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NAVAL OCEAN SYSTEMS CENTER

San Diego, California 92152-5000

J. D. FONTANA, CAPT, USN
Commander

R. M. HILLYER
Technical Director

ADMINISTRATIVE INFORMATION

The Environmental Research and Development (R&D) Technical Workshop was sponsored by the Assistant Commander for Environment, Safety and Health, Naval Facilities Engineering Command and hosted by the Marine Environmental Support Office, Naval Ocean Systems Center. The technical co-chairs were Ms. Elizabeth Wilkins, Director, Environmental Programs Division, Naval Facilities Engineering Command, and Mr. Robert K. Johnston, Marine Environment Branch, Naval Ocean Systems Center. These proceedings were prepared with materials submitted by workshop participants with funding provided by Naval Facilities Engineering Command. This work was performed to support the Navy's Environmental Protection Program.

Released by
P. F. Seligman, Head
Marine Environment Branch

Under authority of
S. Yamamoto, Head
Environmental Sciences
Division

NOTE: The front cover is an artist's depiction of the environmental setting surrounding Naval installations. Navy bases are components of complex coastal and estuarine ecosystems which are both environmentally sensitive and economically important. Environmental protection at Navy activities requires the capability to comply with appropriate environmental laws and regulations.



THE SECRETARY OF DEFENSE
WASHINGTON, THE DISTRICT OF COLUMBIA

10 OCT 1989

MEMORANDUM FOR SECRETARIES OF THE MILITARY
DEPARTMENTS

SUBJECT: Environmental Management Policy

This Administration wants the United States to be the world leader in addressing environmental problems and I want the Department of Defense to be the Federal leader in agency environmental compliance and protection.

Federal facilities, including military bases, must meet environmental standards. Congress has repeatedly expressed a similar sentiment. As the largest Federal agency, the Department of Defense has a great responsibility to meet this challenge. It must be a command priority at all levels. We must demonstrate commitment with accountability for responding to the Nation's environmental agenda. I want every command to be an environmental standard by which Federal agencies are judged.

The first priority of our environmental policy must be to integrate and budget environmental considerations into our activities and operations. This will decrease our future liabilities and costs for our people. The effort begins and ends with our people. We need the right people at the right place with the right training.

It is also extremely important that we communicate clearly what we are doing to address our environmental concerns. We need to work harder at telling our environmental success' stories and solving our problems in an open, cooperative way with the public and also appropriate regulatory authorities. The universal recognition of effective DOD environmental compliance and stewardship activities in the surest way to maintain our access to the air, land, and water we need to maintain and improve our mission capability.

We must be fully committed to do our part to meet the worldwide environmental challenge and I know I can count on your support to ensure that we are successful in that effort.

A large, handwritten signature in black ink, which appears to be "Dick Cheney", is located at the bottom right of the page.



DEPARTMENT OF THE NAVY
NAVAL OCEAN SYSTEMS CENTER
SAN DIEGO, CALIFORNIA 92152-5000

IN REPLY REFER TO

WELCOME TO THE ENVIRONMENTAL R & D TECHNOLOGY WORKSHOP

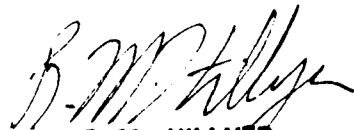
Welcome to the Naval Ocean Systems Center. It is our pleasure to have you here and be able to host this workshop. I hope the time spent here will be productive and that the facilities we have made available will be conducive to a successful meeting.

The mission of the Naval Ocean Systems Center is to provide the Fleet with the best systems and technology possible at the best price. Our primary mission is to support weapons, surveillance, and command control and communications systems as well as other vital components of the Navy's mission, such as environmental compliance. It does not benefit the Navy to have the cutting edge of technology available but not be able to deploy those systems because the proper permits can not be obtained, or that the use of those systems will result in unsatisfactory degradation of our environment or the pollution of our harbors and waterways.

The Naval Ocean Systems Center is committed to a standard of excellence in being able to provide the leading edge of technology to the Fleet. During this era of funding uncertainties it is essential that the Navy gets the highest return possible on its investment in R & D. It is also certain that environmental requirements will not go away, and in fact, will become more and more restrictive. Therefore, it is critical that the Navy has the technology available to meet the expanding requirements and reduce the cost of compliance. NOSC is proud of the contribution we have made to the Navy's Environmental Program, such as the technology base developed to support the Navy's Organotin Program, the establishment of a Marine Environmental Support Office here at NOSC, and the technical support provided for numerous environmental assessments and studies.

The Naval Ocean Systems Center will continue to support the development of quality technology to assist the Navy's environmental programs and help achieve Secretary Cheney's goal of making the Department of Defense "the Federal leader in agency environmental compliance and protection."

I hope you enjoy your stay in "America's Finest City."



R. M. HILLYER

Robert Hillyer
Technical Director
Naval Ocean Systems Center
San Diego, CA 92152-5000

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INTRODUCTION

Environmental protection is becoming one of the top priorities for the Department of Defense and the Navy. How do we achieve compliance with the staggering environmental requirements? How do we maintain mission readiness and meet operational requirements while simultaneously protecting the environment? How do we pay for environmental protection technology? How can we implement available technology and develop needed technology in order to improve our environmental protection record without exceeding budget restraints? These were some of the issues addressed by the Environmental Research and Development (R&D) Technical Workshop. The workshop addressed the technical issues of the Navy's hazardous waste minimization (HAZMIN), installation restoration (IR) and pollution abatement (PA) programs.

The workshop brought together a cross-section of people supporting the Navy's environmental protection programs. Participants included program managers, project engineers, technicians, lawyers, staffers, and researches. The mix of participants helped provide an atmosphere which promoted insightful discussions on the the technical issues of the Navy's environmental protection program. Major Claimant representatives provided an overview of headquarters programs and initiatives. Engineering Field Division (EFD) representatives presented information and specific examples of environmental protection technology needs and provided contrasting experiences of environmental requirements from their geographical regions. Activity level representatives provided yet another perspective on practical aspects of environmental protection.

These proceedings have been compiled to document the information presented at the workshop and to assist in the transfer of the technical information to those unable to attend the workshop. The proceedings are organized roughly according to the workshop agenda and common topical areas. Although it was not possible to include everything which transpired during the workshop, the proceedings have been developed from materials submitted by workshop attendees to provide the essence of the workshop experience and continue the process of developing solutions to the Navy's environmental problems. The first section provides an overview of the environmental R&D program currently being funded by the Naval Facilities Engineering Command (NAVFAC) and the exploratory development program (6.2) being funded by the Office of Naval Technology (ONT). The definition of the Navy's environmental technology requirements was developed from presentations submitted by representatives of Major Claimants, EFDs, and activities and from keeping a tally of technology development issues discussed throughout the workshop.

The remainder of the workshop consisted of technical seminars and demonstrations of technology development projects currently being addressed by R&D initiatives. The proceedings are organized according to the topical areas addressed during the technical seminars. The contributing author's name, address, and phone number is provided as a point of contact for more information on a specific technical area. In some cases, presentations submitted have been edited to conserve space and improve clarity. The final section provides the list of attendees and comments received from those who filled out the workshop evaluation form.

We thank all those who participated in the workshop, especially those who took the time to prepare presentations and contributions for the proceedings. The workshop provided valuable interaction and educational experiences and we thank all who helped make it a success.

Editors:

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**ENVIRONMENTAL RESEARCH AND DEVELOPMENT (R&D)
TECHNICAL WORKSHOP**

**AGENDA
TUESDAY NOVEMBER 7, 1989**

0800 WELCOME - Robert Hillyer, Technical Director,
Naval Ocean Systems Center

0815 VIEW FROM THE TOP - Captain J. Rispoli, Assistant Commander
for Environment, Safety and Health, NAVFACENGCOM Code 18

OVERVIEW OF ENVIRONMENTAL RDT&E PROGRAM

0830 THE NAVY'S SHORESIDE ENVIRONMENTAL PROTECTION RDT&E:
PROGRAM: A STRATEGY FOR ENVIRONMENTAL COMPLIANCE AT
NAVAL SHORE FACILITIES - Elizabeth Wilkins, Director, Environmental
Programs Division, NAVFACENGCOM Code 183

0850 EMERGING TECHNOLOGY FOR ENVIRONMENTAL COMPLIANCE,
Paul Schatzberg, DTRC Code 2830

0910 THE REGULATORY FRAMEWORK FOR COMPLIANCE,
Ray Goldstein, NAVFAC Office of Counsel

0930 BREAK

DEFINITION OF ENVIRONMENTAL R&D REQUIREMENTS

0945-1130

NORTHDIV
CHESDIV
LANTDIV
SOUTHDIV
WESTDIV (San Bruno)
OICC-NW (Silverdale)
SOUTHWESTDIV (San Diego)
PACDIV

1130 - 1300 LUNCH, DOLPHIN FACILITY, Guest Speaker:
"How Clean is Clean?", Dr. Richard Gersberg, San Diego State University,
School of Public Health

DEFINITION OF ENVIRONMENTAL R&D REQUIREMENTS (CONT.)

1300-1500

NAVSEA
NAVAIR
CINCLANT
NAVSUP
OTHER CLAIMANT REPRESENTATIVES
OTHER ACTIVITY REPRESENTATIVES

1500 BREAK

1515 R&D PRIORITIES MATRIX - WHERE SHOULD THE FOCUS BE?
DISCUSSION Elizabeth Wilkins, Moderator

1615 WRAP UP

1630 ADJOURN

WEDNESDAY MORNING NOVEMBER 8

CONCURRENT SESSION A
Building 128 Auditorium

0800-1000 HAZMIN 1: WASTE MINIMIZATION INITIATIVES

MODERATOR: Mr. J. Kaminski, NAVFAC 182
Building 128 Auditorium

0800 Cadmium Removal From Electroplating Rinsewaters,
Ms. J. Koff, NCEL

0820 Conversion of Navy Paint Spray Booth Particulate Emission
Control Systems from Wet to Dry Operations,
Mr. R. M. Roberts, NCEL

0840 Fast Breaking Degreasers,
Mr. T. Torres, NCEL

0900 Recycling Hydroblasting Waste Water,
Dr. B. Y. K. Pan, NCEL

CONCURRENT SESSION B
Building 111, Room 266

0800-1000 SESSION IR 1: MEASUREMENT TECHNOLOGY

Moderator: Dr. Al Zirino, NOSC
Building 111 Code 50 Conference Room

0800 Cone Penetrometer System for Real-Time Chemical Screening
of Hazardous Waste Sites, Dr. S. H. Lieberman, NOSC

0820 Analytical Methods to Monitor Remediation, Ms. C. Dooley,
NOSC

0840 Field QA/QC Strategies in the Installation Restoration
Program, Mr. J. Edkins, NEESA

0900 Automated Instruments for Organometal and Heavy Metal
Analysis, Mr. C. Clavell, NOSC

0920 Remote In Situ Sediment Toxicant Release Sampler,
Mr. S. Lieberman, NOSC

0945-1030 DEMONSTRATIONS

0945 Automated Organometal Analysis
Building 111 Room 239
Mr. C. Clavell, NOSC

0945 Geoprocessing for IR Support
Marge Elliot, NCEL
Building 111, Room 238

0945 Expert System for Hazardous Waste Minimization
R. M. Roberts, NCEL
Building 111, Room 221

1000 Sediment Toxicant Release Sampler
Building 111 Room 148
Mr. B. Chadwick, S. Lieberman, NOSC

1015 Fiber Optic Laser-Based Sensors
Building 111 Room 123
Dr. S. Lieberman, NOSC

WEDNESDAY MID-MORNING NOVEMBER 8

CONCURRENT SESSION A
Building 128 Auditorium

CONCURRENT SESSION B
Building 111, Room 266

1030-1200 HAZMIN 2: POLLUTION PREVENTION PROJECTS
MODERATOR: R. Mike Roberts, NCEL
Building 128 Auditorium

1030-1200 SESSION IR 2: TOXICITY AND RISK ASSESSMENT
Moderator: T. Flor, NEESA
Building 111 Code 50 Conference Room

1030 Three Projects to Reduce Hazardous Wastes From Ships:
Blasting Grit Recycling, Ultra Jet Paint Removal, and
Bilge Oily Waste Treatment, Mr. G. Smith, DTRC

1030 Utility of In Situ Mussel Bioindicators to Monitor
Contamination and Assess Environmental Effects,
Mr. M. Salazar, NOSC

1100 Industrial Improvements for Pollution Prevention: Plastic
Media Blasting, Mr. J. Zimmerle, NCEL

1050 Assessing the Impact of Hazardous Waste Disposal Sites on
the Environment: Case Studies of Ecological Risk
Assessments at NCBC Davisville and NAS Whidbey Island,
Mr. R. K. Johnston, NOSC

5

1110 National Research Council Special Study for Risk
Assessments at Navy Aquatic Sites, Mr. P. F. Seligman

1130-1200 DEMONSTRATIONS

1130 Toxicity Assessments With Microtox - P. Kenis, NOSC
Laboratory Bioassay Demonstration - D. Rosenberger, NOSC
Building 111, Room 152

1130 Expert Systems For Haz Min
Mr. R. M. Roberts, NCEL
Building 111, Room 221

1130 Geoprocessing for IR Support
Marge Elliot, NCEL
Building 111, Room 238

1200-1330 LUNCH

WEDNESDAY AFTERNOON, NOVEMBER 8

CONCURRENT SESSION A
Building 128 Auditorium

CONCURRENT SESSION B
Building 111 Code 50 Conference Room

1330-1600 PA 1: AIR AND WATER POLLUTION CONTROL

Moderator: Dr. E. Douglas, AESO
Building 128 Auditorium

AIR INITIATIVES

1330 Compliance With Air Toxic and California Hexavalent Chromium Emissions, Dr. E. Douglas, AESO

1345 Impact of Montreal Protocols on Navy Operations, R. Waskull, OESO

1400 Architectural Paint Specification for VOC Compliance, Dr. Drisko and Mr. Yanez, NCEL

1420 Used Oil and Solvent Recovery and Reuse, Mr. W. Venable, NEESA

1445-1500 BREAK

WATER INITIATIVES

1500 Development of a Portable Flowthrough Bioassay System, Mr. R. S. Henderson, NOSC

1520 Biomonitoring For Navy Effluents, Ms. S. Salazar, NOSC

1330-1600 SESSION IR 3 REMEDIATION TECHNOLOGIES

Moderator, Mr. P. Schatzberg, DTRC
Building 111 Code 50 Conference Room

1330 Remedial Action Contracts, R. Biggers, NEESA

1350 Technology Transfer Documentation For Remediation: Case Study at MCAS Tustin, Mr. S. McCarel, NEESA

1410 Chemical and Physical Treatment at NAES Lakehurst, N. Olah, NCEL

1425 PCB Remediation at PWC Guam, N. Olah, NCEL

1445-1500 BREAK

1500 Biological Treatment at NAS Patuxent River, Ron Hoeppe, NCEL

1520 Bioreactor Development for Waste Site Remediation, Dr. C. Hui, NOSC

1545-1645 DEMONSTRATIONS

1545 Geoprocessing for Installation Restoration Support
Building 111, Room 238
Marge Elliot, NCEL

1545 Laboratory Bioassay Demonstration
Ms. D. Rosenberger, NOSC
Building 111, Room 152

1615 Automated Defense Priority Model
Building 111, Room 237
K. M. Green, NAVFAC 181C

1615 Toxicity Assessments With Microtox
Paul Kenis, NOSC
Building 111, Room 152

THURSDAY MORNING, NOVEMBER 9

CONCURRENT SESSION A Building 128 Auditorium

0800-1000 PA 2: RUNOFF CONTROL AND ASSESSMENT
Moderator: R. Hoepfel, NCEL
Building 128 Auditorium

0800 Environmental Feasibility of Wetland Enhancement for
Mitigation of Runoff,
Ms. L. Karr, NCEL and Mr. L. Gadbois, NOSC
0820 Assessing the Environmental Impact of Runoff,
Mr. L. Gadbois, NOSC

0840 Technologies for Control of Runoff From Target Ranges,
Mr. J. Heath, NCEL

0900 Preliminary Assessment of Metal Contamination
From Target Ranges. Ms. L. Karr, NCEL

CONCURRENT SESSION B Building 111 Code 50 Conference Room

0800-1000 PA 3: SAMPLING NETWORKS, MONITORING, AND ASSESSMENT
Moderator: LCDR. W. Wild, NOSC
Building 111 Code 50 Conference Room

0800 Overview of the Navy's Underground Storage Tank Program,
Mr. N. Pryor, NAVFAC 181E

0820 Underground Storage Tank Leak Detection,
Mr. N. Olah, NCEL

0840 Marine Environmental Survey Technology,
Mr. B. Chadwick, NOSC

0900 Prediction of Toxicant Dispersion and Environmental Fate,
Dr. K. Richter, NOSC

0930-1000 DEMONSTRATIONS

0930 Automated Organometal Analysis
Building 111 Room 239
Mr. C. Clavell

0930 Geoprocessing for IR Support
Marge Elliot, NCEL
Building 111, Room 238

0930 Fiber Optic Laser-Based Sensors
Building 111 Room 123
Dr. S. Lieberman

THURSDAY MID-MORNING, NOVEMBER 9

1000 EXECUTIVE SESSION
IMPLEMENTATION: THE TRANSITION PHASE
PANEL DISCUSSION
Building 128, Auditorium
Moderator: E. Wilkins, Code 183
Members: CMD J. McCollum, Code 03
Mr. P. Schatzberg, DTRC
Mr. S. Ehret, NCEL
Dr. S. Yamamoto, NOSC
Ms. T. Gandy, NEESA

1115 WORKSHOP WRAP UP
E. Wilkins NAVFAC

1130-1330 DEMONSTRATIONS

1130 Geoprocessing for IR Support
Marge Elliot, NCEL
Building 111, Room 238

1130 Fiber Optic Laser-Based Sensors
Building 111 Room 123
Dr. S. Lieberman, NOSC

1130 Marine Environmental Survey Demonstration
Mr. B. Chadwick, NOSC
San Diego Bay Cruise aboard the Research Vessel ECOS
Pier 159

1130 Automated Organometal Analysis
Building 111 Room 234
Mr. C. Clavell, NOSC

1130 Expert System for HAZ MIN
M. Roberts, NCEL
Building 111, Room 221

1230 Geoprocessing for IR Support
Marge Elliot, NCEL
Building 111, Room 238

1230 Marine Environmental Survey Demonstration
Mr. B. Chadwick, NOSC
San Diego Bay Cruise aboard the Research Vessel ECOS
Pier 159

1230 Toxicology Demonstration
Ms. D. Rosenberger, NOSC
Building 111, Room 152

OVERVIEW OF ENVIRONMENTAL RDT&E PROGRAM

THE NAVY'S SHORESIDE ENVIRONMENTAL PROTECTION	11
RDT&E PROGRAM: A STRATEGY FOR ENVIRONMENTAL COMPLIANCE AT NAVAL SHORE FACILITIES	

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AUTOVON 221-8531, (202) 325-8531

NAVY ENVIRONMENTAL R&D TECHNICAL WORKSHOP	17

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EMERGING TECHNOLOGY FOR ENVIRONMENTAL COMPLIANCE	26

Paul Schatzberg
Code 2830, David Taylor Research Center
Annapolis, MD 21402-5067
AUTOVON 281-3629, (301) 267-3629

THE NAVY'S SHORESIDE ENVIRONMENTAL PROTECTION RDT&E PROGRAM:
A STRATEGY FOR ENVIRONMENTAL COMPLIANCE AT
NAVAL SHORE FACILITIES

Elizabeth F. Wilkins, Robert K. Johnston,
and Deborah A. Rayworth
Naval Facilities Engineering Command
Alexandria, VA 22332 (202) 325-8531

INTRODUCTION

Increasing environmental compliance requirements are impacting on the operational effectiveness of Navy Shore Facilities. This year the Naval Facilities Engineering Command (NAVFACENGCOM) received numerous requests for research, development, test and evaluation (RDT&E) assistance from Navy Major Claimants. These requests were based on potential operational impacts from the inability to comply with current and impending environmental laws and regulations. Operational impacts identified ranged from the high cost of technical solutions and increased manpower requirements to facility shutdowns and possible criminal and civil liability. RDT&E is required to develop new and innovative technologies to assure cost effective compliance with environmental laws and regulations.

An integrated RDT&E program is required to address a broad range of environmental requirements and to meet the challenge of overall environmental protection. NAVFACENGCOM has established specific goals and thrust areas to facilitate the development of an integrated RDT&E program. These goals and thrust areas are listed in Table 1. The legislative and regulatory mandate for each goal is listed in Table 2. The execution of RDT&E projects aimed at achieving these goals is necessary for the Navy to obtain and maintain cost effective environmental compliance for shoreside facilities and operations.

TABLE 1: NAVY ENVIRONMENTAL RDT&E GOALS (NAVFAC PERSPECTIVE)

I. Zero discharge of hazardous wastes from Navy industrial facilities.

THRUST AREAS:

- Waste Stream Treatment for Industrial Processes
 - . Emptying, Cleaning, and Derusting Bilges and Tanks
 - . Painting and Paint Stripping Operations
 - . Boiler Lay-up and Cleaning Operations
- Ordnance Operations and Waste Disposal
- Lubricants and Other Fluids Change-outs
- IWTP Reagents Use and Reuse

II. Acceptable cleanup levels achieved at all Navy past hazardous waste disposal sites.

THRUST AREAS:

- Remediation Technologies
 - . Biological (In situ and bioreactors)
 - . Chemical
 - . Physical
- Risk Assessment and Risk Management Methodologies
- Site Restoration and Closure Techniques

III. One hundred percent reclamation of industrial and municipal waste water at Navy facilities.

THRUST AREAS:

- Conservation
- Reuse and Reclamation of Waste Water
- Reduction of Water Total Toxic Organics
- Groundwater Protection
- Monitoring and Protection of Drinking Water

IV. Zero air emissions and acceptable noise emissions from Navy shore facilities.

THRUST AREAS:

- Air Emissions Control
- Alternatives to Volatile Organic Carbon (VOC) Coatings
- Control of New and Emerging Air Pollutants
- Noise Reduction and Control
- Alternatives to Chlorofluorocarbon (CFC) Applications

- V. Nonpolluting, safe, and state-of-the-science materials and industrial processes for Navy facilities.

THRUST AREAS:

- Improvements for Industrial Processes
 - . Emptying, Cleaning, and Derusting Bilges and Tanks
 - . Painting, Paint Stripping Operations
 - . Boiler Lay-up and Cleaning Operation
- Substitution for Nonhazardous Materials
- Nonpolluting Antifouling Systems

- VI. State-of-the-science methods and instrumentation for cost effective monitoring of Navy unique pollutants and contamination.

THRUST AREAS:

- Sensor Development
 - . Sensor Networks
 - . Real Time Sensors for Process Control and Monitoring
- Biomonitoring for Toxicity and Hazard Assessment
- Monitoring Network Design and Implementation

- VII. Comprehensive prediction and management of environmental effects from Navy systems and operations.

THRUST AREAS:

- Control of Nonpoint Source Pollution
- Modeling and Prediction of Environmental Effects
- Remote Sensing and Remote Detection
- Site Closure and Excess Property Procedures

**TABLE 2: THE STATUTORY AND REGULATORY MANDATE FOR THE NAVY
ENVIRONMENTAL RDT&E GOALS (NAVJFAC PERSPECTIVE)**

I. Zero discharge of hazardous wastes from Navy industrial facilities.

Resource Conservation and Recovery Act (RCRA), Clean Water Act - National Pollution Discharge and Elimination System (CWA-NPDES), Toxic Substances Control Act (TSCA), Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), National Ocean Pollution Planning Act (NOPPL), Used Oil Recycling Act (UORA)

II. Acceptable cleanup levels achieved at all Navy past hazardous waste disposal sites.

Comprehensive Environmental Response Compensation and Liability Act and Superfund Amendment and Reauthorization Act (CERCLA and SARA), National Contingency Plan (NCP), Hazardous and Solid Waste Amendments (HSWA), Applicable or Relevant and Appropriate Requirements (ARARs)

III. One hundred percent reclamation of industrial and municipal waste water at Navy Facilities.

CWA, Safe Drinking Water Act (SDWA), Water Resources Planning Act (WRPA), State Regulations, economic necessity

IV. Zero air emissions and acceptable noise emissions from Navy shore facilities.

Clean Air Act, TSCA, Noise Ordinances, State Regulations

V. Nonpolluting, safe, and state-of-the-science materials and industrial processes for Navy facilities.

RCRA, Occupational Safety and Health Act (OSHA), NPDES, TSCA, FIFRA, State Regulations, economic necessity

VI. State-of-the-science methods and instrumentation for cost-effective monitoring of Navy pollutants and contamination.

National Environmental Policy Act (NEPA), CERCLA and SARA, RCRA, CWA (Dredging Requirements, National Estuary Program, Nonpoint source, NPDES), Ocean Dumping, State Regulations, economic necessity

VII. Comprehensive prediction and management of environmental effects from Navy systems and operations.

NEPA, Coastal Zone Management Act (CZMA), Endangered Species Act, Farm Bill (nonpoint source), Marine Protection, Research and Sanctuaries Act, Exclusive Economic Zone, Outer Continental Shelf - "Ocean Sanctuary", Floodplain Insurance Act (increased liability in coastal areas)

PROGRAM STRUCTURE

The environmental RDT&E program sponsored by NAVFACENGCOM addresses three program areas: hazardous waste minimization (HAZMIN), Installation Restoration (IR), and Pollution Abatement Ashore (PA). The HAZMIN projects are supported with Navy Defense Environmental Restoration Account (DERA) funds set aside to reduce hazardous waste generation at Navy facilities; the IR projects are also supported with Navy DERA funds; and the PA projects are supported with funds from the RDT&E Program Element 0603721N, Y0817.

HAZMIN and IR program RDT&E is required to develop a technology base capable of minimizing hazardous waste generation and reducing the cost of cleaning up hazardous waste sites. Innovative technology development is required for physical, chemical, and biological treatment of hazardous wastes, methods for risk assessment and risk management of hazardous waste sites, and techniques for site restoration and site closure. The majority of technology development projects can be executed as demonstration projects at specific IR sites. However, RDT&E funds are required to support feasibility studies of specific technologies that are not mature enough for demonstrations. These RDT&E funds are used for selected technology development projects and for integrated strategy development for solving technological problems associated with site restoration and hazardous waste minimization.

PA program RDT&E is required to reduce mission impact and cost of compliance with Federal and State laws and regulations primarily driven by the Clean Water Act, Clean Air Act, and the National Environmental Policy Act.

Major program thrust areas include:

Industrial Improvements. RDT&E is required to identify and implement nonpolluting industrial processes for Navy unique industrial and waterfront facilities. New industrial processes and replacement of toxic chemical processes are required to cost effectively meet Federal and state regulations requiring pretreatment of industrial wastewater.

Monitoring and Assessment. The Navy must develop systems to acquire scientifically sound and legally defensible monitoring and assessment data to document the environmental safety of Navy operations.

Water Conservation and Reuse. RDT&E is required to develop water conservation and reuse technology due to increased demand for water supplies, seawater intrusion into coastal aquifers, and the high cost of potable water supplies. Effective management and use of available water resources will be required. This problem will be especially acute in the Southwest and Florida.

Air Emission Control. RDT&E is required to identify: the substitution of materials and emission control technology for volatile organic compound (VOC) emissions from solvents and paints; the substitution of materials for chlorofluorocarbons (CFC) and halon systems that will be banned to prevent ozone depletion; and technology to mitigate and control noise pollution.

Methods and Instrumentation. RDT&E is required to develop methods and instrumentation to measure unique Navy pollutants. These methods and materials will be required for determining the extent of environmental pollution and the effectiveness of the Navy's pollution abatement program.

Comprehensive Prediction and Management. RDT&E is required to develop methods to integrate environmental information that will provide effective management of harbor areas, wetlands, shorelines, and other natural resources. Modeling and prediction of long term impacts will provide tools necessary for management of the Navy's environmental resources. Methods and technologies needed for Navy compliance with requirements of nonpoint source runoff, coastal zone management, and endangered species legislation are the most urgently needed.

NAVY ENVIRONMENTAL R&D TECHNICAL WORKSHOP

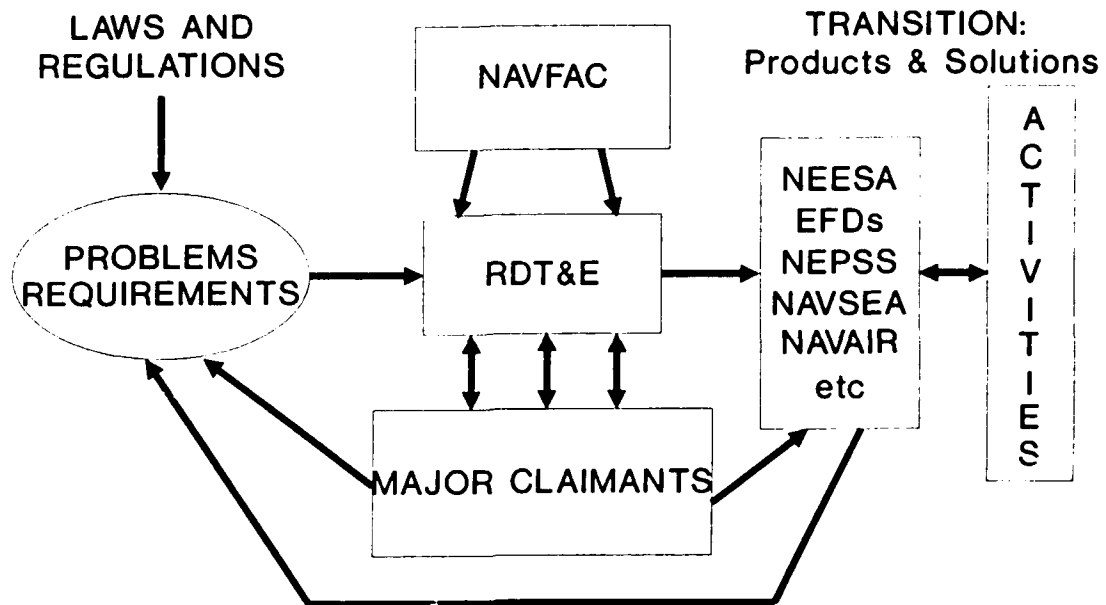
- Introduction
- Goals of meeting
- Program Goals
- Current Program
- Future Plans
- Program prioritization

NAVY ENVIRONMENTAL R&D TECHNICAL WORKSHOP

GOALS OF MEETING:

- IDENTIFY REQUIREMENTS
- REVIEW CURRENT TECHNICAL ISSUES
- FORUM FOR DIALOGUE

ENVIRONMENTAL PROTECTION RDT&E PROCESS



ENVIRONMENTAL R&D GOALS NAVFAC PERSPECTIVE

- I. Zero Discharge From Shore Facilities
- II. Acceptable Cleanups at IR Sites
- III. 100% Reclamation of Waste Water
- IV. Zero Air and Acceptable Noise Emission
- V. Nonpolluting Improved Industrial Processes
- VI. Methods and Instrumentation for Monitoring
- VII. Comprehensive Prediction and Management

I. ZERO DISCHARGE FROM SHORE FACILITIES

- Expert system for HAZMIN
- Non-cyanide electroplating
- Cyanide minimization
- Shelf life specification
- Chrome substitution
- Paint reformulation

II. Acceptable Cleanup at IR Sites

A. Risk Assessment

- Site specific toxicity assessment
- NAS Whidbey Island
- CBC Davisville
- NRC special study
- NAS North Island

II. Acceptable Cleanup at IR Sites

B. Demonstration projects

- PWC Guam
- MCAS 29 Palms
- CBC Port Hueneme
- NAS Lakehurst
- NWS Seal Beach
- NSB Bangor
- NAS Patuxent River

II. Acceptable Cleanup at IR Sites

C. Remedial technology

- Stabilization/Solidification
- Electrolysis Oxygen generation
- Electro-acoustical soil cleanup
- Target range cleanup
- Biotechnical Slope protection
- Tri-Service Bioreactor Technology

IV. Zero Air and Acceptable Noise Emissions

- Environmentally acceptable coatings
- NOx emission reduction
- Asbestos encapsulation guide spec.

V. Non-polluting Improved Industrial Processes

- Recycling hydroblast wastewater
- Sodium Nitrite reduction
- Citric acid reduction
- IWTP technology
- Shipboard HAZMIN
- Blasting grit recycling
- Bilge oily waste
- Ultra Jet Paint removal

VI. Methods and Instrumentation for Monitoring

A. Installation Restoration

- Pipeline cleanup and monitoring
- Benthic flux device
- Tri-service fiber optic sensor
- Remedial analytic methods

VI. Methods and Instrumentation for Monitoring

B. Pollution Abatement

- UST leak detection
- Lead in drinking water
- AFFF detection
- Fiber optic sensor for metals
- Marine environmental survey
- Portable environmental test sys.
- Biomonitoring

VII. Comprehensive Prediction and Management

- Non-point source assessment
- Non-point source control
- Geoprocessing for IR support

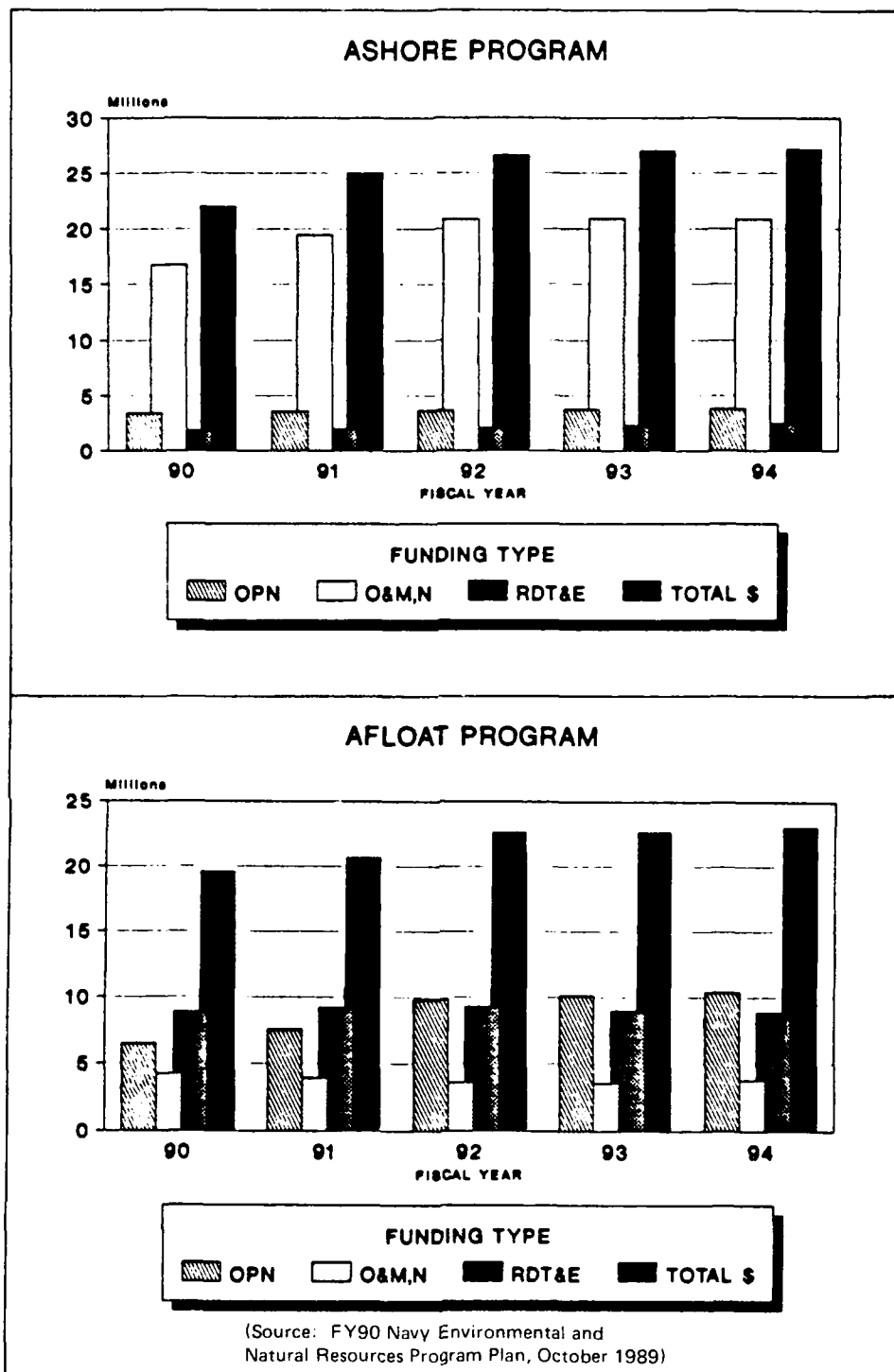
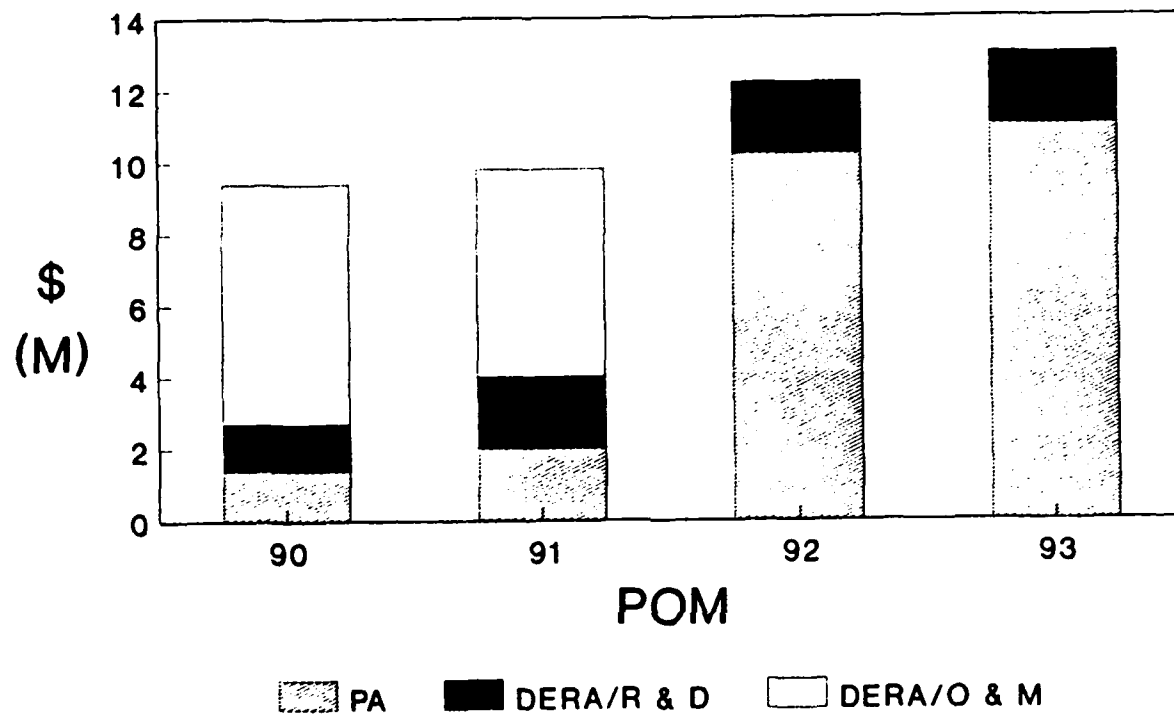


FIGURE 2-2. Funding Profile

R & D FUNDING STRATEGY



EMERGING TECHNOLOGY FOR ENVIRONMENTAL COMPLIANCE

Paul Schatzberg
David Taylor Research Center

Definitions

Let me begin by reviewing some definitions of the different kinds of research we do. The following definitions are taken from the FY90 Department of Defense Small Business Innovation Research Program Solicitation. They are very clear definitions and are better than anything else I have seen.

Basic Research. A systematic, intensive study directed toward greater knowledge or understanding of the subject studied.

Exploratory Development. A systematic study directed specifically toward applying new knowledge to meet a recognized need.

Advanced Development or Engineering Development. A systematic application of knowledge towards the production of useful materials, devices, and systems or methods, including design, development, and improvement of prototypes and new processes to meet specific requirements.

I have underlined what I consider to be the key words. Let me discuss these definitions with an example. Several years ago there was a specific need to separate oil from bilgewater, because when ships pump bilges, an unacceptable slick of oil would appear. A slick of oil, by the way, that could not only be seen by a U.S. Coast Guard helicopter but also by a space satellite. If the oil is emulsified, which is often the case, simple separation by gravity would not work. To respond to that need, new existing knowledge of pressure-driven semi-permeable membrane separation was applied. This is exploratory development or 6.2 research. Once a specific requirement was established, namely, pumped bilgewater could not contain more than 15 parts per million of oil, using the 6.2 results, the application of knowledge was directed to the production of an oil/water separation system to meet that requirement. The important distinction that this example seeks to illustrate, is the distinction between 'need' and 'requirement;' the former term is qualitative while the latter term is quantitative. ONT has made it very clear that 6.2 R&D be need-driven.

At present there is no environmental protection 6.1 program that is structured to transition increased knowledge and understanding to 6.2 in the manner that 6.2 is structured to transition to 6.3, driven by the goal of environmental compliance at affordable costs. Therefore environmental protection technology base development begins with 6.2.

Introduction

It is my job as technical manager for 6.2 to facilitate development of the technology base on which the larger R&D effort can be supported. This program is currently funded at \$1.5M. That is approximately 8.8% of the total Navy environmental protection budget. ONT has given environmental protection the no.1 priority for investment strategy in the logistics 6.2 area; that is, a higher priority than equipment performance monitoring, shore/offshore facilities, acquisition/supply, and replenishment.

In 1989 the Chief of Naval Operations announced two corporate goals for environmental compliance: (1) Ships of the 21st century will have a "Pollution-Free Profile;" that is, these ships will retain and/or treat wastes such that any necessary discharge will comply with very stringent global water quality standards; (2) Shore facilities of the 21st century will be "zero" discharge; that is, these facilities will eliminate the discharge of hazardous wastes so that any necessary discharge will meet the anticipated more rigorous local regulations. A third goal, which has not been institutionalized, is to reduce by 50% the cost of compliance by the year 2000. This goal is endorsed by the President's Blue Ribbon Commission on Defense Management (The Packard Commission) which recommended that "DoD should place greater emphasis on using technology to reduce cost." (June 1986)

These corporate goals structure the investment strategy for the technology base (6.2) environmental protection program. The objectives of the program are to apply emerging technology to recognized needs to facilitate regulatory compliance now and into the 21st century, minimize hazardous waste generation, and reduce the cost of compliance. The transition recipients of this effort will be P.E. 63721N, the Defense Restoration Account (DERA), the Fleet directly; and joint tri-service advanced development projects, a new and growing approach, there being at least one in operation with several more proposed.

The FY90 6.2 program consists of the following tasks: Environmental Biotechnology (NOSC), which is concerned with the development and application of biomarker technology and total toxic organics analysis to assist in the rapid and economical assessment of potential biological effects of Navy wastewater streams; In Situ Bioremediation (NCEL), which is concerned with expanding the tech base on how indigenous microorganisms can be encouraged to biodegrade underground hydrocarbon fuel spills; Cryogenic Paint Stripping from Aircraft and Ships (NCEL), which is developing means to remove paint with a pressurized liquid nitrogen jet stream, generating only paint chips for disposal; Marine Plastics (DTRC), which is developing biopolymer films for shipboard packaging and associated technology to permit compliance with P.L. 100-220 which prohibits the discharge of synthetic plastics from Navy ships anywhere by January 1, 1993; Vacuum Transport (DTRC), which is developing a mathematical design model that optimizes two-phase flow in shipboard vacuum

sewers to achieve maximum total system performance for ships; Graywater Treatment (DTRC), which is developing shipboard volume reduction processes to eliminate untreated graywater discharge from ships in anticipation of a "zero" discharge requirement; Thermal Destruction for Ships' Solid Waste (DTRC), is developing engineering designs for a high capacity thermal destruction prototype to achieve the CNO corporate goal of a Pollution-Free Profile ship for the 21st century; Ship/Drydock Hazardous Waste Cost Reduction (DTRC), a new start, will develop a strategy to reduce the cost of shipyard compliance with hazardous waste disposal by modifying current processes generating such hazardous wastes. I will discuss only a few of these tasks.

In Situ Bioremediation of Underground Fuel Spills

In situ bioremediation of underground fuel spills (Task D-2) is directed to the need to remediate chronic leaks from underground storage tanks and pipe lines. Hydrocarbon fuels, such as JP-5 jet fuel have contaminated subsoil areas, fresh water tables and marine estuaries. Existing and pending court orders require remediation of these sites. Potentially the most cost-effective remediation is in situ biodegradation by indigenous microorganisms. The optimization of this approach as well as its limitations must be determined.

The magnitude of the need is reflected in the cost of ownership. The Navy owns some 6,000 underground fuel storage tanks. Many of these have been leaking, are leaking now, and many more will be leaking in the near future. The cost of site remediation, in so far it requires soil excavation, treatment and replacement represents an expenditure of billions of dollars, primarily because moving the soil is a labor-intensive activity. In addition, there are approximately 50 on-land oil spills per year, representing a cleanup cost of \$7-\$10 million annually. The Defense Restoration Account (DERA) will pay for remediation of events prior to 1984. Approximately 100 leaking fuel tanks at 21 Navy sites qualify; but, DERA will not pay for events after 1984. Therefore, the cost of remediation of most of the problem will fall to the agencies that own the site; namely, the military readiness, deployment or replenishment activities.

This illustrates the growing cost problem faced by DoD; namely, that by the year 2000 an unacceptably large fraction of activity operating budgets will be directed to environmental compliance.

Accordingly, in situ bioremediation of underground hydrocarbon fuel spills, if effective, can save the Navy 75% of the cost of ownership by eliminating excavation, hauling and disposal costs; minimizing disruption of naval operations; and minimizing damage to the environment.

Task D-2 efforts have already identified specific indigenous JP-5 degrading microbes, established fuel-in soil concentration limits for degradation and identified a microbial encapsulation

phenomenon that may enhance containment and degradation strategies. A number of things remain to be done. The solubility in water and the toxicity of various hydrocarbon components of JP-5 will be determined, the encapsulation phenomenon will be investigated, and a numerical model of the life cycle of an underground fuel spill will be determined. This model has the potential of predicting a number of things about an underground fuel spill, including its life and toxicity. However, there is much that remains unknown and still needs to be discovered. Close coordination is being maintained with the Air Force R&D effort and their contractor, Batelle of Columbus.

Cryogenic Paint Stripping from Aircraft and Ships

Current methods of paint stripping from surfaces using organic solvents generate large volumes of toxic chemicals and have potential human health hazards. Alternative methods, gaining some acceptance, such as plastic media abrasive blasting, also generate toxic wastes and may cause mechanical damage to thin aluminum surfaces. The Air Force has announced a large contractual effort to identify and develop alternative approaches to current paint stripping procedures. None of these efforts include the approach being used in Task D-4, in which a jet of pressurized liquid nitrogen (LN2) combines the thermal shock of LN2 with the mechanical energy of the jet to remove paint films, requiring only the collection and disposal of paint particles.

This would result in a very large reduction in volume of disposable waste, reduced human health hazards, and produce a very cost effective paint stripping procedure. The 1985 paint stripping sludge disposal cost was \$31.5M.

What has been achieved so far are paint film chill rates greater than 1000°F per second; maximum thermal shock attained before the substrate chilled; thick films (10 mils) stripped at 200 psi LN2 jet pressure; and cryogenic temperatures have no adverse effects on aluminum. The next step is to apply higher LN2 jet pressures to attempt removal of thin films (< 1 mil).

Plastics for Marine Waste Disposal

Public Law 100-220 prohibits overboard discharge anywhere of synthetic plastics by 1 January 1993. Synthetic plastics as packaging materials are ubiquitous in our society, and so they are on our ships. Navy ships will have to hold their synthetic plastic waste until it can be off-loaded ashore. However, the daily trash generated that can be thrown overboard will have to be contained in a marine biodegradable trash bag rather than the ubiquitous, non-degradable plastic trash bag. A large ship generates several hundred such bags daily. Furthermore, a large amount of synthetic plastic cannot be stored for longer than three days because unacceptable odors develop. Task D-6 is developing a degradable (< 4 weeks) trash bags and odor-barrier bags for storage of food-contaminated plastics. This will

facilitate compliance with P.L. 100-220, retain the benefits of synthetic plastics, and avoid the cost of special non-plastic packaging.

