellant for 2 months. The reactor was initially incubated with activated sludge obtained from a nearby POTW (Public Owned Treatment Works, Bergen County Utility Authority, Bergen, NJ). The pH was maintained slightly above 7, using a phosphate buffer solution. The agitation speed and the temperature of the reaction medium were maintained at 250 rpm and 30 °C respectively.

Samples taken from the reactor were filtered using 0.45μ filters (Whatman International Ltd., Maidstone, England). The nitrate and nitrite concentration were determined by High Pressure Liquid Chromatography (HPLC) on a Varian LC Workstation (Varian Associates, Sugar Land, TX) equipped with a diode array detector, and a Universal Anion 4.6x 150mm, 5 μm (Alltech Associates Inc., Deerfield, IL) chromatographic column. The BOD and COD were also monitored by standard methods[5].

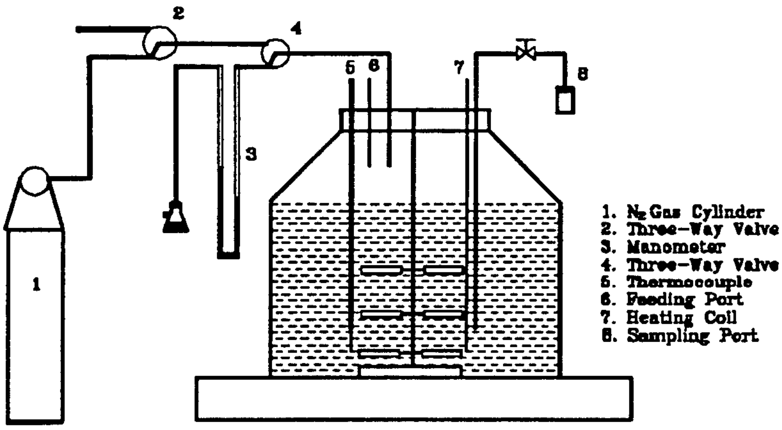

Figure 1. Denitrification reactor.

RESULTS AND DISCUSSION

Preliminary BOD and COD measurements have indicated that the neutralized digested propellant is biodegradable. Since the digested liquor is very rich in nitrates and nitrites, anoxic denitrification experiments were conducted with lead-free digested liquid, to convert them to nitrogen gas. The bioreactor had been acclimated for two months with digested propellant. This acclimation period was necessary because it was observed that high initial shock loads of nitrite were inhibitory. At this point it should be mentioned that, contrary to nitrite, high loading of nitrate is not inhibitory.

Following this acclimation period, biological denitrification experiments were carried out without the addition of an external carbon source. In a typical experiment, initial nitrite and nitrate concentrations were 123.3 mg/L and 90.5 mg/L respectively. Figure 2 shows that these components were reduced completely to nitrogen gas within 30 hours. It should be noted that concentrations of nitrate and nitrite in this figure are reported in terms of nitrogen content. The initial COD in the reactor was 1274 mg/L and after total nitrite and nitrate conversion, 1168 mg/L of COD were remaining in the system. The COD consumed per unit mass of nitrogen (2 mg COD/mg nitrogen) is close to the values reported in the literature[6]. The complete conversion of nitrite and nitrate and a residual BOD of 94 mg/L in the system proves conclusively that external carbon sources are not necessary to denitrify the digested propellant. Since BOD is present in excess of the amount required for nitrite and nitrate conversion, an additional step will be required for complete mineralization of the hydrolysis products. However, after a few months of operation with the same batch of acclimated mixed culture, it was observed that, although nitrate was totally converted, nitrite was building up in the system. As illustrated in Figure 3, nitrate was totally consumed within 47 hours of operation, while nitrite was still detected at high levels after 50 hours of operation. However, few days later, analyses showed that nitrite is no longer detectable. This slow rate of nitrite conversion might be due to a deficiency of microorganisms responsible for the conversion of nitrite to nitrogen gas.

In order to enhance the rate of conversion the following approach was taken: Fresh activated sludge obtained from a nearby sewage treatment plant was added to the reactor by replacing one-third of reaction volume of the prevailing acclimated mixed culture. Following a short acclimation period of 4 days, 135 ml of lead free digested propellant was added to the 2 L reaction volume. Results of the time course of the reaction are shown in Figure 4. The results indicate that nitrate is reduced more rapidly than the nitrite which indicates that the conversion of nitrite to nitrogen gas is the rate limiting step. This figure shows also that nitrite does not build-up and is totally converted to nitrogen gas under these experimental conditions. COD measurements indicate that in this case 2.63 mg COD were consumed per mg of nitrogen. The TSS was 1180 mg/L. The difference with the COD/N ratio of 2 reported above might be attributed to cell synthesis since 700 ml of acclimated mixture culture (acclimated for two months) was replaced by fresh activated mixed culture. The specific denitrification rate was 0.026 mg NO_3^--N/mg TSS.day that was computed based on batch mode of a single-sludge denitrification system. The value of the specific denitrification rate is close to the value reported in the literature[7]. However, it was slightly lower than the value reported in the literature by Beccari, et al.[8] carbon source.

Other experiments carried out with different amounts of propellant added to the reactor have confirmed that the replacement of part of the prevailing mixed culture with fresh activated sludge, allows the total conversion of nitrate and nitrite present in the digested propellant to nitrogen gas. More experimental work is required in order to understand the mechanisms of the biological denitrification of the propellant.

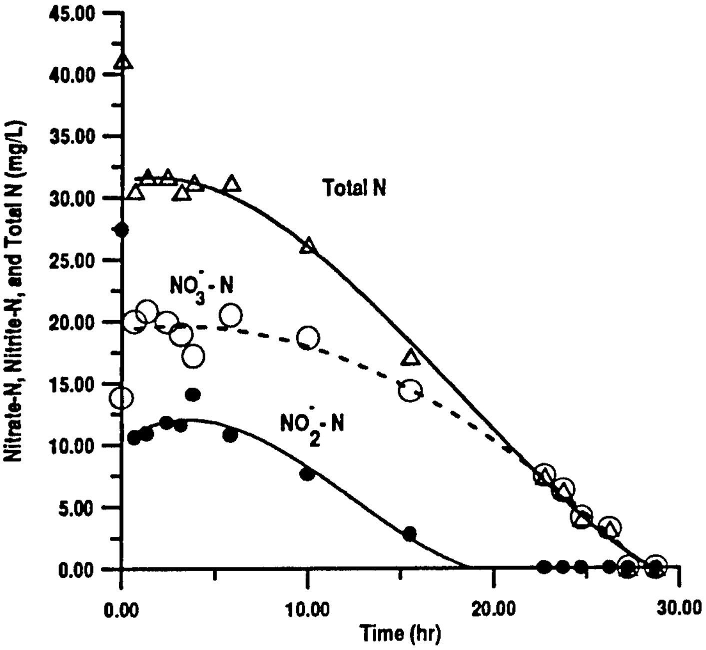

Figure 2: Time history of nitrogen reduction under anoxic conditions.