Several types of bio-polymer films have been made which exhibit adequate mechanical strength and degrade rapidly (< 4 weeks) in the marine environment. Films have been made of chitosan, derived from the waste of consumed shell fish; from a blend of chitosan and starch; and from regenerated cellulose. Manufacturing issues and cost considerations have been a factor in this effort. A promising odor barrier bag for food-contaminated plastics has been identified and will receive an extensive shipboard evaluation.

Laboratory and field evaluations of the most promising bio-polymer films will continue, an accelerated biodegradation apparatus will be used to screen candidates, and the ability to manufacture these films commercially will be further investigated.

All Navy ships will need to meet near zero discharge standards in many bodies of water worldwide by the 21st century. A compact, lightweight, high capacity, thermal destruction system for solids and concentrated sludges would meet that need if it can function within the unique operational constraints imposed by Navy surface ships. To achieve this will require a technology base development effort consisting of a design feasibility analysis, investigation of the best methods of thermal destruction, and investigation of the optimum methods of heat transfer and process temperature.

Successful transition of this task to 6.3 with subsequent implementation will benefit the ship of the 21st century by achieving the near zero discharge corporate goal and specifically by freeing the ship of having to process solid wastes, eliminating the costs and problems of disposal in foreign ports, permitting plastic and medical waste destruction, leaving no traceable discharge while only producing an inert ash that can be retained during deployment, and eliminating the need to transit to 25 nm for trash discharge during coastal and amphibious operations.

So far it looks as if pyrolysis and gasification, with an after-burner is the most feasible, while radiant heat from electric elements or conductive heat in a fluidized bed appear best for rapid processing. An extensive technology assessment is underway. It is useful to present definitions of terms used in this task.

Incineration. Burning of material (gas or solid) in an oxygen-rich atmosphere that converts organic molecules primarily to carbon dioxide and water.

Pyrolysis. Destructive distillation of material in an atmosphere devoid of oxygen that produces primarily gaseous

organic molecules.

Starved Air Incineration or Gasification. Simultaneous distillation and burning of material in an oxygen-poor environment to convert material to a gas without creating fly ash.

Ship/Drydock Hazardous Waste Cost Reduction

This is a new task beginning FY 1990. The emphasis is on cost reduction as distinct from HW volume reduction. The cost of HW treatment and disposal continues to increase and is expected to become a significant portion of activity operating expenses by CY 2000 unless heroic steps are taken to decrease generation rates by the application of new and emerging technology.

The first major deliverable of this new task will be a shipyard drydock case study which will itemize the costs of complying with HW disposal requirements at the Philadelphia Naval Shipyard. The second major deliverable will be a detailed plan to reduce the cost of disposing shipyard HW by 50% by CY 2000, and to eliminate its production in the future.

PROGRAM FUNDING

As stated in the introduction, The ONT FY90 funding for the Exploratory Development Environmental Protection Program is \$1.5M. This includes one ongoing task at the Naval Ocean Systems Center, two tasks by the Naval Civil Engineering Laboratory, and five tasks at the David Taylor Research Center. Funding for these tasks described is shown below.

Exploratory Development Program Funding (\$K)

Task No.	Title	FY90	FY91
D-1	Environmental Biotechnology	260	255
D-2	In Situ Bioremediation	200	245
D-4	Cryogenic Paint Stripping	210	
D-6	Marine Plastics	165	300
D-7	Vacuum Transport	160	-
D-8	Graywater Treatment	155	200
D-9	Thermal Destruction	150	250
D-10	Hazardous Waste Cost Reduction	100	150

The corporate Navy environmental goals described in the introduction are ambitious, but represent an appropriate response to the reality of environmental policy developments. As stated earlier, the R&D technology base response to these corporate goals begins at the 6.2 level. As technology transitions to 6.3, field trials and implementation, the degree of flexibility in making changes decreases accordingly. Therefore, the highest opportunity for innovation and fundamental change in current practices that are necessary for meeting the new corporate goals

lies with Exploratory Development, including the highest potential return on investment. The impact on Navy operations, afloat and ashore, of environmental regulations, already significant in 1990, will be profound by the end of the decade. All indications are that a graduated increase in R&D investment in 6.2 now will show very substantial returns by the end of the millenium. Conversely, maintaining funding at the present level, could jeopardize realization of the corporate goals at a point in the development process when the degree of flexibility in making changes is no longer present.

DEFINITION OF ENVIRONMENTAL R&D REQUIREMENTS

SOUTHWEST-DIV ENVIRONMENTAL R&D GOALS 35

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PROGRAM PRIORITIES MATRIX 51

SOUTHWEST-DIV ENVIRONMENTAL R&D GOALS

SOUTHWEST DIVISION ENVIRONMENTAL DIVISION (SWDIV-ED) IS RESPONSIBLE FOR PROVIDING ENVIRONMENTAL SERVICES TO BOTH MARINE AND NAVAL ACTIVITIES IN THE SOUTHWEST REGION OF CALIFORNIA, AND IN THE STATE OF ARIZONA. PRESENTLY SWDIV-ED CATERS TO 34 NAVY INSTALLATIONS AND 9 MARINE CORPS ACTIVITIES. THE FUNCTIONS OF THE SWDIV-ED INVOLVE HANDLING MATTERS RELATED TO CERCLA, UNDERGROUND STORAGE TANKS (USTs), CURRENT OPERATIONS (RCRA), AND LOCAL REGULATIONS AT EACH OF THE VARIOUS NAVY AND MARINE CORPS ACTIVITIES. TWO OF SWDIV-ED ACTIVITIES ARE CURRENTLY LISTED ON THE U.S. ENVIRONMENTAL PROTECTION AGENCY'S NATIONAL PRIORITIES LIST (NPL). THIS NPL STATUS ENTAILS THAT THESE SITES WILL RECEIVE HIGHEST PRIORITY AMONG NATION'S HAZARDOUS WASTE SITES. TWO ADDITIONAL SWDIV-ED ACTIVITIES ALSO HAVE BEEN PROPOSED FOR NPL LISTING. MOST OF OUR ACTIVITIES ARE LOCATED ALONG THE SHORELINE OF THE PACIFIC COAST.

EACH ACTIVITY AVERAGE ABOUT SIX TO TWELVE CERCLA SITES AND 20 TO 30 UST AND RCRA SITES. THE POLLUTANTS COMMON TO MOST OF THESE ACTIVITIES ARE POLs, SOLVENTS SUCH AS DEGREASING AGENTS, AND PESTICIDES SUCH AS DDTs; GENERATED BY VEHICLE MAINTENANCE, PEST CONTROL, FIRE FIGHTING TRAINING OR IN COMBAT TRAINING OPERATIONS.

UNDER THE PRESENT SELECTION CRITERIA, CONCENTRATIONS OF THE POLLUTANTS AT MAJORITY OF THESE SITES ARE NOT HIGH ENOUGH TO CONDUCT R&D WORK. IF CHANGES ARE MADE TO THE SELECTION CRITERIA TO INCLUDE LESSER CONTAMINANT CONCENTRATIONS, SWDIV-ED WILL BE ABLE TO PROMOTE A NUMBER OF THEIR SITES FOR R&D WORK.

A. COMMON GOALS.

- I. FIRE FIGHTING TRAINING AREAS (FFTAs) ARE HAZARDOUS WASTE SITES COMMON TO MOST ACTIVITIES. THESE ABANDONED SITES ARE CONTAMINATED WITH MIXTURES OF COMPOUNDS SUCH AS WASTE POLs, HEAVY METALS, PCBs, TETRA OR TRICHLOROETHYLENE, OR ANYTHING THAT BURNS OR NEED TO GET RID OF. PRESENTLY OUR ACTIVITIES USE OFF-SPEC JET FUELS FOR TRAINING FIRE FIGHTERS, AND THE FUELS ARE BURNT ON A CONSTRUCTED IMPERMEABLE BASIN-LIKE STRUCTURE. BUT UNFORTUNATELY, IN THE PAST, UNLINED AREAS WITH A 2-FOOT HIGH DIKE WERE USED AS FFTAs. THERE WAS NOTHING TO PREVENT THE INTRODUCED LIQUIDS FROM PENETRATING INTO UNDERLYING SOILS, AND THE FFTAs

HAVE BECOME HAZARDOUS WASTE SITES. SOIL CONTAMINATION HAS OCCURRED WITHIN AN AREA AVERAGING ABOUT 25 TO 50 FEET IN DIAMETER, TO A DEPTH OF ABOUT 20 FEET. WE NEED BETTER DESIGNED FFTAs AND ALSO TECHNOLOGIES TO DEMARCATe CONTAMINATED AREAS AND METHODS TO TREAT THE CONTAMINATED SOILS WITHOUT EXCAVATION.

CURRENTLY WE USE TWO UNSATISFACTORY, BUT POPULAR METHODS FOR CLEANING UP FFTAs. THE FIRST CONSISTS OF EXCAVATION, TRANSPORTATION, AND DISPOSAL IN A RCRA LANDFILL; THIS TENDS TO FILL UP OUR COSTLY LANDFILLS AND ALSO IS DISCOURAGED BY THE SARA DUE TO ASSOCIATED LONG TERM UNCERTAINTIES.

BIO-DEGRADATION IS THE OTHER METHOD. WE USED THIS METHOD TO CLEAN UP A 20,000 CY OF CONTAMINATED SOIL IN A PILE AT BRIDGEPORT MARINE CORPS MOUNTAIN TRAINING CENTER. FIRST PROBLEM WE FACED IN THE METHOD WAS THE NEED FOR SEGREGATION OF PILE MATERIALS BY SCREENING TO COARSE AND FINE PARTICLES. THIS NEEDED HAULING OF THE CONTAMINATED MATERIALS FROM ONE PLACE TO ANOTHER WHICH MAY REQUIRE RCRA PERMITS, AND ALSO THE METHOD WAS INCAPABLE OF TREATING COARSE MATERIALS. TIME REQUIREMENT FOR BIODEGRADATION ALSO WAS EXCESSIVE, THE REGIONAL WATER QUALITY CONTROL BOARD WHO HAD ISSUED A CLEANUP AND ABATEMENT ORDER ON THIS PILE WAS QUITE CONCERNED ABOUT THE TIME IT WAS TAKING TO TREAT THE PILE AND ABOUT THE POSSIBLE DISPERSION OF THE CONTAMINATED MATERIALS BY WIND AND RAIN. MARINE CORPS AIR GROUND COMBAT CENTER AT 29 PALMS ALSO HAS A SIMILAR PILE WHICH NEEDS IMPROVED TREATMENT METHODS. A SPEEDY PROCESS WHICH WILL PERMANENTLY AND SIGNIFICANTLY REDUCE THE VOLUME, TOXICITY OR MOBILITY OF CONTAMINANTS IN HYDROCARBON SPILLED AREAS, WHICH NEITHER NEEDS EXCAVATION NOR PILING NEED TO BE DEVELOPED FOR TREATING CONTAMINATED AREAS.

- II. SLUDGE MINIMIZATION IS ALSO AN IMPORTANT TASK FOR THE SWDIV-ED R&D EXPECTATIONS. SPECIALLY, INDUSTRIAL SLUDGES AT BARSTOW AND EL CENTRO, AND SEWAGE SLUDGE CONTAINING HIGH CONCENTRATIONS OF HEAVY METALS, AND PESTICIDES AT NOSC ARE BIG PROBLEMS; WE ARE RUNNING SHORT OF AREAS FOR DISPOSAL AND THE PERMIT REQUIREMENTS ARE TEDIOUS AND TIME-CONSUMING.
- III. OTHER COMMONLY OCCURRING CONTAMINANTS OF SOIL IN SWDIV-ED ARE NON HALOGENATED SEMI-VOLATILE ORGANICS. PHTHALETES WHICH ARE RCRA LISTED WASTES ARE FREQUENTLY FOUND IN SOILS AND ORIGINATES FROM VARIOUS SOURCES. AN IN-SITU TREATMENT PROCESS IS REQUIRED TO CLEAN UP THESE TYPES OF WASTES SINCE EXCAVATION IS HIGHLY UNDESIRABLE.

- IV. PESTICIDES AND WOOD PRESERVATIVES ARE ALSO COMMONLY FOUND IN SOILS, AND R&D WORK NEEDED TO DISCOVER WAYS TO TREAT THESE CONTAMINANTS IN-SITU.**
- V. R&D HELPS ARE NEEDED TO TREAT WASTES GENERATED FROM PLATING COMPOUNDS WHICH PRODUCE METALS SUCH AS CADMIUM AND ARSENIC.**
- VI. WASTE GENERATED FROM BATTERY ACIDS SPILLS AND OLD BATTERIES ARE ALSO COMMONLY OCCURRING PROBLEMS AT OUR ACTIVITIES.**
- VII. OIL/WATER SEPARATORS OR THE INTERCEPTORS ARE A MAJOR PROBLEM AT VARIOUS ACTIVITIES. THEY ARE OVERLOADED AND DO NOT FUNCTION WELL ENOUGH TO SEPARATE THE OILS. IMPROVED DESIGNS FOR THESE UNITS ARE NEEDED TO INCREASE THE EFFICIENCY SO THAT REGULATORY STANDARDS FOR PERMITTING ARE MET.**
- VIII. WASTE-WATER (PERCOLATING) LEACH-FIELDS ARE ALSO A BIG PROBLEM AT ACTIVITIES. THE REGULATORS INSIST ON CONTINUOUS GROUNDWATER MONITORING AND OTHER EXPENSIVE ANALYTICAL WORKS PERFORMED AT THESE SITES. NEED R&D WORK FOR A BETTER SYSTEM.**

B. SPECIFIC GOALS.

- I. A SPILL OF POTASSIUM FERRY CYANIDE FROM A PHOTO PROCESSING LAB HAS CAUSED PROBLEMS AT NAVAL AIR STATION EL CENTRO. ALTHOUGH ALL VISIBLE CONTAMINATED SOILS WERE REMOVED IMMEDIATELY, A SMALL AMOUNT STILL REMAINED. AFTER SEVERAL YEARS, THE SITE DISCOLORATION IS NOW APPARENT; (WHITISH GREEN COLORATION OF SURFACE SOIL IS NOTICED). SOME MILCON PROJECTS ARE PLANNED AT THIS SITE, AND NEED A COST VIABLE METHOD FOR THE SITE REMEDIATION BEFORE THE PLANNED PROJECTS COULD BE EXECUTED. THE DEPTH TO THE GROUNDWATER IS ABOUT 6 FEET AND IS NOT POTABLE (CLASS III-TYPE WATER).**
- II. SOILS CONTAMINATED WITH ACIDS, CYANIDES, HYDROXIDES, AND CARBON TETRACHLORIDE ARE BIG ISSUES AT NOSC. PCBs AND WASTE OIL CONTAMINATED SOIL ARE PROBLEMS AT THE SUBBASE. THESE NEED R&D COMMUNITY HELP.**

- III.** NAVAL AMPHIBIOUS BASE NORTH ISLAND HAS ENCOUNTERED PROBLEMS WITH STORM SEWERS DISCHARGING INTO THE BAY POTENTIALLY POLLUTING THE BEACH OF SEDIMENTS CONTAINING HEAVY METALS, ALKALIS, PESTICIDES, ACIDS, PAINT SLUDGES, PLATING SOLUTIONS, DEGREASING AGENTS, AND WASTE FUELS. ALTERNATIVE INNOVATIVE TECHNOLOGIES ARE NEEDED TO RESOLVE THESE PROBLEMS.
- IV.** CLASS I-, AND II-TYPES GROUNDWATER HAVE GOT CONTAMINATED WITH TETRA & TRICHLOROETHYLENE, DDTs, AND OTHER PESTICIDES AT SOME OF OUR ACTIVITIES. AQUIFERS ARE ABOUT 150 FEET DEEP. NEED TO MEET MAXIMUM CONCENTRATION GOALS AND OTHER ARARS IN CLEANING UP THEM. R&D EFFORTS NEED TO BE PERFORMED TO IDENTIFY THE EXTENT OF CONTAMINATION, METHODS TO CONTAIN AND TREAT THESE WASTES.
- V.** BETTER METHODS NEED TO BE DEVELOPED FOR PRECISION TESTING, LEAK DETECTION, AND FOR VAPOR RECOVERY SYSTEMS OF USTs. THERE IS A LIMITED AMOUNT OF FUNDS FOR THIS WORK, WE HOPE R&D CAN DO THESE TESTING FOR US.
- VI.** R&D HELPS NEEDED IN IMPLEMENTING REMOVAL ACTION (IMMEDIATE REMOVAL). THIS WOULD ENTAIL COST COMPARISONS AND ENGINEERING EVALUATIONS. WE HOPE R&D CAN HELP US IN THIS AREA TOO.
- VII.** NEED DEMONSTRATED TECHNOLOGIES DISCOVERED BY R&D COMMUNITIES TRANSFERRED TO USERS (i.e. DIVISIONS AND ACTIVITIES) WITHOUT DELAY. NAVY INSTALLATION RESTORATION (IR) MANUAL OF MAY 1988, SECTION 6.0 DESCRIBES THE PROCEDURES FOR TRANSITION OF TECHNOLOGIES.

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CHESDIV ENVIRONMENTAL R/D NEEDS

AIR TOXIC POLLUTANTS

- Accurate Estimates of Emitted Quantities
- Cost Effective Control Methods
- Monitoring Procedures
- Modeling Principles and Accuracy

COST EFFECTIVE REMOVAL OF ASBESTOS TILES

WAIVER OF REGULATIONS WHERE FEASIBLE BY DEMONSTRATIONS

- Search and List Areas where Regs Permit
- Cost Effective Applicability to Navy Processes
- Develop Demonstration Method and Procedures

LANDFILL CLOSURE PROCEDURES AND SPECIFICATIONS

ORDNANCE WASTE

WASTEWATER COLLECTION AND ZERO DISCHARGE

- Process Steam Flow
- Floor and Walls - Cleaning Wastewater

DESIGN ZERO AIR TOXIC VENTS FROM ROOF-TOP

- Alternatives for High Cost Controls

DELISTING OF ORDNANCE WASTE - SLUDGE FROM TREATMENT OF ORDNANCE WASTE

TESTING AND EVALUATION OF LOW FLOW WATER (MINIMIZE USE OF WATER)

FIREFIGHTER - AFFF WASTEWATER

EASY METHOD OF MONITORING Pb (PROBE) WATER COOLER

REVERSE OSMOSIS FOR BOILER WATER TREATMENT— DEMINERALIZATION CAUSES WASTEWATER

TREATMENT OF LOW CONCENTRATION OF OIL-CONTAMINATED DIRT

Commander, Pacific Division
Naval Facilities Engineering Command
Pearl Harbor, Hawaii

Summary of R & D Requirements

- Non-point source pollution
- Oil in ground water at NAVBASE Pearl Harbor
- Hazardous Waste Incinerator
- Recycling of Solvent Wastes from Torpedo Maintenance Operations

Non-Point Source Pollution

- Runoff from industrial areas into receiving waters during heavy rains
- State of Hawaii has developed a Non-Point Source Assessment and Management Plan
- Future compliance requirements highly probable
- Review plan and recommend solution for compliance

Oil in Groundwater

- Oil floats on groundwater at the Pearl Harbor Naval Base
- Layer up to 2 feet thick
- Infiltrates into storm drains and manholes
- Seepage into Pearl Harbor during heavy rains
- Recommend technology for removal of the oil

Hazardous Waste Incinerator

- Long term goal of H-HAZMIN Project
- Will achieve 90% reduction for off-island disposal
- Incinerator must have an approved RCRA Part B Permit
- Design standard incinerator with RCRA Part B Permit for construction at multiple sites

Recycling Solvent Wastes from Torpedo Maintenance Operations

- Wastes from torpedo maintenance operations consist primarily of solvents
- Presently under study
- Very interested in final conclusions and recommendations

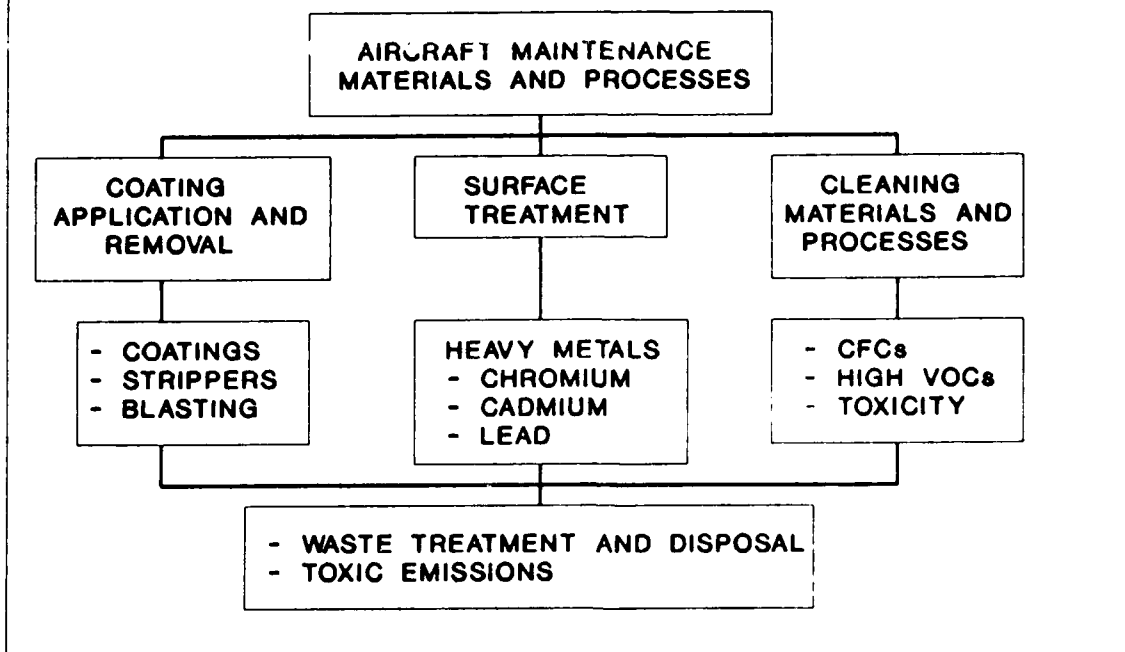
NAVAIR ENVIRONMENTAL R&D NEEDS

- LOW VOC SOLVENTS
- BIOLOGICAL ORGANIC WASTE DESTRUCTION
- BIOLOGICAL SLUDGE REDUCTION
- FREEZE CRYSTALLIZATION
- LIQUID TANK STRIPPER
- AIRCRAFT DEPAINTING
- ADVANCED COATING MAINT PROCESSES
- CHROME REPLACEMENT
- AQUEOUS DEGREASER
- HEAVY METAL REPLACEMENT
- LARGE TANK LEAK DETECTION
- HALON SUBSTITUTE
- CHLOROFLUOROCARBON REPLACEMENT
- TOXIC EMISSIONS SOURCE REDUCTION
- CHROME RECOVERY
- FREON REFRIGERANT REPLACEMENT
- LOW VOC COATINGS

TOTAL NAVAIR PROPOSED 6.3 ENVIRONMENTAL EFFORT

	FY90	FY91	FY92	TOTAL
LIQUID TANK STRIPPER	50	50	20	120
AIRCRAFT DEPAINTING	310	235	400	945
CHROME REPLACEMENT	110	110	55	275
HALON SUBSTITUTE		500	250	750
CFC CLEANER	110	110	110	330
FREON REFRIGERANT	275	345	225	845
LOW VOC COATINGS	115	135	120	370
TOXIC EMISSIONS	240	200	100	540
ADV COATINGS MAINT	<u>170</u>	<u>220</u>	<u>220</u>	<u>610</u>
TOTAL	1380	1905	1500	4785

NAVAL AIRCRAFT MAINTENANCE: ENVIRONMENTAL COMPLIANCE ISSUES



 NEED FOR LONG TERM STRATEGY RESEARCH & TECHNOLOGY AIR-93 FOR NAVAL AVIATION		
PROCESS	SHORT TERM	LONG TERM
<u>APPLICATION:</u>	REDUCTION IN TOXIC EMISSIONS	PERMANENT COATING OR NO COATING NEEDED OR NON-HAZ COATING
<u>CLEANING/REMOVAL:</u>	PLASTIC MEDIA OR SODA BLAST AND/OR LASER STRIP	NOT NECESSARY OR NON-HAZARDOUS 'COMMAND DESTRUCT'
<u>WASTE TREATMENT:</u>	LESS HAZARDOUS LESS CONTAMINATING	BIODEGRADABLE OR NON-CONTAMINATING, NON-TOXIC WASTE-- NO NEED FOR WASTE TREATMENT



CCRT TECHNOLOGIES

RESEARCH &
TECHNOLOGY

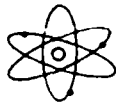
AIR-93

FOR NAVAL AVIATION

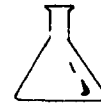
APPLICATION	REMOVAL	• WASTE TREATMENT •
NEW BARRIER COATING	WATER BASED	PMB TREATMENT
LOW VOC COATING	CRYOGENIC	TOXIC SEPARATION
FLUORINATED COATINGS	ULTRASOUND	WASTE PYROLYSIS
PIGMENTED COMPOSITES	TUNED LASER	WASTE BIOTREAT
PERMANENT COATINGS	LOW VOC SOLVENTS	ENZYME TREAT
	NONHAZ STRIPPERS	MICROBIAL TREAT
	ELEC. CORROSION	
	BIO CMD DESTRUCT	
	CHEM CMD DESTRUCT	
	ELEC CMD DESTRUCT	
• NAVAIR SUPPORT OF NAVFAC LEAD		

TECHNOLOGY DEMONSTRATION/ADVANCED DEVELOPMENT NAVAIR LONG TERM CCRT TASKS (6.3 PROGRAM)

DESCRIPTION	90	91	92	93
NEW BARRIER COATING	155	90	100	75
LOW VOC COATINGS	115	135	120	30
FLUORINATED COATINGS	85	110		
PIGMENTED COMPOSITES			130	190
• TOTAL COATINGS (AIR)	355	335	350	295
WATER BASED REMOVAL	125	45	65	
CRYOGENIC REMOVAL	125	165		
ULTRASOUND REMOVAL	60	25		
LOW VOC CONTENT SOLVENTS			120	120
NONHAZ PAINT STRIPPERS			80	110
ELECTROCHEM REMOVAL			75	75
TUNED LASER			60	170
• TOTAL REMOVAL (AIR)	310	235	400	475
WASTE PYROLYSIS	200	35		
WASTE BIODEGRADATION		100	175	160
PMB WASTE TREATMENT	90	55		
TOXIC SEPARATION	85	70		
• TOTAL TREATMENT (FAC)	375	260	175	160
• TOTAL 6.3 CCRT	1040	830	925	930



ORDNANCE POLLUTION ABATEMENT



ENVIRONMENTAL R&D WORKSHOP



**BOB CASSEL
SEA-06APR
202-692-0515**



ORDNANCE POLLUTION ABATEMENT BACKGROUND

**NAVY HAS 19,000 TONS OF ORDNANCE FOR DISPOSAL
- GENERATING ABOUT 5,000 TONS/YEAR**

**ENVIRONMENTAL STANDARDS HAVE DECREASED ABILITY
TO DISPOSE OF ORDNANCE BY OB/OD AND WITH
DEMILITARIZATION FURNACES**

STEAMOUT NOT A VIABLE PROCESS FOR PBX'S

**LARGE ROCKET MOTOR DISPOSAL IS A VERY SIGNIFICANT
PROBLEM (POSEIDON, POLARIS, AND TRIDENT)**

- PROBLEM IMPACTING COASTAL STORAGE AND
ABILITY TO SUPPORT FLEET REQUIREMENTS**

R&D FUNDING SEVERELY REDUCED IN FY 89 AND 90

ORDNANCE POLLUTION ABATEMENT - WATERJET REMOVAL -

**BACKGROUND: PBX LOADED MUNITIONS EVALUATED FOR
WATERJET REMOVAL**

**OBJECTIVES: RECLAIM ENERGETIC MATERIALS AND HARDWARE
PREVENT POLLUTION OF THE ENVIRONMENT
AVOID ENVIRONMENTAL VIOLATIONS**

**APPROACH: DEVELOP AND TEST WATERJET REMOVAL OF PBX
AND PROPELLANTS FROM MUNITION ITEMS**

**PROGRESS: REMOTELY OPERATED PILOT PLANT CONSTRUCTED
SUCCESSFULLY REMOVED PBX FROM SPARROW,
SHRIKE AND HARM WARHEADS**

ORDNANCE POLLUTION ABATEMENT - PYROTECHNIC INCINERATION -

**BACKGROUND: NO PROVEN METHOD FOR DISPOSAL OR
RECLAMATION OF COLORED SMOKES AND
FLARES**

**OBJECTIVES: DESTROY CARCINOGENIC SMOKES AND
FLARES LADEN WITH HEAVY METALS
IN AN ENVIRONMENTALLY ACCEPTABLE
MANNER**

**APPROACH: DEVELOP AN INCINERATOR TO DESTROY
THESE HARMFUL AGENTS**

**PROGRESS: DEVELOPED AND CONSTRUCTED A CONTROLLED
AIR INCINERATOR**

**DEVELOPED A CONTINUOUS MONITOR FOR
POLYNUCLEAR AROMATIC HYDROCARBONS**

**DEVELOPING A CONTINUOUS MONITOR FOR
TRACE METALS**

ORDNANCE POLLUTION ABATEMENT - PBX SEPARATION PILOT PLANT -

BACKGROUND: SCALE UP RECOVERY PROCESS FROM
LAB SCALE TO PILOT PLANT

OBJECTIVE: DESIGN, INSTALL AND OPERATE A PILOT
PLANT FOR SEPARATION AND RECOVERY

APPROACH: DEVELOP A PILOT PLANT THAT WOULD
ACCEPT MATERIAL FROM WATERJET WASHOUT
AND SEPARATE INGREDIENTS FOR RECOVERY

PROGRESS: LAB SCALE COMPLETED, BENCH SCALE IN
PROGRESS AND PRELIMINARY DESIGN STUDIES
ON PILOT PLANT PERFORMED

ORDNANCE POLLUTION ABATEMENT - SOLVOLYSIS -

BACKGROUND: PROPELLANTS AND EXPLOSIVES HAVE BEEN
RECOVERED UTILIZING SOLVOLYTIC
PROCEDURES WITH HIGH YIELDS

OBJECTIVES: DEVELOP SOLVOLYTIC METHODS FOR THE
RECOVERY OF EXPLOSIVES AND PROPELLANTS

PREPARE EXPLOSIVES AND PROPELLANTS
WITH RECOVERED INGREDIENTS

APPROACH: CHEMICAL METHOD WILL BE USED TO RECLAIM
ENERGETIC MATERIALS

PROGRESS: AMMONIUM PERCHLORATE EXTRACTED FROM JATO
PROPELLANT (YIELD 73%)

PBXW-109E AND PBXW-114 MADE FROM
RECOVERED EXPLOSIVES

ORDNANCE POLLUTION ABATEMENT - SBIR CONTRACTS -

ATMOSPHERIC DISPERSION OF ORDNANCE PRODUCTS

**DEVELOP A COMPUTER MODEL TO PREDICT THE
ATMOSPHERIC TRANSPORT OF PRODUCTS CREATED
BY OPEN BURNING**

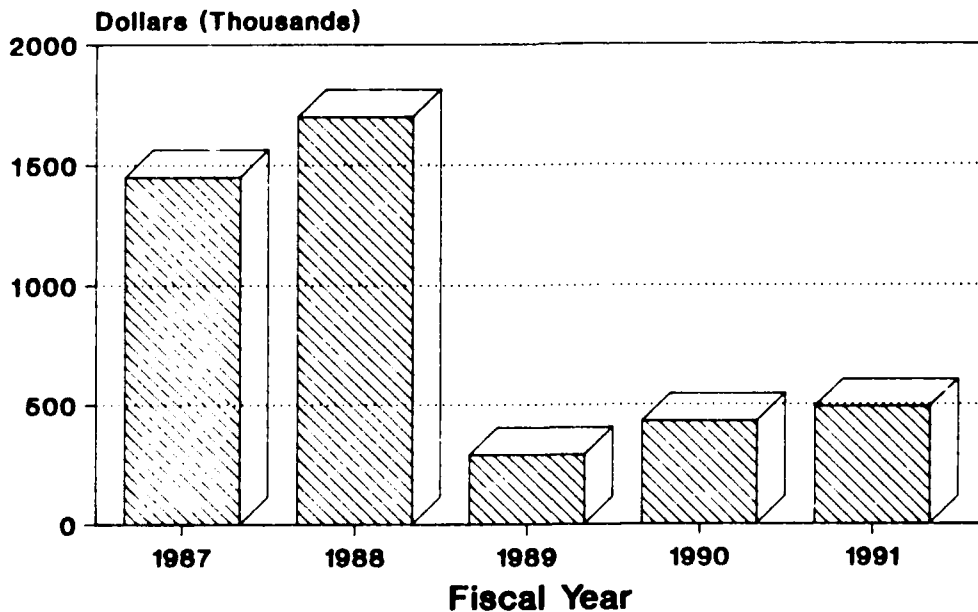
REFORMULATION OF EXPLOSIVES

**DETERMINE FEASIBILITY OF INCORPORATING OR
REFORMULATING PBX EXPLOSIVES REMOVED BY
WATERJET FOR USE IN THE COMMERCIAL MINING
INDUSTRY OR FOR OTHER APPLICATIONS**

ISOLATION AND USE OF PURE COMPOUNDS

**USE OF RECOVERED PBX'S WITH MINIMUM
MODIFICATION**

ORDNANCE POLLUTION ABATEMENT FUNDING



PROGRAM PRIORITIES MATRIX

SUMMARY OF FLIP CHART INPUT FROM PARTICIPANTS

GOAL I: ZERO DISCHARGE FROM SHORE FACILITIES

NORTHDIV	Bilge Water
	Painting/Stripping
PACDIV	HW Incineration
NAVAIR	Paint Stripping
	HW Treatment
SOUTHWESTDIV	Sludge Minimization
NADC	Chrome Plating Elimination
	Corrosion Inhibitor
NSEC Crane	Ordinance

GOAL II: ACCEPTABLE CLEANUPS AT IR SITES

NORTHDIV	PCBs
	Treatment
	Risk Assessment
	USTs
	Acceptable Cleanup Levels
CHESDIV	Landfill Closure
	Low Concentration Contaminated Soil
	PCBs
PACDIV	Oil in Ground Water
NAVSUP	Site Remediation
	Technology Development
	Pb and PCB Cleanup
	USTs
	Risk Assessment
	Oil Spills
SOUTHWESTDIV	In-situ Cleanup
	Battery Acid
	Spill Sites
	PCBs
	Pesticides
PWC San Diego	USTs
NAEC Lakehurst	USTs
	Site Remediation

GOAL III: 100% RECLAMATION OF WASTEWATER

NORTHDIV	Total Toxic Organics
	Ground Water Protection
CHESDIV	Low Flow Water
	AFFF

GOAL IV: ZERO AIR AND ACCEPTABLE NOISE EMISSIONS

NORTHDIV	Volatile Organic Compounds
	Chlorofluorocarbons
CHESDIV	Emissions Estimates
	Modeling
	Control Technology
	Roof Top Vents
	Removal of Asbestos Vinyl Floor Tile
NAVAIR	Halon
	Toxic Emissions
	CFC
	Freon
NADEP North Island	Source Reductions (CR)
PWC San Diego	Toxic Hot Spots

GOAL V: NONPOLLUTING IMPROVED INDUSTRIAL PROCESSES

NORTHDIV	Bilge Water
	Paint Stripping
	Non-HM Substitutes
CHESDIV	Ordinance Wastewater Collection
	Ordinance Steam Flow
	Ordinance Clean Wastewater
	Ordinance Delisting
	Boiler Water Demineralization (Reverse Osmosis)
PACDIV	Recycle Torpedo Solvent
NAVAIR	Chromium Substitution
NAVUSP	Shelf Life of Hazardous Materials
SOUTHWESTDIV	Plating
	Oil/Water Separator
NADEP Jacksonville	Chromium Plating Substitute
	Blasting Media Recycling
	Paint Stripping
NADEP North Island	Plating (Black Oxide, Cd, Cr ⁺³)
PWC San Diego	Bilge Water
	Tributyltin Sand Blast Grit

COMNAVSURFPAC	Bilge Water
	Ballast Water
NADC Warminster	Pastics
	HM Substitution:
	Strippers
	Cleaning Solvents
	Degreasers
	Conversion Coatings
	De-Oxidizers
	Inhibitors
	CFCs
NAEC Lakehurst	Lacquer
	Oil/Water Separator

GOAL VI: METHODS AND INSTRUMENTATION FOR MONITORING

CHESDIV	Air Monitoring
	pH Probe
SOUTHWESTDIV	UST Monitor

GOAL VII: COMPREHENSIVE PREDICTION AND MANAGEMENT

NORTHDIV	Site Closure
	Property Procurement
PACDIV	Non-Point Source
	Modeling

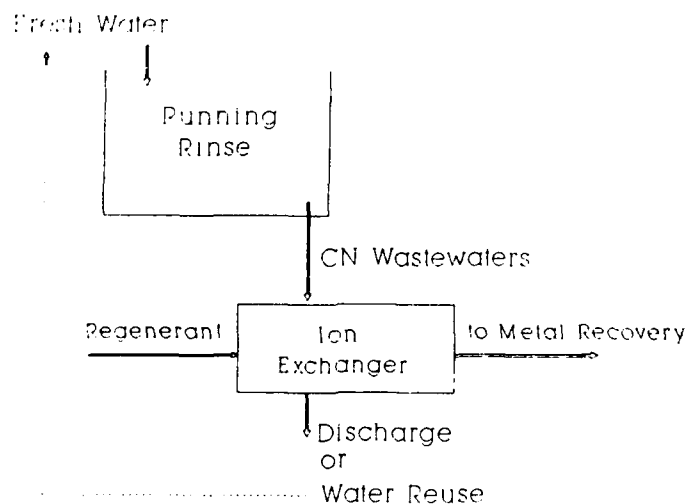
CONCURRENT SESSIONS HAZMIN INITIATIVES AND POLLUTION PREVENTION PROJECTS

CADMIUM REMOVAL FROM ELECTROPLATING Rinsewaters using ION EXCHANGE	57
Jenny Koff Code 674, NCEL Port Hueneme, CA 93043 AUTOVON 551-1669, (805) 982-1669	
CONVERSION OF NAVY PAINT SPRAY BOOTH PARTICULATE EMISSIONS CONTROL SYSTEMS FROM WET TO DRY OPERATION	62
Richard M. Roberts Code L74B, NCEL Port Hueneme, CA 93043 AUTOVON 551-1669, (805) 982-1669	
FAST BREAKING EMULSIFYING DEGREASERS	73
Tom Torres Code 671, NCEL Port Hueneme, CA 93043 AUTOVON 551-1658, (805) 982-1658	
RECYCLING OF HYDROBLASTING WASTEWATER	76
Bingham Y. K. Pan Code L74, NCEL Port Hueneme, CA 93043 AUTOVON 551-1650, (805) 982-1650	
FOUR PROJECTS FOR SHIPBOARD HAZARDOUS WASTE MINIMIZATION: ULTRAJET POINT REMOVAL AND CONTAINMENT SYSTEM; ABRASIVE GRIT RECYCLING; BILGE ONLY WASTE MINIMIZATION; AND SHIPBOARD HAZARDOUS MATERIALS MINIMIZATION PROGRAM	81
Gordon Smith Code 2834, DTRC Annapolis, Md 21402-5067 AUTOVON 281-3831, (301) 267-3831	
PLASTIC MEDIA BLASTING RDT&E PROGRAM	92
Richard M. Roberts Code L74B, NCEL Port Hueneme, CA 93043 AUTOVON 551-1650, (805) 982-1669	

CADMIUM REMOVAL FROM ELECTROPLATING RINSEWATERS USING ION EXCHANGE

Jenny Koff, NCEL

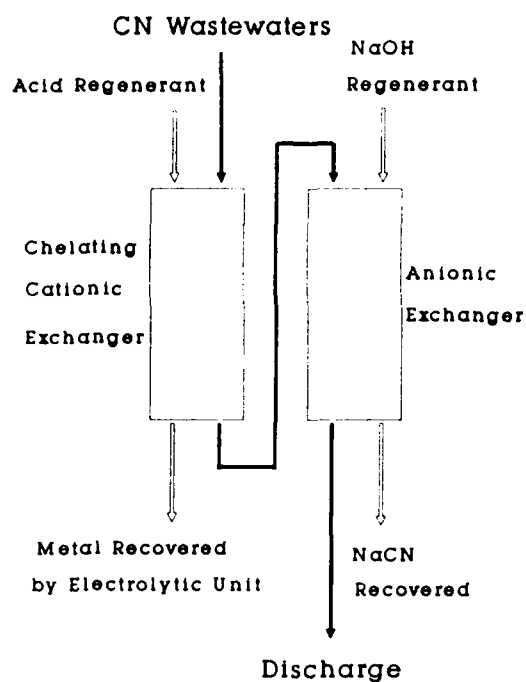
Treatment of CN Wastewaters by Ion Exchange



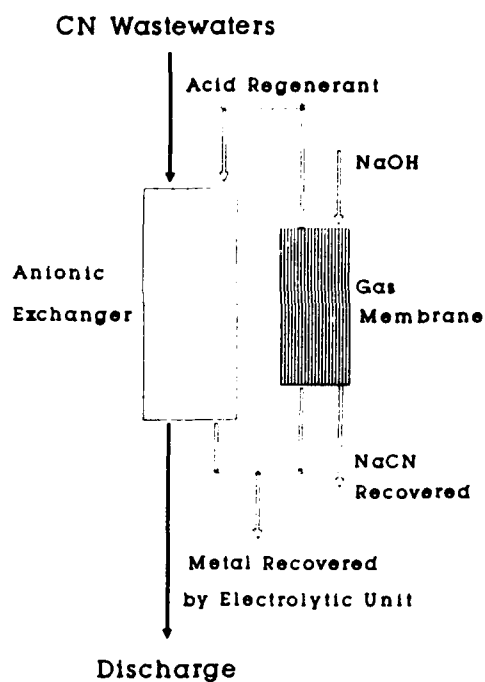
Benefits:

- Eliminate IWTP Sludge from CN Wastewaters
- Recovery of Hazardous Materials
- Meet Stringent Discharge Criteria
- Potential for Water Reuse

Selective Metal Removal



IX-Gas Membrane Process



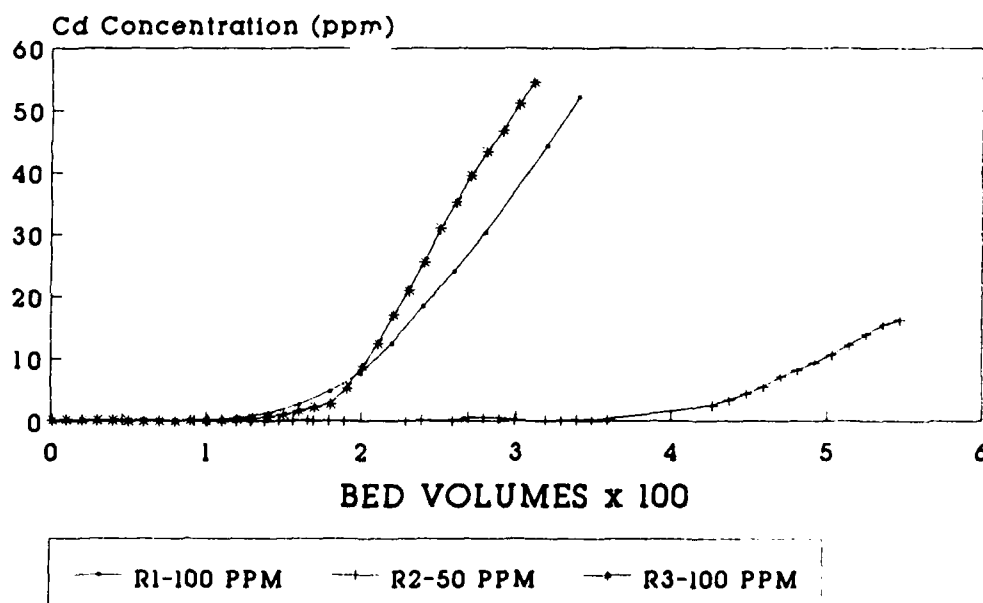
TECHNICAL ISSUES

- IS IX EFFECTIVE FOR Cd REMOVAL UNDER CN COMPLEXING CONDITIONS
- CAN GM/IX PROCESS BE DEVELOPED FOR Cd/CN WASTEWATERS
- WHAT ARE THE BEST CATIONIC AND ANIONIC RESINS
- CAN RESIN REGENERATION AND Cd/CN RECOVERY TECHNOLOGY BE DEVELOPED

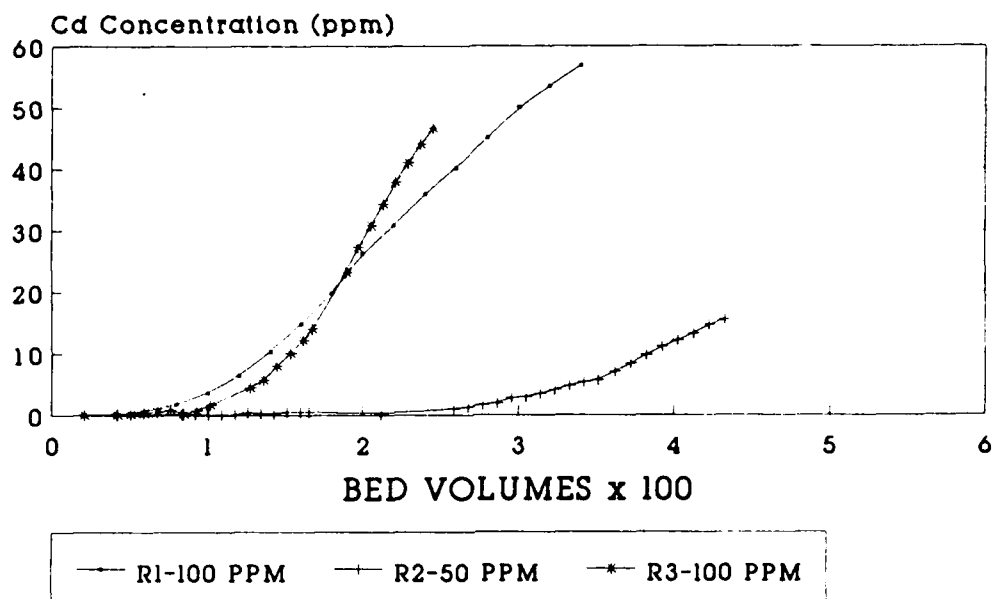
TECHNICAL APPROACH

- EVALUATE SELECTED RESINS
- DEVELOP OPERATIONAL REQUIREMENTS
- DETERMINE REGENERATION PROCEDURES
- INVESTIGATE RECOVERY TECHNOLOGY
- DETERMINE DESIGN CRITERIA
- ASSESS PRETREATMENT REQUIREMENTS

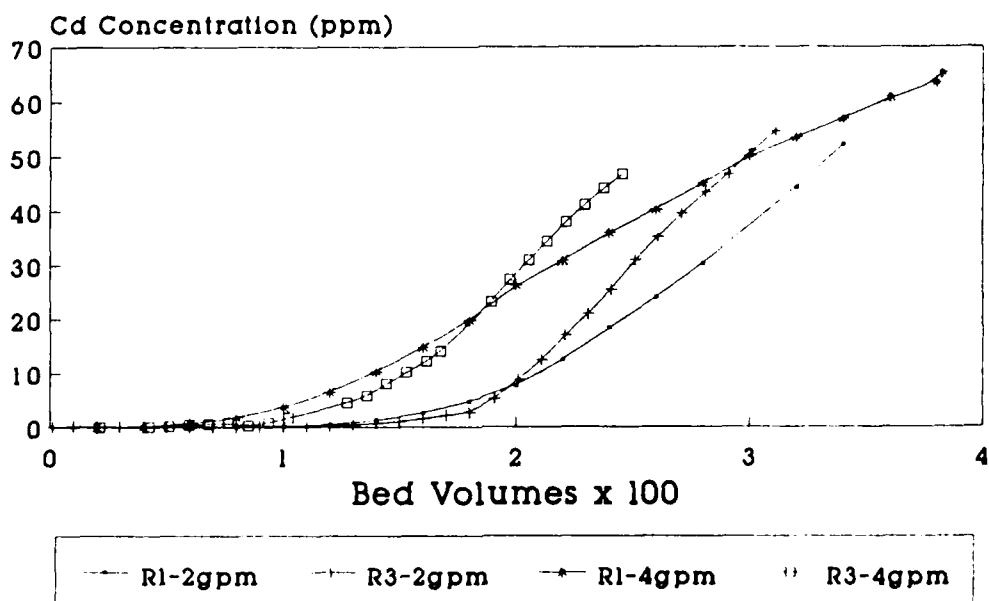
IRC-718 Cd BREAKTHROUGH 2 GPM/FT3 RESIN



IRC-718 Cd BREAKTHROUGH 4 GPM/FT3 RESIN



IRC-718 Cd BREAKTHROUGH 2 and 4 gpm, 100 ppm Cd



CONCLUSIONS

- IRC-718 CAN REMOVE Cd UNDER CN COMPLEXING CONDITONS
- FLOWRATE OF 2 GPM/FT3 RESIN PROVIDES HIGHER RESIN CAPACITY FOR IRC-718
- IRC-718 CAPACITY - 18 MG Cd/ML RESIN
- IRA-400 CAPACITY - 84 MG Cd/ML RESIN
21 MG CN/ML RESIN
- EARLY CN BREAKTHROUGH IN ANIONIC RESIN

FUTURE WORK

- *FINAL FEASIBILITY STUDY*
Evaluate Influence of Flowrate, Conc., Spec.
Establish Operational Parameters
- *DEVELOPMENTAL TESTING*
Pilot Scale at Field Site
- *OPERATIONAL TESTING*
Prototype System
- *PREPARE USER DATA PACKAGE*
Design Criteria, O&M Requirements

CONVERSIONS OF NAVY PAINT SPRAY BOOTHS
R. M. ROBERTS, NCEL

WET-TO-DRY SPRAY BOOTH
PEC SYSTEM CONVERSION



OBJECTIVE : DEVELOP COST EFFECTIVE MODIFICATION
SCHEME FOR CONVERSIONS AFFORDING EQUIVALENT
PEC PERFORMANCE WITH ZERO DISCHARGE.

NAVY NEED: ELIMINATE ENTIRELY SOME 5 KTON/YR
SCRUBBER LIQUID AND PAINT SLUDGE: CUT COSTS
BY \$5M ANNUALLY.

PROGRESS/ACCOMPLISHMENTS: UDP COMPLETED AND
IN JOINT PUBLICATION WITH EPA. NEESA INITIATING
IMPLEMENTATION OPERATIONS FOR DEMONSTRATIONS
AT TWO ACTIVITY SPRAY BOOTHS.

PERFORMANCE EVALUATION OF THE DRY PECS
FOR SPRAY BOOTH APPLICATIONS

- EQUIVALENT EFFICIENCY DEMONSTRATED
IN ACTUAL WET-TO-DRY CONVERSIONS -
 - NIROP POMONA - ALL SPRAY BOOTHS
 - PMTC PT. MUGU, CA - SINGLE BOOTH
 - McCLELLAND AFB, CA - TWO BOOTHS
- USAF PECS EVALUATED BY EPA RTP (AEERL)
(JOINT SPONSORS OF PRESENT PROJECTS)
- PERMITTING PRECEDENT SET WITH MOST
STRINGENT BOARD (SCAQMD) IN U.S.

CRITICAL DESIGN CRITERIA FOR DRY PECS

- ✓ PAINT BOOTH DUTY CYCLE
- ✓ AVERAGE TRANSFER EFFICIENCY
- ✓ DAILY PAINT CONSUMPTION
- ✓ CHARACTERISTICS OF THE PAINTS USED
- ✓ APPLICABLE EMISSIONS REGULATIONS

DRY FILTER SYSTEM CHARACTERISTICS

Filter Type	Filter Characteristics			
	Particulate Capacity	Removal Efficiency	Cost	Replacement Time
Fiberglass Catridge	Moderate	High	High	Very High
Honeycombed Paper	High	High	Low	Low
Cloth	High	High	Low	Low
Pleated Paper	Low	Low	Very High	Very Low

Conversion of a Large Downdraft Paint Booth

- The booth is 20 ft wide, 25 ft high, and 40 ft long.
- The booth floor consists of a large grate covering the water curtain sump.
- There are 4 exhaust ducts, each drawing overspray from a 20 ft by 10 ft area (approximately).
- The flowrate through each exhaust duct is 25,000 cfm (125 linear fpm) x (10 ft width) (20 ft length), and each exhaust fan is rated at 20 hp.
- There are 4 water pumps, each rated at 7.5 hp, that circulate water from the sump.
- The booth is considered an industrial user, therefore lower electrical rates apply.
- The pressure drop across the water curtain PECS is 2.0 inches w.c. due to presence of baffles, underground ducting, etc.
- The booth is used 1.5 shifts per day.
- The average paint usage rate is 70 gallons per week.
- The average transfer efficiency is 30 percent.
- Wastewater from the sump is drained to an IWTP; sludge collected at the bottom of the sump is drummed and disposed of as hazardous waste.
- Sump maintenance occurs three times per year.
- Twenty five drums of sludge are generated per year.
- 120 ft² of major sheetmetal modification and repair work is needed to remove the water curtain baffles, and prepare the site for installation of the dry filter system.

SUMMARY OF ONE-TIME AND RECURRING COST ESTIMATES FOR A LARGE DOWNDRAFT BOOTH BEFORE AND AFTER CONVERSION

RECURRING COSTS

Item	Water Curtain System		Dry Filter System	
	Annual Constant Dollar Cost (\$)	NPV of 10 Year Life Cycle Cost (\$)	Annual Constant Dollar Cost (\$)	NPV of 10 Year Life Cycle Cost (\$)
Utilities	\$12,624	\$90,160	\$6,314	\$45,080
Waste Treatment	\$7,500	\$54,975	\$0	\$0
Labor	\$1,380	\$9,849	\$334	\$2,373
Materials	\$0	\$0	\$2,038	\$14,560
Total	\$21,504	\$154,984	\$8,686	\$62,013

ONE-TIME COSTS

Item	Cost (\$)
Fan Motor Replacement	\$2,320
Equipment & Installation	\$4,982
Major Sheetmetal Work	\$1,888
Floor Grate Covering	\$17,856
Total	\$27,046

SIR = 3.9

PAYBACK = 1.8 YR

Conversion of a Large Crossdraft Paint Booth

- The booth is 15 ft wide, 10 ft high, and 20 ft long.
- The booth is used 1 shift per day.
- The average paint usage rate is 20 gallons per week.
- The average transfer efficiency is 30 percent.
- Wastewater from the sump is drained to an IWTP; sludge collected at the bottom of the sump is drummed and disposed of as hazardous waste.
- Sump maintenance occurs once every 2 months.
- Six drums of sludge are generated per year.
- The flowrate through the booth is 18,750 cfm (125 linear fpm) x (10 ft high) x (15 ft wide).
- The pressure drop across the water curtain PECS is 1.3 inches w.c. due to the baffles, water curtain, etc
- The power ratings of the exhaust fan and water pumps are 10 and 7.5 hp, respectively. The booth is considered an industrial user, therefore lower electricity rates apply.
- 20 ft² of major sheetmetal modification and repair work is needed to remove the water curtain baffles, and prepare the site for installation of the dry filter system.

SUMMARY OF ONE-TIME AND RECURRING COST ESTIMATES FOR A LARGE CROSSDRAFT BOOTH BEFORE AND AFTER CONVERSION

Item	Water Curtain System		Dry Filter System	
	Annual Constant Dollar Cost (\$)	NPV of 10 Year Life Cycle Cost (\$)	Annual Constant Dollar Cost (\$)	NPV of 10 Year Life Cycle Cost (\$)
Utilities	\$1,228	\$8,766	\$702	\$5,007
Waste Treatment	\$1,800	\$13,194	\$0	\$0
Labor	\$144	\$1,026	\$95	\$678
Materials	\$0	\$0	\$582	\$4,159
Total	\$3,172	\$22,986	\$1,379	\$9,844

ONE-TIME COSTS

Item	Cost (\$)
Equipment & Installation	\$996
Sheetmetal Work	\$314
Total	\$1,310

SIR = 10.0

PAYBACK = < 1 YR

Conversion of a Small Crossdraft Paint Booth

- The booth is 9 ft wide, 9 ft high, and 10 ft long.
- The booth is used less than 1 shift per day.
- The average paint usage rate is 10 gallons per week.
- The average transfer efficiency is 30 percent.
- Wastewater from the sump is drained to an IWTP; sludge collected at the bottom of the sump is drummed and disposed of as hazardous waste.
- Sump maintenance occurs once per month.
- Three drums of sludge are generated per year.
- The flowrate through the booth is approximately 10,500 cfm (125 linear fpm) x (9 ft width) (9 ft height).
- The water curtain pressure drop is .8 inches w.c. due to the baffle system and spray curtain
- The power ratings of both the exhaust fan and the water pump are 5 hp. The booth is considered an industrial user, therefore lower electricity rates apply.
- There is no major sheetmetal rust or damage problem; however, 20 ft² of minor sheetmetal work is required.

SUMMARY OF ONE-TIME AND RECURRING COST ESTIMATES FOR A SMALL CROSSDRAFT BOOTH BEFORE AND AFTER CONVERSION

Item	Water Curtain System		Dry Filter System	
	Annual Constant Dollar Cost (\$)	NPV of 10 Year Life Cycle Cost (\$)	Annual Constant Dollar Cost (\$)	NPV of 10 Year Life Cycle Cost (\$)
Utilities	\$702	\$5,007	\$211	\$1,502
Waste Treatment	\$900	\$6,597	\$0	\$0
Labor	\$72	\$513	\$49	\$356
Materials	\$0	\$0	\$338	\$2,413
Total	\$1,674	\$12,117	\$598	\$4,271

ONE-TIME COSTS

Item	Cost (\$)
Equipment & Installation	\$530
Sheetmetal Work	\$176
Total	\$706

SIR = 11.1
PAYBACK = < 1 YR

AUDIT INFORMATION NEEDED FOR DOWNDRAFT PECS

- BOOTH DIMENSIONS, MANUFACTURER, SPECS & DWGS
- BOOTH FLOOR CONFIGURATION (E.G., GRATING OVER SUMP)
- LOCATION OF BAFFLED WATER SPRAY SYSTEM & ACCESSIBILITY
- SYSTEM CONDITION & STRUCTURAL INTEGRITY
- SUPPLY & EXHAUST FAN MFR. SELECTION CURVES, HP & ELEC. RATING
- SUPPLY & EXHAUST FAN INSTALLED ACFM AT WHAT PRESSURE RATING
- PECS PRESSURE DROP W/ & W/O WET SCRUBBER ON
- ACFM & VAC. AT EXHAUST FAN INTAKE IN NORMAL OPERATION

CROSS-/DOWNDRAFT SYSTEM CONVERSION PROCEDURES

- PERFORM EQUIPMENT AUDIT
- SELECT THE APPROPRIATE FILTER SYSTEM
- SELECT A FILTER SYSTEM SUPPLIER
- DESIGN THE RETROFIT PACKAGE
- INSTALL THE DRY PECS

AUDIT INFORMATION NEEDED FOR CROSSDRAFT PECS

- BOOTH DIMENSIONS, MANUFACTURER, SPECS & DWGS
- SYSTEM CONDITION & STRUCTURAL INTEGRITY
- EXHAUST FAN MFR, SELECTION CURVES, HP & ELEC. RATING
- EXHAUST FAN INSTALLED ACFM AT WHAT PRESSURE RATING
- PECS PRESSURE DROP W/ & W/O WET SCRUBBER ON
- ACFM & VAC AT EXHAUST FAN INTAKE IN NORMAL OPERATION

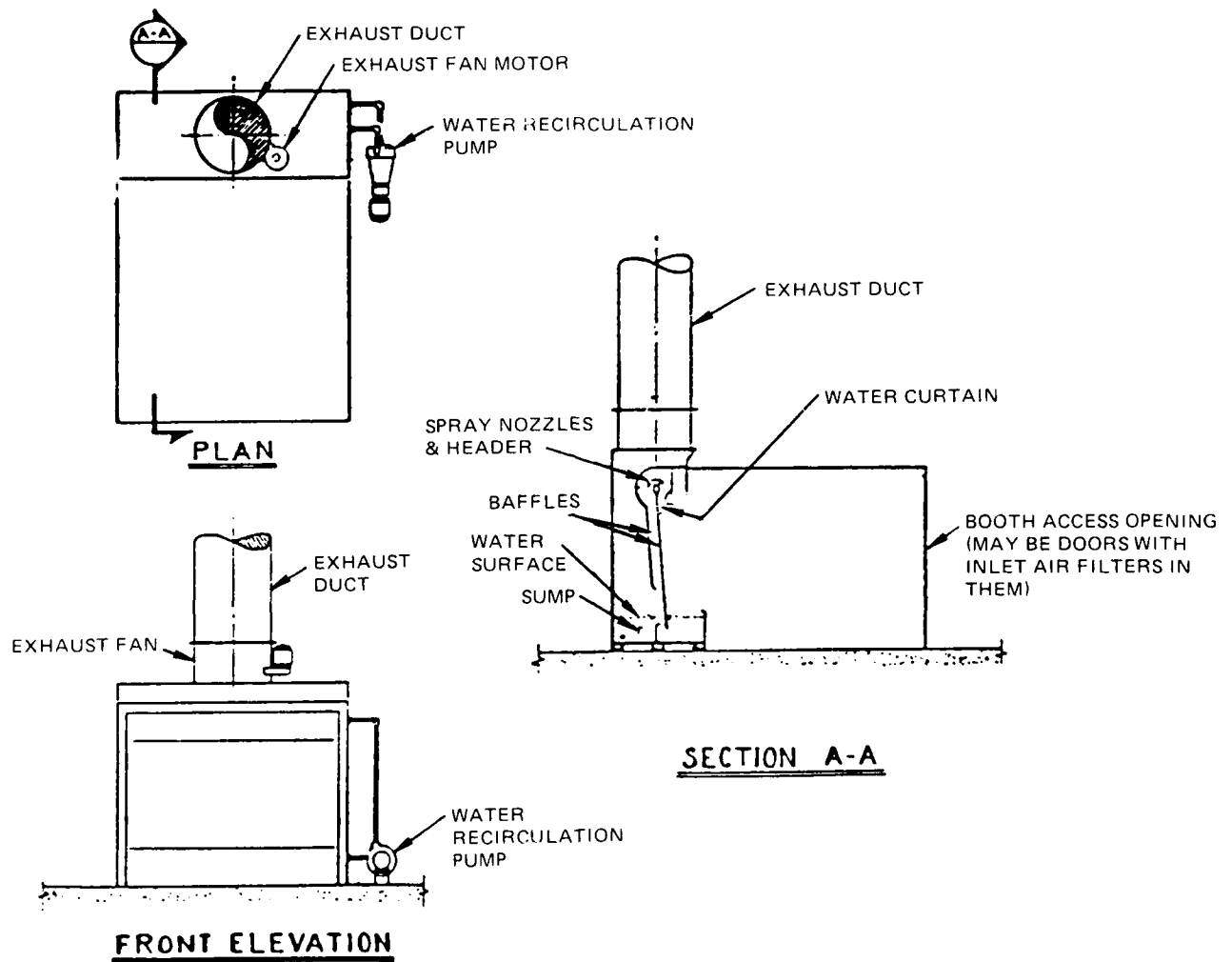


Diagram of a typical crossdraft paint spray booth equipped with a water curtain PECS.

FAST BREAKING EMULSIFYING DEGREASERS
TOM TORRES, NCEL

PROBLEM

SURVEYED EIGHT NAVY SHIPYARDS:

- **CURRENT NAVY BILGE AND TANK
CLEANING PRACTICES**
- **TYPE OF DEGREASERS CURRENTLY BEING USED**
- **PROBLEMS ENCOUNTERED WITH CURRENT DEGREASERS**

REASON FOR STUDY

- **REQUIREMENT TO CHANGE**
- **NAVSEA 05 CONTROLS SPECS.**
- **DEVELOP PERFORMANCE SPECIFICATIONS**
- **VALIDATE (DOCUMENT) PERFORMANCE SPECS.**

PERFORMANCE CRITERIA

- TIME OF EMULSION TO BREAK (12 MINUTES)
- pH OF SURFACE AFTER CLEANING (5.0-9.0)
- AMOUNT OF OIL RESIDUE (MODERATE)
- AMOUNT OF OIL AND GREASE LEFT IN WATER PHASE AFTER SEPARATION (<10 PPM)
- FLASH POINT (>150 F)
- CONTAIN NO DETECTABLE HALOGENS

TECHNICAL RESULTS

<u>CRITERIA</u>	<u>PRELIMINARY</u>	<u>MODIFICATIONS</u>
EFFECTIVENESS	MODERATE	.60 GRAMS
OIL AND GREASE RESIDUE	<10 PPM	<250 PPM
EMULSION BREAK TIME	12 MINUTES	12 MINUTES
DEOILING TIME	15 MINUTES	4 TO 5 HOURS
SURFACE pH	5 TO 9	5 TO 9
OIL QUALITY		FAIR TO GOOD
FLASH POINT	>150 F	>110 F
HALOGENS	NONE	NONE

FUTURE EFFORTS

FIELD TESTS:

UNITOR-CLEANBREAK

PENETONE-FORMULA 730

SUNSHINE-NATRASOL

UNITED LAB-#692

CHEMSEARCH-DUOPOWER

OMEGA-CITRI-FLOAT

PATCLINE-#454 FAST BREAK

RECYCLING OF HYDROBLASTING WASTEWATER (ABSTRACT)

NCEL ENVIRONMENTAL DIVISION, BINGHAM Y K PAN

The hydroblasting wastewater is produced from a high pressure water jet used to clean the boiler tubes of Navy surface ships. The objective of this project is to recycle hydroblasting wastewater, thereby reducing its volume up to 90%.

The initial feasibility study involving bench scale work at NCEL and pilot scale tests at Long Beach and Norfolk Naval Shipyards were completed in FY88. The data and results confirmed the feasibility to recycle the hydroblasting wastewater.

Three series of field tests were conducted in FY89 at Norfolk Naval Shipyard. A complete recycling process consisted of wastewater collecting, settling, filtering, reconditioning, and reusing. The first series of field tests provided a 75% reduction of wastewater. The second series made a 90% reduction of wastewater. The third series resulted in a 92% reduction of wastewater.

Naval Shipyards now generate three million gallons/yr of the hydroblasting waster. This hazardous wastewater has been a part of the combined bilge wastewaters which are contractor hauled at a cost up to \$3.25/gal. A 90% reduction of the wastewater will result in a savings of about \$8 million/yr.

We have paid much attention to the safety of this recycling process. Efforts are being made to implement our technology in a shipyard. A mobile unit will be designed, constructed, and tested. Also, a technical manual shall be prepared in FY90.

OBJECTIVE

To reduce the volume of hydroblasting wastewater up to 90 per cent

Navy Need

- Source: Cleaning ship boiler tubes.
- Volume: Three million gal/yr.
- Haz Was: Mixture of sodium nitrite, heavy metals, oil, grease, and otehr wastes.
- Disposal cost: \$ 3.25/gal.

Technical Approach

- Identify hydroblast condition & problem.
- Make theoretical study & sample analys.
- Conduct laboratory tests.
- Design & conduct pilot scale tests.
- Design & conduct field tests.
- Implement recycling tech. at a NSY.
- Provide reliability & safety.

Solid Particle Analysis

Pilot Scale Test

Size, micron	Wastwatr	50mic	10mic
5 - 10	19,350k	5,014k	1,324k
10 - 25	4,285	1,035	546
25 - 50	232	225	396
50 - 75	29	18	1
>75	13	nil	nil
	23,909	6,292	2,267

Particle count per 100 ml sample

Change of Metal Concentration

pilot scale test

Metal	Water	Feed soln	Wastwat	Discharge Limit
Cd	0.004	0.004	0.008	0.10
Cr	0.007	0.020?	0.007	0.05
Cu	0.006	0.069	12.0 >	2.0
Pb	0.040	0.040	0.550>	0.05
Ni	0.015	0.015	0.331	0.40
Zn	0.082	0.078	0.465	1.48

mg/L

Solid Particles

1st-Washing Wastewater

Size	B.S.	A.S.	50m	10m
10 - 25	5688k	797k	580k	192k
25 - 50	276k	49k	12k	58k
50 - 70	1k	.2k	.04k	1.5k
75 - 100	3k	.4k	.14k	4.2k
100 - 125	.2k	0	0	.05k
>125	.5k	0	0	0
	5968.7	846.6	592.2	255

Size: micron

Legend: B.S. Before setting
A.S. After setting
50m After 50 μ filter
10m After 10 μ filter

Three Field Tests

Recycling of Hydroblasting wastewater

Test #	WW recyl.	No recyl.	% red.
1st	1500 gal	3	75
2nd	500 gal	9	90
3rd	500 gal	12	92

Legend: WW recyl. Wastewater recycled
 No recyl. Number of recycle
 % red. Percent wastewater
 reduced

April to June, 1989

Chem. Analysis

1st-washing wastewater

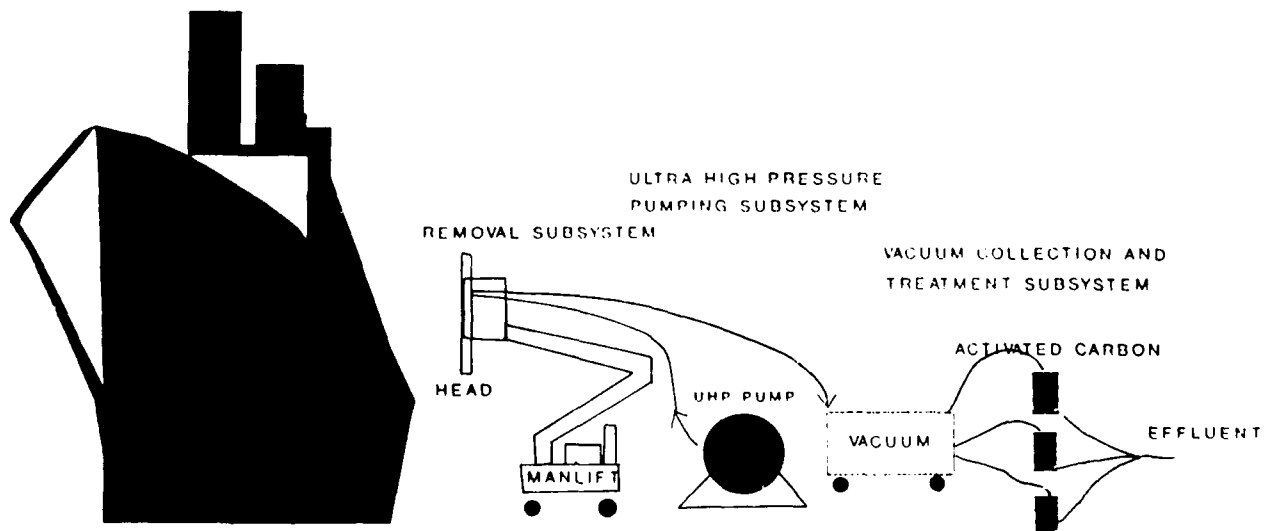
Item	B.S.	A.S.	50m	10m	Discharge Limit
pH	8.01	7.84	9.01	8.00	6.0-9.0
Oil & grease	5.0	5.0	5.0	5.0	30
Nitrite	410	630	590	580	33
Nitrate	6	6	6	?	45
Cd	.004	.003	.003	.007	0.10
Cr	.021	.015	.013	.035	0.05
Cu	8.10	8.00	6.29	5.97	2.0
Pb	.58	.41	.31	.86	0.05
Ni mg/L	.034	.025	.020	.043	0.40

SHIPBOARD HAZARDOUS WASTE MINIMIZATION
GORDON SMITH, DTRC

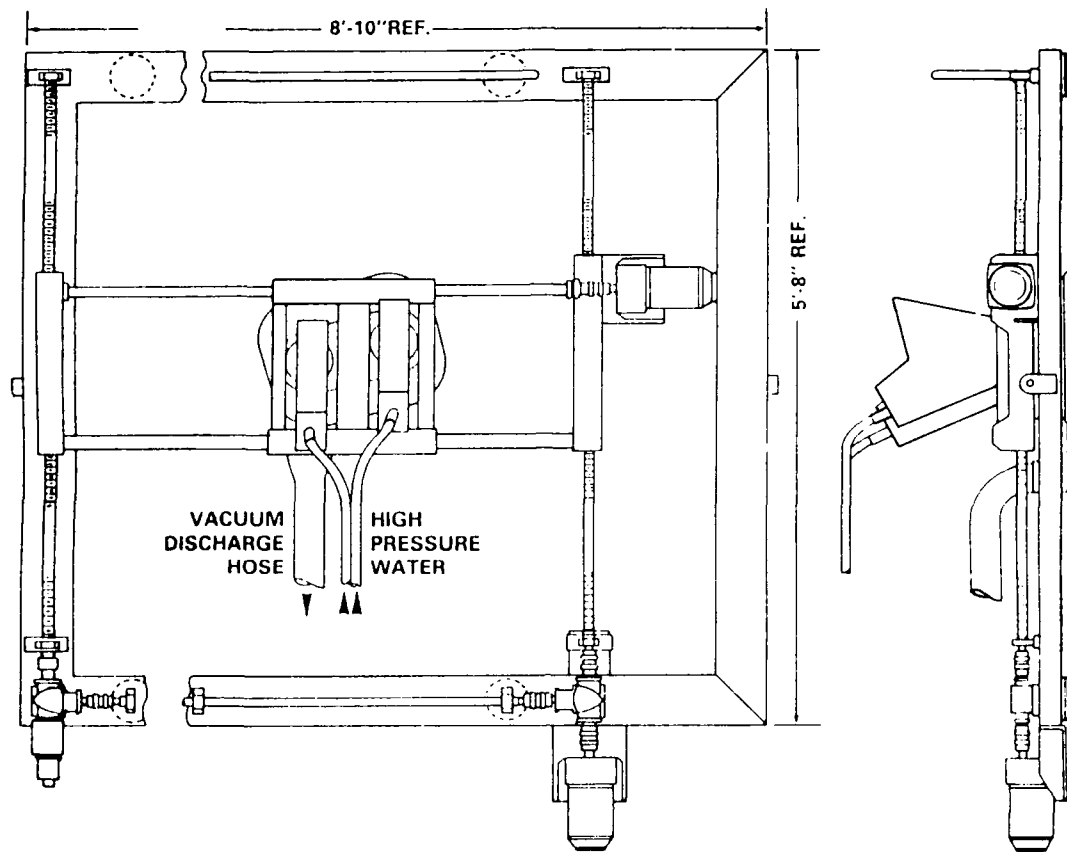
**ULTRAJET PAINT REMOVAL AND
CONTAINMENT SYSTEM - PROGRESS**

- MANUAL 10,000 PSI SYSTEM DESIGNED, BUILT AND TESTED
- MANUAL 35,000 PSI UNCONTAINED SYSTEM TESTED
- AUTOMATED 35,000 PSI CONTAINMENT HEAD DESIGNED
- AUTOMATED 35,000 PSI SYSTEM REQUIREMENTS DETERMINED
- PRELIMINARY COST COMPARISON STUDY COMPLETE

**SCHEMATIC,
ULTRAJET PAINT REMOVAL SYSTEM**



ULTRAJET PAINT REMOVAL HEAD



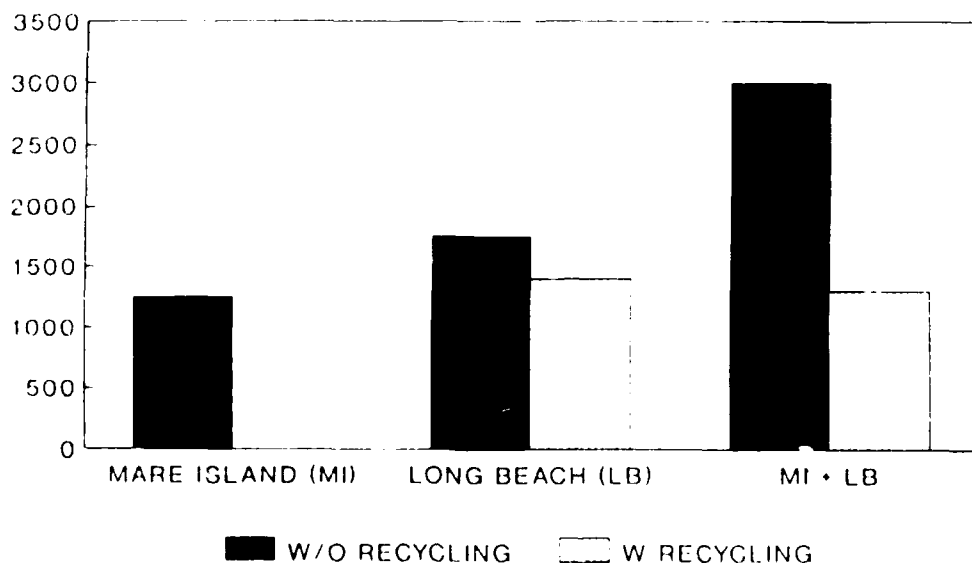
ULTRAJET PAINT REMOVAL AND CONTAINMENT SYSTEM - STATUS

- WORK ON ULTRAJET PROJECT WILL BE HALTED THIS YEAR WITH A COMPLETED AUTOMATED HEAD DESIGN, A CLEARLY DEFINED SET OF SYSTEM REQUIREMENTS, AND A FINAL COST COMPARISON STUDY.
- FINAL REPORT BEING PREPARED.

RECYCLING REQUIREMENTS

- PRODUCT MUST MEET MIL-A-22262A (SH)
"ABRASIVE BLASTING MEDIA-SHIP HULL BLAST
CLEANING"
 - REMOVE PAINT CHIPS, OIL, WATER, DEBRIS
 - RECLASSIFY PARTICLE SIZE DISTRIBUTION
 - MEET TOTAL AND SOLUABLE METAL
CONCENTRATION LIMITS
 - MEET FRIABILITY LIMIT (DUST PLUME
REQUIREMENT)
 - PROVIDE COMPARABLE PAINT REMOVAL
RATE
 - PROVIDE COMPARABLE SURFACE PROFILE

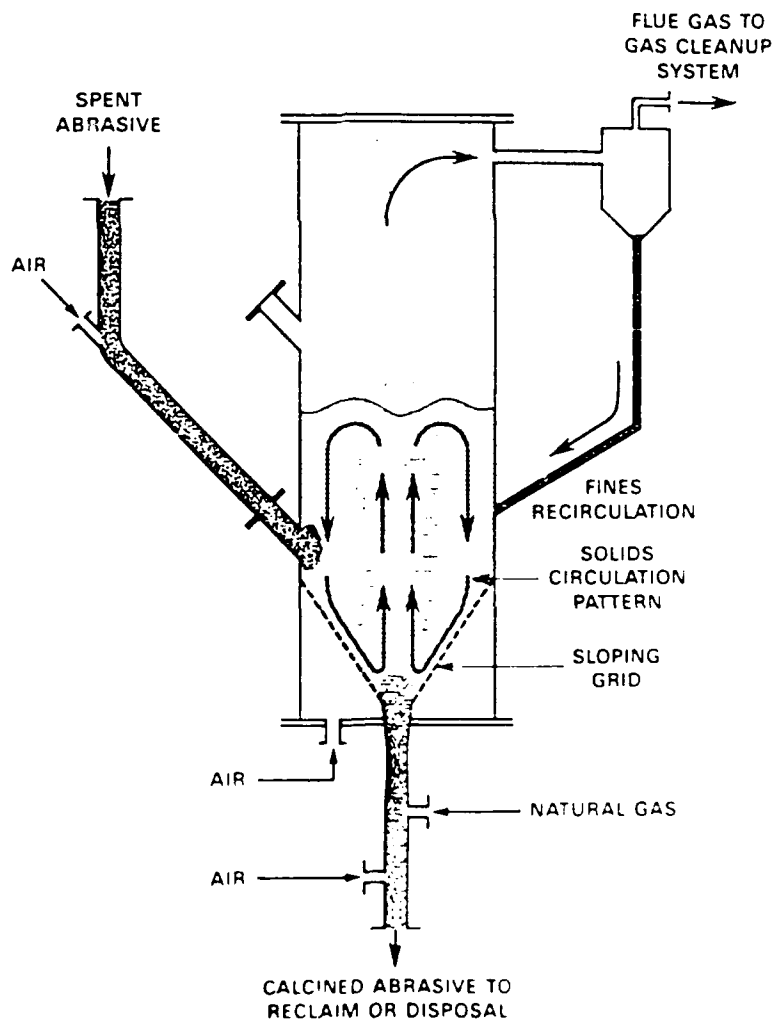
COST OF GRIT DISPOSAL (\$K/yr)



INSTITUTE OF GAS TECHNOLOGY (IGT) FLUIDIZED BED SLOPED GRID (FBSG) CALCINER

- INITIAL PROPOSAL TO NAVSEA 07 – 1985
- IGT BENCH-SCALE TESTS ON NAVY SUPPLIED SPENT ABRASIVE SHOWED REMOVAL OF COPPER PAINT CHIPS – 1986
- NAVFAC PROVIDED \$140K OF DERA FUNDS FOR PILOT-SCALE TESTS

SCHEMATIC DIAGRAM OF THE FBSG CALCINER



BLAST ABRASIVE TEST BURN SUMMARY

ABRASIVE TYPE	COAL/Cu	COAL/TBT	Cu/Cu
ABRASIVE FEED RATE, lb/h	843	1,119	1,509
CALCINER TEMPERATURE, °F	1,481	1,470	1,476
ORGANICS,* $\mu\text{g/g}$ (ppm)			
FEED	12,300	15,000	7,200
DISCHARGE	1,500	200	200
FINES	13,500	64,700	32,400
TOTAL TIN/ORGANOTIN, $\mu\text{g/g}$ (ppm)			
FEED	—	50/32	—
DISCHARGE	—	30/<0.00005††	—
FINES	—	160/<0.011	—
FINES** IN PRODUCT, wt %	14.70†	6.10	13.65

*MEASURED AS CARBON AND HYDROGEN

**U.S. SIEVE SIZE SMALLER THAN 80 MESH

†AVERAGE OF INDIVIDUAL SAMPLE ANALYSES RATHER THAN FINAL COMPOSITE SAMPLE

††INDICATES DETECTION LIMIT OF ANALYTICAL PROCEDURE

IGT-FBSG CALCINER PILOT TEST

RESULTS - COPPER

	LIMIT	VIRGIN ABRASIVE		SPENT ABRASIVE		RECYCLED ABRASIVE	
		COAL	Cu	COAL/Cu	Cu/Cu	COAL/Cu	Cu/Cu
TTLC	2,500	20	4,200	440	4,800	460	4,020
STLC	25	< 0.2	8.5	49	130	33	14

Evaluation of Recycled Abrasive Mare Island Naval Shipyard

REMOVAL RATE (sq ft/min)

New Cu	Recycled Cu	Recycled Coal	New Cu/ Recycled Cu	New Coal/ Recycled Coal
4.9	4.5	3.8	4.4	3.9

PROFILE (mils)

4-4.5	2-3	3-4	2-3	3.5-4

IGT FBSG CALCINER

PROGRESS:

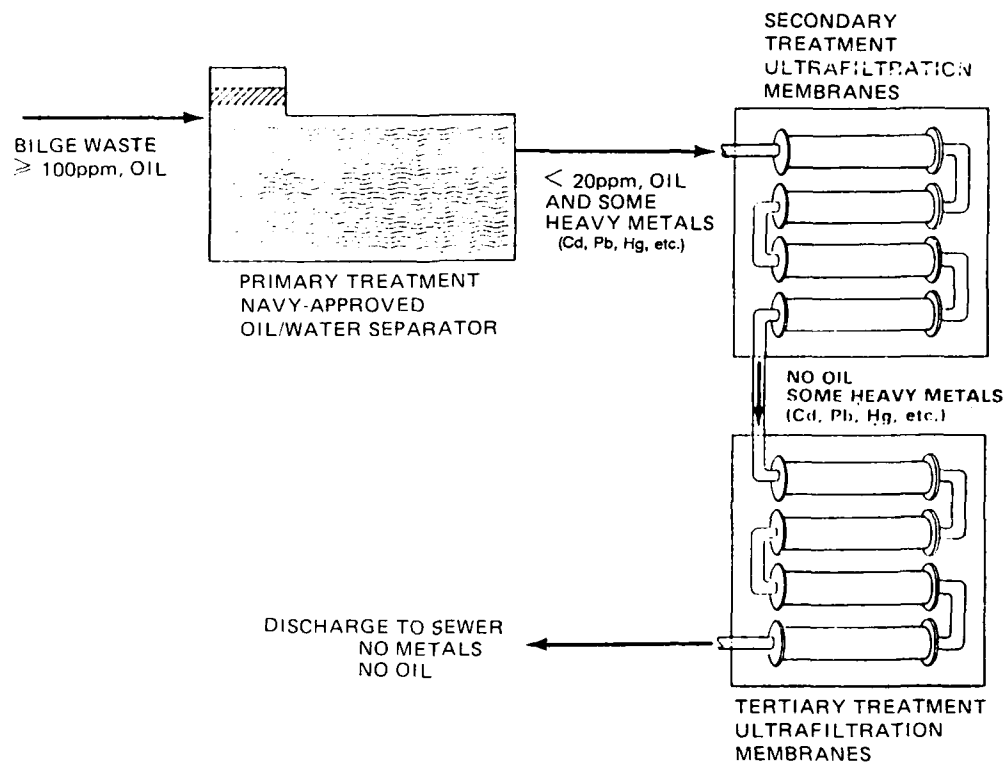
- Completed survey of existing technology
- Completed bench-scale evaluation
- Completed pilot-scale evaluation

PLANS:

- Fulfill SEA 07 Requirements
- Prepare technology Comparison
- Evaluate 2nd Recycle of Abrasive
- Design and construct 5 ton/hr Unit
for Demonstration

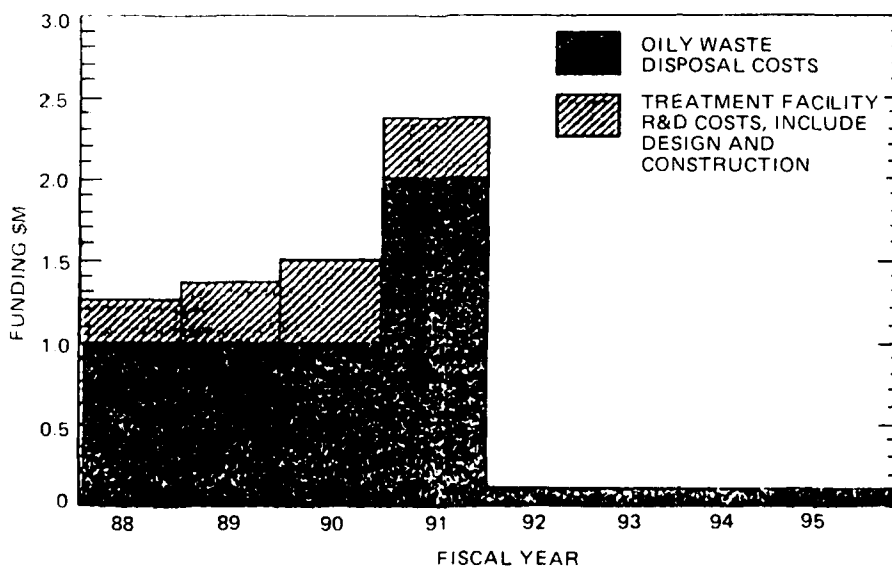
HAZARDOUS BILGE OILY WASTE TREATMENT SYSTEM FOR NAVAL WEAPONS STATION EARLE

TREATMENT SYSTEM DESCRIPTION

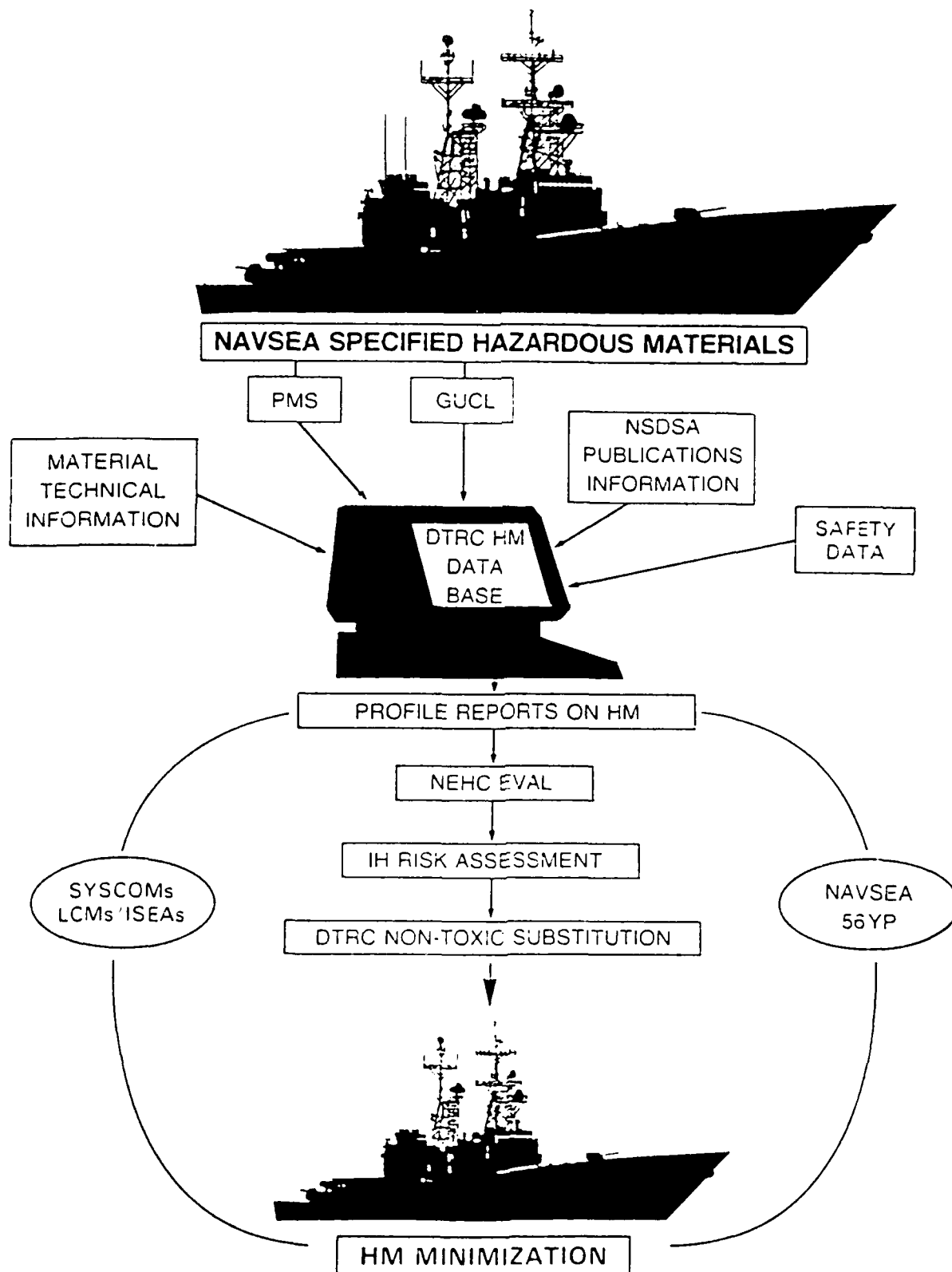


HAZARDOUS BILGE OILY WASTE TREATMENT SYSTEM FOR NAVAL WEAPONS STATION EARLE

DISPOSAL COST REDUCTION



SHIPBOARD HAZARDOUS MATERIALS MINIMIZATION

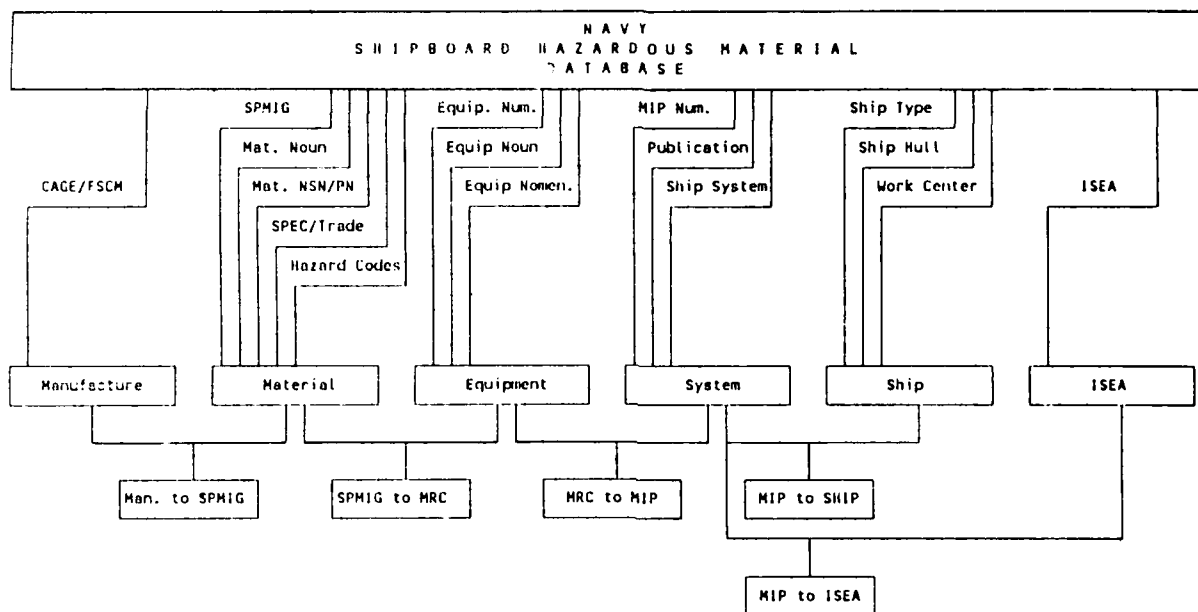


OBJECTIVE

DEFINE, MINIMIZE, AND CONTROL
NAVSEA SPECIFIED
HAZARDOUS MATERIALS USED ABOARD SHIP

APPROACH

- IDENTIFY HM
- ESTABLISH DATABASE
- ESTABLISH IN-HOUSE REFERENCE CAPABILITIES
- PROVIDE LIST OF NAVSEA SPECIFIED HM TO SEA 56YP
- INITIATE MINIMIZATION STUDIES
- INTERFACE WITH SYSCOM CODES AND ISEAs
- OBTAIN NEHC TOXICITY/HAZARD EVALUATION OF HM
- OBTAIN RISK ASSESSMENT OF NEHC IDENTIFIED HM
- INITIATE STUDY FOR NON-TOXIC, NON-HAZARDOUS SUBSTITUTES
- RECOMMEND ELIMINATIONS AND SUBSTITUTIONS FOR HM
- ISSUE FINAL REPORT



PMS - CROSS REFERENCE RETRIEVAL

RETRIEVAL SELECTIONS

Search (Select One Item)	Retrieve (Select One Item)
Material ___ SPMIG Num. ___ Noun ___ MILSPEC/Trade ___ NSN ___ P/N Equipment ___ MRC Num. ___ Nomenclature ___ Noun System ___ MIP Num. ___ System/Equip. ___ Publication Ship ___ Type ___ Hull ___ Work Center ISEA	___ Material ___ Equipment ___ System ___ Ship ___ ISEA

Key Value: _____

Restrict Search By:

Ship Type: _____	Hull: _____	WC: _____
SYSKOM: _____	Directorate: _____	

PMS - SYSTEM EDITOR

SYSTEM EDITOR	
MIP Number: _____	MIP Date: _____
CS Code: _____	
Ship System: _____	
ESWBS: _____	
SYSCOM: _____	
Directorate: _____	
TYCOM: _____	
MRC: _____	
System/Equip.: _____	
Publication: _____	
Configuration: _____	
ISEA: _____	

SAMPLE CROSS REFERENCE SEARCH BY MATERIAL

1. MATERIAL RETRIEVAL REPORT HEADER:

SPMIG NUMBER:	NSN
MATERIAL NOUN:	P/N
MILSPEC/TRADE NAME	MSDS

2. RETRIEVAL DATA:

a) BY EQUIPMENT:

EQUIPMENT NOUN:	MRC CONTROL CODE:	NOMENCLATURE:

b) BY SYSTEM:

SHIP SYSTEM:	MIP NUMBER:	SYSCOM:	DIRECTORATE:

c) BY SHIP:

SHIP TYPE:	SHIP HULL:	WORK CENTER:	UIC:

d) BY ISEA:

ISEA:	COG CODE:	ADDRESS:	TELEPHONE:

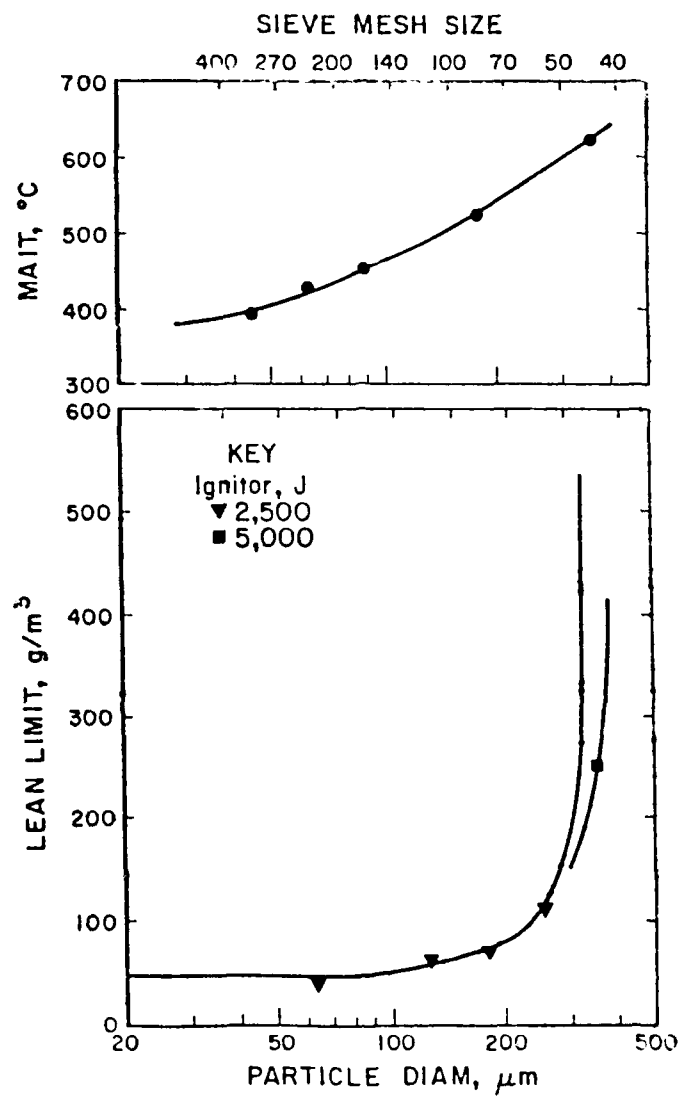
PLASTIC MEDIA BLASTING

R. M. Roberts, NCEL

- REPLACE:** Chemical Paint Stripping Produced
Toxic Liquids and Sludges
- WASTE:** Tons of Dry Waste with Lead,
Cadmium, and Chromium
- PURPOSE:** Improve Efficiency of FMB Operations
- GOAL:** Reduce Haz Waste Generation by 50%
Save \$25,000/Booth for Explosion
Monitors
Save \$400,000/yr in Ventilation Costs
Save \$400,000/yr in Media Replacement
and Disposal by Greater Reuse

Safety and Health RDT&E Explosion Hazard Studies

- Bureau of Mines
- Plastic media (12-60 mesh) is not explosive
- LEL - 45 g/cubic meter for dust <200 mesh
- Never exceeded 1 g/m³ of fine dust
- No need for explosion prevention
in blast booth



Effect of particle size on explosibility and ignitability for Polyextra

Safety and Health RDT&E

Ventilation Requirements

- ANSI recommends 100 fpm as a guideline
- Air Force standard is 75 fpm
- NCEL studied the large PMB booth at McClellan AFB
 - toxic concentrations were below exposure limits outside safety hoods
 - worker safety/productivity is maintained at the lower rate
- Recommended to NAVAIR that the Navy conform with the Air Force standard

McClellan AFB PMB Booth

Average Contaminant Concentrations (mg/m³)

Contaminant	TWA	Inside hood	Outside hood
Lead	0.15	ND	0.021
Chromium	0.5	0.004	0.035
Cadmium	0.05	ND	0.014
Formaldehyde	1.5	ND	ND
Diisocyanate	0.02	ND	ND*

* previous study - Hill AFB

Safety and Health RDT&E

Offgas Analysis

- Analyzed different medias for gas release at high temperature
- Did not detect any isocyanates
- Showed formaldehyde might be a problem
- Blasting and media storage areas should be tested

Safety and Health RDT&E

Waste Analysis

- Lead, chromium, cadmium are consistently a problem

Leachable Concentration (mg/l)
Contaminant Limit Range

Lead	1.0	0.05 - 15
Chromium	5.0	0.10 - 72
Cadmium	5.0	0.08 - 16.5

- Most waste should be disposed as hazardous waste

Operational RDT&E Recycling Equipment

- Improperly designed systems lose 10% good media per pass
- Booth - 2 nozzles - 70% operation will lose 65 tons of media at \$260,000/yr
- Recommended system
 - Large cyclone w/ or w/o air wash set to remove media >80/100 mesh from the air stream
 - Vibrating screens - 12 and 60 mesh
 - Large, self-cleaning magnetic separator
 - Critical applications, hard particle separator

Operational RDT&E Blasting Equipment

- Evaluated equipment produced by several manufacturers
- Developed a list of minimum design criteria - CR 89.010
- Oct 89 - Examined performance of Schlick equipment in Cherry Point including hard particle separator

Operational RDT&E Recycling Floors

- Evaluated different kinds of floors
 - Pneumatic
 - Conveyor belt
 - Screw
 - Partial and full floor systems
- Each design has benefits and limitations
- Partial floor with pneumatic recovery is the best option

INSTALLATION RESTORATION - MEASUREMENT TECHNOLOGY AND TOXICITY AND RISK ASSESSMENT

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DEVELOPMENT OF INNOVATIVE PENETROMETER
TECHNOLOGY FOR THE DETECTION
AND DELINEATION OF CONTAMINATED SOILS

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San Diego, CA 92152-5000

ABSTRACT

Truck-mounted cone penetrometers capable of quickly and economically measuring soil strength properties from the surface to depths of approximately 50 meters in suitable soils (sand, silts and clays) are in routine use in engineering studies for subgrades and foundations. A project is currently underway to develop contaminant sensors that can be built into soil penetrometer equipment to allow the detection and delineation of contaminants in soils as the penetrometer is forced through the soil. A goal of this research effort is to develop a family of sensors that can be used to produce real-time data on-site as the penetrometer is forced through the soil at speeds as fast as 2 cm/sec. Two types of sensors, a module for measuring soil resistivity and a module for measuring soil fluorescence, are discussed as examples of sensor technology integrated into the penetrometer.

The soil resistivity module uses an array of electrodes mounted on the penetrometer rod to determine the presence of anomalous electrical resistivity in soil adjacent to the penetration hole. Soil contaminants containing easily ionized components such as salt will produce decreased soil resistivity. Changes in resistivity in a uniform soil type can be used as a preliminary indication of soil contamination. The soil resistivity module has successfully located closed landfills and evaporation ponds.

The soil fluorescence module can detect soil contaminants that will fluoresce under ultraviolet light. Fluorescence is a promising approach for the detection of contamination from fuels, lubricants, and certain explosives wastes. The fluorescence module has been successfully employed in a tracer dye study on a dredged material site.

The economy obtained by using a penetrometer rather than a conventional drill-and-sample approach easily justifies the cost of development of additional sensors. Techniques for low-level detection of toxic metals and specific organic contaminants are currently being researched. Spectral characteristics of contaminated soil show great promise in contaminant detection. Combining sensors with a location/positioning capability can produce a system for real-time, on-site mapping of subsurface contamination.

INTRODUCTION

A typical cone penetrometer system designed for foundation investigations consists of a 35.7-mm diameter steel rod terminating in a 60-degree cone. The cone and a section of the rod behind the cone (the sleeve) are instrumented to allow the forces acting on the cone and the sleeve to be measured as the penetrometer is forced through soil or unconsolidated sediments. The tip resistance and the sleeve friction are measured continuously as the penetrometer is advanced through the soil at a standard rate of 2 cm/sec. The force needed to move the rod is produced by a hydraulic load frame mounted on a truck equipped for off-road operation. With a truck loaded to produce a 20-ton reaction mass, penetrations as deep as 40 to 50 meters can be achieved in most normally compacted, uncemented soils. The sleeve friction and tip resistance vary systematically with the soil type (clayey, sandy or mixed silt and sand), and this allows the soil type to be continuously estimated from the cone response data. Cone penetrometer testing is considered the most useful in-situ soil test method available and most countries have established cone penetrometer test standards (Campanella and Robertson, 1982). A cone penetrometer can collect data from penetrations totalling approximately 200 m in one day at a cost of approximately \$30 per m. Drilling, sampling and testing would produce only 20 percent of the data within the same time period and would have a unit cost ten times that of a penetrometer.

Since the cone penetration system provides a rapid and economical method for moving instruments and even samplers into the soil, there has been interest in developing geophysical tools or chemical sensors and samplers that could be operated with the standard cone penetrometer equipment. The sensors allow the presence of contaminants to be detected while the soil stratigraphy is being established from the standard cone response (Amann, Berigen and Wollenhaupt, 1986). When the cone penetrometer and specialized sensors are combined with a location/positioning system for the penetrometer truck, the combination will allow for real-time, on-site mapping of contamination in the subsurface.

The purpose of this report is to discuss the operation of two sensor systems that have been used with penetrometer

equipment and to provide an outline for the development of a cone penetrometer-based system for detection and delineation of contaminated soils at hazardous waste sites. The goal is to show what has been achieved with this technology to improve our ability to characterize waste sites and to describe the logical next step in specialized penetrometer system development.

CONE PENETROMETER-BASED SENSOR SYSTEMS

The cone penetrometer unit is designed to provide information on the type of soil in the subsurface from strength characteristics measured by internally mounted strain gages as the instrument moves through the soil. The cone is advanced at a uniform rate of 2 cm/sec over 1-m intervals. After each 1-m advance, the cone is halted while an additional 1-m rod segment is added to the rod string. Technically, a sensor can operate either continuously as the rods are advanced or the sensor can be read at 1-m intervals if response time is slow. Both methods of operation would fit into the standard pattern of advance of the cone penetrometer and would not interfere with collection of data on the soil stratigraphy. While it is possible to envision specialized sensors that might require long delays for equilibration or might have a nonreversible response, first efforts in sensor development have emphasized techniques that have rapid, reversible response and can provide a continuous record of soil characteristics. Sensors that involve measurements of electrical properties and spectral properties are prominent candidates for development because they involve rapid, reversible responses that can be related to the presence of anomalous materials (contaminants) in the soil.

Sensors Based on Electrical Properties

Electrical resistance (or conductance) of groundwater is routinely measured as a gross estimate of inorganic contamination. Because electrical resistance of saturated soil is related to the resistance of the pore fluid, it is possible to make estimates of the relative levels of contamination from differences in soil resistivity observed in similar soil types (Rhoades and others, 1989).

Instruments designed to measure soil resistivity from the cone penetrometer typically are built by mounting a series of conductive bands or buttons a few centimeters apart on the exterior of the rod so that soil comes in contact with these electrodes as the rod moves through the soil column. The electrodes are separated by an abrasion-resistant insulator that holds the electrodes in place and maintains the constant diameter of the rod (Figure 1). The measuring surface wipes itself clean as soil is forced across the surface. Response is rapid and no equilibration is required. With close spacing of the electrodes,

the volume of soil investigated is small, but resistivity interfaces are very sharply defined.

Electrical resistivity modules have been most successful in locating closed landfills (Amann, Beringen and Wollenhaupt, 1986) or evaporation ponds (Cooper and others, 1988a, 1988b). The high concentrations of inorganic contaminants associated with these targets provide excellent contrast with uncontaminated soils.

The major disadvantage in the use of electrical resistivity measurements involves the effects of the soil. Soils with clay present conduct electricity through soil water and through the outside conductive layer (bound water layer) of the clay itself. Clays and clay-sand mixtures can be conductive even when the pore fluid is resistive (Rider, 1986). Cone resistance and sleeve friction can provide data on the soil type that can assist in many instances in obtaining a correct interpretation of the variation in electrical resistivity.

Sensors Based on Spectral Properties

Sensors based on spectral properties such as fluorescence or absorption have been employed in investigation of contaminants in surface and groundwater, but adaptation of this technology to the cone penetrometer is a new and potentially very useful development. By using fiber optics it is possible to produce a compact unit that can provide a remote excitation and light collection system that permits examination of spectral properties of fluids or solids without building complex optical equipment into a small probe. Chudyk, Carrabba and Kenny (1985) and Chudyk and others (1989) reported on units developed for measuring fluorescence from organic contaminants in monitoring wells. Lieberman, Inman and Stromvall (1987) showed how a fiber optic fluorescence unit could be used for measuring trace amounts of inorganic contaminants remotely in seawater using fluorogenic ligands.

A prototype fluorescence sensor for the cone penetrometer was fabricated at USAE Waterways Experiment Station and tested in a subsurface dye tracing experiment. The unit has two 0.25 watt mercury vapor lamps, emitting light at the 254 nm wavelength and above, mounted inside a 35.7-mm diameter penetrometer rod (Figure 2). The lamps are positioned behind an 8-mm diameter round sapphire window. The window is 4-mm thick, transparent to ultraviolet and is ground optically flat. The termination of a 500-micrometer diameter optical fiber is mounted directly behind the window so that light from the soil moving past the window is captured by the fiber and passed through 50 meters of fiber to a spectrophotometer or optical multichannel analyzer on the surface. The fluorescence sensor unit attaches to standard penetrometer rod (Figure 3) and can be mounted above the instrumented cone and friction sleeve unit.

In an initial field test to the unit, 8 liters of a non-toxic, fluorescent optical brightener (Fluoretrack II, Formulabs, Escondido, CA) was injected in saturated sand at a depth of 4 m in an area underlain by approximately 10 m of hydraulically placed sand and silt. Over 35 penetrometer pushes were made in a pattern crossing over the penetration point. Data on fluorescence were taken with a Guided Wave Model 260 fiber optic spectrophotometer (Guided Wave, Inc., El Dorado Hills, CA) interfaced with a personal computer. The sensor was calibrated on standards prepared from water-saturated sand samples containing known amounts of optical brightener (Figure 4). The intensity (power in picowatts) of the fluorescence signal was measured at 517 nm at 0.1 sec (0.2 cm depth) intervals as the rod moved downward. Figure 5 shows the pattern of the dye detected with the fluorescence sensor. A water sampler designed for use on the penetrometer was used to collect ground-water samples over the plume and confirm that dye was present in the pattern the sensor indicated.

Laboratory testing conducted with an optical multichannel analyzer indicates that complete spectral data can also be collected. Ultraviolet or visible absorbance as well as fluorescence can be used to detect and delineate soil contamination (Figure 6).

DEVELOPMENT OF A SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM (SCAPS)

Advances in sensor technology have pointed to the possibility of developing a real-time, multi-parameter measurement system for detecting and delineating pollutants in soil. The system could couple measurements from a suite of chemical and physical sensors to a location/positioning system. Soil contaminant distribution could be displayed as a series of map overlays as they are collected. This approach would be similar to the system discussed by Lieberman, Clavell and Bower (1989). The systems approach has the advantage that it allows the use of real-time sensor data collected with the penetrometer and associated equipment to guide the intelligent placement of borings for the collection of large volume soil samples and/or the installation of permanent monitoring wells for the collection of groundwater or soil gas. Since the SCAPS equipment would collect and analyze data while the unit is still on-site, gaps in sensor data can be identified and additional data can be collected until the objective of selecting optimum locations for more expensive and time-consuming drilling and sampling is completed. The SCAPS unit can also be equipped to collect small-volume, high-quality water or soil samples to confirm sensor readings. Field-based screening tests on SCAPS samples can be used to provide the justification for a full-scale sampling and

analytical program such as would be required by regulatory considerations or litigation.

A full SCAPS system would include the following:

a) A suite of geophysical equipment (magnetometers and ground-penetrating radar) for scanning the area ahead of the penetrometer to avoid hazards from unknown wastes or unmapped utilities.

b) The penetrometer with physical and chemical sensors and real time data acquisition and location/positioning equipment.

c) Data analysis and mapping equipment to present contaminant distribution data in the field.

d) Field sampling and analysis equipment to provide confirmation of sensor data as required.

e) Grouting pumps and injection equipment to seal the penetrometer holes and maintain the integrity of the site.

f) Safety equipment to protect the work crew and ensure containment of toxic or hazardous materials on-site during the site investigation.

By integrating site investigation efforts and undertaking each activity (from sweeping the site for buried hazards to taking samples for regulatory compliance and litigation) in a step-wise progression, we can provide a safe and economical waste site investigation. The key features in accelerating site clean-up efforts are rapid screening with sensors to optimize our monitoring efforts and prompt on-site integration of data so that questions can be answered as fully as possible before critical and expensive decisions on permanent monitoring programs or cleanup activities are made.

ACKNOWLEDGMENTS

The authors wish to thank Messrs. Donald H. Douglas, E. A. Graves, Bryant Peterson, H. L. Blake, and W. H. Dulaney of USAE Waterways Experiment Station (WES), who collected the field data used in this report. Mrs. Tina H. Dykes (WES) assisted in the preparation of this manuscript and her efforts are gratefully acknowledged. The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the Cone Penetrometer Development Program of the U. S. Toxic and Hazardous Materials Agency by the

USAE Waterways Experiment Station. Permission was granted by the Chief of Engineers to publish this information.

The views, opinions, and/or findings contained in this report are those of the authors and should not be construed as an official Department of Defense position, policy or decision, unless so designated by other documentation. The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial products. This report may not be cited for purposes of advertisement.

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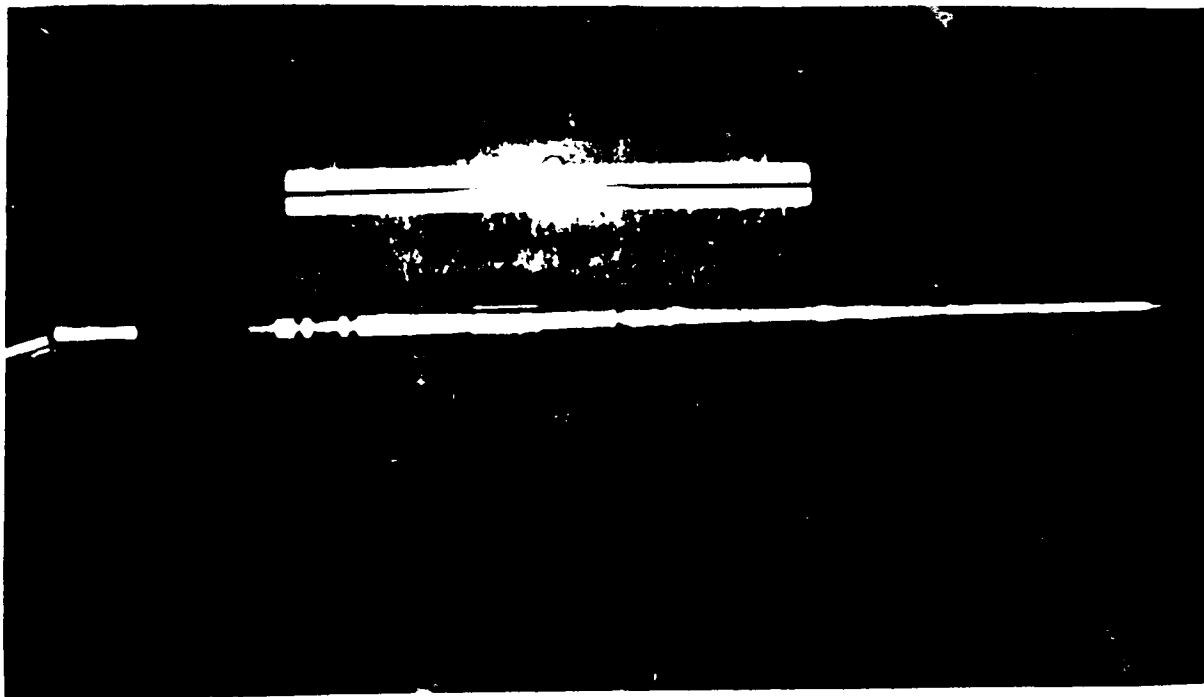


Figure 1. Photo of penetrometer with soil resistivity module attached. The electrodes are formed from stainless steel bands. The dark sections of the module are abrasion-resistant insulators.

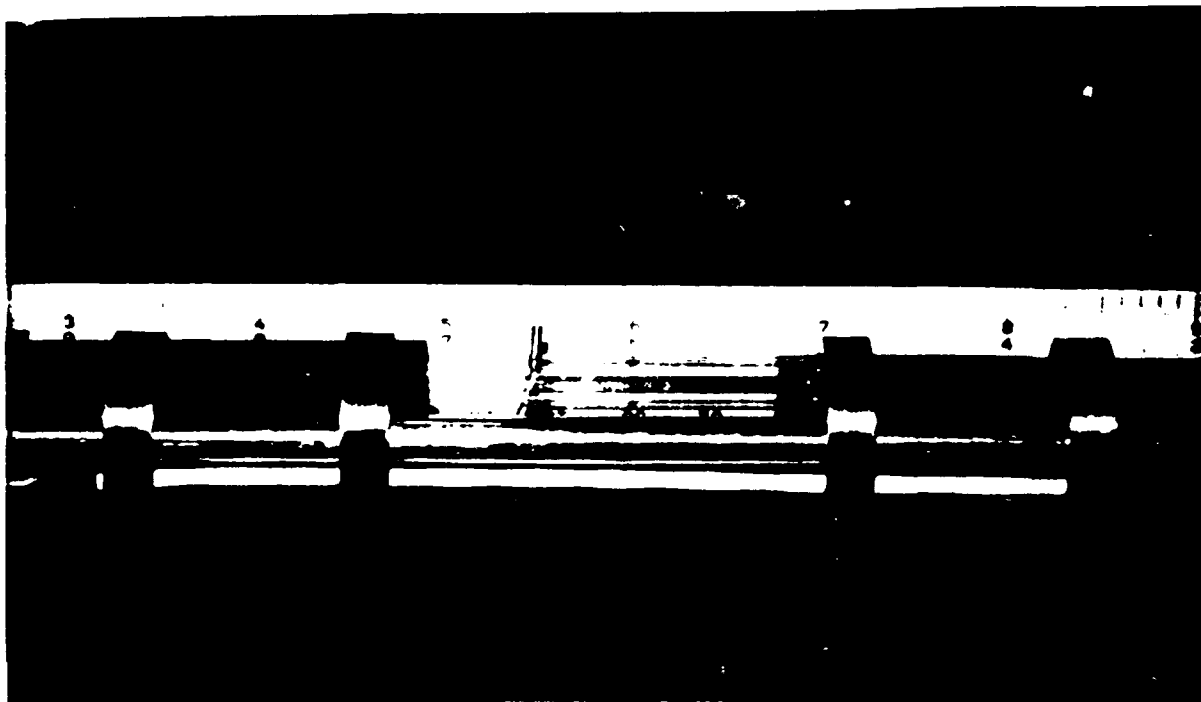


Figure 2. Photo of disassembled fluorescence sensor showing the mercury vapor lamps. The optical fiber termination is located in the tube between the two lamps.

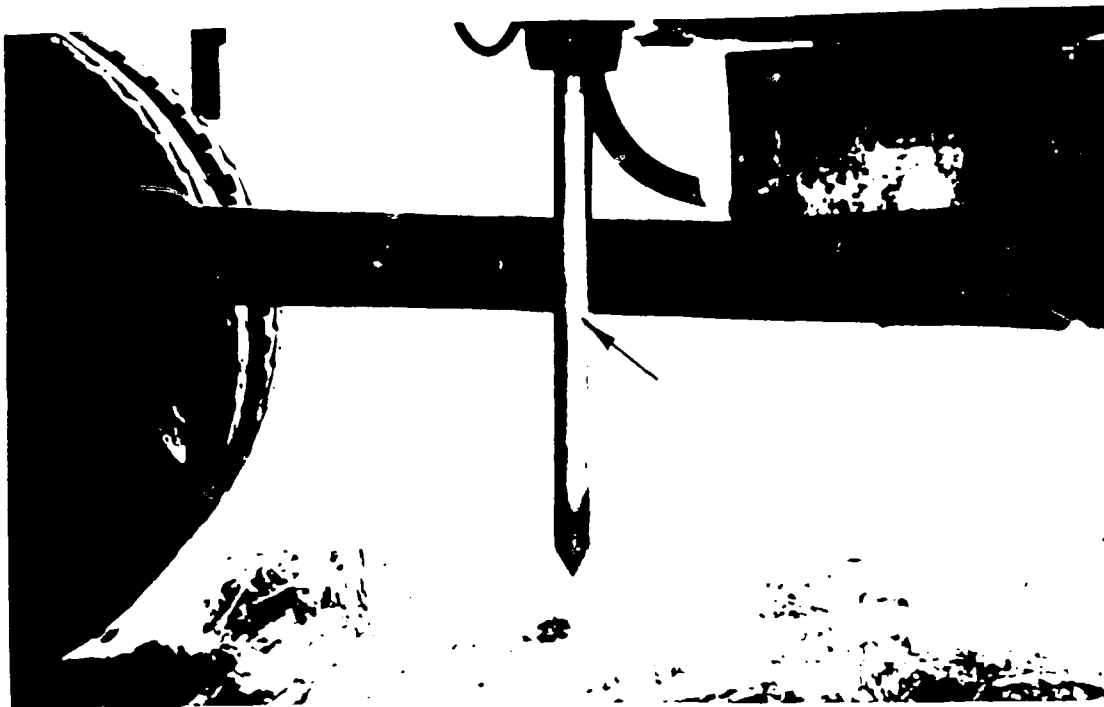


Figure 3. Photo showing the fluorescence sensor mounted on the penetrometer rod. The arrow marks the position of the small window located on a section of the rod that has been milled flat.

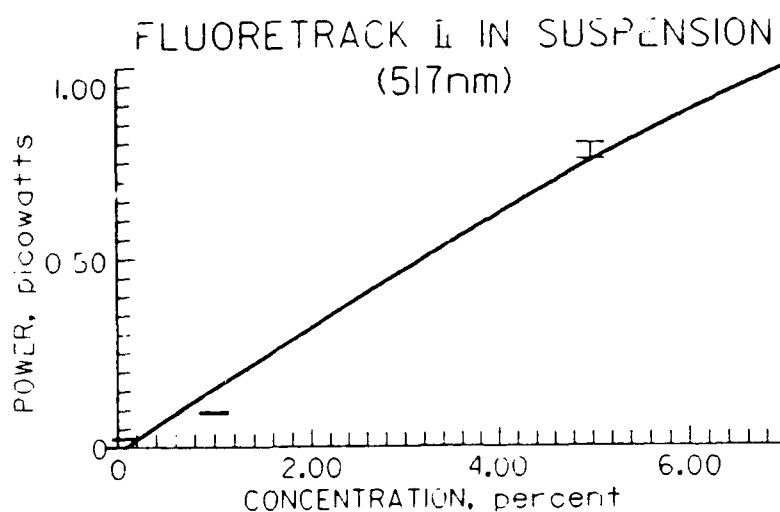


Figure 4. Low-level calibration curve prepared for the fluorescence of Fluoretrack II suspension in sand. Error bars represent one standard deviation from the average reading.

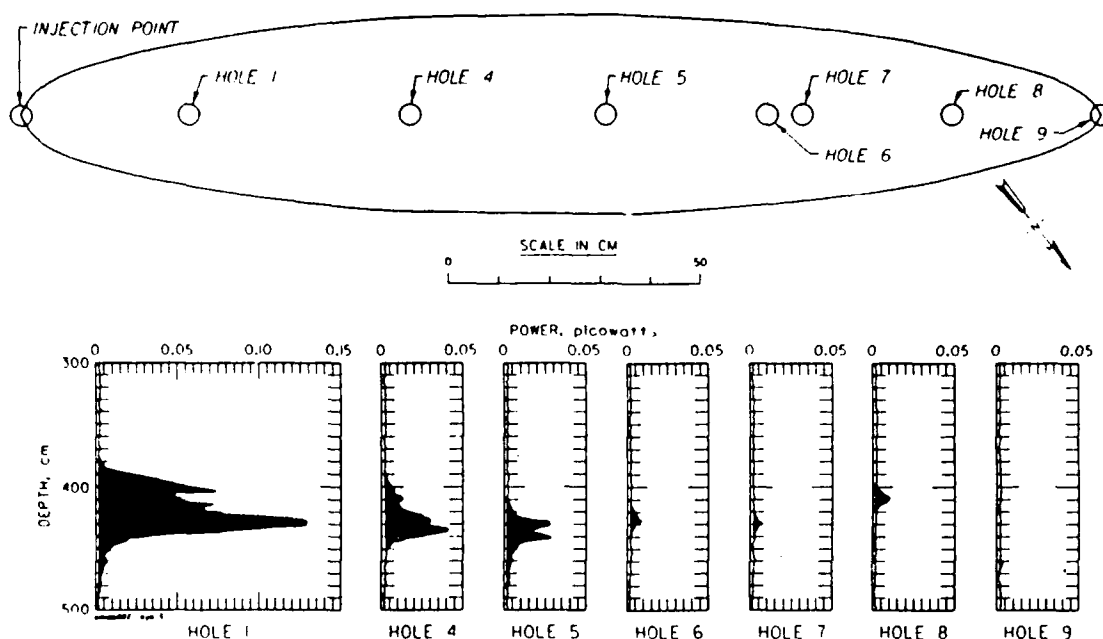


Figure 5. Map view and readouts from the fluorescence sensor showing the dilution and movement of the dye as it is carried away from the injection point. The width of the plume was estimated from readings made across the plume path near Hole 5. The reduction of fluorescence intensity is due to filtration of the suspended solid dye, adsorption of the dissolved dye on clays and silts and dilution by the surrounding groundwater.

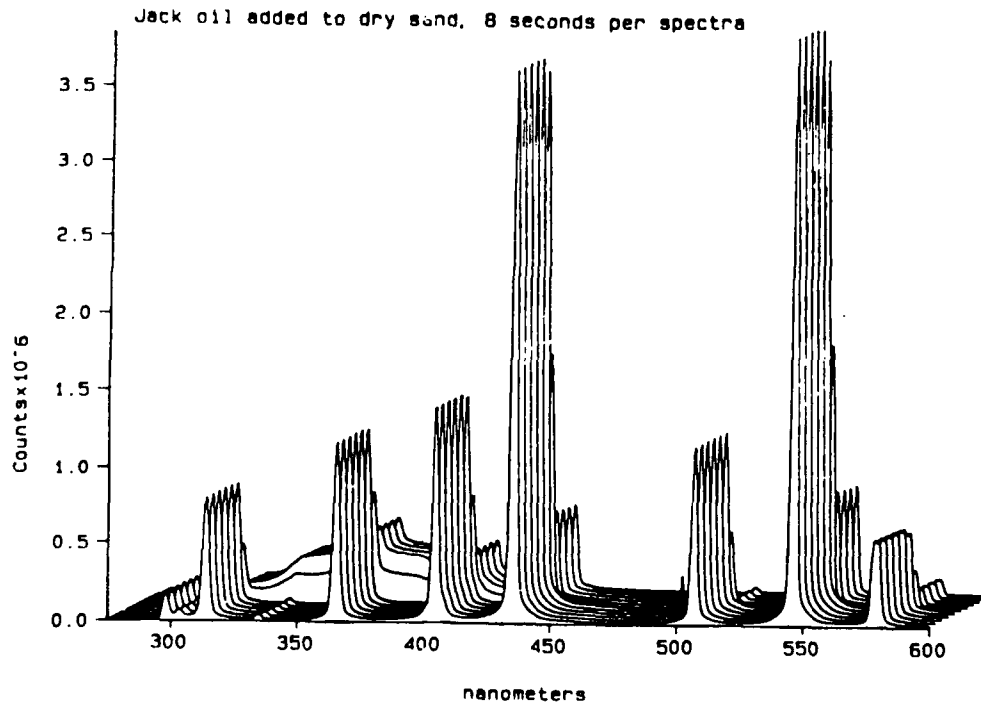


Figure 6. Spectral data collected with an optical multichannel analyzer. The spectra in the foreground were collected in clean sand, the spectra in the background were collected as the sand was contaminated with hydraulic oil. Fluorescence excitation and collection of the reflectance/fluorescence energy was done using the penetrometer fluorescence sensing unit.

Title: Development of Analytical Methods to Monitor Remediation at NWS Seal Beach.

Principal Investigator: Carol A. Dooley, NOSC Code 522
San Diego, CA. 92152-5000

OBJECTIVES

The objectives of this proposal are to develop a rapid tool to 1) map the extent (impacted area) of the hazardous site before, during and after the application of remedial measures, thereby achieving cost reduction by identification of those samples needing detailed chemical analysis by conventional methods, and 2) monitor clean-up measures in the field. The effort will be initially directed toward measurements of fuel oils in contaminated soils and groundwater.

BACKGROUND: Improper disposal of hazardous wastes and indirect runoff and ground water transport of contaminants from land sites have resulted in the contamination of many Navy sites with toxic organic compounds. The preferred method of remediation of contaminated sites is with on-site measures.

Detection and identification of hazardous organic substances and monitoring of clean-up measures are important problems. The conventional approach to these problems involves the collection of numerous field samples and off-site detailed chemical analyses.

Although analytical methods for all the priority pollutants are available, thorough qualitative and quantitative analysis is time-consuming and labor intensive, requires expensive and sophisticated instrumentation and may involve considerable delay in obtaining needed results. These analytical procedures do not lend themselves to field analysis. Further, interpretation of the analytical results can be ambiguous. Measurement of biodegraded fuels presents a significant analytical problem because not only are the parent substances poorly defined mixtures, but each component possesses its own degradation rate. In addition, specific intermediates of the degradative process usually cannot be identified because of the low concentration of any one substance in a complex mixture and because no standard for that substance is available for calibration of the instrument.

This proposal addresses the need for rapid general identification, semi-quantitation and hazard assessment of selected chemical compounds and their degradation products in the field.

A 3-year research project by NCEL has commenced to investigate various aspects of gasoline hydrocarbon degradation by native groundwater microorganisms at Seal Beach NWS. Since, as mentioned above, fuels are a complex mixture of hundreds of hydrocarbon compounds, analytical measurement of cleanup progress is a significant challenge. Rapid group assessment of parent

compounds and their likely degradation products, rather than attempted measurement of the individual chemical species, would be far more desirable and realistic approach.

TECHNICAL APPROACH: Simple, rapid, chemical methods suitable for field utilization will be developed to minimize time-consuming conventional analyses. This approach is based on the fact that related chemical substances have structural characteristics in common. These structural characteristics can be the basis for the identification and estimation of the substance by, for example, the presence or absence and intensity of distinctive ultraviolet or infrared absorption bands. Simple appropriate chemical measurements characteristic of the various categories of pollutants, such as UV absorbance for aromatic fuel components, will be determined.

A literature search for microbial and other degradation modes and common products will be conducted. Those degradative schemes amenable to simple chemical measurement, such as UV absorption or colorimetric reaction, will be selected and used to develop a simple and reliable field measurement technique. An example of this would be to determine the ratio of an easily measured primary pollutant to a distinctive breakdown product and use this changing ratio to monitor progress of the clean-up actions. Specifically, aromatic hydrocarbons might be estimated by their UV spectra; a common mode of microbial degradation produces hydroxylated products which form aldehydes before further degradation. The products can be detected by simple colorimetric measurements of the produced aldehyde.

The validity of this approach will be verified using artificial mixtures, simulated contaminated samples, laboratory scale bioreactors and finally field samples in support of the NWS Seal Beach remediation effort.

TECHNICAL WORK PLAN

FY90

A database of simple, field-adaptable chemical tests that identify and estimate the concentrations of selected hazardous substances and their expected breakdown products.

Laboratory demonstration that the measurement approach is feasible in complex mixtures. Technical report.

FY91

Demonstration of the feasibility of monitoring the progress of a specific clean-up effort using a laboratory scale bioreactor. Technical Report.

FY92

Integrated system consisting of documentation and simple instrumentation for on-site determination of the progress of remedial measures.

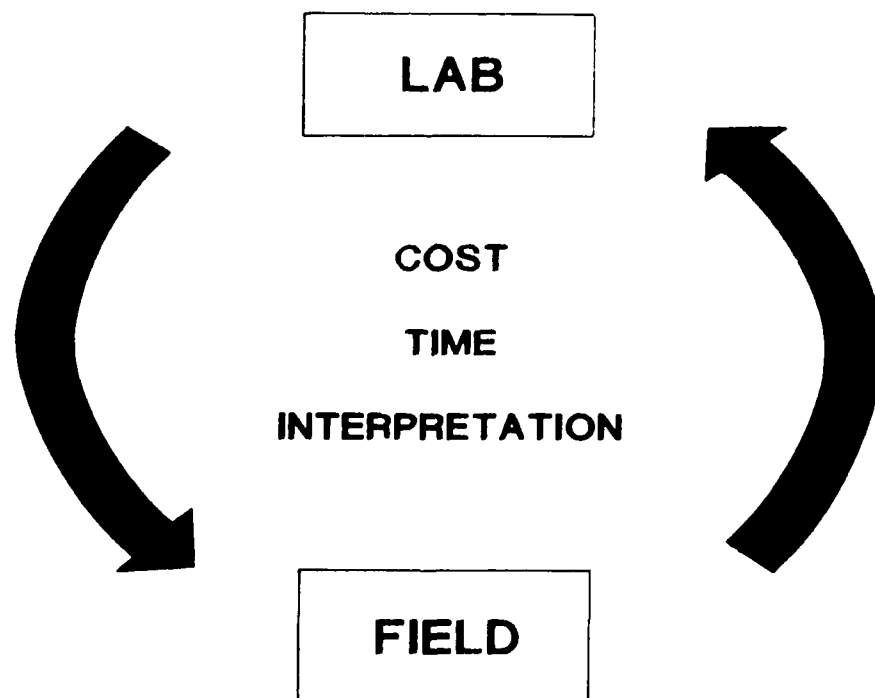
Protocol for use of the integrated system by monitoring personnel or contractors involved in site clean-up. Technical

ANALYTICAL METHODS TO MONITOR REMEDIATION

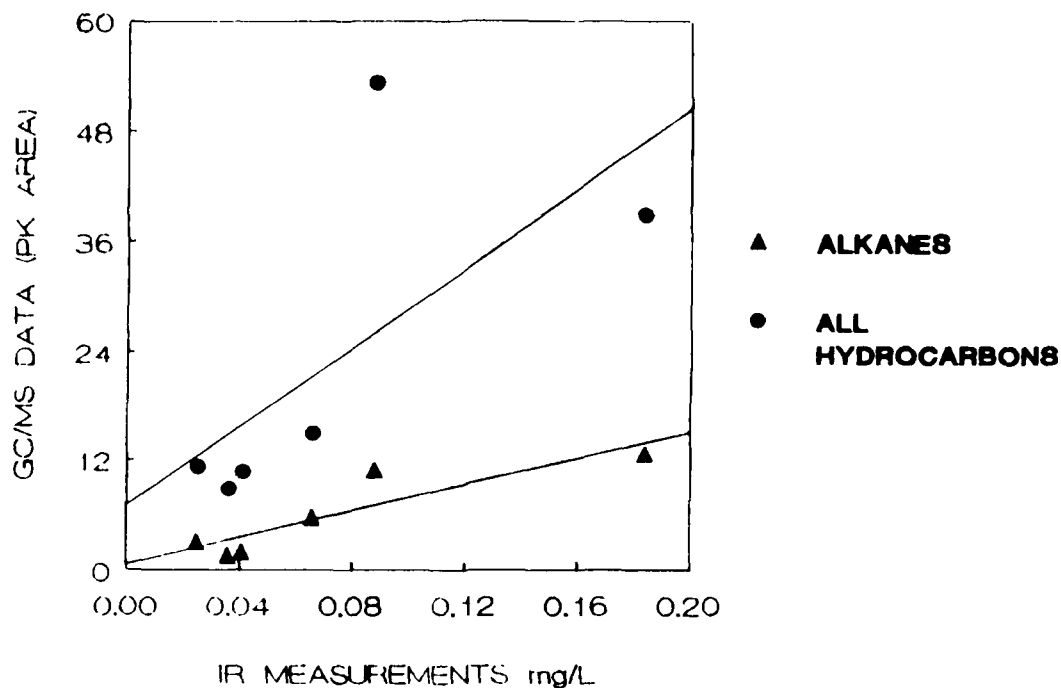
**DEFINE PROBLEM
DELINEATE EXTENT OF DAMAGE
DETERMINE REMEDIATION SUCCESS**

NWS SEAL BEACH

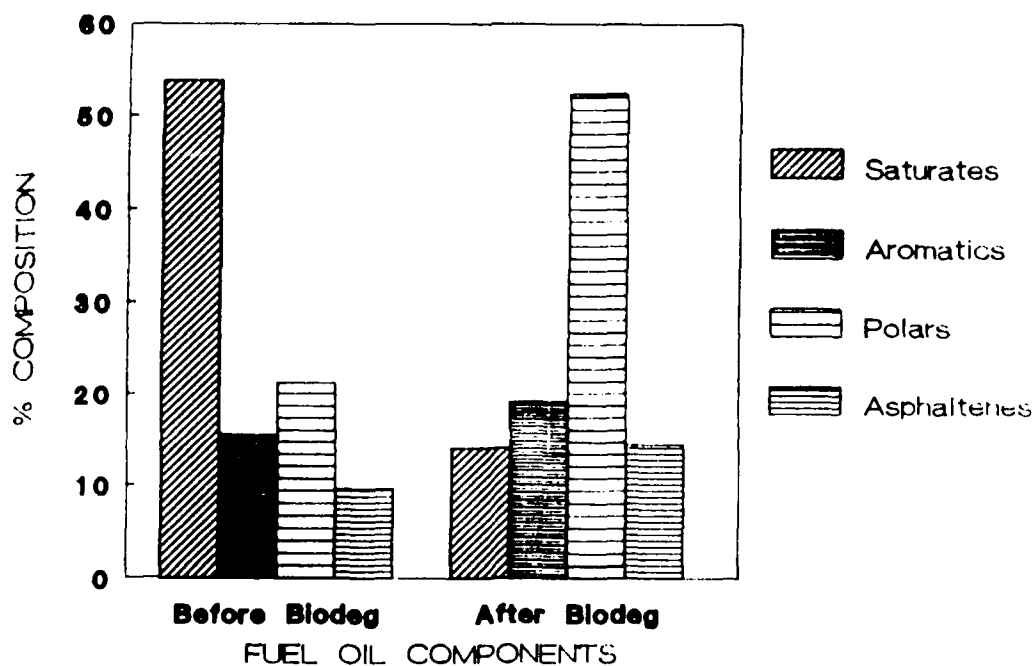
CONVENTIONAL ANALYSIS



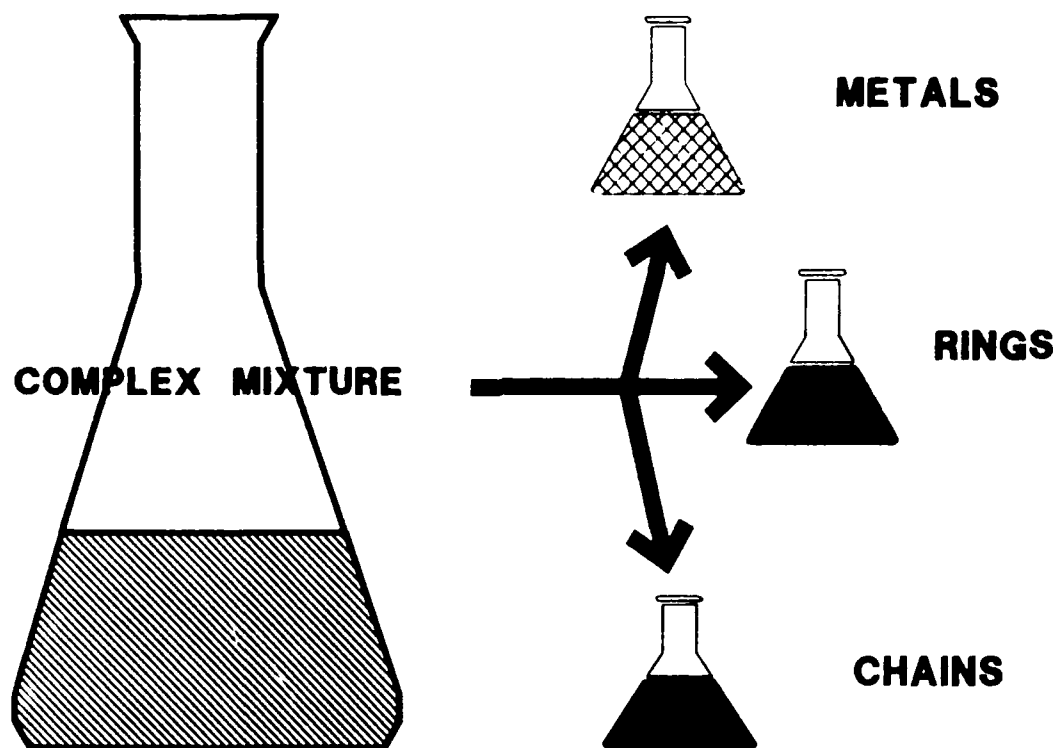
IR AND MS DATA CORRELATION



CRUDE OIL COMPOSITION BEFORE & AFTER BIODEGRADATION



RESOLUTION OF COMPLEX MIXTURE



DEVELOPMENT OF ANALYTICAL METHODS TO MONITOR REMEDIATION AT NWS SEAL BEACH

PROBLEM	FUEL HYDROCARBONS		
POLLUTANTS	ALKANES	AROMATICS	HEAVY METALS
CHARACTERISTICS	- CH ₂ -	RING	COLORLED COMPLEX
MEASUREMENT	IR	UV FLUORESCENCE	COLORIMETRY
DEGRADATION PRODUCTS	-COOH -C=O	-COOH -C=O RING	NONE
MEASUREMENT	IR COLORIMETRY	IR COLORIMETRY UV FLUORESCENCE	

AUTOMATED ORGANOMETALS ANALYZER

C. Clavell, NOSC

Workshop

Automated Organometals Analyzer

BACKGROUND

The fouling of ship hulls has been a major concern to world navies and merchant seaman since the first ships put to sea. Since that time, the prevention or mitigation of the detrimental effects of fouling has been a much sought after but elusive goal. With the development of copper-based antifouling paints at the turn of the century, a reliable means of protection lasting 1 to 2 years was achieved. However, as the size and speed of ships increased with an equivalent escalation in the cost of fuel, economics dictated the development of coating systems which could dramatically extend the service time between haul-outs.

Other paints did not provide a significant performance improvement over copper-based paints until the development, in the 1970s, of Organotin-based formulations. These new paints can provide effective protection for 5 to 7 years due to the much lower and better controlled release rate for the antifouling toxicant.