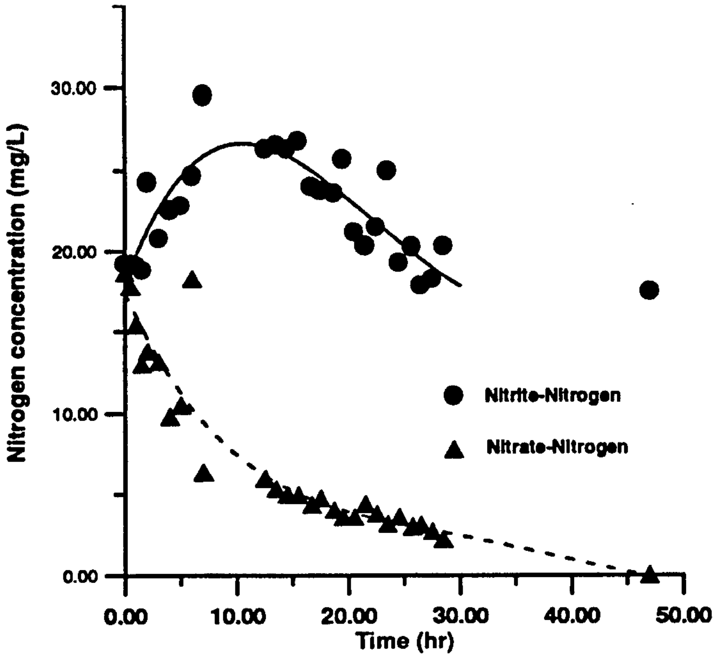

Figure 3 : Nitrite build-up after few months of operation.

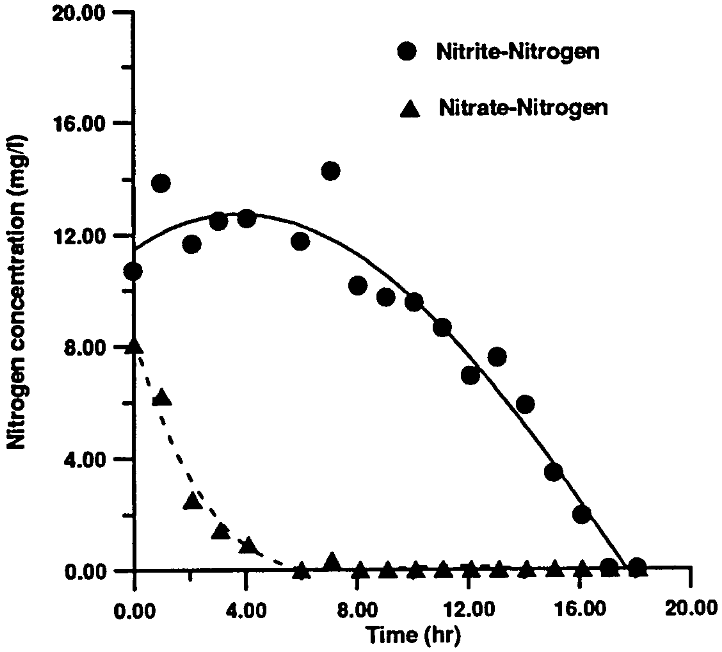

Figure 4: Nitrate/Nitrite removal after sludge replacement.

CONCLUSIONS

Denitrification of digested propellant (AHH) liquor rich in nitrates and nitrites was achieved without the addition of an external carbon source. Proper acclimation of the microorganisms is necessary to obtain sufficiently high removal rates of nitrates and nitrites. The rate of conversion in the bench scale reactors was 0.026 mg NO_3^--N/mg TSS.day.

ACKNOWLEDGMENT

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BENCH-SCALE EVALUATION OF THE ENVIROMETAL PROCESS (METAL ENHANCED REDUCTIVE DEHALOGENATION) AT A U.S. AIR FORCE BASE

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INTRODUCTION

Metal-Enhanced Reductive Dehalogenation of Volatile Organic Compounds

Research at the University of Waterloo and elsewhere during the last four years has shown that certain metals are highly effective in promoting the abiotic degradation of halogenated volatile organic compounds (VOCs) in aqueous solution[1,2]. Based on experimental evidence from laboratory and field tests, the metal produces reducing conditions and also participates in the degradation reaction. The process has been effective in degrading a range of halogenated methanes, ethanes and ethenes in groundwater from various sites, over a wide range of initial VOC concentrations. Because of its availability, low cost, and ability to induce rapid VOC degradation, specially prepared granular iron has been used in these tests. One application of the technology involves the placement of the metal in *in-situ* permeable treatment zones, or gates, across the path of groundwater containing VOCs, flanked by impermeable walls (sheet piles, slurry walls, etc.) which serve to funnel groundwater through them. This passive "funnel and gate" treatment system offers many advantages over conventional pump and treat systems, particularly in the area of reduced operation and maintenance requirements.

Over the past 2 years, more than 25 treatability studies have been undertaken to evaluate the potential of *in-situ* permeable reactive walls to remediate VOC contaminant plumes. These treatability studies are initiated with bench-scale laboratory tests, which simulate conditions of groundwater flow, followed by pilot-scale field tests of the technology. This paper presents the results of a bench-scale treatability study using groundwater from Fairchild Air Force Base, WA, and describes a two-dimensional groundwater flow model used to assist in the field-scale designs of a funnel and gate system at the site.

SITE DESCRIPTION

A shallow sandy aquifer downgradient of a stormwater lagoon at Fairchild Air Force Base is contaminated with VOCs, primarily trichloroethene (TCE) at concentrations of up to 0.5 ppm. The aquifer is 5 to 10 feet thick and is underlain by a similar thickness of silty clays. The water table is about 5 feet below grade. The combination of shallow construction depths and a confining layer at the base of the aquifer make it a favourable candidate for *in-situ* remediation using a funnel and gate system. A pump and treat system is currently planned to capture the portion of the plume that has moved off base property. However, successful installation of an *in-situ* remedy closer to the suspected source area will prevent additional contaminant migration off site, and allow the pump and treat system to be turned off sooner than otherwise expected.