In 1984, with the issuance of an environmental assessment, the Navy announced its intention to slowly implement the fleetwide use of organotin antifouling paints containing tributyltin (TBT) as the biocide. In anticipation of a need for extensive monitoring of Navy-impacted receiving waters, due to concerns of potential environmental damage from the extensive use of TBT paints, the Marine Environmental Branch at the Naval Ocean Systems Center initiated an effort to develop an automated instrument to facilitate the measurement of TBT directly in sea water. The Automated Organotin Analyzer (AOA) represents a state of the art chemical analysis instrument system designed to provide rapid, on-site analyses for several organotin and arsenic compounds.

SYSTEM DESCRIPTION

The prototype AOA system has been described previously in reference 1. The AOA-II system is shown in figure 1.

The hydride derivatization method, described in references 2 and 3, can be used to analyze selected organic and inorganic tin and arsenic compounds directly in sea water. The volatile hydride reaction products formed are swept out of the 0.5-liter sea water sample by a stream of helium gas and concentrated in a cryogenic trap. Following the concentration period, the compounds are volatilized and separated by electrothermal heating and detected by atomic absorption spectroscopy using a hydrogen-flame quartz burner. Analysis of 3 to 4 samples per hour has been accomplished with a sensitivity of 0.5 ng at the detector or 1 ng/L (1 part per trillion (ppt)) in environmental samples.

Figure 2 is a diagrammatic representation of the system showing the interconnections between the major system components.

The analyses for arsenic and tin compounds cannot be conducted together since the analytical parameters differ slightly for the two elements. To switch from analyzing organotin compounds to arsenic compounds entails the replacement of the tin hollow cathode lamp with an arsenic lamp, changing the packing material in the trap, and loading a different set of analysis parameters into the computer's memory.

Although the tin and arsenic analyses use the same chemical methodology (hydride derivatization), each requires different settings for the programmed set point and holding temperatures, sodium borohydride addition rate, acid type and concentration, sample size, and dilution ratio. Arsenic samples must be diluted significantly prior to analysis due to the high concentrations of arsenic present in natural waters. This is easily accomplished using the auxiliary syringe pump to add a small volume of sample to blank water in the reaction vessel.

The instrument software contains a menu window which permits selecting which element is to be analyzed and then automatically loads all the required parameters for that analysis. The operator then must install the proper hollow cathode lamp, install a new trap, and readjust the wavelength on the spectrometer. Conversion from tin to arsenic analysis would take approximately 30 to 45 minutes.

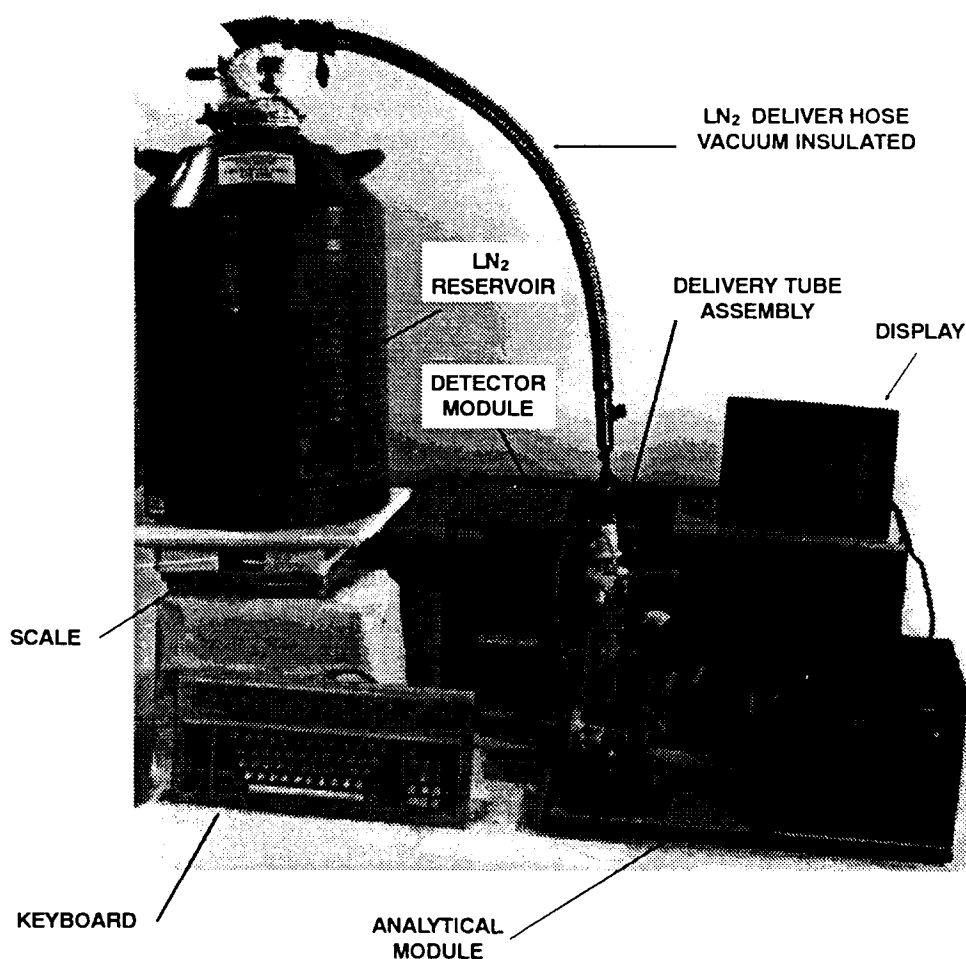


Figure 1. Arrangement of system components.

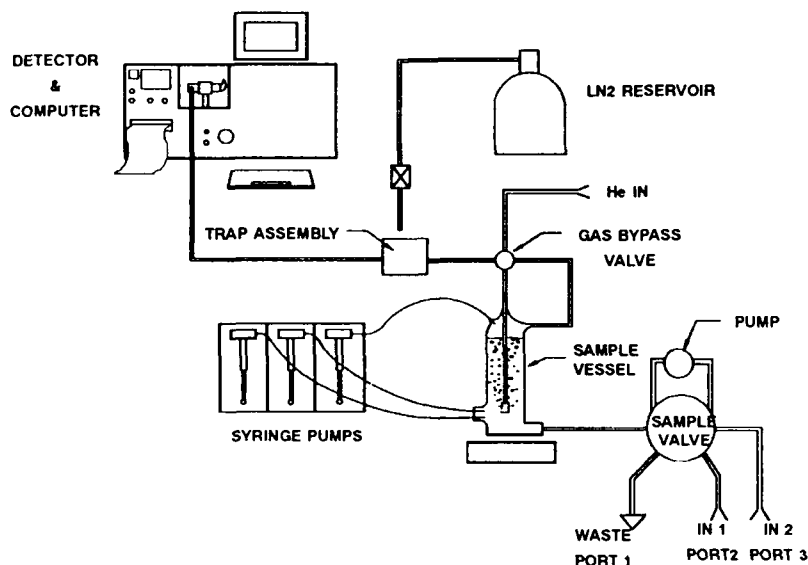


Figure 2. Instrument system diagram.

The instrument has three main subsections: The *System Controller*, the *Analytical Module*, and the *Detector Module*. The controller and detector are packaged as a single unit with the analytical section comprising a separate module.

SYSTEM CONTROLLER

The controller is based on a board-level IBM-AT compatible computer, together with memory, display, input, and interface peripherals.

Software is written in the PolyFORTH[®] (Forth, Inc) version of the Forth language, which provides a multi-user, multitasking environment. The system program is composed of several 'tasks' which can run simultaneously, permitting input or retrieval of parameters or data at any time. This feature enables the user to review system status and alter parameters; to input free form notes relating to the current analysis; and to adjust previous run data, with a peak editor function, during an analysis cycle without interrupting the analysis process. The operator interacts with the system through a menu-driven interface implemented as function key selections with pop-up windows. All data collected is automatically archived.

ANALYTICAL MODULE

The analytical unit implements the hydride derivatization analysis method. It contains hardware to automatically perform three required functions:

(1) **Sample handling:** Samples can be pumped from any source into the 500-ml reaction vessel. Following an analysis, the system can be instructed to flush the reaction vessel, using an alternate water source or the sample source, and then refill the vessel with a fresh sample.

(2) **Reagents and standard additions:** Additions to the reaction vessel are made by a set of three computer-controlled syringe pumps.

(3) **Reaction product concentration and separation:** Trapping and concentrating the reaction products is accomplished with a patented variable temperature trap assembly (figure 3). The computer-controlled trap and its liquid nitrogen source can provide temperature sequencing of up to six selectable set points, where the temperature can be held for a specified time. The trap temperature range is -200 to $+180$ °C. Traps are made of quartz tubing packed with a chromatographic support material centered in tube. The trap tube is inserted coaxially in a graphite tube heater which is under computer control. The trap assembly (trap tube and heater) is inserted into a vacuum-insulated, quartz reservoir which is filled with liquid nitrogen to maintain the trap tube temperature at -198 °C during the concentration period.

The system can operate continuously (processing 3 to 4 samples per hour) or on an individual sample basis. To begin an analysis run, a sample is pumped into the 500-ml reaction vessel and 0.5 ml of 10% acetic acid is added. Simultaneously, the trap reservoir is filled with liquid nitrogen. When the trap has cooled to -150 °C, the gas bypass valve directs helium gas (80 ml/min) into the reaction vessel and then 5 ml of a sodium borohydride (NaBH_4) solution is added. Helium is bubbled through the sample for 5 minutes purging the hydride derivatives from the reaction vessel and concentrating them in the cold trap. After the concentration period, the gas valve redirects the helium to the trap, bypassing the reaction vessel. This process is followed by the simultaneous initiation of the heating program, the acquisition of data from the atomic absorption spectrometer, and the real-time plotting of the raw data. The trap temperature is raised in dis-

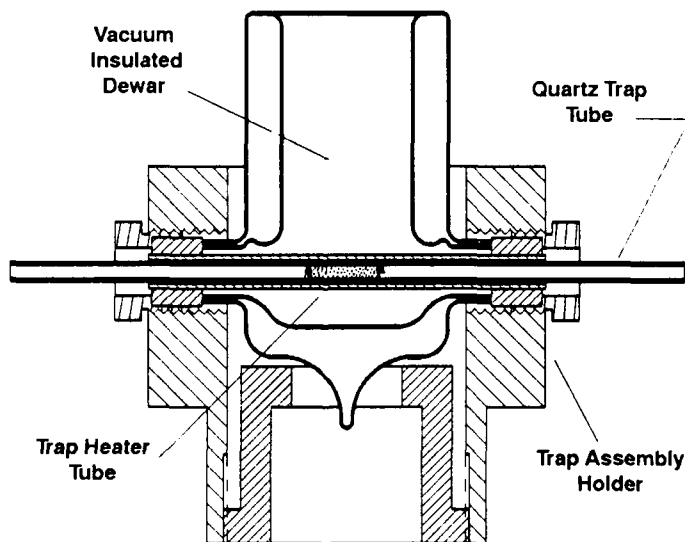


Figure 3. Variable temperature trap assembly.

crete steps, with a holding time between steps, yielding well-resolved chromatograms (figure 4). The trap is maintained at the final temperature of 180 °C for 10 minutes to remove all traces of moisture. During this time, the computer processes the data and outputs an annotated plot with temperature vs. mv scales, peak areas, and concentrations for each component, and any notes input by the user. If the automatic peak detection has incorrectly identified the limits of a peak, the operator may call up the peak editor, correct the limits, and then reprocess the data to generate a new plot. The multitasking capability of the software allows all these functions to be performed concurrently.

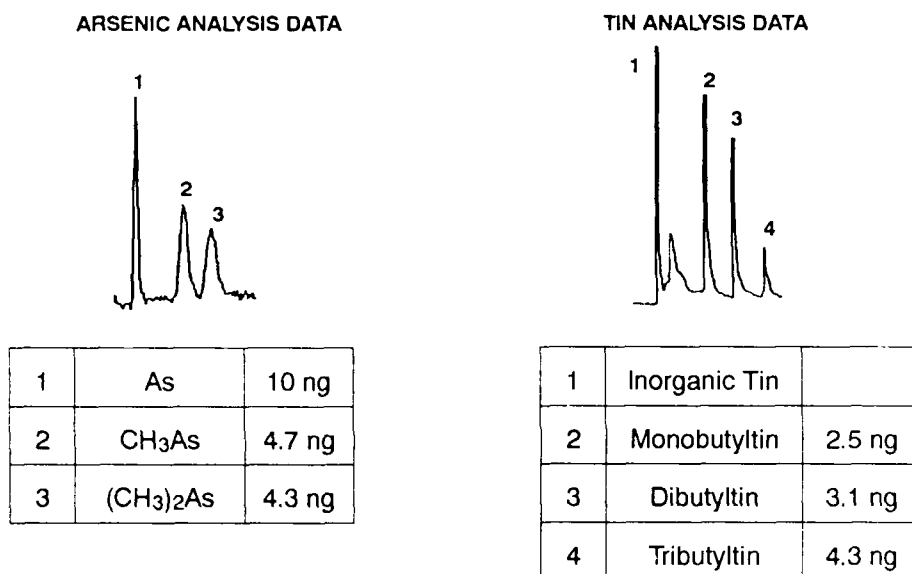


Fig. 4 Sample chromatogram

DETECTOR MODULE

The detector is based on a Buck Instruments Model 200 atomic absorption spectrophotometer repackaged and ruggedized for field operation. Sensitivity for the butyltin and arsenic compounds of interest is in the sub-ppt range.

EXAMPLE FIELD TEST DATA

Several 24-hour surveys were conducted in August 1989 to test the systems performance and reliability. The instrument was installed aboard the NOSC survey craft *ECOS* which was moored at the NOSC small boat piers (figure 5). Sampling data from the 2-3 Aug are presented in figure 6. Although the peak shapes were broad and required considerable editing, the data showed good inverse correlation between TBT concentrations and tidal height. This correlation is due to the extremely low TBT concentration in coastal waters and the high TBT concentrations found in Shelter Island yacht basin, which is located immediately north of the small boat piers where the *ECOS* is tied up (figure 5). As the tide ebbs, highly loaded water is drawn out of the Shelter Island yacht basin and towards the mouth of the bay, passing under the *ECOS*. When the tide turns and begins to flood, clean coastal water flows back into the bay and organotin concentrations at the piers fall, approaching those in the coastal water.

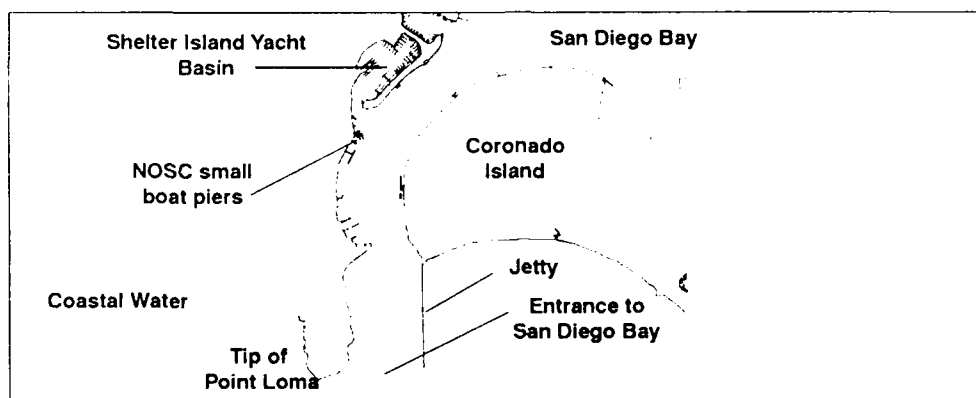


Figure 5. Expanded portion of chart showing the area from the entrance to San Diego Bay up to the Shelter Island yacht basin.

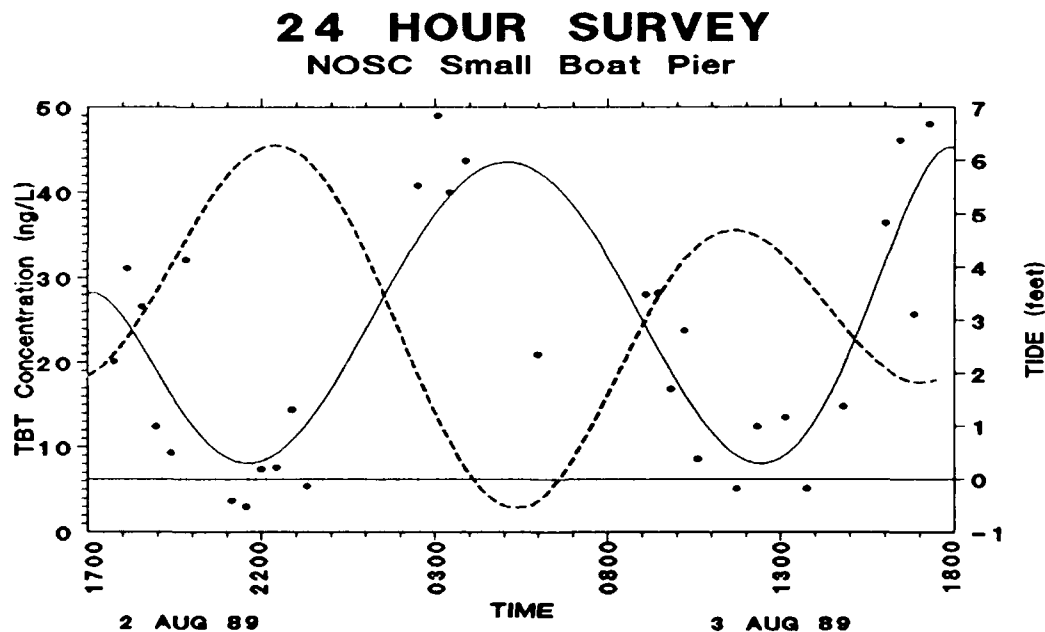


Figure 6. TBT concentration and Tidal height vs. time.

This data set provided an excellent example of the potential problems encountered with automatic computer data analysis. Recorder/integrators and computers frequently are not capable of accurately determining the correct beginning and end points of a poorly shaped peak and therefore can produce erroneous area calculations. The ability to manually edit a peak to adjust its limits can save an otherwise unusable data point.

A second 24-hour test was run on 27-28 August 1989. The system operated extremely well, requiring almost no operator intervention. Thus the operator was free to complete other tasks while the samples were analyzed. Peak shapes for the data collected on this survey were well formed, reducing the need for most post peak editing.

Nine samples were also collected for arsenic analysis, using the manual laboratory system, at intervals spanning a complete tidal cycle. The tin data are shown graphically in figures 7 to 9, and the arsenic data are presented in table 1.

There is exceptionally good inverse correlation between TBT concentration and tidal heights. The line through the 34 TBT data points is a sixth-order polynomial curve fit. The maximum value at low tide was 49.2 ng/L and the minimum value at high tide was 2.4 ng/L.

Dibutyltin (DBT) also showed exceptionally good inverse correlation between concentration and tidal height. The data shown in figure 8 were not edited with the peak editor. The average DBT concentration was 18.6 ng/L, $\sigma=14.3$. The maximum concentration was 45.5 ng/L and the minimum concentration 2.9 ng/L. Figure 9 shows a composite plot of the TBT and DBT data.

The arsenic data (table 1) show no changes correlating to tidal flux. This is expected since both the bay and coastal waters contain approximately the same arsenic concentrations.

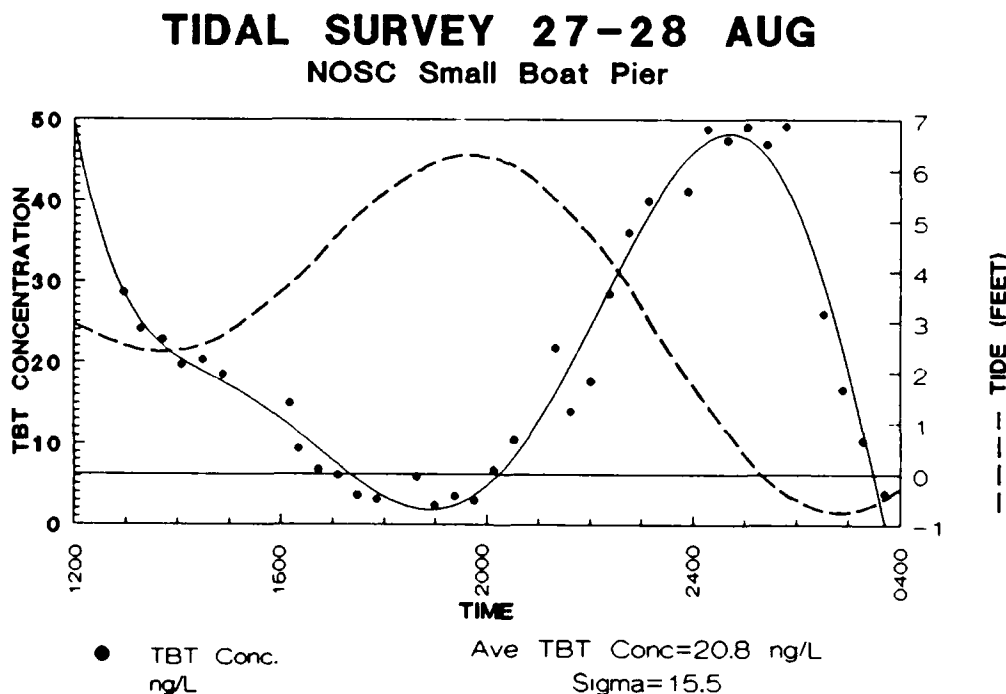


Figure 7. TBT concentration and tidal height vs. time.

TIDAL SURVEY 27-28 AUG

NOSC Small Boat Pier

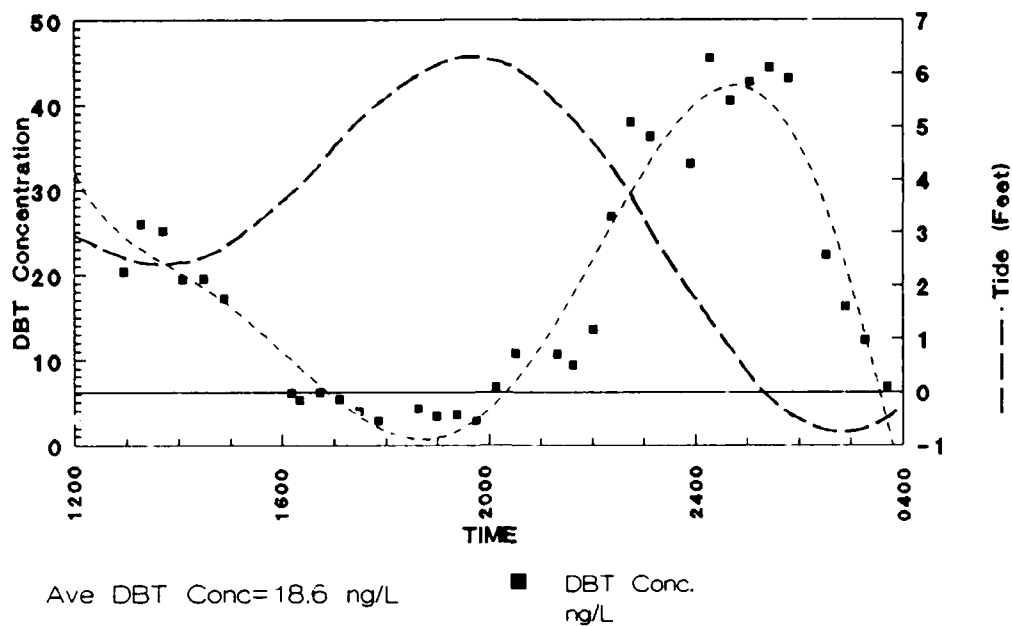


Figure 8. DBT concentration and tidal height vs. time.

TIDAL SURVEY 27-28 AUG

NOSC Small Boat Pier

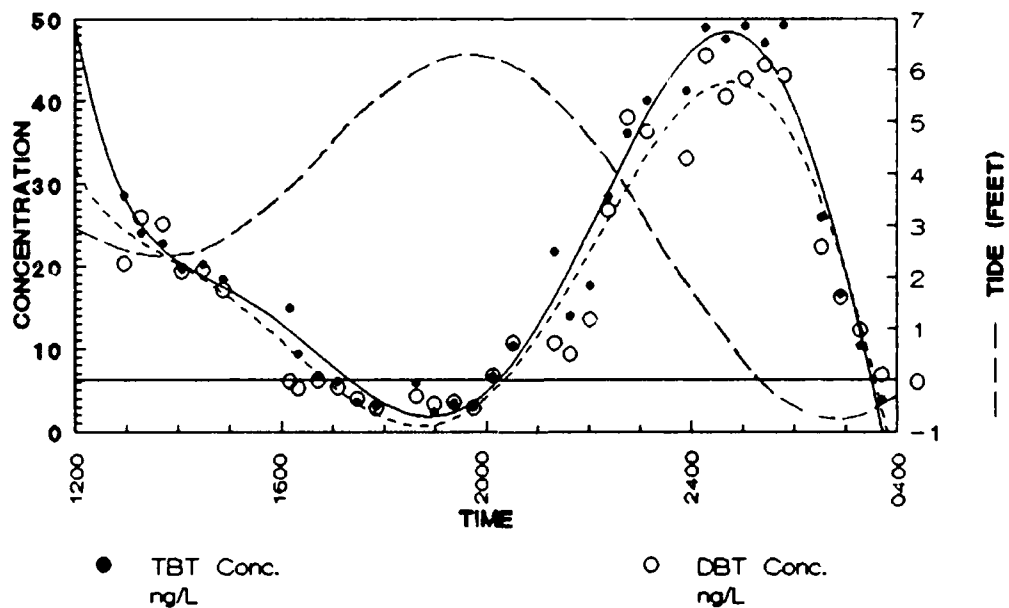


Figure 9. TBT and DBT concentrations and tidal height vs. time

Table 1. Samples collected during 27-28 August Tidal Survey at NOSC small boat pier #159. Concentrations for all species are calculated in terms of elemental arsenic.

ARSENIC DATA (ppb)				
Sample ID	Tide (ft)	Inorganic As	Methyl-As	Dimethyl-As
27 Aug 1342	2.4	0.90	0.04	0.11
27 Aug 1640		0.83	0.04	0.11
27 Aug 1940	6.3	0.79	0.03	0.11
27 Aug 2240		0.73	0.03	0.08
28 Aug 0251	-0.7	0.67	0.02	0.08
28 Aug 0551		0.65	0.02	0.07
28 Aug 0913	4.6	0.92	0.03	0.11
28 Aug 0913		0.87	0.09	0.11
28 Aug 1213		0.75	0.03	0.10
28 Aug 1426	2.0	0.67	0.07	0.09
Average Values		0.78	0.04	0.10
Sigma		0.09	0.02	0.01
Scripps Institute of Oceanography sea water		1.09	0.05	0.12
NOSC, Bldg. 111 sea water system		1.04	0.09	0.09

RECOMMENDED USE

PRIMARY CONFIGURATION

Fitted with the current large port sample valve and 0.5-inch ID tubing, the AOA is optimized for continuous monitoring directly from a body of water or performing discrete analyses when sample volumes greater than 1.5 liters can be collected. It is somewhat cumbersome for analyzing small (1 liter or less) discrete samples due to the relatively large volume retained in the sample lines. Discrete samples would have to be poured into the reaction vessel manually if there is not sufficient volume to flush the lines completely.

ALTERNATE CONFIGURATIONS

The system can easily be adapted for discrete small sample (500 ml) operation by substituting a smaller port sample valve and using 1/4-inch or 3/16-inch Teflon tubing of minimum lengths. In this configuration, samples could be pulled directly from small sample bottles (<1 liter). It would also be possible to incorporate an automatic sample carousel with the system.

Another option is to arrange the AOA as a semiautomated system in which only the trap assembly, the liquid nitrogen valve, and the liquid nitrogen level sensor are automated. A standard reaction vessel (no reagent addition ports) is connected directly to the trap with or without the gas bypass valve, and the sample and all reagents would be added manually. AOA-I has been converted to this configuration and is currently being evaluated for its suitability to perform routine laboratory analyses.

The semiautomated system provides the advantage of simplified cleaning if contaminated, which is commonly encountered in the laboratory with samples having large concentration differences or high loadings of organic matter. However, it retains the computer control of timing and temperature as well as automated data collection, analysis, raw data archiving, and the ability to edit peaks. Computer control of these parameters eliminates the majority of operator variation and induced errors.

CONCLUSION

The AOA system has been tested and proven under field and laboratory conditions. It has been demonstrated that the complex chemical analysis for TBT can be successfully conducted aboard small crafts while underway as well as at anchor.

HARDWARE

The field tests have identified possible enhancements to the system to facilitate analyses of small discrete samples. These enhancements would be simple to effect and would still permit using the system for continuous monitoring at a slightly reduced sample throughput.

A second instrument system has been fabricated, AOA-II, which incorporates several improvements.

The instrument has been shown to be insensitive to the normal small boat vibration and shocks encountered in protected waters. Although the electronics are off-the-shelf commercial grade, the system has experienced no component failures in over a year of testing.

SOFTWARE

The current software version number is 3.8. The operator-machine interface is implemented as a windows-oriented menu program. The menus allow access to all system functions and are largely self-explanatory, which permits operation of the instrument by lesser skilled technicians. The software package has been refined based on the comments and suggestions from several operators with widely divergent backgrounds and training.

The software design has proven to be extremely amenable to enhancement and extension. Future upgrades to extend the instruments' present capabilities will be simple to implement. A list of enhancements has been compiled, based on experience gained during the last two 24-hour monitoring tests. The suggested additions will be implemented in version 3.9 as funding permits.

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Benthic Flux Sampling Device

S. H. Lieberman, NOSC

- **Objective**

Determine *in situ* release rate (flux)
of chemical toxicants from contaminated
sediments in aquatic environments

Benthic Flux Sampling Device

- **Operational Specifications**

- Autonomous Operation
- Max operating depth: 50 m
- Max operating period: 3 days
- Minimizes disturbance at
sediment/water interface
- Max bottom current: 5 knots
- Accommodates variety Sediment Types
- Deployed/recovered small vessel

Benthic Flux Sampling Device

- **Applications**

- Measure flux from contaminated sediments
- Evaluate effectiveness of capping procedures
- Evaluate flux from dredge spoils

Benthic Flux Sampling Device

- **FY90 Plans**

- Test device at NOSC pier
- Test prototype at NAS North Island
- Test prototype at PACO copper ore loading facility on San Diego Bay

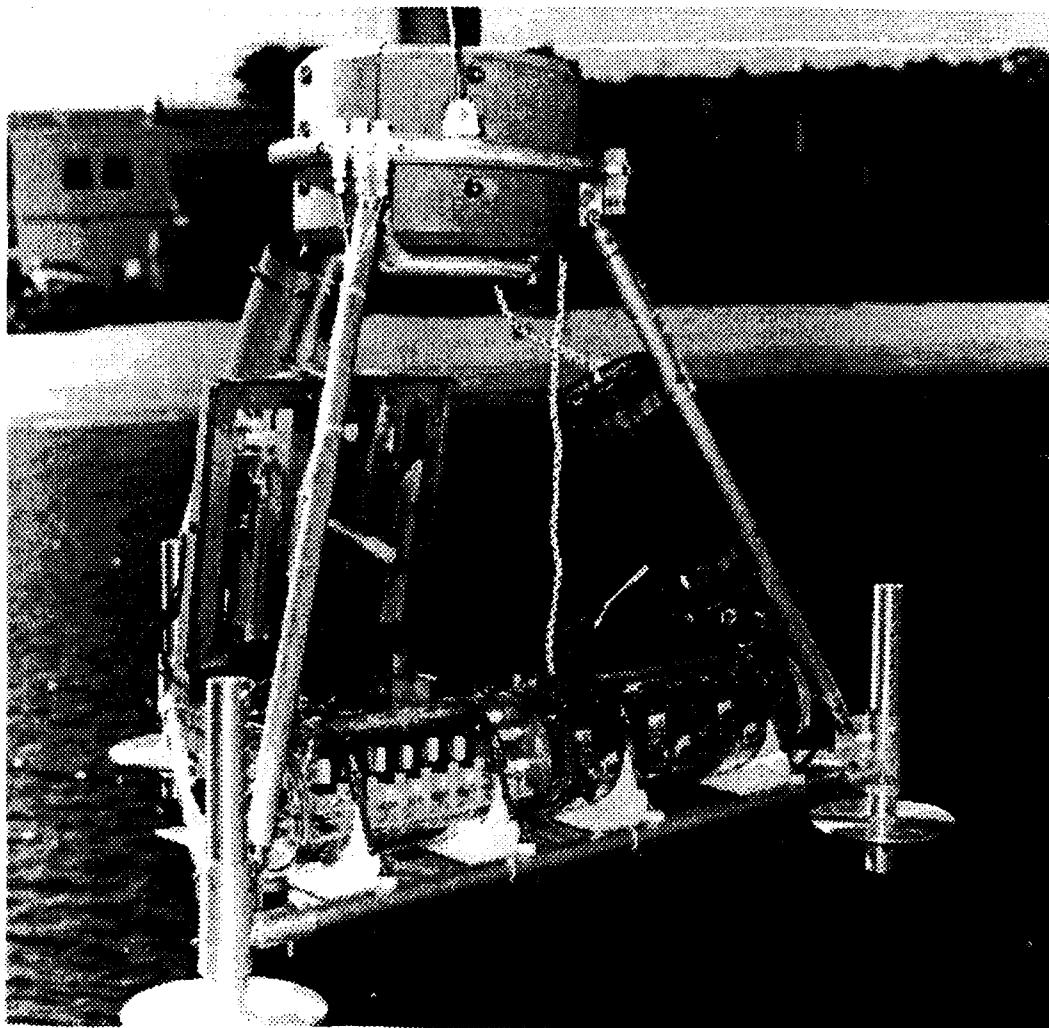
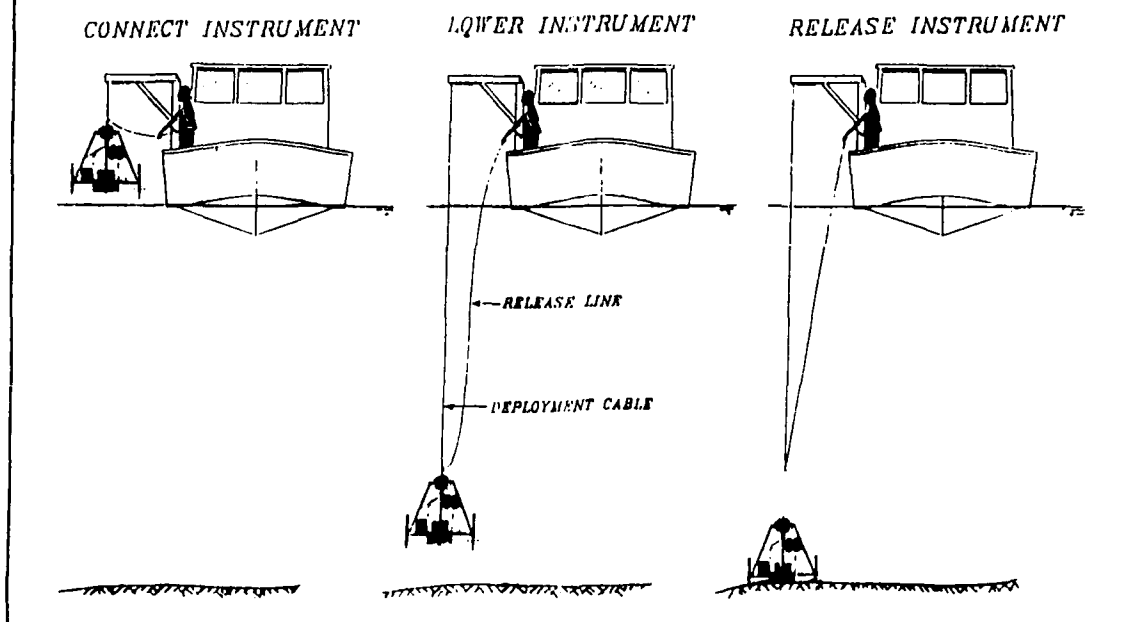
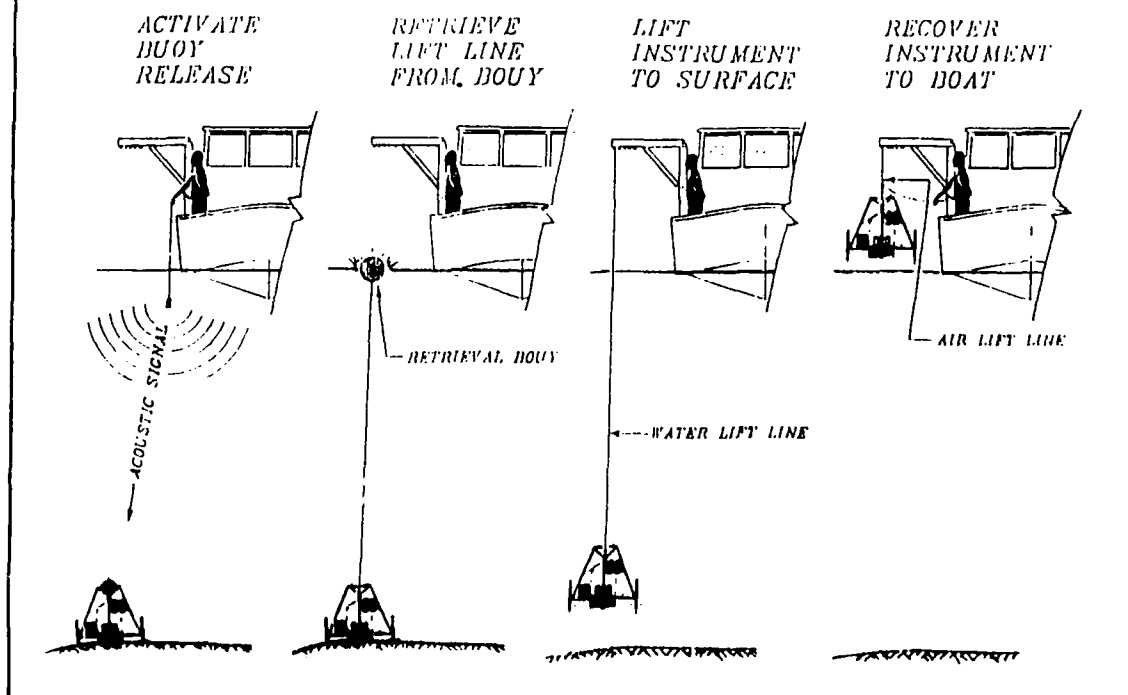


Fig 1. Photograph of Benthic Flux Sampling Device.

Benthic Contaminant Flux Sampling Device - Deployment -



Benthic Contaminant Flux Sampling Device - Retrieval -



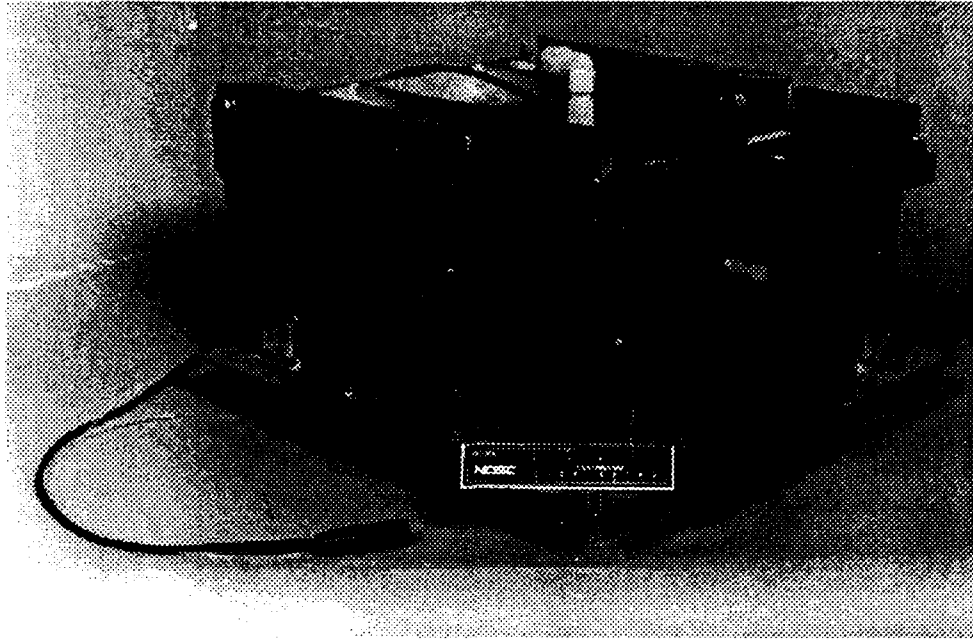


Fig 2. Photograph of chamber from benthic flux sampling device (shown with lid in closed position).

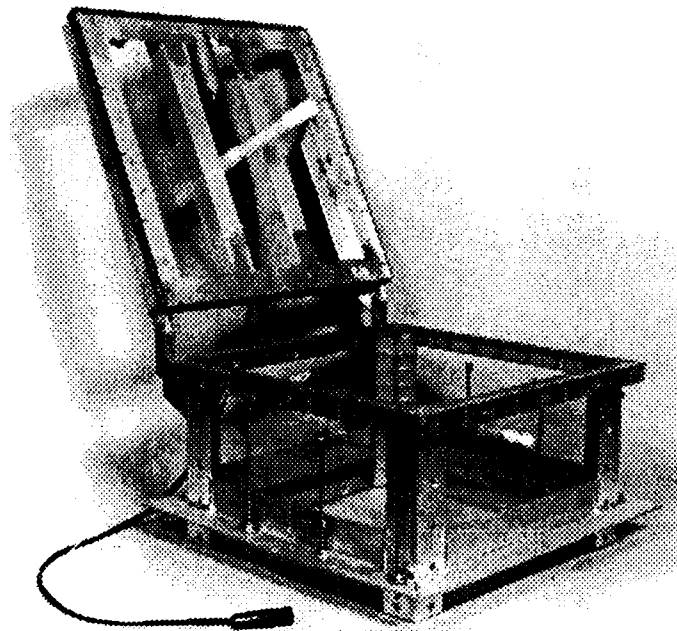


Fig. 3. Photograph of benthic flux chamber with lid in open position. Chamber is lowered to the sediment surface with lid in this position.

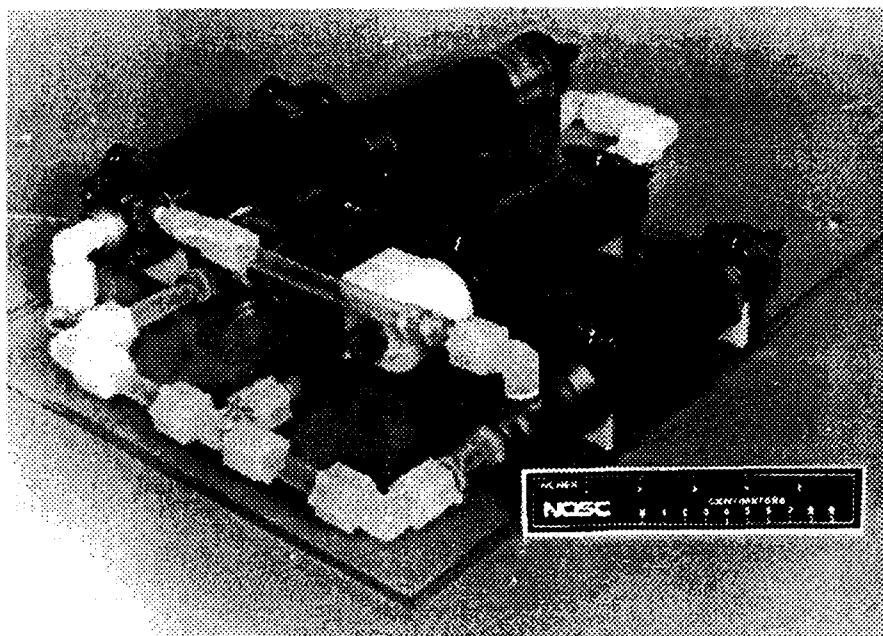


Fig. 4. Photograph of chamber lid showing temperature, conductivity and oxygen sensors used to record conditions within the chamber during depolyment. A pump mounted on the lid is used to circulate water from within the chamber through the sensor manifold. This also ensures that the volume of water within the chamber is uniformly mixed.

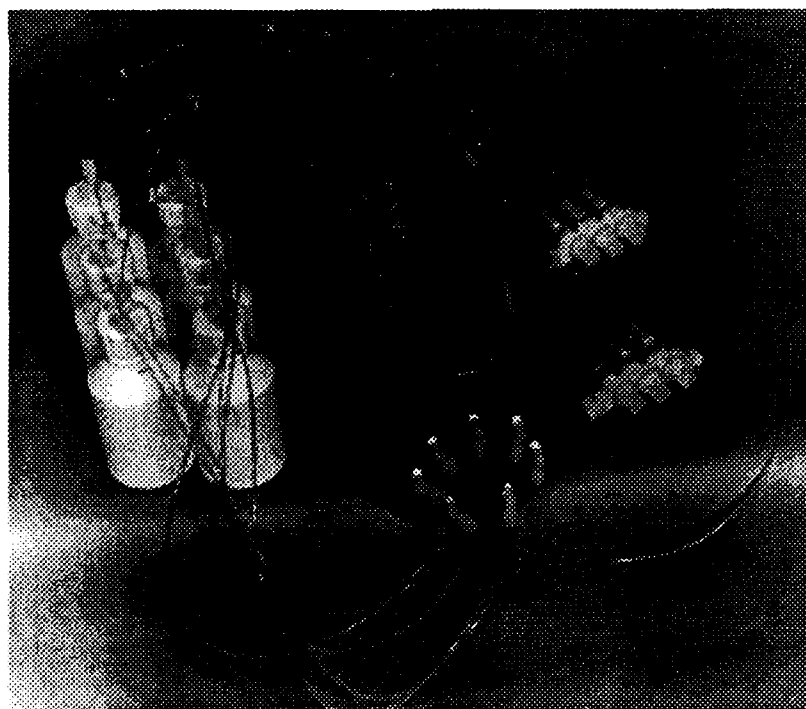


Fig 5. Photograph of valve manifold and sample bottles. Bottles are filled with water from within the chamber at intervals controlled by the onboard microprocessor.



Fig 6. Photograph of microprocessor control unit. This unit provides all control functions for the benthic sampling device (eg., closing of the chamber, filling of sample bottles and recording of sensor data). Data is dumped to laptop personal computer after retrieval of device.

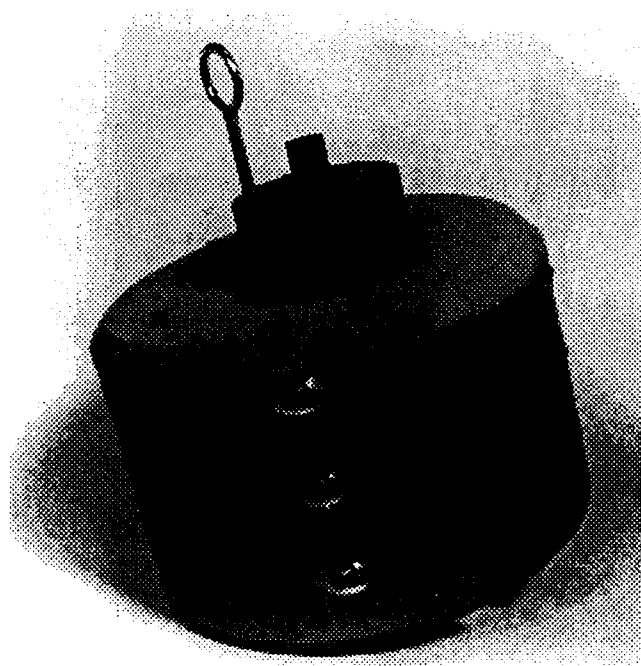


Fig. 7. Photograph of acoustic release mechanism. The device is retrieved from the bottom by sending an acoustic signal to the device which releases a float that rises to the surface. A cable attached to the float is then used to raise the chamber to the surface.