LABORATORY TEST METHODS

In order to estimate VOC degradation rates that could be expected in the field, groundwater from the site was pumped through two columns, one containing 100% reactive iron, and one containing 50% iron and 50% silica sand. Measurements were taken at groundwater velocities of 4.3 and 6.5 ft/day in the 100% iron column and the 50% iron column, respectively. These velocities are within the range of the groundwater velocity expected in the gate of the funnel and gate treatment zone installed in the shallow aquifer at the site. The column tests were performed at a room temperature of approximately 25°C. The groundwater contained 250 to 285 µg/L of TCE, 15 to 20 µg/L of cis-1,2-dichloroethene (cDCE), and 5 to 15 µg/L of trans-1,2-dichloroethene (tDCE). The groundwater contained about 16 mg/L magnesium, 60 to 70 mg/L calcium, and the alkalinity ranged from 270 to 294 mg/L HCO^-_3. The organic and inorganic chemical concentrations in the water entering the columns during the tests remained quite stable, indicating that sample storage prior to use in the columns did not appreciably influence the results.

The columns were constructed of Plexiglass™ with a length of 50 cm (20 in) and an internal diameter of 6.5 cm (2.6 in). Water samples for organic and inorganic analyses were obtained from several ports positioned along the length of the column (Figure 1). Samples were also collected from the influent and effluent ends of the columns. The columns were sampled over time, roughly at every 5 pore volumes, until steady-state concentration profiles were achieved. Redox potential (Eh) and pH electrode measurements were also made at each port, as well as from both the influent and effluent solutions.

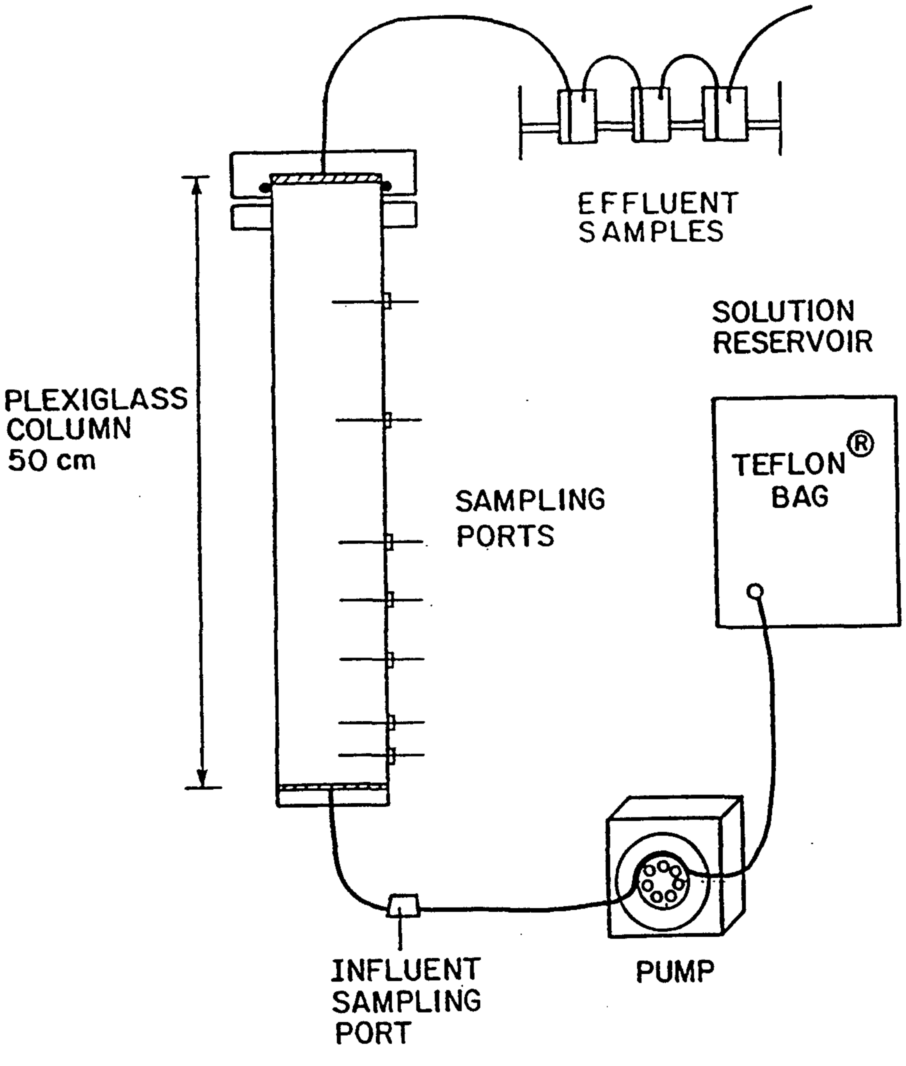

Figure 1: Schematic of the apparatus used in the column experiments.

Analyses for TCE were performed on aqueous phase samples derived using a pentane micro-extraction technique and an electron-capture detector. Cis-1,2-dichloroethene and vinyl chloride (VC) analyses were completed on samples obtained from the headspace above an aqueous sample, using a photoionization detector. Analyses for major cations and anions were completed using atomic-absorption spectrophotometry and/or ion chromatography as appropriate.

LABORATORY TEST RESULTS

Observed Degradation of VOCs

The VOC degradation observed during the column test may be summarized as follows:

i) TCE degraded rapidly in both columns, with steady-state half-lives (the time needed to remove one half the contaminant mass) of 0.71 hrs in the 50% iron column, and 0.34 hrs in the 100% iron column. Figure 2 shows the measured declines in TCE concentration in each column at steady state.

ii) Small amounts of cDCE (between 5 and 6% of the original TCE concentration) were produced as a result of TCE degradation. Less than 2 ppb of VC also appeared due to dechlorination of TCE and cDCE as groundwater moved through the columns. Both cDCE and VC subsequently degraded in the iron. Half lives of 1.4 hrs for cDCE and 1.58 hrs for VC were calculated from concentration profiles measured in the 100% iron column.

These degradation rates are comparable to those observed in other laboratory treatability studies, and were used to calculate the residence time needed in a field-scale funnel and gate system.

Inorganic Results

Expected changes in inorganic chemical constituents were observed in the groundwater as it moved through the columns. Calcium, magnesium and alkalinity concentrations decreased, and the dissolved iron concentrations increased. These changes occur in response to increasing pH due to the corrosion of iron:

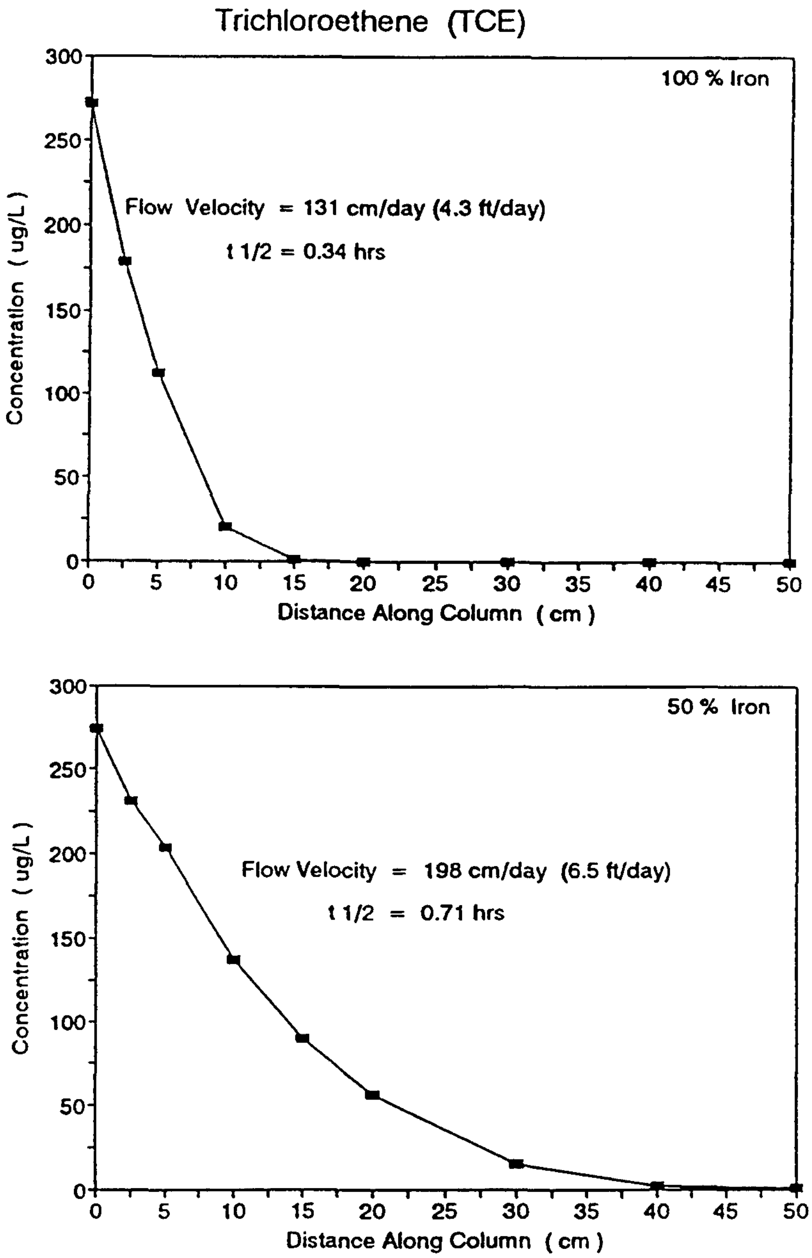

Figure 2- Observed TCE concentration profiles in bench-scale columns

$$Fe_{(o)} + 2H_2O \longrightarrow Fe^{+2} + 2OH^- + H_{2(g)}$$

As the pH of the solution increases, bicarbonate (HCO_3^-) ions are converted to carbonate ions (CO_3^{-2}) to buffer this increase. The CO_3^{-2} ions formed then combine with cations present in solution (i.e., Ca^{+2}, Mg^{+2}, Fe^{+2}) to form carbonate mineral precipitates. The changes in concentration which reflect mineral precipitation in the columns are given below.

	50% Iron 6.5 ft/day		100% Iron 4.3 ft/day	
Parameter	Change (mg/L)	Change (mmol/L)	Change (mg/L)	Change (mmol/L)
Calcium	-50.5	-1.26	-62.6	-1.56
Iron	+2.95	+.05	-.29	-.005
Alkalinity as HCO_3^-	-153	-2.51	-202	-3.31

Comparing the above results for the two columns, roughly 30% more calcium, magnesium and alkalinity was lost from the 100% iron column than the 50% iron column. This is due to the larger percentage of iron and greater residence time in the 100% iron column, which contributes to higher pH values. A pH of under 9.0 was measured at steady state in the 50% iron column effluent, while a pH of over 9.5 was measured in the 100% column effluent at steady-state. Upon comparison of calculated theoretical dissolved iron increases due to corrosion, and measured effluent iron concentrations, it appears that considerable iron precipitation occurred in the columns. From measured declines in alkalinity, much of the dissolved iron produced in the columns likely precipitated as siderite.

Modeling results obtained with MINTEQA2[3] indicated that the influent groundwater was oversaturated with respect to calcite and siderite prior to entering the column. This indicates that precipitation of carbonate species observed during the column tests may not occur to the same extent *in-situ*, as groundwater entering a treatment zone *in-situ* would not likely exhibit this degree of oversaturation. This oversaturation may be an artifact of CO_2 degassing during groundwater sampling.

Required Residence Time

In a funnel and gate system, the dimensions of the permeable reactive (iron-containing) gate are based on the degradation rate of the compounds in the groundwater and the velocity of the groundwater moving through the gate. The length of the gate in the direction of groundwater flow must be large enough to allow adequate time for VOCs to be reduced from influent concentrations to the relevant water quality criteria. Historical TCE concentrations near the possible field location for *in-situ* treatment were used as the estimated influent concentration of TCE to calculate the required residence time. These residence times were used in conjunction with the groundwater model results described below to derive possible *in-situ* treatment zone dimensions.

Percentage of Reactive Iron	Estimated TCE Concentration in Groundwater Entering Gate (ppb)	Target Effluent Concentration (ppb)	Measured Half-Life (hrs)	Required Residence Time (hrs)
100%	190	5	.34	1.8
50%	190	5	.71	3.7

As mentioned previously, small amounts of cDCE and VC were produced due to TCE degradation. However, these VOC concentrations did not exceed regulatory requirements. Based on previous studies, we do not expect the concentrations of these breakdown products to increase when the technology is applied in the field, relative to laboratory observations.

GROUNDWATER MODELING

The groundwater flow model FLOWPATH[4] was used to examine the effect of installation of a funnel and gate treatment system on existing groundwater flow patterns in the vicinity of the proposed installation. FLOWPATH is a two-dimensional steady-state groundwater flow model which includes a particle tracking routine to calculate groundwater pathlines and travel times. The main objective of the modeling exercise was to determine the residence time of groundwater in the permeable gate, given existing aquifer characteristics and the positioning of impermeable funnels and a permeable gate of given dimensions. The width of the upgradient aquifer funneled through and treated by the *in-situ* system (the capture zone) was also evaluated.

The shallow aquifer was modelled as a homogeneous aquifer using a plan-view model domain of 80 feet parallel to groundwater flow by 160 feet perpendicular to groundwater flow.