RISK ASSESSMENT PHILOSOPHY FOR CONTAMINATED SEDIMENTS AT NAVY AQUATIC HAZARDOUS WASTE SITES

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Abstract

Contaminated marine sediments have always been a potential problem for the Navy since the majority of their facilities are located adjacent to the marine environment and Navy vessels spend a great deal of time in port. The magnitude of the problem has escalated with increases in facilities and deep-draft vessels, the volume of contaminated material and more restrictive environmental regulation. The scientific problem is ecological and without straightforward answers to important questions like contaminant flux from sediment, bioavailability of contaminants, and biological effects of accumulated contaminants. Relevant information is best obtained with an integrated risk assessment philosophy that includes the following measurements: 1) water and sediment; 2) chemistry and biology; and 3) laboratory and field. Environmental compliance will be costly and often controversial. The best possible scientific data will assist Navy managers in making cost effective engineering decisions for environmental compliance.

INTRODUCTION

Marine sediments adjacent to Naval facilities and Naval vessels have become contaminated over the years from a variety of sources (Figure 1). These sources include antifouling paints, oil-water separators, industrial processes, and non-point sources. Some of the sources may even be non-Navy. The problem has been largely ignored since marine sediments associated with Naval activities are covered by water and not highly visible. The effects of contamination are often subtle, long-term, and not easily quantified. Historically, there have been no regulations to force measurement and cleanup procedures but environmental requirements are escalating. Several states are developing sediment criteria and some regional regulatory agencies are beginning to regulate Navy sediments. Several studies have shown that sediments are the ultimate sink for many contaminants. More importantly, potentially harmful levels of hazardous materials can concentrate in sediments even if water column levels are lower than existing regulatory requirements. Other studies have shown that in certain situations it may be more hazardous to remove contaminated sediments than to leave them in place. The Navy should use environmental science to formulate appropriate environmental compliance options.

INTEGRATED RISK ASSESSMENTS FOR CONTAMINATED SEDIMENT

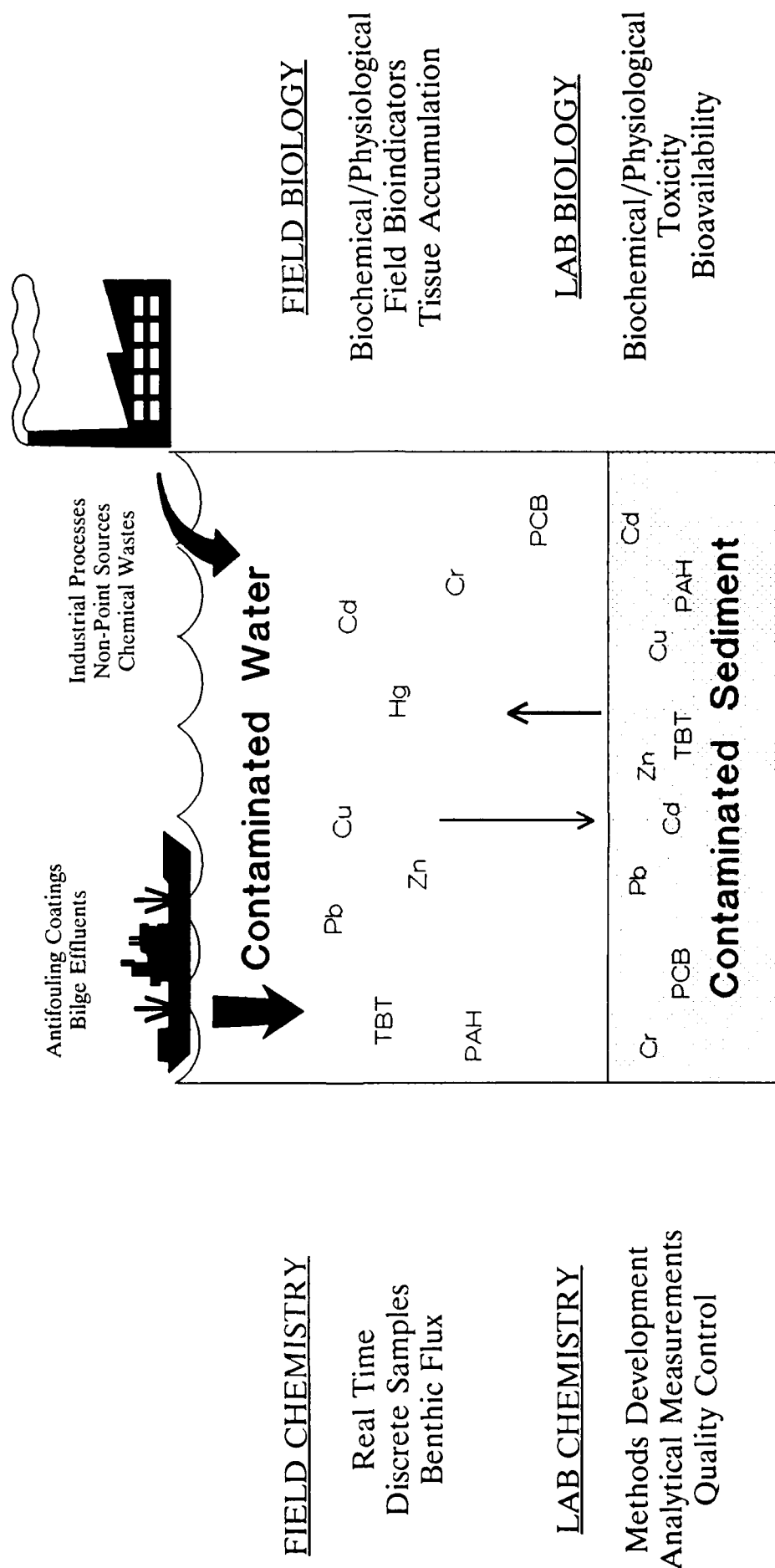


Figure 1. Problem and approaches to assess contaminated sediments at Navy aquatic hazardous waste sites.

Environmental concerns and resulting public laws have led to the development of an Installation Restoration program for all Department of Defense activities. Although the emphasis of this program has been to clean up terrestrial sites which potentially threaten human health, identification and management of contaminated aquatic sediments are also serious problems for the Navy. Aquatic contamination is a significant portion of the total contamination and traditionally is more difficult to assess. In most cases where contaminated sediments have been suspected in Navy areas, chemical sampling has confirmed the potential for significant environmental impacts. The next step is far more difficult. Generally available techniques are inadequate to properly define the extent of contamination in the marine environment and accurately quantify environmental effects. Environmental science is relatively new with continually emerging technologies. Adding to the problem is the extremely transitory nature of the water column overlying contaminated sediment and the enigmatic chemical relationship between the concentration of contaminants in sediment and the concentration in water. This is confounded by attempts to predict environmental effects on marine organisms. Further, once the degree of contamination has been quantified, it may be difficult to determine the most appropriate course of action. For example, "Cleaning up" the contaminated sediment by dredging can often cause more of an adverse impact on the marine environment than leaving the material in place.

The Navy needs the best possible measurement tools to quantify the degree of contamination and to assist in assessing the most appropriate course of action during the remedial investigation. Contaminated sediments have always been a potential problem for the Navy that will only increase with more facilities and deep-draft vessels. Regulatory requirements for environmental assessment of contaminated sediments is also increasing and environmental considerations have already impacted Navy operations in a variety of ways. The purpose of this paper is to outline an assessment philosophy that includes a critical evaluation of the scientific uncertainties in the process as well as some practical considerations in conducting meaningful risk assessments for contaminated marine sediments at Navy aquatic hazardous waste sites.

ASSESSMENT PHILOSOPHY

The general scientific approach to evaluating environmental effects of contaminated sediments in risk assessments is an ecological problem that can best be solved by integrated approaches (Figure 1). The potential problem must be considered as part of the larger ecological framework and this makes the situation much more complex. There are three basic questions to be answered. First, are contaminated sediments the source of contaminants in the water column? Second, are these contaminants bioavailable to marine organisms? Third, are the accumulated contaminants having an adverse effect on marine organisms? Answering these types of questions through risk assessments require the following integrated approaches:

1) **WATER and SEDIMENT.** Since contaminated sediments at Naval installations are part of the entire ecosystem, it would be naive to assume that one could predict environmental impact by measuring the chemical constituents of sediments. Although it is generally assumed that contaminated sediments will have a detrimental effect on the marine environment, several studies have shown that many chemical contaminants in sediments are not generally bioavailable to marine organisms. Conversely, it is possible to have sediments that appear uncontaminated which could have an effect on the marine environment. Recent work at an aquatic hazardous waste site at NAS North Island has shown elevated levels of petroleum hydrocarbons in both sediments and transplanted mussels. However, it is believed that the petroleum hydrocarbons accumulated by our test animals are actually coming from an adjacent fuel facility. This has significant ramifications for the Installation Restoration assessment program. It is essential to demonstrate a cause-and-effect relationship between contaminants measured in the sediment and those measured in the water column. The methods described in "Technical Approach" will be used to address this issue.

2) **CHEMISTRY and BIOLOGY.** In 1977 the Environmental Protection Agency and the Army Corps of Engineers issued requirements for ecological evaluations of dredged material that emphasized laboratory bioassays instead of bulk chemical analysis. Since then, other regulatory agencies have also shifted emphasis from chemical criteria to biological criteria. The rationale is that the ultimate effects will be on the biological community so that is where the measurements should be made. The presence of contaminants in sediments does not *a priori* indicate adverse biological effects. Another problem is that it is impossible to guarantee that chemical measurements have identified all the contaminants that could have a potential biological effect. Further, real-time chemical measurements in the water column have shown a substantial temporal and spatial variability in several contaminants that must be accounted for when explaining biological results. In the final analysis, integrated risk assessments of contaminated sediment must have complementary chemical and biological measurements to help explain potential environmental impact.

3) **LABORATORY and FIELD.** Inherent differences between biological responses in the laboratory and the field include differences in test species, test water and test conditions. The biological problem is defining the genetic stock and environmental conditioning of test animals while the chemical problem is addressing bioavailability and defining the exposure dose. It is generally acknowledged that laboratory tests have a very high degree of experimental control and a very low degree of environmental realism. The opposite is true for field studies (Figure 2). In many cases laboratory tests are conducted with unstabilized test animals maintained under inadequate environmental and nutritive conditions. Animal health is usually not quantified at the start or end of the test. In general, bioassays do not simulate the natural environment very well and their use by regulators as a predictive tool is extremely limited. Yet, most regulatory criteria are based on laboratory bioassays and once the criteria have been established, research often stops due to funding constraints. Conversely, field tests are much

PREDICTING ENVIRONMENTAL IMPACT

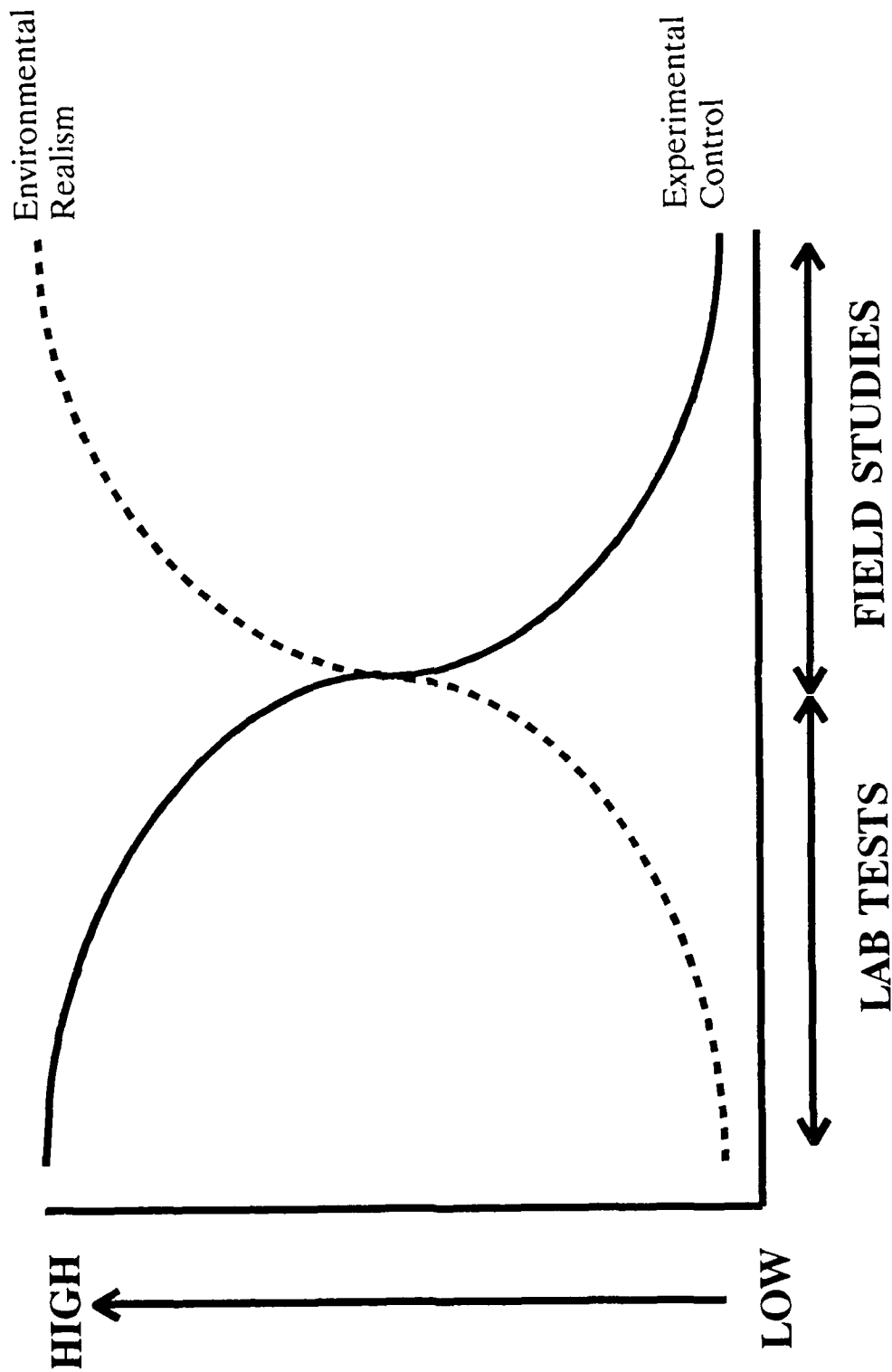


Figure 2. Lab tests generally have a high degree of experimental control and a very low degree of environmental realism while field studies have a very high degree of environmental realism and a very low degree of experimental control. This adds uncertainty to predicting environmental impact.

more realistic but there are so many variables it is difficult to use these data to establish regulatory criteria either. The Navy must utilize the advantages of environmental realism from the field and experimental control in the laboratory to provide meaningful and integrated risk assessments with the following technical approach.

TECHNICAL APPROACH

One goal of environmental research programs at Navy laboratories is to provide a real-time multidimensional approach for assessing the chemical and biological implications of contaminants in marine sediments. It includes: 1) State-of-the-art chemical measurement techniques to quantify the degree and extent of marine sediment contamination, and 2) Sensitive biological measurement techniques to assess the impact of the contamination on marine organisms. These advanced methods should be used wherever possible to give the Navy an accurate representation of potential problems without overestimating or underestimating the potential for environmental impacts.

Chemical Analysis

1. Methods Development: The key to marine environmental measurements is the continued development of advanced chemical methods to quantify the amount of specific contaminants and the particular molecular species present in different environmental compartments. This includes sediment, water, and tissues. These measurements are essential to quantifying the fate of these contaminants within the ecosystem and predicting potential effects on marine organisms.
2. Real-Time Chemistry: It is also critical to define the temporal and spatial variability in contaminants in order to accurately predict potential toxic effects on marine organisms. Real-time chemistry refers to semi-continuous chemical measurements that reflects actual changes in the water column as they occur. Discrete sampling usually cannot provide these numbers in a cost-effective manner. Variability must be quantified to relate biological effects to actual exposure concentrations.
3. Benthic Flux: The innovative thrust of this chemical analysis approach for evaluating contaminated sediments is combining an automated analyzer to document temporal and spatial variability of metals in the water column with a benthic flux device for *in-situ* measurement of contaminant flux from the sediment into the interstitial water and the water column. These types of measurements are essential to determining whether biological effects are attributable to contaminants from sediments or other unidentified sources. This is crucial to the remedial investigation and development of remediation options for the Installation Restoration Program.

Biological Methods

1. Biochemical/Physiological Methods: Biochemical and physiological measurements of marine organisms in laboratory and field studies can be used as an indicator of stress on the population. They will be used to assess the seawater overlying the contaminated sediment as well as extracts from the sediment. In much the same way blood chemistry and respiratory measurements are used to detect illness in humans, biochemical and physiological measurements will be used to quantify stress in marine organisms. These internal changes occur in marine organisms under stress before other more obvious changes in the population.
2. Field Bioindicators: Biological indicators are selected organisms with easily measured responses that are used as surrogates of the biological community for stress measurements. They are more cost effective than community studies because community effects are difficult to understand or interpret. Appropriate bioindicators must be selected with caution. Reduced growth rates have also been shown to indicate stress attributable to contaminants. The innovative thrust of this particular biological approach to evaluating contaminated sediments is the combination of growth rate measurements and biochemical/physiological measurements with bioaccumulation measurements. This documents the extent of contamination and potential environmental effects.
3. Laboratory Bioassays: Specific laboratory experiments must be used to answer specific questions like the relationship between dose and response that cannot be adequately answered in the field. A key issue to be addressed is bioavailability of contaminants in sediments. In most cases the accumulation process and the significance of accumulation are poorly understood. Although field measurements provide more environmentally realistic answers, the degree of control necessary to address all pertinent questions is often not available. This is why integrated risk assessments should include both laboratory and field experiments.

PRACTICAL CONSIDERATIONS

There are certain misconceptions regarding the environmental significance of scientific measurements, the cost of those measurements and the relationship between those measurements and the regulatory community. Many environmental scientists have perpetuated those perceptions. For example, when submitting proposals it is customary to amplify the utility of the work and downplay the cost. There is also a tendency to cast the regulatory community in an adversarial role. Science is often abused and agencies misled when politics enters the risk assessment arena. However, it is the responsibility of scientists to document the limitations of their work. Therefore, although the first sections of this paper dealt with these "state-of-the-art" approaches with inferences that this would surely provide conclusive data, the limitations of all these approaches and their relationship to regulatory process should be addressed.

1. Scientific Limitations. Unfortunately, even state-of-the-art methods for environmental assessment cannot always provide the definitive answers sought by Navy environmental managers. Few definitive answers are available today or in the near future. There is a significant amount of scientific uncertainty in all environmental measurements and this uncertainty has fueled the controversy over potential environmental effects. It also leads to potential adversarial positions between the Navy and regulatory agencies over the evaluation of Navy aquatic hazardous waste sites. Poorly understood phenomena are frequently controversial. It is essential for the Navy to establish a scientifically defensible position, albeit inconclusive in certain situations, to reduce the potential for environmental controversy.

2. Funding Solutions. There also seems to be certain misconceptions among Navy engineers that since cost-effective methods are being used, these controversial answers will be cheap. There may even be some who believe that significant increases in funding will solve all environmental problems. Due to current scientific limitations, this is not the case. Environmental solutions are often more complex than engineering solutions. Concerned environmental managers may wonder why they should proceed with such costly and ill-defined information. Scientists, regulators and engineers are together in the environmental process whether they like it or not. Expensive state-of-the-art answers are the best that science can provide and the Navy must use these in environmental management.

3. Navy Positions. Beginning about 1980, the Navy attitude seemed to shift from fighting environmental compliance to capitulation. Neither approach is in the Navy's best interest. The Navy needs to establish a position on contaminated sediments at aquatic hazardous waste sites that is not only scientifically justifiable but politically viable. The scientific approaches have been outlined previously. Navy engineers should contact appropriate regulatory agencies as soon as possible to get them involved in the risk assessment process. Historically, regulators are much more receptive to suggestions early in the process rather than later. Both sides benefit from this approach and it ameliorates potentially adversarial positions. In the final analysis the regulators, engineers and consultants are all limited by a cursory understanding of contaminated sediments and their environmental significance. By working together and using the basic scientific approaches described here, many potential problems can be avoided.

CASE STUDIES OF ECOLOGICAL RISK ASSESSMENTS AT

NAS WHIDBEY ISLAND, WA AND NCBC DAVISVILLE, RI[#]

Robert K. Johnston^{1*}, Paul E. Woods², Gerald G. Pesch³,
and Wayne R. Munns, Jr.⁴

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ABSTRACT

The current status of ecological risk assessments being conducted for hazardous waste disposal sites located at Naval Air Station (NAS) Whidbey Island, WA, and Naval Construction Battalion Center (NCBC) Davisville, RI, are reported. The sites being investigated at NAS Whidbey Island include a fire fighting training area, a pesticide disposal site, and the air station's runway ditches. Toxicological impacts are being evaluated using starling (*Sturnus vulgaris*) nesting and reproductive biology as an indication of contaminant migration into the food chain. Toxicological impacts are also being monitored in small mammals, hawks, owls, herons, and selected prey species located on or near the hazardous waste disposal sites.

The sites being investigated at NCBC Davisville are a landfill and disposal site located directly adjacent to Allen Harbor and Narragansett Bay. Ecological impacts are being assessed by characterizing the sediment and water quality in Allen Harbor and nearby Narragansett Bay and evaluating the toxicological impact on quahog clams (*Mercenaria mercenaria*), soft shell clams (*Mya arenaria*), oysters (*Crassostrea virginica*), mussels (*Mytilus edulis*), and amphipods (*Ampelisca abdita*). In addition, biomarker assays are being conducted to evaluate the mutagenic potential of sediments collected from Allen Harbor and the surrounding Narragansett Bay.

The sampling designs and rationale being used for the investigations at NCBC Davisville and NAS Whidbey Island are presented. The procedures for incorporating the toxicology data into the remedial investigation and feasibility study process, and supporting the development of risk management plans are also discussed.

[#] Paper presented at the Environmental Research and Development (R&D) Technical Workshop, 7-9 November 1990, San Diego, CA

INTRODUCTION

Remedial actions conducted at hazardous waste disposal sites must meet cleanup levels that will insure protection of human health and the environment (Comprehensive Environmental Response Compensation and Liability Act, 42 U.S.C. 9604 (a)). The development and application of biological assessment methods to determine the impact of disposal sites on the environment is the focus of the research described in this paper. Biological assessment techniques are required to provide the data necessary to conduct ecological risk assessments of the impact of disposal sites on the surrounding environment. Ecological risk assessment involves quantitative estimation of the likelihood of adverse ecological impact resulting from exposure to toxic substances (Beck and Conner 1987). Ecological risk assessments are accomplished by collecting data relating exposure levels to biological effects (Gentile et al. 1989) and provide a framework for interpreting and predicting potential adverse impacts (Phelps and Beck 1989). With appropriate assessment techniques it will be possible to obtain direct measures of environmental health and implement monitoring programs to assess and verify the environmental risks of hazardous waste disposal sites.

Demonstrations of biological assessments aimed at assessing the ecological risk of hazardous waste disposal sites are currently being conducted at the Naval Air Station (NAS) Whidbey Island, Washington, and the Naval Construction Battalion Center (NCBC) Davisville, Rhode Island. At NAS Whidbey Island the impacts of three disposal sites on wildlife and the surrounding environment are being evaluated. The sites being investigated are a former fire school, a pesticide disposal area and the runway ditches. At NCBC Davisville a landfill and disposal area located directly adjacent to Allen Harbor in Narragansett Bay are being investigated to determine the impact of leachate from the disposal sites on shellfish and sediment quality of Narragansett Bay.

The toxicological assessment for NAS Whidbey Island is being performed by The Institute of Wildlife and Environmental Toxicology (TIWET), from Clemson University, Clemson, SC, in cooperation with Huxley College of Environmental Studies, Western Washington University, Bellingham, WA. The risk assessment at NCBC Davisville is being executed under a cooperative research agreement between the Naval Ocean Systems Center, San Diego, CA, and the Environmental Protection Agency Environmental Research Laboratory, Narragansett, RI, with the cooperation and assistance of the Narragansett Bay Project, Providence, RI, the Food and Drug Administration Northeast Technical Services Unit, Davisville, RI, and the University of Rhode Island Graduate School of Oceanography, Narragansett, RI.

RELATIONSHIP OF TOXICITY ASSESSMENTS TO THE REMEDIAL INVESTIGATION PROCESS

The relationship of toxicity assessments to the remedial investigation and feasibility study (RI/FS) process at hazardous waste sites is outlined in Figure 1 (Johnston and Lapota 1989, Lapota et al. 1989). The RI/FS can consist of three phases: information gathering, verification and evaluation of site conditions, and, if required, remediation. Onsite investigations carried out in accordance with EPA Superfund Guidance (EPA 1986) are primarily concerned with quantifying site contamination levels, and relating those levels to potential health risks. The objective of the toxicology studies described in this paper is to determine the toxicological impact of the disposal site on the surrounding environment.

During the toxicology study data are collected to determine exposure levels and the consequences of exposure to receptor organisms. The toxicology study seeks to answer the question: Is there a toxicological impact? If the answer is no, the goal for the second phase of the toxicology study is to confirm the nonimpact and provide monitoring data necessary for site closure. However, if significant toxicological impacts are detected then the goal of the second phase will be to provide a detailed evaluation of the impact. This information will be necessary to determine what corrective action is required and evaluate toxicity reduction during feasibility studies of remedial options. If remediation is required, the toxicity data will be used to measure the effectiveness of cleanup and help determine when remediation can be terminated. Interaction between the toxicology and onsite investigations is required to assure that the data collected are complementary and comparable. Obtaining complementary and comparable data can be accomplished by intercalibrating analytical methods to be used (A in Figure 1), providing significant information feedback to facilitate an accurate description of toxicological effects and contaminant source and loading (B and C in Figure 1), and the selection of appropriate cleanup levels (D in Figure 1) (Johnston and Lapota 1989, Lapota et al. 1989).

DESCRIPTIONS OF SITE INVESTIGATIONS

Toxicology Demonstration Project at NAS Whidbey Island, WA

The Naval Air Station (NAS) Whidbey Island has been proposed for addition to the National Priorities List (NPL). Twenty eight sites have been recommended for investigation as part of the Navy's Installation Restoration Program (NEESA 1984a, SCS Engineers 1987). NAS Whidbey Island is located in a fairly pristine area of the Puget Sound and provides habitat for a variety of game birds, water fowl, and mammals. The endangered peregrine falcon and the threatened bald eagle have been sighted in areas on NAS Whidbey Island and a great blue heron colony is also located on the air station. Beaches and bays around NAS

RI/FS Process

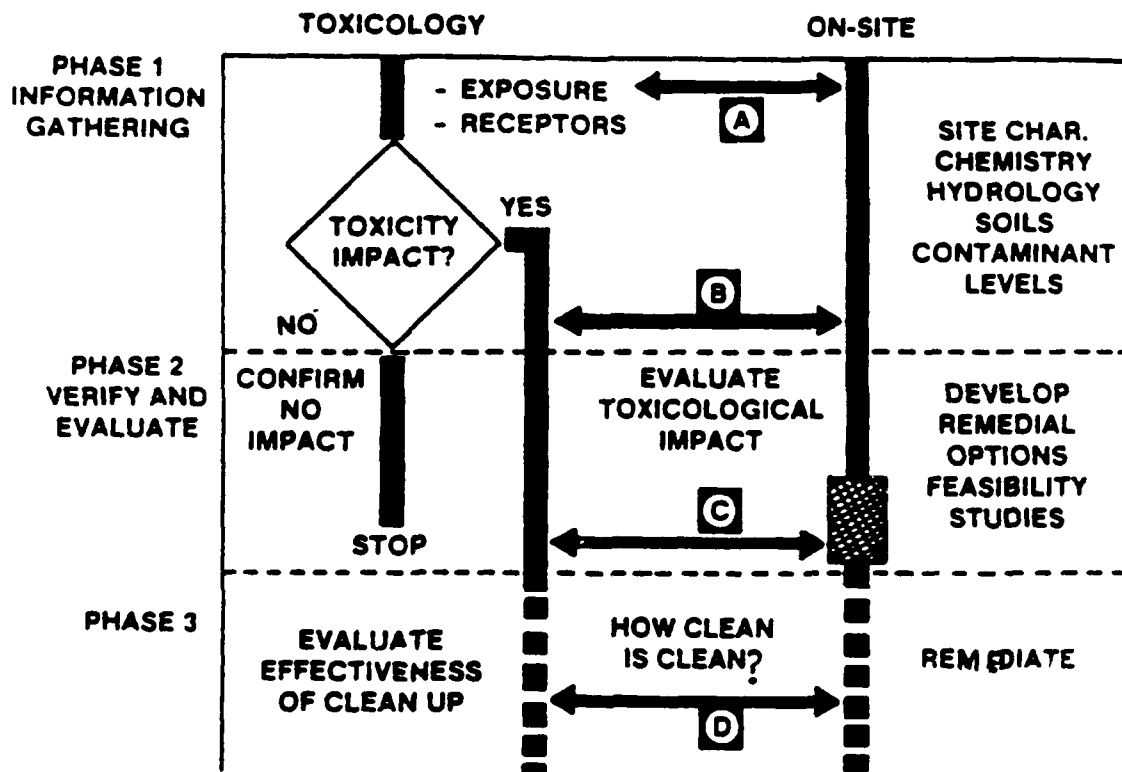


Figure 1. Integration of toxicological assessment information into the Remedial Investigation and Feasibility Study (RI/FS) process (Johnston and Lapota 1989).

Whidbey Island are popular fishing and shellfish gathering areas. Past disposal practices may have contaminated lowland areas and the accumulation of persistent and biomagnifying contaminants could affect higher order predators and humans (NEESA 1984a). The primary purpose of the toxicological investigation is to determine if contaminants from disposal sites are significantly impacting wildlife and degrading environmental quality. The study will also demonstrate the effectiveness of in situ toxicological assessment techniques.

The sites selected for toxicological assessment are the Clover Valley Fire School, the Pesticide Disposal Area, and the Runway Ditches. These sites were selected for evaluation based on the possible presence of surface contamination and concern for migration of contaminants into the food chain (TIWET 1989).

The contaminants of concern at the Clover Valley Fire School include aromatic hydrocarbons and heavy metals released when waste oils were burned during fire fighting training exercises conducted between 1951 and 1966. An estimated 50,000 to 75,000 gallons of waste fuels contaminated with solvents, oils, and paint strippers were burned and disposed of at the fire school (NEESA 1984a). The Pesticide Disposal Area was used for rinsing equipment used during insecticide and herbicide applications. During the period between 1973 and 1983 a variety of pesticides, including 2,4D, malathion, and chlordane were disposed in a dry well located at the site (NEESA 1984a). The network of ditches around the air station's runways comprises the third site being investigated. The ditches run south and east of the runway and collect runoff from the flight line as well as from storm sewers near the hangar operations area, and eventually discharge into a marshy area around Duqualla Bay in the Puget Sound. Since 1965 jet fuels, waste cleaning solvents, caustic agents, motor oils, paints, and paint thinners have been periodically spilled around the air station's flight line and hangars and washed into the runway ditches (NEESA 1984).

The approach of the toxicological investigation of impacts from the disposal sites is designed to assess the extent and nature of possible contamination using free-living species residing on the sites of interest (TIWET 1989). Assessments of reproductive success and biochemical function are being made between populations sampled on the disposal sites and populations sampled from sites which have no known history of contamination. To accomplish this goal several parallel lines of inquiry among different animal species are being conducted. Additionally, organic chemical analyses of soil and invertebrates will be conducted to determine which contaminants are likely to be incorporated into the food chain.

Food chains are frequent pathways for environmental contaminants to penetrate into biological communities. Numerous studies from both agricultural (Anderson et al. 1982, Telford et al. 1982, Stoewsand et al. 1986) and natural settings (Cooke 1973, Rudd et al. 1981) have demonstrated extensive contamination

from anthropogenic sources.

A representation of a simplified food web, emphasizing the monitored species is shown in Figure 2. This generalized figure shows the complexity of the ecosystem at NAS Whidbey Island. Plants may accumulate soil contaminants and expose herbivorous insects (e.g., grasshoppers) and mammals (e.g., voles), and omnivorous mammals (e.g., mice), which in turn will expose animals feeding on higher levels of the food web. The primary route of exposure is being assessed with the European starling (Sturnus vulgaris). Starlings feed on carnivorous insects, herbaceous insects, grubs, earthworms, and larvae of various insects which may be living in close association with the soil. Many of the latter organisms are particularly important as detritivore-decomposer organisms. Plant materials become important food sources on a seasonal basis (Feare 1984). Consequently, starlings may be exposed to a wide array of contaminants in the grazing (e.g., grasshoppers, caterpillars) and detritivore food chains (e.g., earthworms). Other possible routes of exposure are being assessed by evaluating toxicological impacts on small mammals, primarily mice, voles and shrews, and birds of prey, such as the northern harrier (Circus cyaneus) and great blue heron (Ardea herodias).

The primary investigatory tool used at the Clover Valley Fire School and the Pesticide Disposal Area is the enhanced avian bioassay. The starling presents numerous advantages as an indicator wildlife species. In general, birds possess characteristics which tend to maximize their exposure to environmental contaminants. First, birds possess high metabolic rates with attendant elevated food intake rates. Secondly, their complex air sac respiration system (Fedde 1976) is structurally unique and maximizes inhalation exposure. Finally, birds frequently dust bathe and use surface water for bathing. Behaviors such as these would likely result in increased dermal exposures through contact with contaminated soils and surface water.

The starling is an introduced species which is abundant throughout most of North America (Robbins et al. 1983) and is frequently considered a pest. Starlings are easily induced to nest in artificial nest boxes (Figure 3) facilitating experimental manipulations and assuring investigators of a viable experimental population to work with (Robinson et al. 1988). Starlings usually feed within 200 m of their nest site (Feare 1984) and frequently feed closer if resources allow (Tinbergen 1981). Thus starlings should forage a substantial amount of time within the confines of the study sites. At nesting time the parents may have difficulty maintaining a positive energy balance when striving to feed their offspring. At this crucial juncture starlings are representative of most songbirds. Starlings have proven to be excellent research subjects in field studies exploring the effect of organophosphorus pesticides on wildlife (Robinson et al. 1988). The USEPA has recently issued a guidance document for starling nest box studies for use in determining

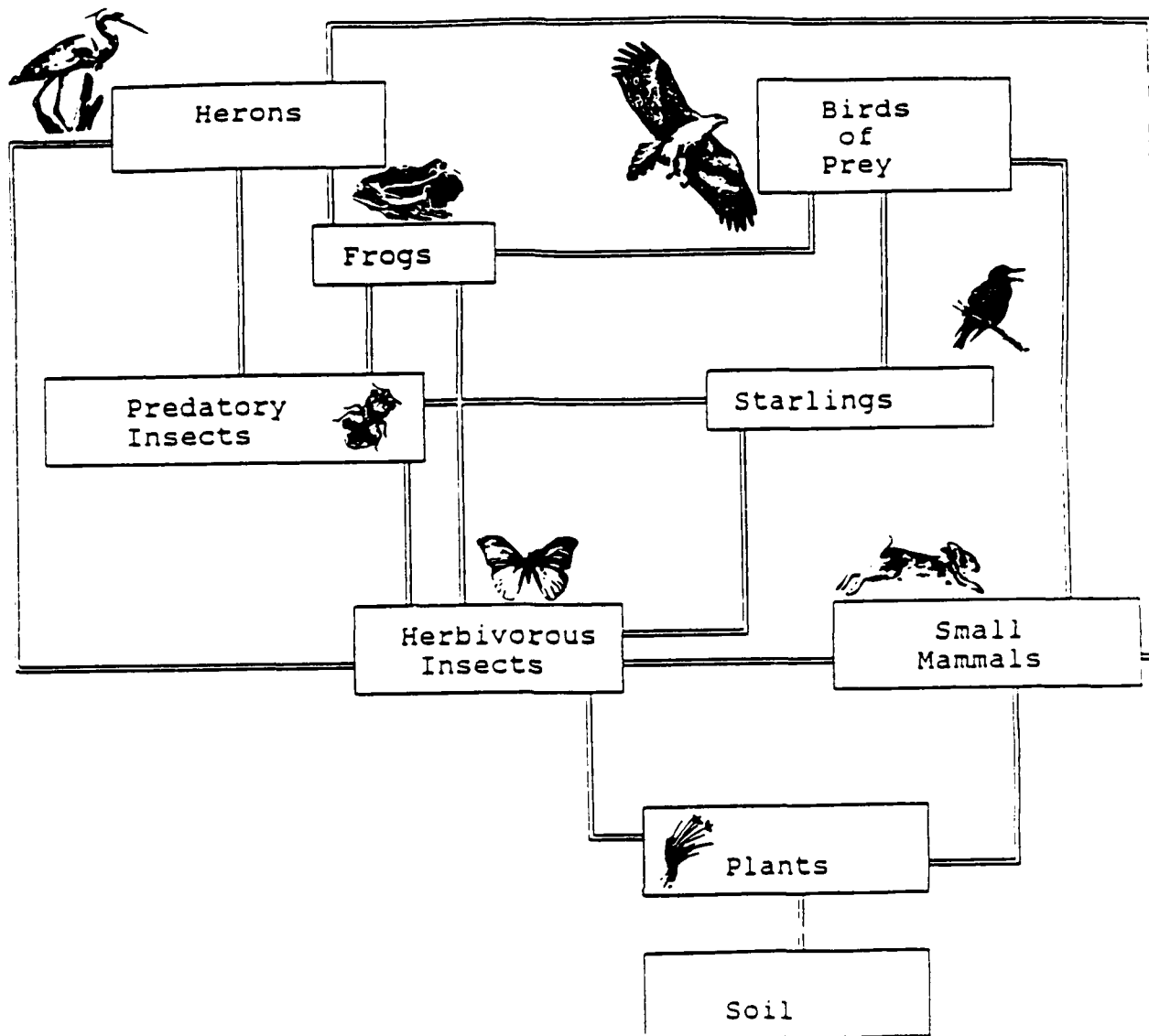


Figure 2. A diagram illustrating a simplified food web for NAS Whidbey Island. The soil compartment represents both the physical components of the soil and decomposer organisms such as earthworms. This extremely important component connects with virtually every other compartment. The small mammal compartment includes both herbivorous (e.g., voles) and carnivorous species (e.g., shrews). The birds of prey compartment contains both diurnal and nocturnal species (TIWET 1989).

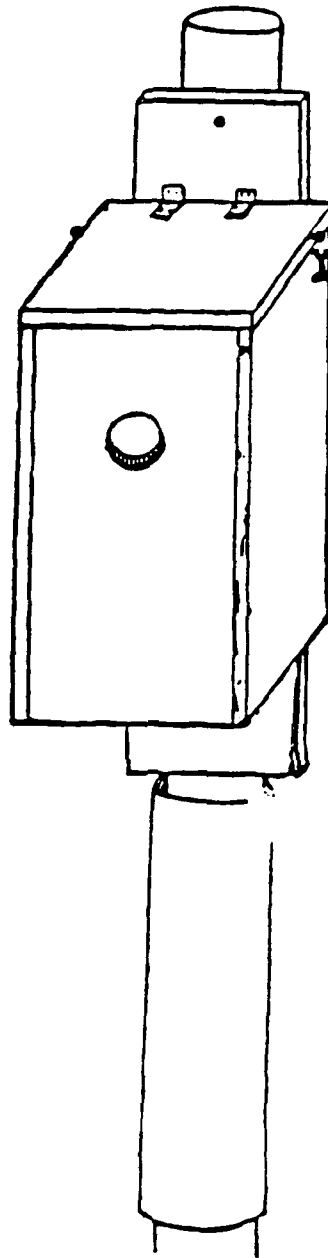


Figure 3. Nest box design used in the enhanced starling bioassay (IWT 1988).

effects of pesticides on nontarget organisms in agricultural settings (IWT 1989). The study at NAS Whidbey Island is the first use of the starling bioassay for assessing impacts of hazardous waste disposal sites.

Starling nest boxes have been erected at the Clover Valley Fire School and the Pesticide Disposal Area (Figure 4). An exposure gradient was created by placing the nest boxes in transects radiating out from the focal point of contamination in concentric rings. Starlings defend a territory which is normally less than 0.5 m in diameter around the nest hole (Kessel 1957), but on occasion the defended area extends to 10.0 m (Feare 1984), especially just before egg-laying. Therefore nest boxes on all sites were spaced a minimum of 12 meters apart (Figure 4) to reduce the possibility of intraspecific conflict. Statistical analyses of ecological endpoints such as clutch size, hatching success and fledging success will be conducted to determine differences along the exposure transects and differences between the disposal sites and three reference sites located in Western Washington (TIWET 1989).

Based on past studies (Whitten et al. 1989, Robinson 1988, Brewer et al. 1988, 1989) up to 80% occupancy can be expected, with an average of four nestlings per box. During the first year of the study high occupancy was not achieved because nest boxes were erected too late in the season. In order to determine what food items adults starlings are feeding to nestlings, approximately 10% of the active boxes on each site were sampled for invertebrate prey items by taking crop samples. Crop sampling involves placing a restrictive ligature about the throat of the nestling. The ligature is tight enough to prevent swallowing but loose enough to avoid injuring the nestling. Ligatures are left in place for a short period of time (maximum one hour) and the food items are collected and analyzed for species composition and tissue burdens of contaminants in the juveniles' diet. Since post-fledging survival is key to parental reproductive success and the long-term survival of songbird populations, a subsample of juvenile hatchlings were banded before fledging. If there is no effect of the study sites on fledging survival and subsequent behavior, then return rates should be equal to those at the reference sites.

Small mammals have also been shown to be excellent indicator organisms in field studies of various contaminants (e.g., Anderson and Barrett 1982, Maly and Barrett 1984, Barrett 1988, Hall et al. 1989). Small mammals such as mice and shrews, live on the soil surface and some species burrow within the litter and upper levels of the soil itself, thereby maximizing chances of dermal exposure. Their diet is varied, and ranges from nearly strict herbivory (e.g., some voles, Microtus spp.) to an omnivorous (e.g., deer mice, Peromyscus maniculatus) and completely carnivorous condition (e.g., the shrews, Soricidae). Studies of small mammals were initiated on all three sites during spring and summer of 1989.

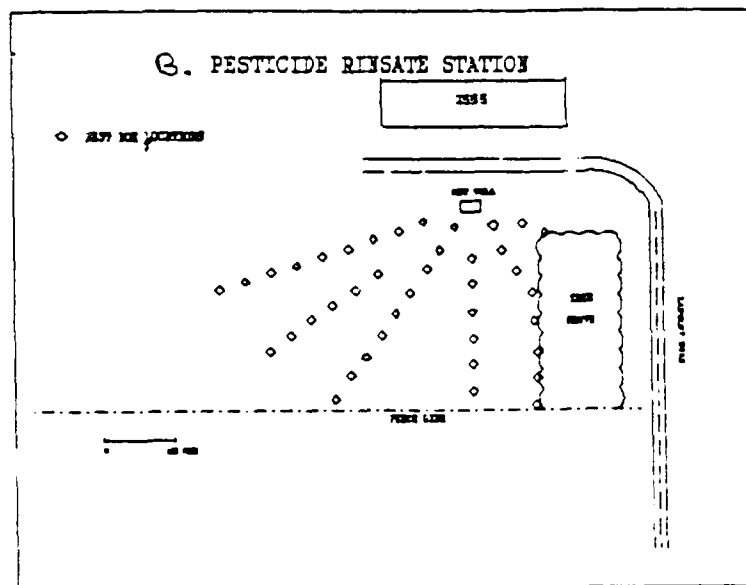
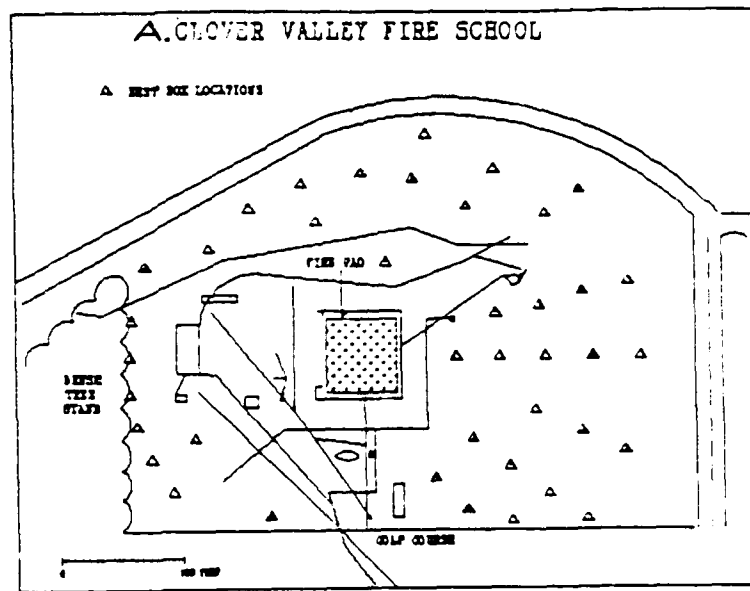


Figure 4. A diagram illustrating the placement of starling nest boxes at the Clover Valley Fire School (A) and the Pesticide Disposal Area (B) (TIWET 1989).

Raptors, by virtue of feeding on higher trophic levels may be indicators of contaminants which move up through the food chain (Moriarity and Walker 1987). Red-tailed hawks (Buteo jamaicensis), great-horned owls (Bubo virginianus), western screech owls (Otus kennicottii), and northern harriers (Circus cyaneus) are being evaluated for radio-tracking to determine their feeding and foraging ranges. Owls and raptors feed quite extensively on small mammals and occasionally on songbirds. The pathway of contaminants from soil to vegetation to herbivore to carnivore is being evaluated by monitoring biochemical responses in the raptors.

Hérons are similar to raptors in their position on the food chain. Herons consume fish, amphibians, and small rodents. Observations on heron foraging will be conducted to determine where adults are feeding and prey items. The great blue heron colony will be visited twice to acquire nondestructive samples (e.g. fecal matter, discarded eggshells, and dead nestlings that have fallen from the nest). Methods using the chorio-allantoic membrane (CAM) of discarded eggshells has proven to be a useful technique in assessing the chemical burden of heron chicks in a nondestructive bioassay (Norman et al. 1989). Data obtained from the heron colony at NAS Whidbey Island will be compared to data previously collected from other heron colonies in the Puget Sound. If preliminary investigations indicate abnormal concentrations of contaminants, more in-depth studies will be planned for ensuing years. If no indications of impact are determined, a monitoring program will be established to verify on-going health of the heron colony.

The use of wildlife populations for the monitoring of chemical contaminant availability in the environment is enhanced by the evaluation of "marker enzymes" which respond to the presence of contaminants in the body (Lee et al. 1980, Payne et al. 1987, Rattner et al. 1989). These enzymes are found in the blood, liver, and brain of most species (Walker 1978). Marker enzyme response to contaminants can provide a measurable toxicological endpoint. A biochemical response, once traced back to an offending contaminant, can then serve as an indicator of toxic insult as well as a method to monitor mitigation attempts on the contaminated site. Biochemical evaluation of the wildlife on NAS Whidbey Island will entail the measurement of several bioindicator enzymes from the liver, brain, and plasma tissues of starlings, mice, and amphibians. In addition, tissue burdens of contaminants of concern will be analyzed to obtain a complete picture of exposure and toxicological effects. The complete sampling plan and protocols for the toxicology study at NAS Whidbey Island are documented in the work plan (TIWET 1989).

Risk Assessment Pilot Project at NCBC Davisville, RI

Allen Harbor, located in Narragansett Bay at the Naval Construction Battalion Center (NCBC) Davisville, RI, has been closed for shellfishing by the Rhode Island Department of Environmental Management due to suspected hazardous waste contamination from a landfill and disposal area adjacent to the harbor. The landfill, about 15 acres in size, received a wide variety of wastes including sewage sludge, solvents and paints, chromic acid, PCB contaminated waste oils, preservatives, basting grit, and other municipal and industrial wastes generated at NCBC Davisville and NAS Quonset Point between 1946 to 1972 (NEESA 1984b). Another site, located on Calf Pasture Point, was used for disposal of calcium hypochlorite, decontaminating solution, and chloride (NEESA 1984b). Previous analyses of sediment and bivalve tissues from Allen Harbor have shown increased levels of heavy metals and organics (TRC Environmental Consultants, Inc. 1986). The purpose of the risk assessment pilot project is to determine the impact of the disposal sites on environmental quality and shellfish resources in Allen Harbor and to develop and field validate ecological risk assessment methods.