The following aquifer characteristics were used as inputs into the model, based on data from various hydrogeologic studies conducted at the site:

• hydraulic conductivity	300 ft/day (1.06x10^{-1} cm/sec)
• horizonal gradient	0.005
• porosity	0.25

Initially, the funnel and gate design shown in Figure 3 was simulated. The design consists of a square central permeable treatment zone containing granular iron, which is 3.5 feet on a side and flanked on both sides by 15 feet of sheet piling. The reactive iron in the centre section is separated from the aquifer material on the upgradient and downgradient sides by a section of pea gravel. The pea gravel acts to terminate the effects of any high conductivity zones present in the aquifer upgradient of the gate by spreading this flow vertically, and also provides for the installation of monitoring wells.

For the initial, or base-case simulations, the hydraulic conductivity of the pea gravel was assumed to be 2,830 ft/day (1 cm/sec). Values of hydraulic conductivity and porosity based on a number of laboratory tests were used for the reactive iron. For 50% iron, a hydraulic conductivity of 37 ft/day and a porosity of 0.33 were used, while values of 142 ft/day and 0.40 were used for 100% iron. The sheet pile funnels were assigned a hydraulic conductivity of 2.8x10^{-3} ft/day (1x10^{-6} cm/sec). Following an examination of the groundwater residence times in the gates under these initial conditions, a sensitivity analysis was performed to examine the effects of variation in aquifer, pea gravel, sheet piling, and reactive iron hydraulic conductivity on groundwater residence time within the central treatment zone and on the width of the capture zone.

Results of the initial model runs are summarized in Table 1. Figure 4 shows the capture zone upgradient of a funnel and gate containing 100% iron, using the base-case material properties. Residence times in the reactive iron zone were determined to the nearest hour, using the particle-tracking and time-marker functions of FLOWPATH (Figure 4). For the base case, a minimum residence time in the reactive iron section of about 10 hours was determined for the 100% iron treatment zone. The minimum residence time was approximately 21 hours for the 50% iron mixture due to its lower hydraulic conductivity. Upgradient capture zone widths of 5.2 feet and 9.7 feet were determined for 50% iron and 100% iron, respectively.

Smaller values for the hydraulic conductivity of the aquifer were associated with larger residence times in the reactive iron, due to reduced groundwater velocities in the aquifer and a reduction in volumetric discharge through the gate. The increased residence times were accompanied by an increase in the upgradient width of aquifer treated by the gates. Variation in the hydraulic conductivity of the gravel pack had little effect on residence times in the central reactive zone.

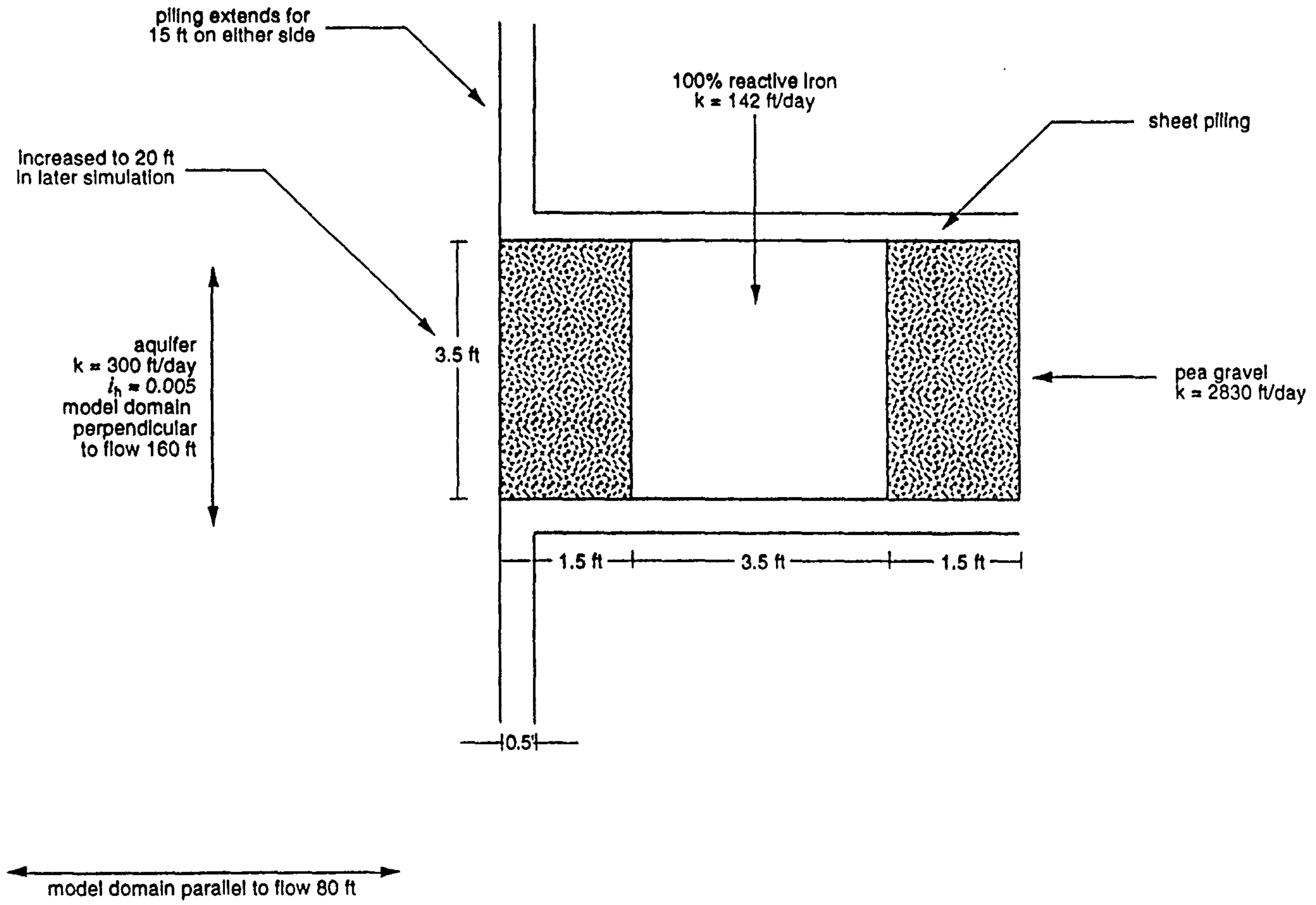

Figure 3- Base case material properties used in pilot-scale groundwater model

TABLE 1: SUMMARY OF RESULTS OF GROUNDWATER MODELING

Material Hydraulic Conductivity (K) Adjusted	Hydraulic Conductivity Value	Treatment Zone Width	Minimum Residence Time in Central Treatment Zone	Notes
Aquifer K	24 ft/d	14.7 ft	40 hr	min. K value reported in previous reports
	300 ft/d	9.7 ft	10 hr	base case K in aquifer
	584 ft/d	7.0 ft	8 hr	max. value reported in previous reports
Gate K	37 ft/d	5.2 ft	21 hr	gate porosity = 0.33; min. K value for 50% Fe
	142 ft/d	9.7 ft	10 hr	gate porosity = 0.4; base case K in Fe gate
	284 ft/d	11.6 ft	7 hr	gate porosity = 0.4; max. K value for 100% fe
Gravel pack K	566 ft/d	7.9 ft	10 hr	
	2,830 ft/d	9.7 ft	10 hr	base case K in gravel pack
	14,150 ft/d	10.8 ft	10 hr	
Funnel wall K	2.8 x 10E-03 ft/d	9.7 ft	10 hr	base case K in funnel wall
	2.8 x 10E-05 ft/d	9.6 ft	10 hr	
Increased treatment zone width (20 feet)				
	142 ft/d	30 ft	17 hr	base case and 100% iron properties used in model run

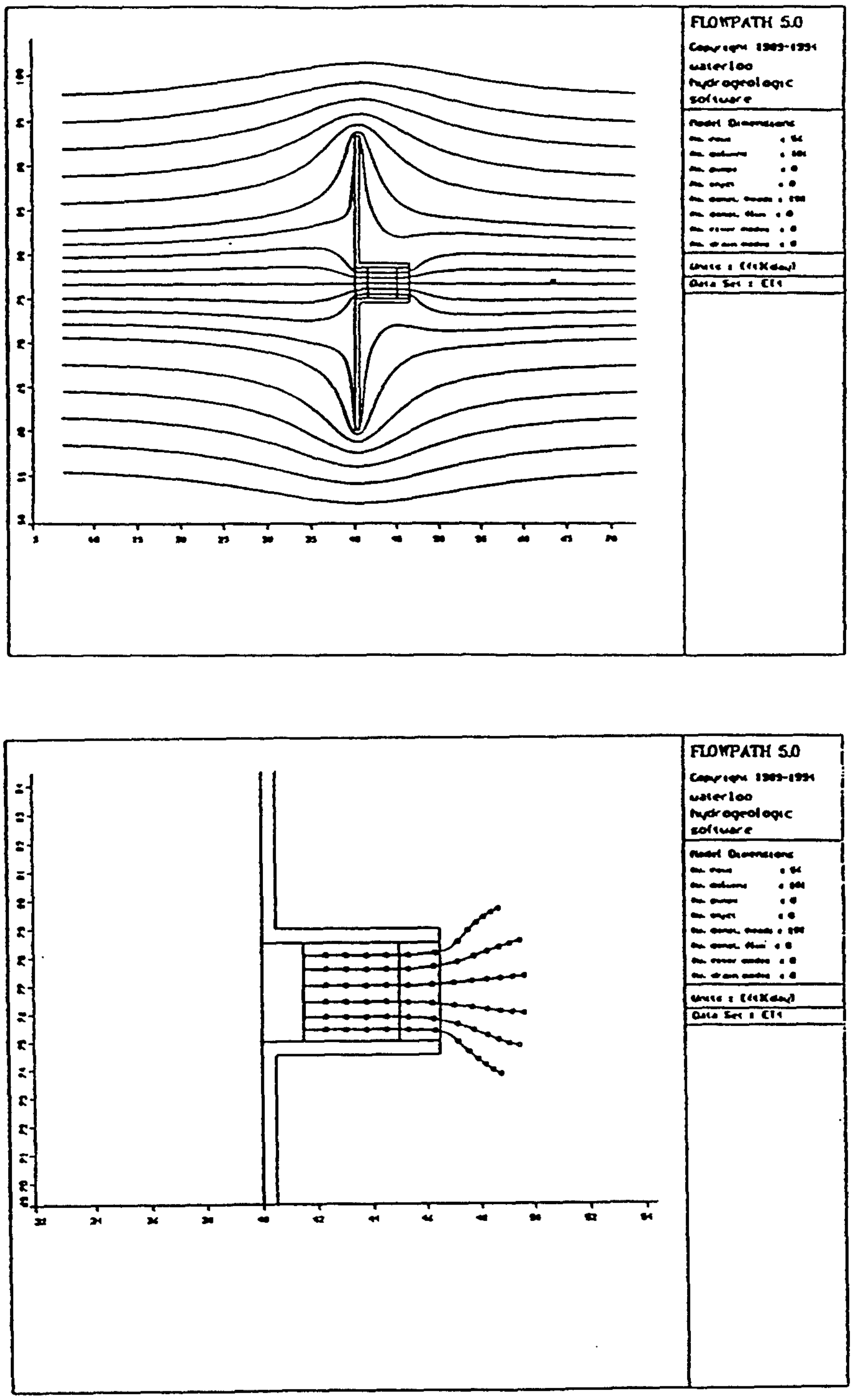

Figure 4- Determination of capture zone and groundwater residence time in pilot-scale model, using base case material properties. Distance between each time-marker in lower figure represents two hours of residence time.

When the hydraulic conductivity for the 100% reactive iron was increased to 284 ft/day (the maximum measured laboratory value), the residence time decreased further, to 7.0 hr. Decreasing the hydraulic conductivity of the sheet pile funnel by two orders of magnitude had a negligible effect on residence times in the gate. While not investigated in detail, the modeling results indicated that residence times in the reactive zone would increase linearly with increased reactive zone length in the direction parallel to groundwater flow.

FIELD TEST RECOMMENDATIONS BASED ON LABORATORY AND MODELING STUDIES

From the column tests, the required groundwater residence time for TCE degradation in reactive media containing 50% iron was about 4 hours. Groundwater modeling results suggested that a minimum residence time of 8 to 12 hours would occur in a treatment zone 3.5 feet long in the direction of groundwater flow, depending on the pertinent material properties. Given this safety factor, and the fact that a 50% iron media is 25 to 30% less expensive than a 100% iron media, it was recommended that the performance of 50% iron be examined in the field trial. If successful, considerable cost savings could be realized in full-scale technology application if 50% iron is used in the reactive zone, relative to 100% iron.

The groundwater modeling results showed that the configuration initially proposed for the funnel and gate system resulted in a relatively small treatment zone width (approximately 10 feet) upgradient of the gate. Because equipment mobilization and construction costs represent a significant portion of the expense associated with the installation of a funnel and gate system, we therefore examined the cost and feasibility of increasing the permeable treatment zone width with a goal of increasing the width of plume treated by the pilot-scale installation while not greatly increasing costs. We modelled this case using the base case aquifer and 100% iron properties, and increased width of the permeable treatment section (Figure 3) from 3.5 feet to 20 feet perpendicular to flow. As shown in Table 1, the width of aquifer captured increased to 30 feet, and a residence time of 17 hrs through the reactive iron zone of the 20 foot wide gate was calculated. It was consequently recommended that a wider treatment zone (≥20 feet) be constructed.