During the first phase of the risk assessment consists of three components: waste site characterization, exposure assessment, and effects assessment. The site characterization portion of the study centers primarily on identification of chemicals residing in the disposal sites (TRC Inc 1988). The exposure assessment focuses on quantification of contaminant levels in the sediment and water column of Allen Harbor and reference areas in Narragansett Bay (EPA-ERL 1989a). The biological effects assessment evaluates toxicity responses of selected organisms, determines physiological and histological conditions of shellfish, and examines chemical bioaccumulation in shellfish tissues (EPA-ERL 1989a).

The primary responsibility for characterizing the Allen Harbor landfill resides with TRC Inc (TRC Inc 1988). Sample splits obtained from groundwater, visible seeps on the face of the landfill, and sediment samples adjacent to the face of the landfill were obtained for analysis by both Environmental Protection Agency Environmental Research Laboratory (EPA-ERL) and TRC Inc. The intercalibration exercise between EPA-ERL and TRC Inc ensures a good description of potential contaminant fluxes into Allen Harbor, accomplishes a quality assurance and quality control (QA/QC) check between EPA-ERL and TRC Inc, and assures that the two data sets will be complementary and comparable. In addition, the Food and Drug Administration Northeast Technical Services Unit (FDA-NETSU) and the University of Rhode Island Graduate School of Oceanography (URI-GSO) are also participating in the intercalibration procedure.

The degree of exposure to resident biota to contaminants from the Allen Harbor landfill is being identified by a qualitative and quantitative description of the contaminants in

sediments and seawater. The approach for sediment characterization consists of collection and analysis of an extensive grid of samples within Allen Harbor (Figure 5) and in reference stations in Narragansett Bay (Figure 6). One-gallon scoop samples were collected intertidally at four locations each within Allen Harbor, Marsh Point (MP in Figure 6), and at two locations at Coggeshell Cove (CC in Figure 6) on Prudence Island. Soft shell clams (*Mya arenaria*) were also collected at these locations.

Subtidal sediments were collected on a grid of eleven stations within Allen Harbor, at seven stations along a "T" transect out of Allen Harbor (Figure 5) and at Mount View (MV), Greenwich Bay (GB), North Jamestown (NJ), and Potter Cove (PC) (Figure 6). A Smith-McIntyre grab sampler was used to obtain five grabs per station in Allen Harbor and vicinity (Figure 5). The top 2 cm of sediment was saved from each grab for subsequent analysis. The four stations representing mid-bay conditions (Figure 6) were sampled using five replicate grabs per five locations per station for a total of twenty five grabs per station. This scheme ensured comparability of data for statistical purposes.

Additional subtidal sediments were obtained at five selected stations within Allen Harbor by gravity coring to a depth of 30 cm, the estimated depth of disturbance due to shellfishing activity. Subsamples were taken from these cores at three depths (top, middle and bottom), and were composited by depth for subsequent analysis. To reduce the number of sample analyses, a subset of both intertidal and subtidal stations were selected for initial chemical determinations. If these results indicate the need for more detailed analysis the archived samples are available for examination. Since all sample were obtained in a single collection, comparability of results will be maintained. In addition, this method of sampling guarantees available material for other purposes. Aliquots from each of five replicate grabs were composited (1 gal total) for each of the Allen Harbor and mid-bay stations, thus reducing the number of chemical analyses needed without sacrificing the ability to detect strong chemical signals.

Chemical analyses were conducted for a "working list" (Table 1) of contaminants developed based on previously identified problem compound in marine environments, existing information on the disposal sites, and information generated by the extensive analytical screen conducted on a preliminary subset of samples. In addition to the analyses identified in Table 1, sediment and tissue samples (from Allen Harbor and from MV) were analyzed for organotin compounds by the Naval Ocean Systems Center (NOSC).

Water column samples were collected in Allen Harbor and at the MV station. Analysis of these samples was related to the analysis of seeps on the face of the landfill. Timing of sampling was scheduled so that samples were collected during

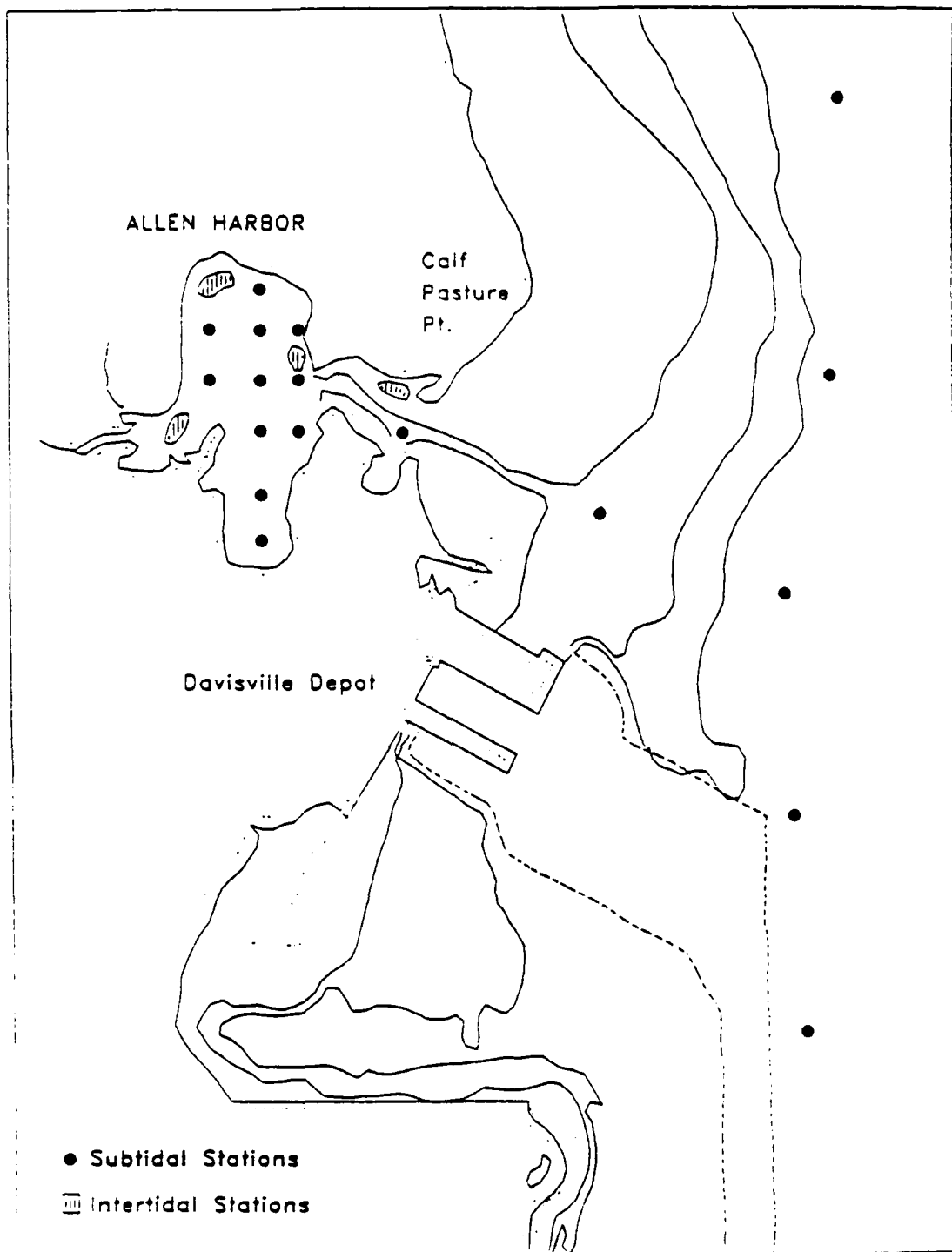


Figure 5. Station locations for characterizing sediments and shellfish in Allen Harbor and nearby Narragansett Bay (EPA-ERL 1989).

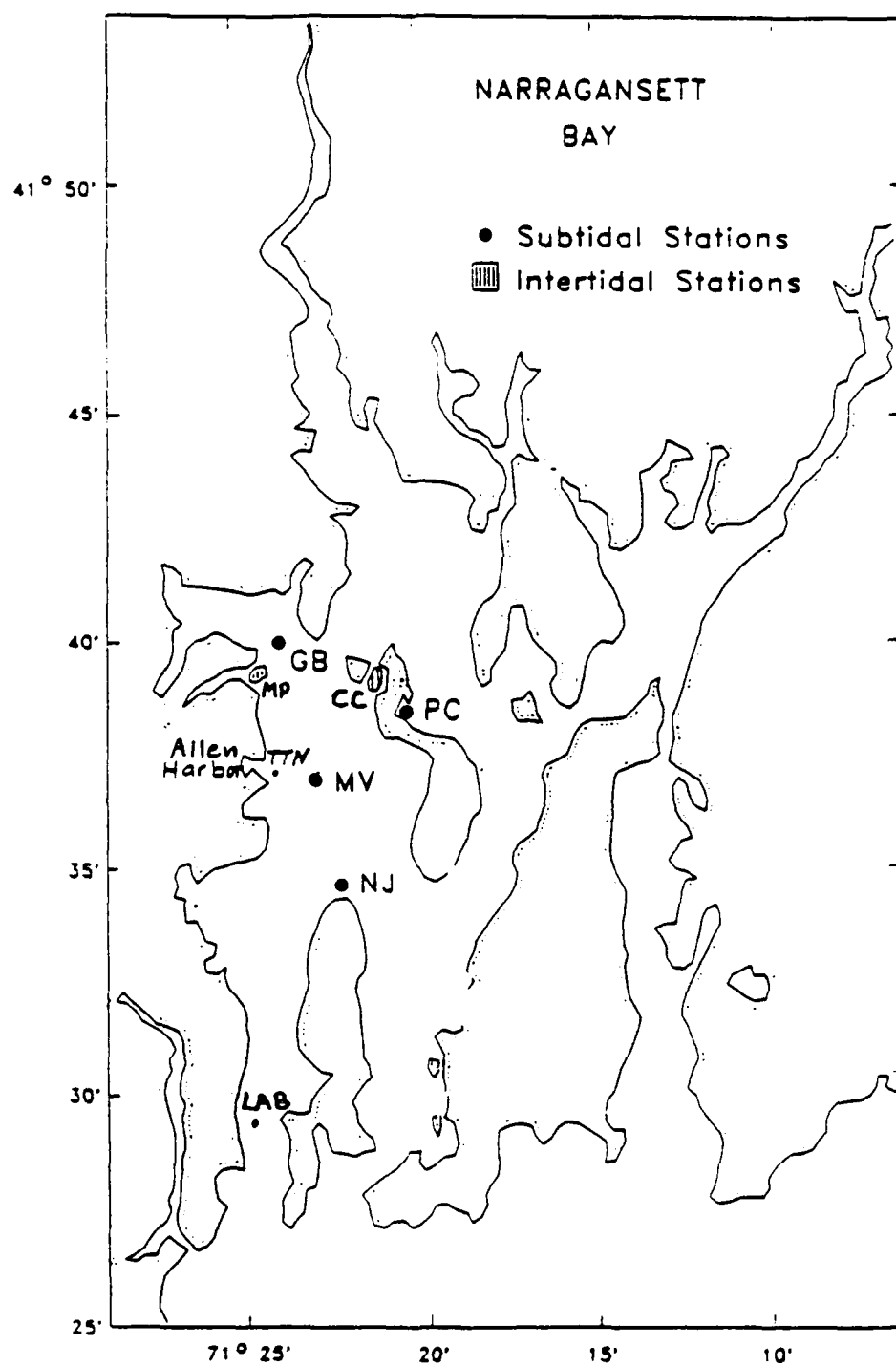


Figure 6. Reference stations locations for characterizing sediments and shellfish in Narragansett Bay (EPA-ERL 1989).

Table 1. Compounds known to cause problems in marine environments and therefore, routinely analyzed at the U.S. Environmental Research Laboratory at Narragansett, R.I.

Parameter	Matrix	Units ^{***}	Detection Limits	Method	Reference	Maximum Holding Time
Volatiles	Sediment tissue seawater	PPB		Purge & Trap GC/MS	**URI SOP's	2 Weeks
Pesticides	Sediment tissue seawater	NG/G NG/G NG/L	0.6 0.6 0.3	Extraction/ GC-ECD	*EPA SOP's	Prior to extraction indefinite if frozen (sediments and organisms) or refrigerated (water)
F-1 (PCBs)	Sediment tissue seawater	NG/G NG/G NG/L	2 2 1	Extraction/ GC-ECD	*EPA SOP's	After extraction indefinite if stored in tightly sealed vials with maximum amount of solvent in vial. Must be stored in dark refridgerator.
F-2 (aromatic)	Sediment tissue seawater	NG/G NG/G NG/L	0.6 0.6 0.3	Extraction/ GC-MS	*EPA SOP's	
F-3 (more-polar)	Sediment tissue seawater	NG/G NG/G NG/L		Extraction/ GC-FID	*EPA SOP's	
Trace Metals						
Cr, Cu Pb, Ni, Ag	Sediment tissue seawater	$\mu\text{g/g}$ $\mu\text{g/g}$ $\mu\text{g/L}$	1-3 0.5-1.5 0.5-1.0	ICP ICP Graphite AA	*EPA SOP's	
Cd	Sediment tissue seawater	$\mu\text{g/g}$ $\mu\text{g/g}$ $\mu\text{g/L}$	1.0 0.5 0.1	ICP ICP Graphite AA	*EPA SOP's	6 months after extraction
Hg	Sediment tissue seawater	$\mu\text{g/g}$ $\mu\text{g/g}$ $\mu\text{g/L}$	0.1 0.05 0.5	Cold vapor AA Cold vapor AA Cold vapor AA	*EPA SOP's	*EPA SOP's referenced in appendix 2
Zn	Sediment tissue seawater	$\mu\text{g/g}$ $\mu\text{g/g}$ $\mu\text{g/L}$	0.5 0.3 0.05	ICP ICP Graphite AA	*EPA SOP's	**Method listed in section 12
Arsenic	Sediment tissue	$\mu\text{g/g}$ $\mu\text{g/g}$	4 2	ICP ICP	*EPA SOP's	***Sed and tissue on dry wt. basis

"dry" and "wet" periods to identify whether there was a contaminant plume in Allen Harbor. Bacteriological indicators were measured by FDA-NETSU and volatile organics (VOCs) were quantified by URI-GSO.

The biological effects assessment portion of the study included toxicity response demonstrations, measurements of physiological and histological condition of bivalves, and quantification of chemical bioaccumulation in shellfish tissues. Shellfish were emphasized because of their ecological and commercial importance in Allen Harbor and Narragansett Bay. Approximately fifty animals of either quahogs (Mercenaria mercenaria) at subtidal stations or soft shell clams (Mya arenaria) at intertidal stations were collected at each station. Where present, oysters (Crassostrea virginica) were also collected. These samples were used to estimate resource density and condition indices. A subset of samples were processed for chemical analysis of tissue residues and to evaluate health via histopathological observations. The remaining samples were archived for future chemical analysis as required. Past experience has shown that tissue samples may be effectively preserved for many years by careful sealing and freezing (EPA-ERL 1989a).

Because of its dense distribution and economic importance the quahog is being used as the primary organism for evaluating benthic impacts. It is sedentary and filters large volumes of water, making it an ideal organism for evaluating environmental quality. Quahogs were sampled at all subtidal stations (Figures 5 and 6) during the fall of 1988 for observations of resource density and size distribution. At a subset of five stations corresponding to the subset of stations selected for chemical screening, five composites of five animals each were sampled for tissue burdens; twenty five animals were sampled at each station for condition index (shell length/whole weight/tissue wet weight ratios) and for histopathological examination. Quarterly sampling of quahogs will continue for a year at a subset of five stations for histological observations and determination of condition indices (EPA-ERL 1989a).

The soft shell clam is very common in intertidal areas of mid and upper Narragansett Bay including Allen Harbor, and its abundance supports an active recreational fishery. Samples of soft shell clams were obtained at the intertidal stations in Allen Harbor, Marsh Point, Coggeshell Cove and Calf Pasture Point. Observations similar to those for the quahog were made on the soft shell clam including analysis of tissue burdens, condition indices, and histopathology. The latter observations are being made quarterly for one year at three of the stations. Oysters were sampled once at two stations, Allen Harbor and CC. Similar observations are being made on the oysters.

Composite sediment samples from Allen Harbor and MV, GB, NJ, and PC, and selected sediments from the bay-wide Narragansett Bay Project survey were tested with the amphipod (Ampelisca abdita)

assay. A. abdita is a euryhaline benthic, tube-building, amphipod inhabiting fine intertidal and subtidal sediments. It is a filter feeder which ingests suspended particles and is a common food source for bottom fish. A. abdita has been shown to be sensitive to contaminated sediments and can be used to evaluate the relative toxicity of sediments (Redmond 1988). The amphipod assay was used to evaluate the relative toxicity of sediments collected in Allen Harbor and in reference areas of Narragansett Bay (EPA-ERL 1989a).

The physiological condition of water column organisms was examined using cages containing the blue mussel, Mytilus edulis (Figure 7). The mussels were collected from a clean reference site in Narragansett Bay and deployed in plastic mesh cages at four stations (four replicate cages/station, fifty animals per cage) for a spring and fall deployment period of twenty eight days. One station was located in Allen Harbor, and outside Allen Harbor in Narragansett Bay at TTN, MV, and LAB (Figure 6). Mussel cages were moored 1 m above the bottom. Clearance rate, assimilation efficiency, and respiration rate were determined for the mussels at the end of the deployment to calculate the scope for growth (SFG) index. The SFG index provides an integrated index of the mussels' physiological well-being and has been shown to highly correlated with environmental conditions and the presence of toxic contaminants (Nelson et al. 1987).

Sediment conditions in Allen Harbor were further evaluated through characterization of benthic community condition using the REMOTS camera system. This work was sponsored by the Narragansett Bay Project and the Allen Harbor stations were included as part of the bay-wide survey (SAIC 1989). Benthic habitat quality, organic enrichment, dissolved oxygen concentration, and the distribution of Clostridium perfringens were examined at fifty-nine stations in the bay to provide information on the sediment quality of areas of Narragansett Bay (SAIC 1989).

Biomarkers tests on two of the sediment samples collected for the amphipod assay, one from Allen Harbor and one from Mount View, were conducted to evaluate cytotoxicity and mutagenicity of contaminants in the sediments. The V79 Metabolic Cooperation Assay (V79/MC) was used as a short-term test to identify tumor promoters. The assay is based on the discovery that the tumor promoters inhibit the gap junctional-mediated transfer of materials between cells (EPA-ERL 1989a). The V79/Sister Chromatid Exchange Assay (V79/SC) was used to evaluate the mutagenic effects of the complex mixtures and fractions of contaminants extracted from the sediment. In this assay chromosomal damage is measured by induction of micronuclei in the interphase cell. Micronuclei represent acentric chromosome or chromatid fragments which give rise to one or more small secondary nuclei that are excluded from daughter nuclei. Sister chromatid exchange represents the breakage and reciprocal exchange of identical DNA material between the two sister chromatids of a chromosome. Both micronuclei and sister

In Situ Array

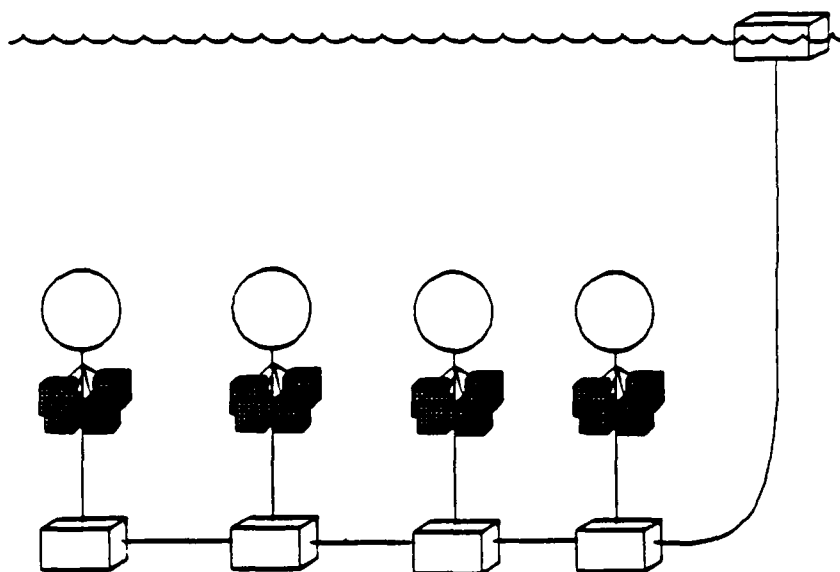


Figure 7. Mussels cages used to deploy mussels at stations located in Narragansett Bay, RI (Nelson et al. 1987).

chromatid exchanges have been found to increase in cells exposed to mutagenic compounds (Mueller et al. 1989).

The results obtained during the first phase of the risk assessment are summarized in the interim (EPA-ERL 1989b) and the draft final reports (EPA-ERL 1990). General observations show no dramatic differences in the chemical composition of the sediments collected from Allen Harbor and those from other areas of Narragansett Bay. Low bacterial counts and no evidence of sediment toxicity from the amphipod assay support this conclusion. The tissue residues and bacterial counts measured in Allen Harbor were also relatively low in comparison to other areas of Narragansett Bay. The histopathological observations and abundance estimates shows that the bivalve population in Allen Harbor is relatively healthy and the benthic community, as measured by the REMOTS system, is relatively undegraded. However, evidence of possible pollution impact on organisms in Allen Harbor was detected in the water column and benthos. Water column pollution stress was detected in sporadic elevated microbial levels and reduced SFG in mussels deployed in Allen Harbor, relative to reference areas. Impacts on benthic dwelling organisms were detected by elevated hemopoietic neoplasia in soft shell clams and elevated levels of tributyltin (TBT) in quahogs. It is not clear that these impacts can be attributed to the landfill and, in fact, are most likely a result of pollution entering Allen Harbor from runoff or boating activities at the marina located in the harbor (Milliken 1989, EPA-ERL 1990).

Work currently planned for the second phase of the risk assessment will address the contributions of the landfill to observable environmental impacts in Allen Harbor by partitioning exposure and toxicity amongst the potential sources. These sources include the landfill itself, runoff from storm drains and nonpoint sources, and effects from increased boating activity during the summer months. Additional sampling will address the relative affliction rates of neoplasia in soft shell clams in Allen Harbor and Narragansett Bay to determine if Allen Harbor is a locus of the disease or whether neoplasia is endemic to soft shell clams in Narragansett Bay. Results of these investigations will be interpreted within an ecological risk assessment framework. A long-term monitoring strategy will be developed to support the risk management plan (EPA-ERL 1989c).

BENEFITS OF ECOLOGICAL RISK ASSESSMENTS

The primary benefit of conducting the studies described in this paper is that direct measures of environmental health are made with actual exposure conditions which are related to biologically significant endpoints. This process provides the risk framework for interpreting and managing impacts from the disposal sites (Phelps and Beck 1989). Ecological risk assessment allows investigators to identify the source and extent

of the problem and delineate between hot spots and nonproblem areas that can be prioritized accordingly. Since ecological risk assessment is an emerging science, a potential drawback is that sometimes results can be ambiguous and subject to conflicting interpretations. Therefore, it is very important that decision criteria are selected that consists of: "... well defined, conveniently measured, and easily understood set of endpoints on which to base management action" (Phelps and Beck 1989, p2351). By selecting the proper endpoints for a particular ecosystem uncertainty can be quantified to allow reduction, rather than elimination, of risk and the identification of appropriate cleanup levels (Greenberg 1989).

Ecological risk assessments also provide information on ecotoxicity or how contaminants affect ecosystems. Continued studies of ecotoxicity will lead to the development of methods and databases that can provide a risk assessment framework for other applications and result in biologically-based models to assess risk, rather than the statistical models currently in use (Paustenbach and Keenan 1989). Finally, ecological risk assessments and monitoring programs can provide a direct verification of environmental safety. This information can be used to facilitate site closures and determine how clean a hazardous waste disposal site actually is.

ACKNOWLEDGMENTS

The work reported in this paper was funded by the Assistant Commander for Environment, Safety and Health of the Naval Facilities Engineering Command, Alexandria, VA, in support of the Navy's Installation Restoration Program. The Environmental Programs Director is Ms. Elizabeth Wilkins and the Engineer in Charge is Mr. William Judkins. The authors wish to thank all those who contributed to the work reported in this paper, including Lcdr. William Wild, Mr. Aldis Valkirs, Ms. Susan Kola, and Ms. Laura Keir, of NOSC; Mr. Roy Hummel, Ms. Terri Donovan, Mr. Brian Westra, Ms. Jeanine Capizzi, Dr. George Cobb, III, Dr. Michael Hooper, Dr. Larry Brewer, Ms. Cathy Bens, and Dr. Ron Kendall of TIWET; Ms. Kathy Souders, Mr. Matt Klope, Ms. Diana Tener, Ms. Sheila Ashton, and Ms. Mary Lou Gonzales of NAS Whidbey Island; Mr. Brian Haelsig and Ms. Beth Anderson of EFANW; Ms. Cornelia Mueller, Mr. Bruce Reynolds, Mr. Timothy Gleason, Dr. W. Skip Nelson, Dr. Richard Pruell, Mr. George Gardner, Ms. Michele Redmond, and Mr. Donald Cobb of EPA-ERL; Cdr. Sam Saltoun, Lt. Don LaChance, Mr. Louis Fayon, and Mr. Mathew Maliki of NCBC Davisville; and Mr. Jim Valenti and Mr. Thomas Schekels of Northern Division, Naval Facilities Engineering Command. Managerial and administrative support for this research was provided by Mr. Peter F. Seligman, Head, Marine Environment Branch, and Dr. Sach Yamamoto, Head, Environmental Sciences Division, Naval Ocean Systems Center. Any citation of trade names does not constitute an endorsement or approval of such commercial products for use by the US Government.

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SCOPE OF WORK
FOR A NATIONAL RESEARCH COUNCIL STUDY:

Improving Environmental Impact Evaluation and Risk Assessment of
Xenobiotic Compounds in the Aquatic Environment

P. F. Seligman, NOSC

INTRODUCTION

The Comprehensive Environmental Response Compensation and Liability Act (CERCLA) as amended by the Superfund Amendment and Reauthorization Act (SARA) of 1986 requires remedial actions at hazardous waste disposal sites to attain a degree of clean up that at a minimum will insure protection of human health and the environment. The law further requires that cleanup of hazardous waste disposal sites meets with the standards, criteria or limitations under any applicable, relevant and appropriate statute or federal law, including the Federal Water Pollution Control Act (FWPCA). Within the Department of Defense (DOD), the Defense Environmental Restoration Program (DERP) has been funded by Congress to cleanup hazardous waste disposal sites. Many DOD sites, particularly those of the Navy, are located on or near bodies of water and represent potential entry points of toxicants into the aquatic ecosystem. Assessing the environmental risk of toxicants at these sites is paramount in choosing the degree and type of remedial procedure required. For example, dredging at some aquatic sites may remobilize highly toxic compounds, thus increasing environmental risk over the no action alternative.

PROBLEM

The DOD has many installations with disposal sites that can impact aquatic environments. More than fifty percent of the Navy's hazardous waste disposal sites are adjacent to water bodies and represent unknown risks to aquatic ecosystems and human health. The Army and Air Force also report many hazardous waste disposal sites which may impact aquatic resources. Contaminants at DOD disposal sites includes toxic organic compounds, organometals, and heavy metals, collectively referred to as xenobiotics, which are either not found in nature or are at doses which far exceed the range of concentrations that organisms would experience under natural conditions. Traditional risk assessments of these compounds has been based on dose-response data from laboratory bioassays and an exposure assessment based on measured or predicted environmental concentrations. Moreover, current approaches to environmental risk assessments only consider single compounds and does not adequately address the effects of complex mixtures which are present at almost all DOD disposal sites. In addition, emphasis of current risk assessment practice is focused on human health concerns and which do not assess the risk to environmental quality and ecosystem impact.

Laboratory bioassays generally do not address the question of toxicant bioavailability in the natural environment and can

induce significant stress on test organisms which may alter experimental results. Likewise, measurement technology attempts to maximize compound yield (recovery) rather than address bioavailability in the matrix of impact (e.g. sediment, water, particulates, surface microlayer). Some xenobiotics present at DOD disposal sites are largely unique to military applications (e.g. TNT, RDX) and data must be developed to determine the environmental fate and effects of DOD unique compounds.

Current risk assessment methods are inadequate for accurately determining the risk to aquatic ecosystems because they tend to overestimate risk, which would greatly increase the cost of cleanup. Overly conservative risk estimates may be translated into a very low standard and thus become highly restrictive or amount to a defacto ban or significantly increased cleanup requirements. With the increasing requirements for cleanup and the limited availability of funds, it is necessary to prioritize site cleanup based on risk and to develop risk-based cleanup levels that adequately protect human health and the environment.

Risk assessment and risk management of xenobiotics, particularly those of high economic or social benefit, or those present at disposal sites where cleanup would represent excessive economic costs, need to address the environmentally relevant questions of toxicant fate, loading capacity, and bio-availability. When regulation of xenobiotics for site remediation requirements under CERCLA are determined by risk assessments that are not environmentally relevant, unnecessary costs and the potential for increased environmental damage may occur.

OBJECTIVE

Develop specific recommendations for improving risk assessment methods for determining the impact of xenobiotics on aquatic ecosystems.

RECOMMENDED TASKING

Recommendations for improving risk assessments of xenobiotic impact on aquatic ecosystems would result in the identification of state-of-the-art approaches that are readily applicable to site investigations and the delineation of areas that require additional research. The following recommended tasks would support this broad objective:

1. Evaluate the process by which the aquatic environmental impacts of xenobiotics from disposal sites are assessed (see Appendix A for examples of risk assessment case studies).

2. Assess the adequacy of using existing laboratory bioassays for predicting aquatic ecosystem effects of xenobiotic compounds from disposal sites. Identify appropriate approaches

for evaluating contaminant exposure from sediment, soil, surface water, and groundwater matrices and complex mixtures as compared to single compounds.

3. Evaluate and recommend emerging methodologies, and identify basic research needs for improving aquatic risk assessment, with quantifiable biological endpoints, including but not limited to:

a. The use of site specific assessment tools such as micro- and mesocosms, deployments of caged or introduced organisms, and in situ toxicity assessments to investigate impacts on aquatic ecosystems. Evaluate and identify methods and research needs for measuring xenobiotic impact on recruitment, community structure, significant sublethal chronic effects, with emphasis on physiological and biochemical endpoints and bioaccumulation or biomagnification of toxicants, that can be used at specific sites.

b. Field validation methods for validating toxic effects observed in bioassays or site specific microcosm studies and other techniques for evaluating exposure scenarios.

c. Development of improved life cycle testing procedures to provide environmentally realistic conditions to evaluate reproductive and genetic effects.

4. Based on assessments and recommendations identify cost-effective methods appropriate for assessments at sites impacting aquatic ecosystems (i.e. runoff, sediment, leachate, etc.) that can be used in the Remedial Investigation and Feasibility Study (RI/FS) process to support the selection of optimal remedial options and evaluate the effectiveness of cleanup.

5. Investigate the status and capability of environmental simulation models (emphasizing probabilistic rather than deterministic models) to predict environmental impact. Evaluate whether modeling can be used in environmental risk assessments and regulation of xenobiotics and appropriate applications of such models. Identify research needs for improved modeling of ecological risk.

RECOMMENDED COMMITTEE COMPOSITION

A committee composed of persons with expertise in aquatic ecology, aquatic toxicology, environmental chemistry, analytical chemistry, environmental engineering, aquatic ecosystem modeling and environmental biochemistry is necessary to perform this study. Committee members should all have an environmental orientation with expertise in aquatic or estuarine systems and familiarity with the requirements of CERCLA and SARA. One or more members actively involved in aquatic risk assessment and risk management should be included on the committee.

PROPOSED FUNDING AND COORDINATION

The chairman of the DOD Installation Restoration Technical Coordinating Group (IRTCG) will provide the coordination and direction for the NRC study through the IRTCG Committee on NRC Special Study (Health and Environmental Toxicology). The proposed level of funding is \$300K per year for Fiscal Years 1990 and 1991. Periodic reviews of the NRC study and acceptance of final reports will be provided by the IRTCG Committee (Health and Environmental Toxicology).

DELIVERABLES

The NRC/NAS will issue special publication(s) on risk assessment methods for aquatic environments. Publication will identify currently applicable methods and basic research needed to support aquatic risk assessments. A draft interim report will be issued before final publication for DOD and EPA review. A series of working meetings with DOD and EPA representatives and position documents will be developed for input into the final report.

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APPENDIX A

A bibliography of risk assessments at hazardous waste disposal sites and issues involving risk assessments of xenobiotics.

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AIR AND WATER POLLUTION CONTROL, AIR INITIATIVES, AND WATER INITIATIVES

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REGULATORY STRATEGY
FOR
TOXIC CHEMICAL RELEASES

E. L. Douglas, AESO

REGULATION OF TOXIC CHEMICALS IN
THE 90's WILL EMPHASIZE:

- * MANDATORY PUBLIC DISCLOSURE
- * RISK COMMUNICATION

EXAMPLES:

- * COMMUNITY RIGHT-to-KNOW
PROVISIONS of SARA TITLE III
- * PROPOSITION 65 & RELATED
LEGISLATION
- * CALIFORNIA'S ASSEMBLY BILL
2588 (TOXIC "HOT SPOTS" ACT)
- * Title III, Hr 3030 to CAA

STATE PROGRAMS: AN EXAMPLE

CALIFORNIA'S TOXIC HOT SPOTS ACT

1. EMISSION INVENTORY PLANS
 - * IDENTIFY TOXIC SPECIES
 - * PROPOSE ESTIMATION TECHNIQUES
2. EMISSION INVENTORIES/ESTIMATION
3. REGULATORY REVIEW PERIOD TO EVALUATE INVENTORIES
 - * HIGH PRIORITY
 - * INTERMEDIATE PRIORITY
 - * LOW PRIORITY

HIGH PRIORITY EMITTERS MUST
SUBMIT RISK ASSESSMENTS!

CONSEQUENCES OF DEMONSTRATING
SIGNIFICANT RISK INCLUDE:

- * PUBLIC DISCLOSURE
- * MEASURES TO MITIGATE
THE RISK

AFFECTED PROCESSES & CHEMICALS

1. ELECTROPLATING FACILITIES

- * CADMIUM * HYDROCHLORIC ACID
- * CHROMIUM * HYDROFLUORIC ACID
- * COPPER * SODIUM HYDROXIDE

2. ENGINE TEST CELLS

- * FUEL CONTAMINANTS
- * INCOMPLETE COMBUSTION PRODUCTS

3. PAINTING & SOLVENT CLEANING

- * CHLORINATED FLUOROCARBONS
- * 1,1,1-TRICHLOROETHANE
- * METHYLENE CHLORIDE
- * GLYCOL ETHERS
- * PHENOL
- * TOLUENE
- * XYLENES

4. ANY AIR PERMITTED SOURCE

5. OTHERS

SPECIALIZED EMISSION SOURCES NOT CLEARLY AFFECTED BY REGULATION OF AIRBORNE TOXICS

- * FIRE FIGHTING SCHOOL
- * STATIC FIRING OF ROCKET MOTORS
- * OPEN BURNING
- * ORDNANCE DETONATION
- * LANDFILLS
- * MOBILE SOURCES

TOXIC CONTAMINANTS
FROM
GAS TURBINE ENGINE TEST CELLS

ACROLEIN	ACETALDEHYDE
BENZENE	BENZANTHRACENE
PHENOL	BENZO[a]PYRENE
TOLUENE	1,3-BUTADIENE
XYLENES	NAPHTHALENE
STYRENE	FORMALDEHYDE
PROPYLENE	

ESTIMATED TOXIC EMISSIONS FROM
TEST CELLS IN SAN DIEGO COUNTY
ARE < 2 TONS ANNUALLY.

WILL THIS TRIGGER REGULATORY
CONCERN?

- * RISK ASSESSMENT?
- * EMISSIONS CONTROLS?
- * REDUCED OPERATIONS?

CALIFORNIA'S TOXIC CONTROL
MEASURE FOR HEXAVALENT CHROMIUM

FACILITY EMISSIONS lb/yr	CONTROL OPTIONS	
	EQUIPMENT EFFICIENCY	STACK EMISSIONS mg/amp-hr
< 2	95.0%	0.15
2 - 10	99.0%	0.03
> 10	99.8%	0.006

WHO CONSTITUTES THE PUBLIC?

- * THE MEDIA
- * SPECIAL INTEREST GROUPS
- * PRIVATE CITIZENS

EXPLAINING RISK TO THE PUBLIC
INVOLVES MORE THAN DISCLOSURE!

OBSTACLES TO OVERCOME:

- * MEDIA SENSATIONALISM/
DISTORTION
- * "CHEMOPHOBIA" / "PSEUDOSCIENCE"
- * PUBLIC PERCEPTION & OUTRAGE -
HOW SAFE IS SAFE?

IMPACT OF CALIFORNIA CHROMIUM
EMISSION REGULATIONS ON NAVY
CHROME PLATING AND CHROMIC ACID
ANODIZING FACILITIES
D. A. Newton, NEESA

EXECUTIVE SUMMARY

In February 1988, the California Air Resources Board (CARB) adopted an Airborne Toxic Control Measure to control hexavalent chromium emissions from chrome plating and chromic acid anodizing facilities. Regulatory requirements depend upon facility-wide annual chromium emissions. Large plating shops emitting over 10 lbs/yr of hexavalent chromium (measured after control equipment) must meet 99.8% control efficiency or 0.006 mg/amp-hour mass emission limit.

Recent tests performed by CARB and the Metal Finishing Association show the control requirements are achievable.

Navy plating shops average 95% chromium control efficiency using mist eliminator or wet scrubber based control systems. However, 95% control only meets regulatory requirements for small plating shops.

All states will eventually adopt a hexavalent chromium control measure for chrome plating processes. Washington's Puget Sound Air Pollution Control Agency plans to adopt California's regulations in June 1990. U.S. EPA plans to develop a chromium emission standard for plating shops by the end of 1991. The federal standard will not be as strict as California. We recommend navy activities prepare for chromium regulations.

We recommend the following for all navy activities:

- Install a non-resettable totalizing ampere-hour meter on each chrome plating and chromic acid anodizing tank. Record meter readings monthly. Plating shops need accurate ampere-hour usage records to determine actual shop size. Over estimating ampere-hour usage will yield a higher annual chromium emission rate and may subject a facility to stricter emission requirements. Under estimating ampere-hour usage will result in a notice of violation when regulatory personnel compare actual usage to permitted usage.

- Make sure plating tank ventilation flow rate is correct and operating well. If plating personnel need respirators to enter a chrome plating area there is a ventilation problem.

- Improve plating efficiency at existing shops.

Specify an economical combination of more efficient plating processes, process modifications (if possible), and higher efficiency control equipment for new plating shop designs. Specify ampere-hour meters for all new chrome plating tanks. Specify enough straight ducting before and after the chromium control system to allow installation of EPA approved emission sampling ports.

1.0 INTRODUCTION

The purpose of this paper is to inform all navy environmental engineering field division directors, environmental coordinators, and plating facility management personnel of California's recent regulation for control of hexavalent chromium emissions. The information will help navy environmental personnel determine impact and compliance strategy when other states adopt similar air pollution control regulations.

The Naval Energy and Environmental Support Activity (NEESA) provides a wide variety of services including criteria development, design review, start up, evaluation, and compliance testing of combustion units and air pollution control systems. NEESA has performed several emission tests at navy electroplating facilities.

2.0 BACKGROUND

In January 1986, the California Air Resources Board (CARB) identified hexavalent chromium as a toxic air contaminant without specifying a permissible exposure limit. In February 1988, CARB approved a Hexavalent Chromium Control Plan¹ and adopted an Airborne Toxic Control Measure² (ATCM) for chrome plating and chromic acid anodizing facilities.

The control plan recommends regulation of several chromium sources. Recommendations include: eliminate chromate corrosion inhibitors in cooling towers, require baghouses to control chromium emission from fuel oil combustion in boilers, limit chromium content of fuel oils, and strict control of chrome plating and chromic acid anodizing facilities.

Table 1 summarizes the ATCM for chrome plating and chromic acid anodizing.

TABLE 1
California Air Resources Board
Airborne Toxic Control Measure
for Chrome Plating and Chromic Acid Anodizing Facilities

Process	Cr ⁺⁶ Emissions Facility-wide (lbs/vr)	Control Efficiency	Mass Emission Limit (mg/amp-hr)
Decorative Chrome	ALL	95%	or N/A
Hard Chrome & CrO ₃ Anodize	2 OR LESS (SMALL)	95%	or 0.15
Hard Chrome & CrO ₃ Anodize	BTWN 2 AND 10 (MEDIUM)	99%	or 0.03
Hard Chrome & CrO ₃ Anodize	10 OR GREATER (LARGE)	99.8%	or 0.006

Large plating facilities emitting over 10 lbs/yr of hexavalent chromium (measured after control equipment) must meet 99.8% control efficiency or 0.006 mg/amp-hour mass emission limit. Pre-1989 chromium emission test results, reviewed by CARB, do not document achievement of the high control efficiency requirements. CARB was confident the requirements were technologically feasible based on performance of air emission control equipment used in the sulfuric acid production industry.

ATCM mass emission limits are stricter than control efficiency requirements. However, it may be easier and cheaper to comply with mass emission limits.

Plating shops have four compliance strategies: workload reduction, control device improvement, plating process modifications, or a combination of the three. Process modifications can substantially reduce generated chromium emissions. However, process modifications can also reduce some control system efficiencies. Control system performance improves with increasing inlet chromic acid mist concentration and mist size.

Each California air pollution control district (APCD) adopted a chromium control rule identical to or stricter than CARB's ATCM. Table 2 compares the rules for California's two largest APCDs; South Coast (SCAQMD) and Bay Area (BAAQMD). Both rules are stricter than CARB's ATCM. SCAQMD regulates decorative chrome processes as strict as hard chrome processes.³ BAAQMD requires hard chrome processes to meet CARB's mass emission limits; control efficiency is irrelevant.⁴

TABLE 2
Comparison of Hexavalent Chromium Control Rules for
South Coast and Bay Area Air Quality Management Districts

Process	Cr+6 Emissions Facility-wide (lbs/yr)	SCAQMD Rule 1169			BAAQMD Reg. 11, Rule 8	
		Control Efficiency		Limit (mg/amp-hr)	Control Efficiency	Limit (mg/amp-hr)
Decorative Chrome	ALL	SAME AS or 0.05 HARD CHROME			95%	N/A
Hard Chrome & CrO ₃ Anodize	2 OR LESS (SMALL)	95%	or	0.15	N/A	0.15
Hard Chrome & CrO ₃ Anodize	BTWN 2 AND 10 (MEDIUM)	99%	or	0.03	N/A	0.03
Hard Chrome & CrO ₃ Anodize	10 OR GREATER (LARGE)	99.8%	or	0.006	N/A	0.006
Monitoring Requirements		Proof Of Compliance (Source Test)			Initial Source Test To Determine Emission Factor	
Recording Requirements		*Ampere-hours ^a *Anti-mist Additive Concentration *Submit Upon Request			*Ampere-hours *Bath Chemistry *Submit Annually	
Other Requirements					10 m Minimum Stack Height 10 m/s Minimum Stack Vel.	

^aSCAQMD requires a non-resettable, totalizing amp-hour meter on each tank.

3.0 HEXAVALENT CHROMIUM CONTROL DEMONSTRATION PROJECT

In response to concerns voiced by the Metal Finishing Association (MFA), CARB provided emission test support to a MFA sponsored project designed to demonstrate feasibility of the requirements. CARB agreed to modify the requirements if warranted by the project.

The demonstration project evaluated both process modifications and control devices. Process modifications include adding anti-mist chemicals to the plating bath, covering the bath surface with floating plastic balls, eliminating air agitation, and increasing freeboard height. Table 3 shows results of preliminary tests performed to assess the benefit of process modifications.⁵ Process modifications can reduce uncontrolled chromium emissions (emissions leaving the plating bath) by 99%. Increasing freeboard height did not reduce emissions.

TABLE 3
Emission Reduction Benefit of Plating Process Modifications

ANTI-MIST ADDITIVE	PLASTIC BALLS	ELIMINATE AIR AGITATION	INCREASE FREEBOARD 6" TO 12"	UNCONTROLLED CHROMIUM EMISSION REDUCTION
YES	YES	YES	NO	98% TO 99%
NO	YES	YES	NO	86% TO 87%
NO	NO	YES	NO	5% TO 80%
NO	NO	NO	YES	NO BENEFIT

CARB initially planned to evaluate wet electrostatic precipitators, however high capital cost and lack of vendor cooperation made these devices "unreasonable" available control technology for plating shop facilities.

Tables 4 through 6 summarize results of the demonstration project.⁶

Table 4 identifies four emission control systems evaluated during the demonstration project; two full-scale and two pilot-scale systems.

Table 5 shows emission test results of each control system. Plating shop personnel used 3/4" plastic balls and no air agitation for all four tests. All outlet emission rates were below the 0.006 mg/amp-hr CARB limit. All four emission control systems demonstrated greater than 99% control efficiency. Two of the control systems achieved the 99.8% CARB control efficiency requirement. The test results show that CARB's chromium control requirements are achievable.

Table 6 shows additional test results of systems #3 and #4. Plating shop personnel used different combinations of process modifications for each test.

Comparison of Tables 5 and 6 shows the impact of process modifications on uncontrolled (inlet) emission rates, controlled (outlet) emission rates, and control system efficiencies. In Table 6, the inlet and outlet emission rates and control efficiency of system #4 are 5.93 mg/amp-hr, 0.011 mg/amp-hr, and 99.9%, respectively. This test used no process modifications. In Table 5, adding 3/4" polyballs to the plating tank, the emission rates and efficiency of system #4 are 0.61 mg/amp-hr, 0.004 mg/amp-hr, and 99.3%, respectively. With the process modification, system #4 met the 0.006 mg/amp-hour limit but not the 99.8% efficiency requirement. With no process modifications, system #4 met the 99.8% efficiency requirement but not the 0.006 mg/amp-hr limit. Notice that the environment benefits from plating process modifications even though control efficiency decreases. Process modifications reduce the controlled chromium emission rate by 63%.

It is important to note that system #4 complies with SCAQMD's large shop requirements with or without process modifications. However, system #4 must use process modifications to comply with BAAQMD's large shop requirement. (Refer to Table 2.)