CURRENT STATUS

The report on this study is currently undergoing review by on-base and AFCEE technical staff. If the project proceeds, a pilot-scale structure similar to the one described above may be constructed and monitored. Costs of alternative construction techniques, and the costs of a full-scale treatment system are being evaluated.

CONCLUSIONS

Bench-scale studies conducted using groundwater from Fairchild Air Force Base indicate that the EnviroMetal process may serve as a passive *in-situ* method of remediating groundwater containing TCE at this site. Rapid TCE degradation occurred in reactive iron columns. Half-lives of 0.34 and 0.71 hours were measured in columns containing 100% and 50% iron, respectively. The small amounts of cDCE and VC produced did not exceed regulatory criteria and these compounds subsequently degraded. At these degradation rates, less than 0.5 days residence time in a reactive gate would be needed to reduce influent TCE concentrations to acceptable levels. A simple groundwater model proved quite useful in determining the required dimensions of *in-situ* treatment zones needed to achieve this residence time.

ACKNOWLEDGEMENTS

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EPA DATABASES FOR THE REMEDIATION OF HAZARDOUS WASTE SITES

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ABSTRACT

The Environmental Protection Agency (EPA) developed several computer databases to support remedial investigations of hazardous waste sites. This paper overviews the ATTIC system and provides a directory of other pertinent databases and on-line bulletin board systems.

The Alternative Treatment Technology Information Center (ATTIC) system was developed pursuant to the 1986 Superfund law amendments. It provides up-to-date information on innovative treatment technologies to clean up hazardous waste sites. ATTIC v.2.0 provides access to several other databases as well as a mechanism for retrieving full-text documents of key literature. It can be accessed with a personal computer (PC) and modem 24 hours a day without user fees. In addition to these separate databases, ATTIC allows immediate access to a number of disk-based database and software systems. A user may download these programs to his PC via a high-speed modem. Also via modem, users are able to download entire documents from the ATTIC system. Currently, over one hundred publications are available, including the Superfund Innovation Technology Evaluation (SITE) program documents.

Other EPA databases and on-line bulletin board systems of interest to hazardous waste site project managers include CLU-IN (Cleanup Information Electronic Bulletin Board) and the ORD BBS (Office of Research and Development Bulletin Board System), Vendor Information System for Innovative Treatment Technologies (VISITT), the Records of Decision System (RODS) database, and several others referenced in the paper.

INTRODUCTION

The Environmental Protection Agency (EPA) has developed several computer databases to support remedial investigations of hazardous waste sites. Some are on-line, accessed through telephone connections, and others are disk-based programs sent to the public, usually free of charge. This paper reviews these systems and comments on strengths and weaknesses of the computerized databases currently available.

GENERAL CONSIDERATIONS

Any database is only as good as the information contained in it. The primary concern of the database manager is to assure that the data in the system is current, complete, and the best attainable. With the mountain of information available, it is imperative to include only top quality information; poor, obsolete, or extraneous information should be excluded. Data quality varies, so several EPA databases have added quality assurance (QA) indicators. Ultimately, a standard system of data quality objectives and indicators should be established.

The appearance, speed and ease of use of the database is a secondary consideration. Improvements in programming have brought forth dramatic enhancements in user friendliness, use of graphics, and responsiveness to user needs. Ongoing software development will continue to make databases easier to use.

Many of EPA's databases are accessed by telephone with modems. This approach offers great advantages in that a central system operator can keep the records current. However, there are several drawbacks associated with transmission over telephone lines. For example, for BBS systems that use ASCII, graphics and tables are severely limited, programming features such as pop-down menus are not available, and low-speed modems (less than 9600 baud) make use cumbersome, especially in areas where telephone line noise exists. These drawbacks are overcome by making programs downloadable for the user's own personal computer.

Other EPA databases are available in disk form only. EPA widely distributes these, normally free of charge. However, some of the larger systems will not fit on high density disks, so they are distributed on compact disks (CD-ROMs), sometimes with a fee.

EPA has been criticized for having too many databases, with tremendous duplication, and inadequate cross referencing. This derives in part from the decentralized nature of the Agency and the fact that the databases are funded separately, with the funding coming from different environmental statutes. The user is not able to connect to a single source; "one-stop shopping" is not available. To a limited extent, EPA is currently addressing this problem.

ATTIC DATABASE SYSTEM

The Alternative Treatment Technology Information Center (ATTIC) system was developed pursuant to the 1986 Superfund law amendments. It provides up-to-date information on innovative treatment technologies to clean up hazardous waste sites. It can be accessed with a personal computer and modem 24 hours a day, and there are no user fees. Currently, ATTIC receives approximately 1000 calls monthly, mostly from hazardous waste consultants.

In an effort to provide one-stop shopping, ATTIC v 2.0 provides access to several discrete databases and software packages as well as a mechanism for retrieving full-text documents of key literature. The databases provide information on alternative treatment options, and include:

- **Treatment Technology Database**: this contains abstracts from the literature on all types of treatment technologies, including biological, chemical, physical, and thermal methods. The best literature as viewed by experts is highlighted.

- **Treatability Study Database**: this provides performance information on technologies to remove contaminants from wastewaters and soils. It is derived from treatability studies. This database is available through ATTIC or separately as a disk that can be mailed to you.

- **Underground Storage Tank Database**: this presents information on underground storage tank corrective actions, surface spills, emergency response, and remedial actions.

- **Oil/Chemical Spill Database**: this provides abstracts on treatment and disposal of spilled oil and chemicals.

In addition to the above, ATTIC allows access to other disk-based systems (databases, software packages, and computer models). These include:

- **Vendor Information System for Innovative Treatment Technologies (VISITT), v.3.0**: this disk-based database displays information on cleanup technologies as provided by equipment and technology vendors. Over 277 technologies offered by 171 vendors are described on the system.

- **Bioremediation in the Field Search System (BFSS), v.1.0:** this disk-based database provides site-specific information on sites where bioremediation is being tested or implemented or has been completed. Currently, 160 sites are on the database; an update doubling this number is expected soon.

- **Pollution Prevention Progress (P2P), v.1.5:** this software package is used for measuring progress in pollution prevention (P2) resulting from product redesign, reformulation or replacement. It compares the pollution generated in the manufacture of a product before and after improvements in the manufacturing process are made, taking into account one or more lifecycle stages.

- **Records of Decision System (RODS):** this information database was developed to track site clean-up under the Superfund program and to document the type of treatment chosen at each site. The system is provided on a CD-ROM, which may be purchased at a current cost of $325.00.

A user may download these programs to his own PC via a high-speed modem. We recommend use of at least a 9,600 baud modem, with 14,400 baud preferred for efficient transmissions.

Users can download entire documents from the ATTIC system. About a hundred publications are available, including the Superfund Innovation Technology Evaluation (SITE) program documents. Other key documents in the system are engineering bulletins and technical resource documents issued by EPA's National Risk Management Research Laboratory (NRMRL).

Other features of the ATTIC system include: a bulletin board system for communication between system users and the establishment of conferences/special interest groups (see discussion under the ORD BBS below) and a calendar of events, updated quarterly, which informs on conferences, etc. in the environmental field.

In the future, EPA intends to upgrade the ATTIC database system by:

- critically reviewing and improving the content of the database through the use of periodic technology expert conferences

- adding additional key documents for on-screen review and full text retrieval

- adding a hypertext feature to downloaded documents

- adding additional data (e.g., drinking water treatment performance data, treatability studies from DOD) into the ATTIC treatability/performance study database

- integrating ATTIC with other EPA and federal databases (ATTIC could be made a component of the DOD Defense Environmental Information Exchange - DENIX system)

- making ATTIC directly available on the Internet (ATTIC is currently available only through FedWorld, via telephone modems)

For more information, call the ATTIC hotline (703-908-2137) or EPA (908-321-6677 or fax 908-906-6990).

OTHER ON-LINE DATABASE/SOFTWARE PACKAGES

CLU-IN Bulletin Board System (CLU-IN BBS). CLU-IN (Cleanup Information Electronic Bulletin Board) is a bulletin board system used for finding information on innovative technologies, consulting among cleanup professionals, and accessing other databases. It allows downloading of full-text documents, including bulletins on how the system operates. Users can tie in at no cost; the system operator is at 301-589-8368. CLU-IN is accessible via the Internet.

ORD Bulletin Board System (ORD BBS). EPA's Office of Research and Development (ORD) established a BBS in 1990 to improve communication and technology transfer among EPA staff, state and local personnel, academia, researchers and the private sector.

There are eleven conferences on the system. These are special interest groups within the BBS who routinely confer and exchange information. The groups on the BBS include Expert Systems, Biotechnology, Regional Operations, the Groundwater Information Tracking System (GRITS), the Environmental Monitoring and Assessment Program (EMAP), the Integrated Risk Information System (IRIS), and the Science Advisory Board (SAB). These conferences provide for the exchange of information and are a forum for the outlet of information, publications and reports.

A special feature of the ORD BBS is a text-searchable database of all ORD publications produced since 1976 (over 20,000 citations). A user may order a copy of the publications directly over the BBS system. Users can tie in at no cost; the system operator (SYSOP) is at 513-569-7272.

Other Databases. In August 1992, EPA published a guide to federal databases[1] that pertain to the clean-up of hazardous waste sites. Twenty-five databases were cited in that manual, several of which have since been abandoned or incorporated into other database systems. This manual is currently being updated by EPA. For further information, contact Ms Naomi Smith at 703-308-8848.

COMPUTER ASSISTED SITE EVALUATION SOFTWARE

Currently, EPA-NRMRL and its consultants are evaluating computer software (federal and commercial) that can be used to depict hazardous waste sites and predict results from alternative treatments. These can:

- assist in characterization of hazardous waste sites, based on data collected in the field
- produce site maps to identify potential and confirmed contaminant sources
- produce geologic cross sections to visualize geology and likely contaminant flow paths in groundwater
- produce maps of groundwater to determine groundwater flow direction and potential contaminant receptors
- produce maps of contaminant plumes (isopleth maps) to identify the vertical and lateral extent of contamination, contaminant hot spots, and contaminant plume migration direction
- identify surface water bodies and pathways for contaminant migration to surface waters
- model 2- and 3-dimensional migration of groundwater contaminant plumes over time
- allow geologic, hydrogeologic, and analytical data to be easily stored, retrieved, updated and statistically analyzed
- allow visualization of the site and the extent of site contamination that might not be possible with conventional maps and tables
- add remedial options (i.e., pumping wells, slurry walls, treatment plants) to the site and model the changes in groundwater contaminant migration over time
- model the costs associated with the selected remedial options

A major feature of this effort is to allow the remedial project manager (RPM) to perform "what if" queries on the data to evaluate remedial alternatives.

EPA-NRMRL is reviewing three software packages: the ICASE (Integrated Computer Assisted Site Evaluation) package developed for EPA over the past several years, the SiteView/EQuIS software package developed by the ConSolve corporation, and the GISKey™

package developed by GIS/Solutions.

TECHNOLOGY REMEDIATION GUIDE - SOFTWARE AND CD-ROM

In 1994, the Department of Defense Environmental Technology Transfer Committee published the second edition of the "Remediation Technologies Screening Matrix and Reference Guide"[2]. This handbook brings together information on technologies used to clean up hazardous waste sites and provides a matrix that can be used to screen which technologies might be applicable to a particular site. It gives profiles/descriptions of over fifty treatment technologies used to treat contaminated soil, groundwater, and air emissions. It also discusses data requirements, common properties and behaviors for groups of contaminants and gives case histories for sites at which treatment has been instituted.

The Guide has been issued in hard copy as well as in electronic form, using WordPerfect 6.0 DOS and Envoy (Windows). It has been converted to hypertext so that the user may easily move around and search the document. The disk version of the Guide is available through the ATTIC system; a portion of it is readable on-screen and the entire document may be downloaded.

Currently, EPA and DOD (Army, Air Force) are collecting the Guide references for addition to the electronic version of the Guide. Hard copies of documents will be converted to electronic form through scanning, using a combination of optical character recognition (OCR) and image scanning. This will greatly enhance the usability of the Guide; future issuances will likely require a CD-ROM version due to the quantity of information/data that will be available.

CONCLUSIONS

There is a wealth of information on technologies to remediate hazardous waste sites. EPA has focused the capturing of this information in its ATTIC database system; other on-line and disk-based database/software systems are also available. Furthermore, EPA is currently involved with development of computer assisted site evaluation software and the electronic collection of pertinent treatment technology information to support the DOD "Remediation Technologies Screening Matrix and Reference Guide".

ENDNOTES

1. U.S. EPA. "Accessing Federal Data Bases for Contaminated Site Clean-Up Technologies - Third Edition". EPA/542/B-93/008. October 1993. 40 pages.

2. Federal Remediation Technologies Roundtable. "Remediation Technologies Screening Matrix and Reference Guide - Second Edition". EPA/542/B-94/013. NTIS PB95-104782. October 1994. Approximately 400 pages.

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