For more information regarding the demonstration project contact NEESA or CARB. CARB personnel prepared an excellent paper discussing the demonstration project.⁷

TABLE 4
California Air Resources Board
Hexavalent Chromium Control Demonstration Project
Evaluated Emission Control Systems

System No.	Scale	Manufacturer	Device Type
#1	Pilot	Monsanto EnviroChem Systems, Inc.	fiber bed mist eliminator
#2	Full	CM&E International	tank covers, low flow exhaust, combination mist eliminator and wet packed scrubber
#3	Full	Tri-Mer Corporation	wet packed scrubber
#4	Pilot	CECO Filters, Inc.	fiber bed mist eliminator

TABLE 5
California Air Resources Board
Hexavalent Chromium Control Demonstration Project
Test Results of Four Emission Control Systems
(Note: All plating baths contained floating polyballs)

SYSTEM NO. TEST DATE CHROME PROCESS PROCESS MODS.	TEST- RUN	INLET? OUTLET?	Cr tot EMISSION RATE (mg/hr)	TOTAL AMPERES (amp)	Cr tot EMISSION RATE (mg/amp-hr)	Cr tot REMOVAL EFF. (%)
#1 MONSANTO	11-S	INLET	541.5	3101	0.1746	
JANUARY 89	12-S	INLET	978.5	3085	0.3172	
CHROME PLATE	13-S	INLET	1177.2	3264	0.3607	
3/4" POLYBALLS						
NO AIR AGITATION	AVG	INLET	899.1		0.2842	
	11-E	OUTLET	7.62	3145	0.0024	98.59
	12-E	OUTLET	5.45	3085	0.0018	99.44
	13-E	OUTLET	4.49	3264	0.0014	99.62
	AVG	OUTLET	5.85		0.0019	99.35
#2 CM&E	23-S	INLET	2109.7	1089	1.9373	
JANUARY 89	24-S	INLET	2111.9	1064	1.9848	
CHROME PLATE						
3/4" POLYBALLS	AVG	INLET	2110.8		1.9611	
NO AIR AGITATION						
	23-E	OUTLET	4.81	1089	0.0044	99.77
	24-E	OUTLET	5.38	1064	0.0051	99.75
	AVG	OUTLET	5.09		0.0047	99.76
#3 TRI-MER	32-S	INLET	584.5	714	0.8186	
FEBRUARY 89	33-S	INLET	846.9	627	1.3507	
CHROME PLATE						
3/4" POLYBALLS	AVG	INLET	715.7		1.0846	
NO AIR AGITATION						
	32-E	OUTLET	0.50	703	0.0007	99.91
	33-E	OUTLET	2.25	627	0.0036	99.73
	AVG	OUTLET	1.38		0.0022	99.80
#4 CECO	41-S	INLET	3912.2	6808	0.5746	
FEBRUARY 89	42-S	INLET	3743.1	6196	0.6041	
CHROME PLATE	43-S	INLET	3930.4	6016	0.6533	
3/4" POLYBALLS						
NO AIR AGITATION	AVG	INLET	3861.9		0.6107	
	41-E	OUTLET	25.13	6808	0.0037	99.36
	42-E	OUTLET	25.37	6196	0.0041	99.32
	43-E	OUTLET	27.14	6016	0.0045	99.31
	AVG	OUTLET	25.88		0.0041	99.33

CARB PROJECT NO. C-88-028b DATED 16 OCTOBER 1989

TABLE 6
California Air Resources Board
Hexavalent Chromium Control Demonstration Project
Test Results of Two Emission Control Systems
(Note: Tests varied use of air agitation, anti-mist additives, and polyballs)

SYSTEM NO. TEST DATE CHROME PROCESS PROCESS MODS.	TEST- RUN	INLET? OUTLET?	Cr tot EMISSION RATE (mg/hr)	TOTAL AMPERES (amp)	Cr tot EMISSION RATE (mg/amp-hr)	Cr tot REMOVAL EFF. (%)
#3 TRI-MER MARCH 89 CHROME PLATE NO POLYBALLS AIR AGITATION ON	51-S	INLET	2926.2	943	3.1031	
	51-E	OUTLET	2.68	943	0.0028	99.91
#3 TRI-MER MARCH 89 CHROME PLATE 3/4" POLYBALLS NO AIR AGITATION ANTI-MIST ADDITIVE	52-S 53-S AVG 52-E 53-E AVG	INLET INLET INLET OUTLET OUTLET OUTLET	461.6 778.2 619.9 1.35 0.74 1.04	839 734 839 734 	0.5501 1.0602 0.8052 0.0016 0.0010 0.0013	 99.71 99.91 99.84
#4 CECO MARCH 89 CHROME PLATE NO POLYBALLS NO AIR AGITATION NO POLYBALLS NO ANTI-MIST ADDITIVE	54-S 54-E	INLET OUTLET	14473.6 16.55	1458 1458	9.9270 0.0113	 99.89

CARB PROJECT NO. C-88-028b DATED 16 OCTOBER 1989

4.0 HEXAVALENT CHROMIUM EMISSION TESTS AT NAVY PLATING SHOPS

Most navy plating shops do not use process modifications. Reasons for this include: inconvenience, tank overheating, plating quality problems, and absence of chromium regulations.

NAD Alameda and NOS Louisville use plastic balls in chrome plating tanks. Other shops have tried plastic balls but had problems with balls lodging in workpiece cavities, recirculation pumps, and between the anode and workpiece. Tanks with poor temperature controllers have overheated because of the insulation benefit of plastic balls.

Most navy attempts to use anti-mist additives in hard chrome plating tanks have been disastrous. The problem has been pitting in the plated material. Chemical companies are trying to solve this problem for California chrome platers. Results look promising for non-fluorinated chemicals.

Navy plating shops use various plating bath agitation methods. Most shops use air agitation, but several use mechanical methods.

Table 7 shows chromium emission test results from four navy plating shops. Navy plating shops use several types of pollution control devices. Navy mist eliminators and wet scrubber based control systems average 95% chromium control efficiency. However, 95% control only meets regulatory requirements for a small shop.

Comparison of emission rates between shops is difficult. Some shops have more tanks, better ventilation systems, better plating efficiencies, etcetera. Be cautious when drawing conclusions by comparing test results from different shops.

U.S. Navy Plating Shop Chromium Emission Test Results

TEST SITE/DATE TEST TEAM CHROME PROCESS CONTROL DEVICE	TEST- RUN	INLET? OUTLET?	Cr tot EMISSION RATE (mg/hr)	TOTAL AMPERES (amp)	Cr tot EMISSION RATE (mg/amp-hr)	Cr tot REMOVAL EFF. (%)
TEST SITE D	15-1	INLET	25171.6	2398	10.497	
AUGUST 88	15-2	INLET	46283.6	2010	23.027	
NEESA	15-3	INLET	48397.5	2010	24.078	
CHROME PLATE						
AIR AGITATION	AVG	INLET	39950.9		19.201	
NO POLYBALLS, ETC						
CHEVRON M.E. &	15-1	OUTLET	1158.2	2398	0.483	95.4
MESH PAD M.E.	15-2	OUTLET	1540.2	2010	0.766	96.7
	15-3	OUTLET	2747.2	2010	1.367	94.3
	AVG	OUTLET	1815.2		0.872	95.5
TEST SITE C	3-4	INLET	25071.0	954	26.280	
JUNE 87	3-5	INLET	26772.5	960	27.888	
NEESA	3-6	INLET	28289.6	1000	28.290	
CHROME PLATE	3-7	INLET	20921.5	1110	18.848	
AIR AGITATION						
NO POLYBALLS, ETC	AVG	INLET	25263.7		25.326	
CHEVRON M.E. &						
WET SCRUBBER	3-4	OUTLET	899.5	954	0.943	96.4
	3-5	OUTLET	1721.4	960	1.793	93.6
	3-6	OUTLET	998.5	1000	0.998	96.5
	3-7	OUTLET	1343.9	1110	1.211	93.6
	AVG	OUTLET	1240.8		1.236	95.1
TEST SITE B	1-1	INLET	5654.8	2810	2.012	
MARCH 85	1-2	INLET	8884.0	2500	3.554	
NEESA	1-3	INLET	10939.7	2186	5.004	
CHROME PLATE						
AIR AGITATION	AVG	INLET	8492.8		3.523	
NO POLYBALLS, ETC						
DEMISTER	1-1	OUTLET	458.8	2810	0.163	91.9
	1-2	OUTLET	436.3	2500	0.175	95.1
	1-3	OUTLET	268.4	2186	0.123	97.5
	AVG	OUTLET	387.8		0.154	95.6
TEST SITE A	4-1	INLET	7155.5	4340	1.649	
MAY 84	4-2	INLET	5062.3	4650	1.089	
NEESA	4-3	INLET	19550.0	5995	3.261	
CHROME PLATE	4-4	INLET	8171.0	6135	1.332	
AIR AGITATION						
NO POLYBALLS, ETC	AVG	INLET	9984.7		1.833	
WET SCRUBBER						
	4-1	OUTLET	< 628.8	4340	< 0.145	> 91.2
	4-2	OUTLET	< 862.1	4650	< 0.185	> 83.0
	4-3	OUTLET	< 497.1	5995	< 0.083	> 97.5
	4-4	OUTLET	< 1002.2	6135	< 0.163	> 87.7
	AVG	OUTLET	< 747.6		< 0.144	> 92.1

5.0 COMPLIANCE CALCULATIONS

The following calculations will help determine a compliance strategy for navy plating shops.

1. Determine maximum annual ampere-hour usage for facility-wide chromium plating operations. The accuracy of this number is very important. Over estimating ampere-hour usage will yield a high annual chromium emission rate and may subject a facility to stricter emission requirements. Under estimating ampere-hour usage will result in a notice of violation when regulatory personnel compare actual usage to permitted usage.

2. Estimate annual chromium emission rate (shop size) using emission test data or state approved emission factors. Some states may provide a maximum uncontrolled emission factor for use in calculating control efficiencies. This will prevent shops from purposely increasing uncontrolled emissions in order to show higher control efficiencies.

3. Consider compliance options.

- a. For medium and large shops, determine level of control needed to reduce facility-wide emissions to 2 lb/yr. The control efficiency specified for each shop size is not absolute. For example, a medium size shop (between 2 and 10 lb/yr) is subject to 99% control efficiency. However an efficiency between 95% and 99% is acceptable if annual chromium emissions reduce to 2 lb/yr. Similarly a large shop (10 lb/yr or greater) will comply with an efficiency between 99% and 99.8% if annual chromium emissions reduce to 2 lb/yr.

- b. Determine annual ampere-hour usage required to qualify as a small or medium shop. Restricting ampere-hour usage may be an option. Improving plating efficiency and minimizing excess plating thickness will reduce annual ampere-hour usage.

- c. Determine impact of process modifications or additional control equipment on the annual emission rate. Many calculation iterations will show how variations in uncontrolled emission rates, controlled emission rates, and annual ampere-hour usage affect compliance status. Figure 1 shows a computer spreadsheet to help evaluate compliance strategies.

Table 8 shows how four navy plating shops compare with California hexavalent chromium emission regulations. Compliance evaluation integrity depends upon accuracies of the annual ampere-hour usage assumption and the emission test data.

FIGURE 1
COMPUTER SPREADSHEET TO HELP EVALUATE
COMPLIANCE STRATEGIES FOR CALIFORNIA CHROMIUM REGULATIONS

The input values shown in bold print are variables. The other values are calculated using the equations shown below.

Changing the assumed (or actual) annual ampere-hour usage changes the uncontrolled emission rate variable. Improving control system efficiency by retrofit or addition of control equipment affects the control system efficiency variable. Using process modifications affects the uncontrolled emission rate however this affect is evaluated separately using the process modification efficiency variable. Remember that reducing the uncontrolled emission rate may reduce the control system efficiency; consult control system manufacturer. The overall control efficiency must comply with requirements for the shop size.

The annual uncontrolled emission rate (E_{unc}) is actually a product of two variables: the assumed (or actual) annual ampere-hour usage and the measured (or assumed) uncontrolled emission rate per ampere-hour. You can modify the spreadsheet to include all variables.

	A	B	C	D	E	F
1		ER_{unc}	E_{cs}	E_{pm}	E_c	E_{oa}
2		(lb/yr)	(%)	(%)	(lb/yr)	(%)
3						
4	Input Value	338.00	95.50	0.00	15.21	95.50
5	Plating Shop Size				Large	
6	Value Req'd for $ER_c = 2$	44.44	99.41	86.85		
7	(Other values constant)					

Equations:

$$\begin{aligned}
 E4 &= B4*(1-F4/100) \\
 F4 &= 100-(1-C4/100)*(1-D4/100)*100 \\
 B6 &= 2/(1-C4/100)/(1-D4/100) \\
 C6 &= 100*(1-2/B4/(1-D4/100)) \\
 D6 &= 100*(1-2/B4/(1-C4/100)) \\
 E4 &= @IF(E4<=2," Small",@IF(E4<10 " Medium"," Large"))
 \end{aligned}$$

Definitions:

ER_{unc} = uncontrolled emission rate (measured before control system)
 E_{cs} = control system efficiency
 E_{pm} = process modification efficiency
 ER_c = controlled emission rate (measured after control system)
 E_{oa} = overall control efficiency

TABLE 8
U.S. Navy Plating Shops
Compliance With California Chromium Regulations

	Site A	Site B	Site C	Site D
Assumed Annual Amp-hr Usage (amp-hr/yr)	24 M	16 M	4 M	8 M
Chromium Emission Rates				
Uncontrolled	1.833	3.523	25.326	19.201
Controlled	< 0.144	0.154	1.236	0.872
(mg/amp-hr)				
Annual Chromium Emission Rates				
Uncontrolled	96.8	124.0	223.0	338.0
Controlled	< 7.6	5.4	10.9	15.3
(lb/yr)				
Shop Size	Medium	Medium	Large	Large
CARB Requirements				
Control Efficiency (%)	97.9	98.3	99.1	99.4
or Emission Limit	0.03	0.03	0.006	0.006
(mg/amp-hr)				
Ampere-hour Limit for				
Small Shop Rating	6.3 M	5.9 M	0.7 M	1.0 M
Medium Shop Rating	31.5 M	29.5 M	3.6 M	5.2 M
(amp-hr)				

M = million

6.0 CONCLUSION AND RECOMMENDATIONS

California hexavalent chromium regulations are strict but achievable. All states will eventually adopt a hexavalent chromium control measure for chrome plating processes. Washington's Puget Sound Air Pollution Control Agency plans to adopt California's regulations in June 1990. U.S. EPA plans to develop a chromium emission standard for plating shops by the end of 1991. The federal standard will not be as strict as California. We recommend navy activities prepare for chromium regulations.

We recommend the following for all navy activities:

- Install a non-resettable totalizing ampere-hour meter on each chrome plating and chromic acid anodizing tank. Record meter readings monthly. Accurate ampere-hour usage records are invaluable to compliance negotiations.
- Make sure plating tank ventilation flow rate is correct and operating well. If plating personnel need respirators to enter a chrome plating area there is a ventilation problem.
- Improve plating efficiency at existing shops.
- Specify an economical combination of more efficient plating processes, process modifications (if possible), and higher efficiency control equipment for new plating shop designs. Specify ampere-hour meters for all new chrome plating tanks. Specify enough straight ducting before and after the chromium control system to allow installation of EPA approved emission sampling ports.

1.0 REFERENCES

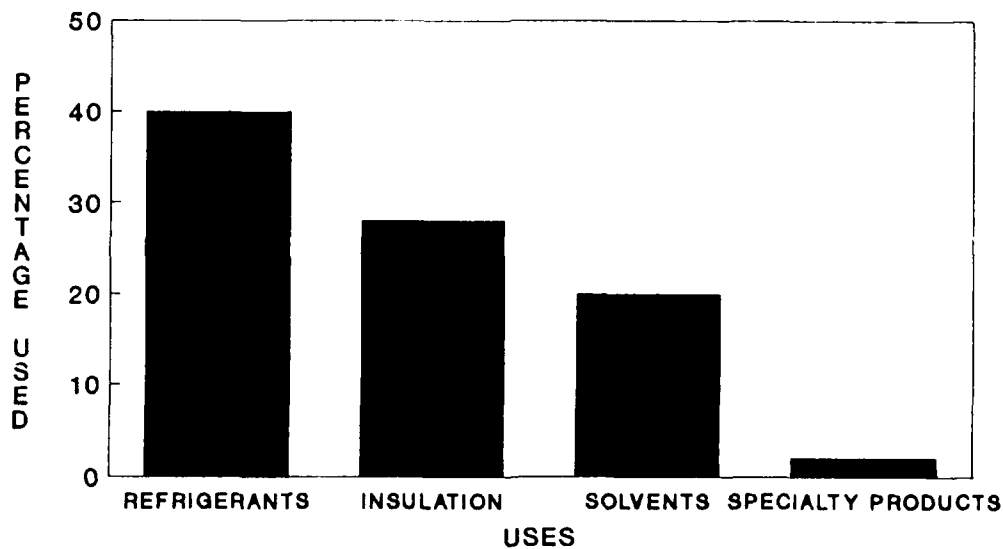
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ENVIRONMENTAL REGULATION OF OZONE DEPLETING SUBSTANCES

The Montreal Protocol: Actions and Impacts

RANDY WASKUL
NAVY ORDNANCE ENVIRONMENTAL SUPPORT OFFICE

U.S. CONSUMPTION OF CFCS



Estimates Based on 1989 EPA Reports

CHLOROFLUOROCARBONS PROPERTIES

- CHEMICALLY VERY STABLE
- NON-TOXIC
- NON-FLAMMABLE
- NON-CORROSIVE
- NON-EXPLOSIVE

HALONS PROPERTIES

- SIMILAR IN PROPERTIES TO CFCs
- CHEMICALLY VERY STABLE
- LOW TOXICITY
- NON-FLAMMABLE
- NON-EXPLOSIVE
- EXCELLENT FIRE EXTINGUISHER

THE MONTREAL PROTOCOL PARTICIPATION

- 23 NATIONS SIGNED THE AGREEMENT IN SEPTEMBER 1987
- AS OF OCTOBER 1989, 54 NATIONS HAD SIGNED THE AGREEMENT
- 45 NATIONS HAVE RATIFIED THE PROTOCOL AND ARE ENFORCING ITS GUIDELINES

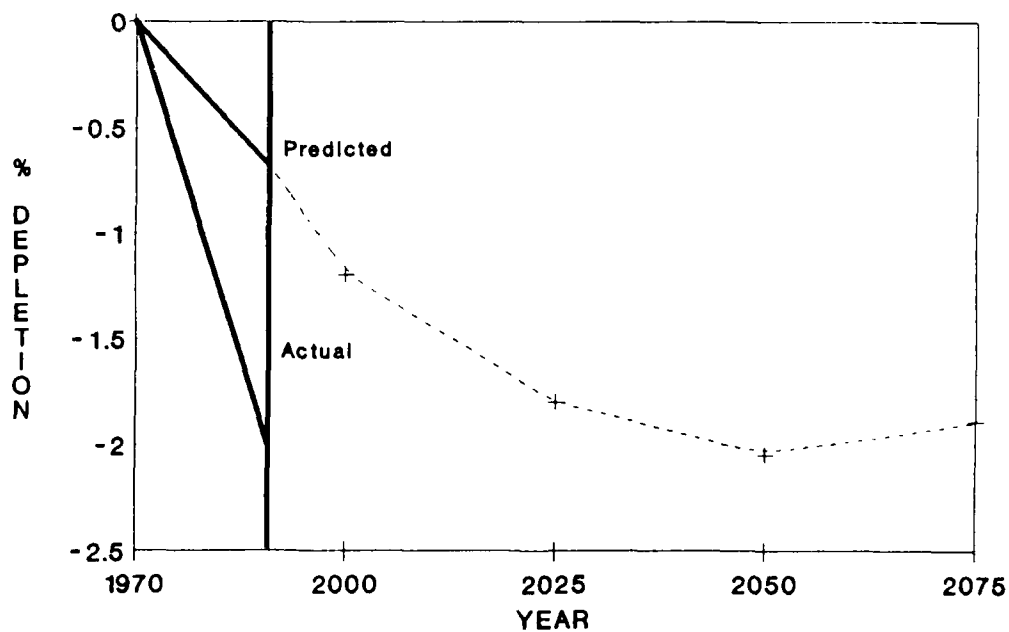
THE MONTREAL PROTOCOL INITIATIVES

- FREEZE CFC PRODUCTION AT 1986 LEVELS BY 1989
- A 20% REDUCTION IN PRODUCTION BY 1993
- AN ADDITIONAL 30% REDUCTION BY 1998
- FREEZE HALON PRODUCTION AT 1986 LEVELS BY 1992

THE MONTREAL PROTOCOL

- DEPLETION OF THE OZONE LAYER WOULD NOT EXCEED 2% OVER THE NEXT 50 YEARS
- THE ANTARCTIC OZONE HOLE WAS NOT TAKEN INTO ACCOUNT

OZONE DEPLETION



SOURCE: OZONE TRENDS PANEL
SUMMARY REPORT (MAR 88)

EPA ACTIONS

- MR. LEE THOMPSON, EPA DIRECTOR, CALLED FOR A TOTAL BAN ON CFCS IMMEDIATELY IN SEPTEMBER 1988
- EPA HAS PROPOSED THE REGULATION OF ADDITIONAL CHEMICALS
 - METHYL CHLOROFORM
 - CARBON TETRACHLORIDE
- ADVANCED NOTICE OF PROPOSED RULE MAKING RELEASED IN APRIL 1989 FOR METHYL CHLOROFORM

EPA ACTIONS (CONT)

- EPA IS ESTABLISHING AN ADVISORY COMMITTEE
- THE POC FOR ADDITIONAL INFORMATION ON THIS COMMITTEE IS
MR. DAVID LEE
GLOBAL CHANGE DIVISION
ENVIRONMENTAL PROTECTION AGENCY
401 M ST
WASHINGTON, D.C
(202) 475-7497

CONGRESSIONAL ACTIONS

- IN 1989 THERE HAVE BEEN NO LESS THAN 15 BILLS INTRODUCED IN CONGRESS
- SEVERAL CALL FOR ACCELERATING THE PROTOCOL TIME FRAME
- SEVERAL CALL FOR FEES ON THE PRODUCTION OF OZONE DEPLETING SUBSTANCES

INDUSTRIAL ACTIONS

- A NUMBER OF CFC/HALON MANUFACTURERS ANNOUNCED PHASE-OUT PLANS
 - Du PONT WILL COMPLETE ITS PHASE-OUT BY 2000
 - THIS WILL DECREASE THE GLOBAL SUPPLY BY 1/4
- IF A COMPANY STOPS OR REDUCES PRODUCTION NO OTHER COMPANY MAY USE THOSE PRODUCTION RIGHTS
-

INDUSTRIAL ACTIONS

- CONSUMERS ARE VOLUNTARILY DISCONTINUING USE OF CFCS IN PRODUCTS AND PRODUCTION
 - AT&T
 - IBM
 - GE
 - NORTHERN TELECOM
- RISK INSURERS ARE ADVOCATING THE REDUCED USE OF HALONS FOR FIRE PROTECTION
 - FACTORY MUTUAL IS EMPHASIZING ALTERNATIVES

COMPANIES WORKING ON DEVELOPING RECYCLING EQUIPMENT

GOVERNMENTAL AGENCY ACTIONS

- NASA ISSUED GUIDANCE CALLING FOR
 - IMPROVED FIRE DETECTION SYSTEMS
 - CHANGING PORTABLE EXTINGUISHERS TO SOLELY CO2 AND WATER
 - MAKING SPRINKLER SYSTEMS MANDATORY
 - INCREASING THE DEPENDANCE ON WATER

DEPARTMENT OF DEFENSE INITIATIVES

- DOD DIRECTIVE 6050.9 (13 FEB 89)
- ESTABLISHES POLICY FOR OZONE DEPLETING MATERIALS IN 5 AREAS:
 - MANAGEMENT OF CFCS/HALONS IN DOD
 - IDENTIFICATION OF APPLICATIONS AND PRIORITIZATION IN DOD
 - LONG-TERM PROCESS OF DECREASING DEPENDANCE ON CFC/HALON BECAUSE OF REDUCED AVAILABILITY DUE TO REGULATORY LIMITATIONS

DEPARTMENT OF DEFENSE INITIATIVES (CONT)

- R&D PROGRAMS TO DEVELOP/EVALUATE SUBSTITUTES FOR HALONS AND MISSION-CRITICAL CFC APPLICATIONS
- A TRACKING SYSTEM TO DOCUMENT DOD'S ANNUAL REQUIREMENTS FOR CFCS AND HALONS

U.S. NAVY GUIDANCE

- SEVERAL GUIDANCE INSTRUCTIONS ARE CURRENTLY UNDER DRAFT
 - SECRETARY OF THE NAVY
INSTRUCTION AWAITING SIGNATURE
 - CHIEF OF NAVAL OPERATIONS
INSTRUCTION AWAITING SIGNATURE
- PROGRAM PLAN FOR CFCS AND HALONS
IS NEARLY COMPLETE

U.S. NAVY GUIDANCE

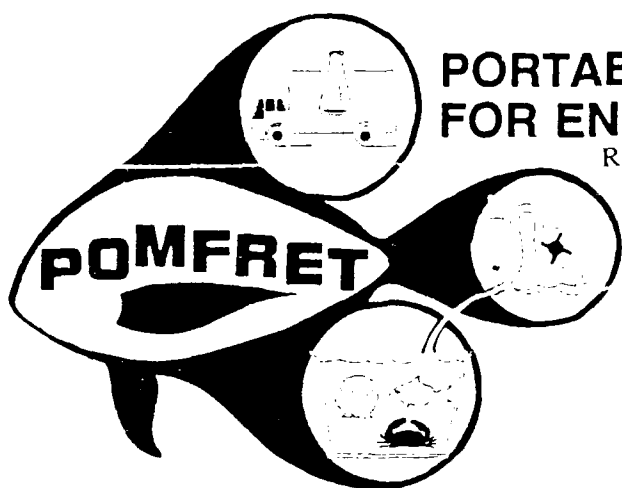
- SECNAVINST ASSIGNS SPECIFIC RESPONSIBILITIES TO VARIOUS NAVAL COMMANDS
- OPNAVINST GIVES SPECIFIC GUIDANCE ON
 - PROCUREMENT GUIDANCE
DIRECT AND INDIRECT PROCUREMENTS
 - ANNUAL REPORTING REQUIREMENTS
 - TRAINING GUIDELINES
 - R&D REQUIREMENTS
 - CONSERVATION MEASURES
 - DELINEATES RESPONSIBILITIES AND ACTIONS

CONCLUSIONS

- THERE ARE NO QUICK SOLUTIONS TO OZONE DEPLETION
- DOD WILL BE IMPACTED BY THE REDUCED AVAILABILITY OF CFCS AND HALONS
- NAVY COULD BE VERY SERIOUSLY AFFECTED
SHIP BOARD USES
FIRE SUPPRESSION
WEAPONS SYSTEMS
- RETROFITTING WILL BE EXPENSIVE AND TIME CONSUMING

CONCLUSIONS

- RETROFITTING WILL BE EXPENSIVE AND TIME CONSUMING
- ADDITIONAL MATERIALS MAY BE REGULATED
- CONSERVATION MEASURES MUST BE INITIATED



PORTABLE MICROCOSMS FOR ENVIRONMENTAL TESTING

R. S. Henderson, NOSC

POMFRET is a system that can be deployed at specific aquatic sites (e.g. Navy-used harbors) to evaluate the chronic effects of pollutants on resident marine organisms. The core of the system consists of twelve outdoor 100-gallon aquaria (microcosms) capable of maintaining low- to medium-diversity assemblages of organisms for periods of several months. The microcosms are provided with continuous flowthrough of unfiltered seawater and are exposed to normal sunlight. As such, they are linked energetically to the natural world, receiving input of ambient sunlight and nutrients, and are colonized by larval organisms entering in the supply water.

Conventional valve-controlled methods are very unreliable for long-term control of unfiltered natural waters because of clogging and fouling problems. POMFRET flow control is accomplished with a unique "batch-delivery" system. A series of paired adjustable-volume bins are periodically filled with ambient or pollutant water and are automatically emptied by activation of flapper valves driven by an adjustable-speed motor. The flow control/pollutant dilution unit is mounted on a small trailer for easy towing transport.

A motorized van provides portable laboratory and workshop space for field experiments, and the aquaria, aquaria stands, delivery pumps and system plumbing components are transported in the van. POMFRET requires about 700 square feet of nearshore area with access to freshwater and 110 VAC power. The system can be assembled by two technicians in about five working days and operation during experiments requires one full-time technician.

Typical experiments run for one to six months. Data produced relate to effects of pollutants such as heavy metals, pesticides, sewage effluents, elevated temperatures, altered salinities, dredge spoils, hydrocarbons and miscellaneous hazardous wastes. Typical measures of pollutant effects on organisms include growth rates, survival, abundance, reproduction and toxin bioaccumulation. Algae, bivalve molluscs, crabs, microcrustaceans, polychaete worms, corals, anemones, small fish and complex invertebrate fouling communities are examples of organisms that have been maintained in POMFRET systems.

Potential applications include:

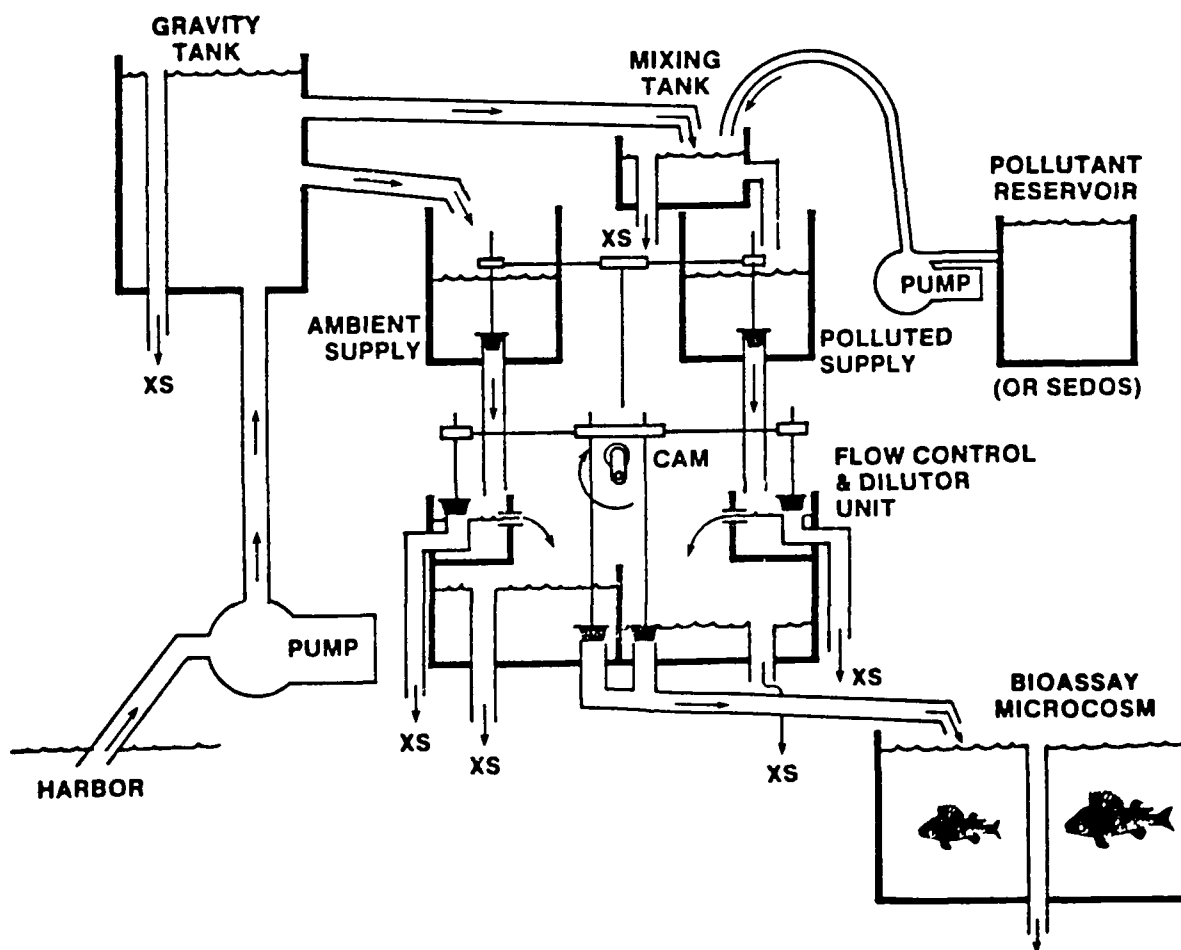
- Determination of realistic LC_{50} 's for harbor pollutants/organisms
- Bioaccumulation studies
- Dredge spoil bioassays
- Evaluation of pollution abatement programs
- Environmental assessments and impact statements
- Pollutant fate and degradation studies

Primary advantages of experimentation performed in a POMFRET system over existing short-term, static, laboratory bioassay methods are:

- Tests are site-specific, utilizing organisms and water actually derived from the study site of interest. The specific characteristics of biota and water quality can be important factors controlling the degree to which organisms are stressed by pollutants.
- Organisms are maintained for long time periods under near-natural conditions providing a realistic view of their response to pollutants. Processes such as toxin bioaccumulation will occur at rates close to those found in the field.
- The response of a wide spectrum of species of biota to a pollutant can be determined in one experiment.

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Funding for development and operational testing of this system was provided by Naval Facilities Engineering Command and David Taylor Research Center.



BIOMONITORING OF NAVY EFFLUENTS

S.M. Salazar, D. Lapota,
D.E. Rosenberger and W.J. Wild

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San Diego, CA 92152

Introduction

The Water Quality Act of 1987 instructs the Environmental Protection Agency (EPA) and State agencies to control toxic pollutants in wastewater discharges. This is being accomplished by lowering the acceptable limits of pollutants in discharge effluents and assessing/limiting toxicity with whole effluent testing. Facilities renewing NPDES permits are often faced with costly biomonitoring procedures. Routine application of biomonitoring tests by some States will lead to monthly testing for some discharges and receiving waters. The NPDES permitting procedures can vary from state to state resulting in different requirements for the Navy. Permit requirements that call for a "Toxicity Reduction Evaluation" or TRE are also being used by some states. The TRE process requires that sources of toxic pollutants in discharges be "found and corrected" which often means additional biological and chemical testing. Some industries have spent up to \$300,000 to comply with their TRE requirements. Unfortunately, some TRE procedures and biomonitoring requirements are selected by states with little or no knowledge of appropriate technical bioassessment protocols. Scientifically defensible environmental evaluations concerning contaminated effluents can only be made with the proper biological and chemical assays. As the requirement of biomonitoring for toxic control increases, the ability to assess, comment on and, if need be, rebut State proposals must also increase. It is imperative that the Navy be able to scientifically evaluate the sampling burden placed on an activity. To do this, biomonitoring experts are needed to review draft permits and provide valid comments or alternatives to State agencies. The risk to the Navy in lacking such expertise is that unnecessarily expensive and inappropriate testing programs may be implemented and, once established as a permit requirement, they are very difficult to modify or eliminate.

What Is Biomonitoring?

- ... Plants and animals used to assess wastewater discharges for toxicity.
- ... One approach for Water Quality-based Toxics Assessment and Control.

Who Must Biomonitor?

- ... NPDES Permit Applicants - Individuals wanting to discharge wastewater into freshwater or saltwater environments.

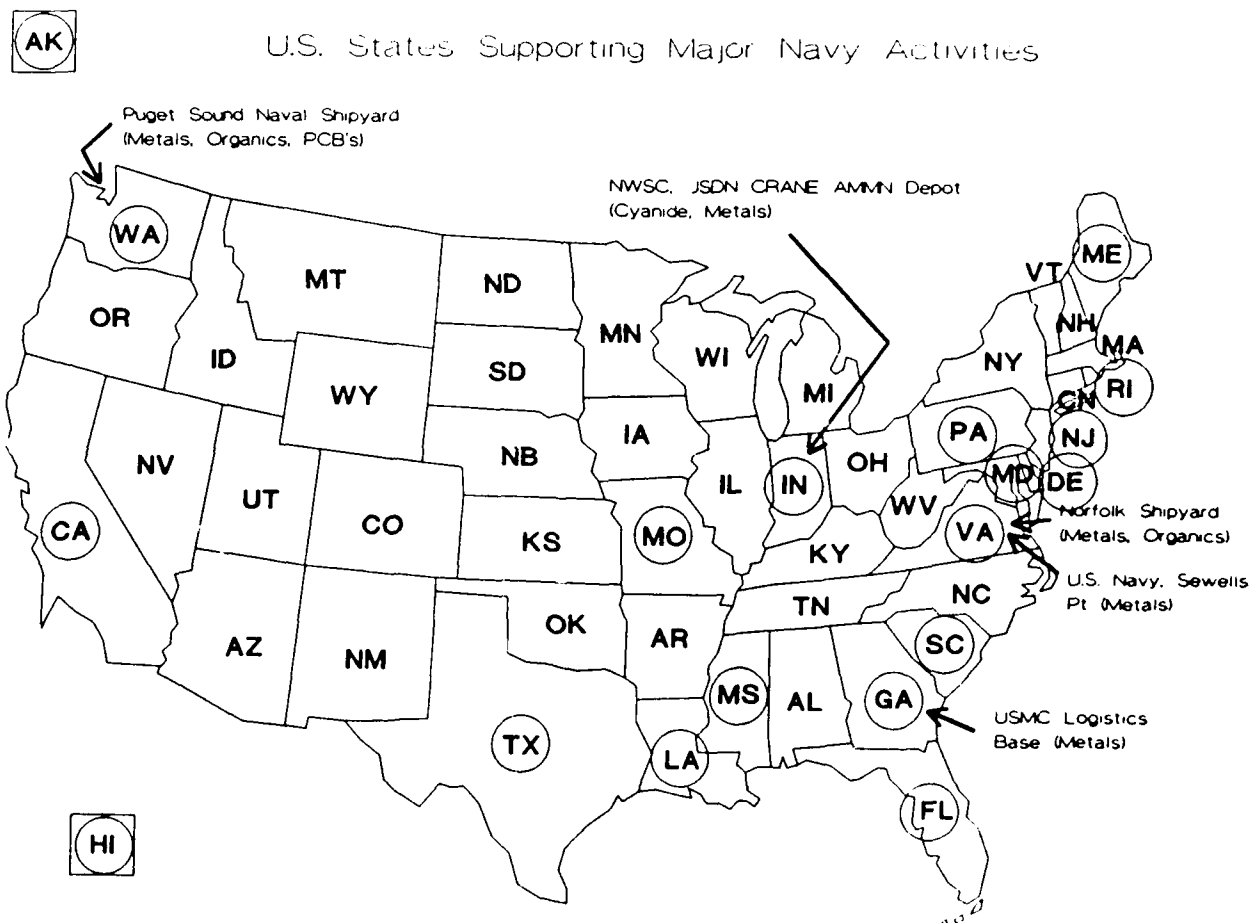
What is the Effect on the Navy?

Naval facilities such as Air Stations and Shipyards must demonstrate industrial wastes meet acceptable limits of pollutants in discharge effluents.

This is accomplished by effluent toxicity testing
- BIOMONITORING -

What Is the Problem?

- **38 States Require Biomonitoring**
- **Navy has major activities in 19 States**
- **Permitting procedures vary for each State:**
 - **EPA Administration/Protocol**
 - **State-Delegated Authority**
 - **Limited Biological Effects Testing**



INDIVIDUAL STATE'S NPDES PERMIT REQUIREMENTS (AS OF 1986)

<u>STATE</u>	<u>AUTHORITY</u>	<u>REQUIREMENTS</u>
AK	EPA - 10	3 permits require bioassays; each individually designed - 96 hr LC ₅₀ : Salmonid, Amphipod, Crustacean - In-situ: 2 Filter Feeders & 2 Sediment Dwellers - Continuous Flow: Salmonids Latest EPA Guidance: Echinoderm Fertilization, Mussel Larvae & Algal Reproduction
CA	9 SRWQCB	Frequency of testing depends on industry 96-hr static Fish assay; Mussel Watch
DE	State	Resident Fish Bioassays; 3 consecutive 24-hr whole effluent tests
FL	EPA - 4	Biomonitoring required for all renewed permits with flow > 0.5 mgd; if $\geq$ 1% waste concentration must do 7-day Daphnid & Larval Minnow Survival Test.
GA*	State	48-hr acute static Daphnid & Minnow Bioassays On-site flow-through testing
HI	State	"Most dischargers to the marine environment and appropriate aquatic species & types of bioassays remain unclear." EPA - 9 has recommended standard freshwater species for freshwater discharges.
IN*	State	48-hr acute static Daphnid Bioassay or 7-day chronic Daphnid & Embryo-larval Fathead Minnow
LA	EPA - 6	48-hr acute static Daphnid Bioassay Both EPA & State discharge permits required
ME	EPA - 1	7-day chronic Daphnid Bioassay 14-day Brook Trout Growth Study
MD	State	One-time 96-hour Static renewal bioassay with a locally important fish & invertebrate. Estuarine: mysid, sheepshead minnow.
MO	State	Chemical Specific, no biological testing
MI	State	7-day Daphnid & Fathead Minnow Bioassays
NJ	State	Acute static renewal Fathead Minnow (FW) Mysid or Sheepshead Minnow (SW)
PA	State	Chemical Specific, no biological testing
RI	State	All major permits; 48-hr static Daphnid, 96-hr Fathead Minnow
SC	State	As permits reissued; 7-day Daphnid Bioassay
TX	EPA - 6	As permits reissued for all major dischargers 48-hr acute static Daphnid Bioassay Both NPDES permit & a State permit for Point Source
VA*	State	Semiannual 96-hr acute, static or static renewal Daphnid & Fathead Minnow or appropriate SW species
WA*	State	As permits reissued 96-hr Salmonid Bioassay, Daphnid Bioassay Puget Sound - special emphasis

* = NAVY/MARINE COPRS FACILITIES ON EPA LIST OF TOXIC DISCHARGERS

Approach

- Up-Date 1986 State Survey for current NPDES requirements.
- Determine Naval Activities Current Problem Areas
- Propose Less-Costly, More Meaningful Approaches when applicable
- Apply New and Existing Techniques to Navy-Related Problems

Site-Specific Environmental Quality Assessment Laboratory (SEQUAL)

Site-Specific

- * Designed to use on various toxicant types and site conditions
- * Hazardous waste disposal sites
- * Nonpoint source discharge sites
- * Land-based (trailer) or floating (platform)

Environmental Quality Assessment

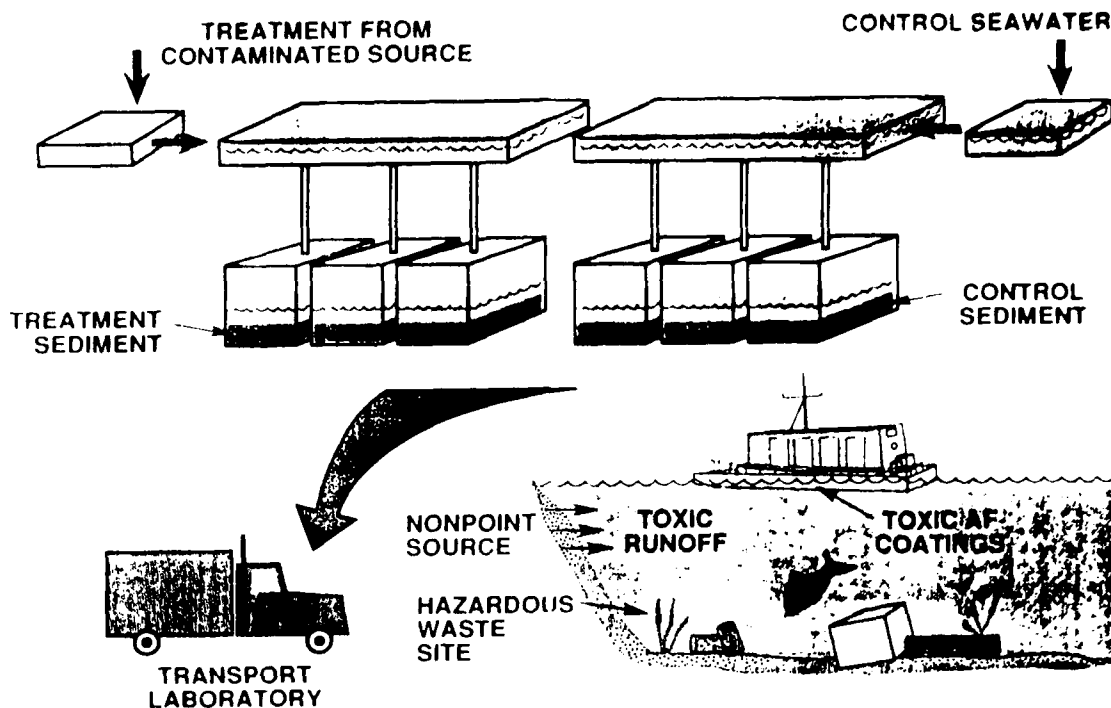
- * Assess extent of contamination and effectiveness of cleanup
- * Potential toxicant media: effluents, sediments, water
- * Optimize biological response for an appraisal of site-specific conditions

Laboratory

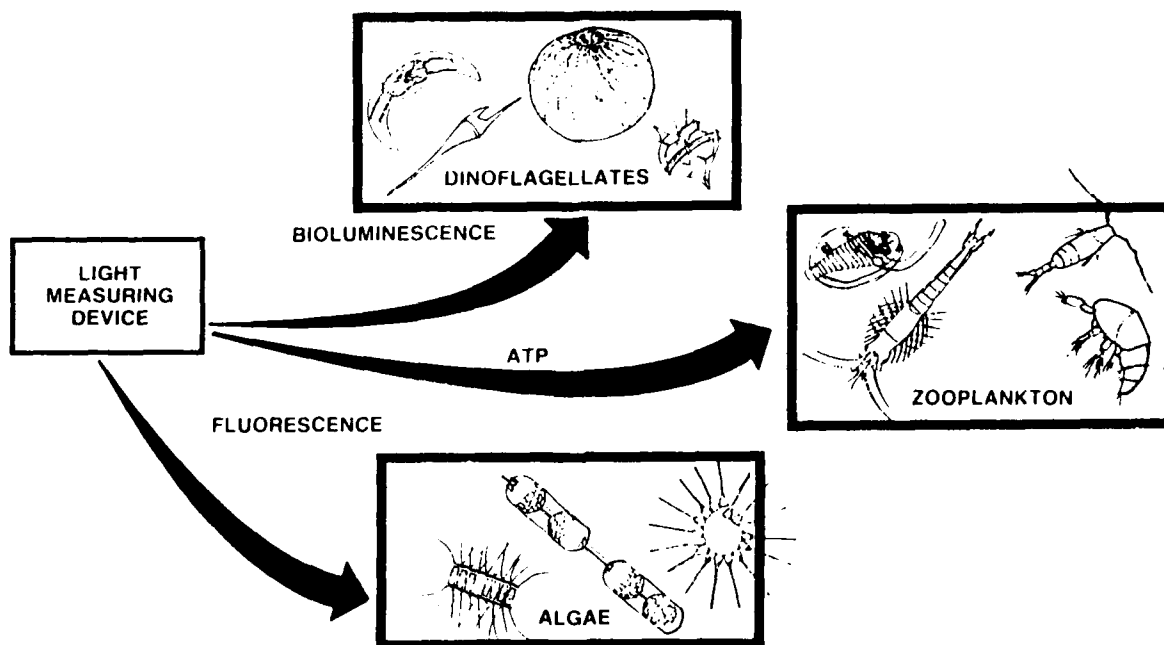
- * Generic, standardized test system
- * Transportable, flow-through
- * Acute and/or chronic assays on individual species
- * Sensitive, reliable test species
- * Growth studies
- * Reproduction/Live cycle tests



SEQUAL Site-Specific Environment Assessment Laboratory



QWIK-LITE Assays



**BIOMONITORING OF EFFLUENTS
INFORMATION SURVEY**

Date _____

Name of Activity _____

POC at EFD _____

Phone Number AV _____ COMM _____

Is Biomonitoring of Effluents a NPDES requirement? _____

NPDES Permit Number _____ State _____

What types of pollutants are being discharged (i.e., metals, organics, PCB's)? _____

What types of assessments are required (i.e., 48-hr static acute Daphnid bioassays, Rainbow Trout growth studies) _____

How often are tests required? _____

How long has testing been performed? _____

To whom have results been submitted? _____

Has a Toxicity Reduction Evaluation been required/performed? _____

If Yes, When: _____

Have you had any problems with the State Agencies or EPA in obtaining permits or defining the procedures to follow? _____

If you have any comments regarding biomonitoring of effluents or the NPDES permit procedures, please take the time to present them here.

What future problems or requirements do you anticipate? _____

Please Return the Survey to:

(619) 553-2776

Sandra Salazar, Code 522
Naval Ocean Systems Center
San Diego, CA 92152-5000

INSTALLATION RESTORATION AND REMEDIATION TECHNOLOGIES

LAKEHURST ADVANCE PHOTOOXIDATION	219

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<i>IN SITU</i> BIOREMEDIATION OF NAS PATUXENT RIVER FUEL FARM	234

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BIOREMEDIATION TECHNOLOGY	244

Clifford Hui
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San Diego, CA 92152-5000
AUTOVON 553-5475, (619) 553-5475

LAKEHURST ADVANCED PHOTOOXIDATION

N. J. Olah, NCEL

The matrix of processes investigated included all binary combinations of ozone, hydrogen peroxide, and ultraviolet radiation (UV). To date, all candidate processes except ozone alone have been investigated. For reasons which will be given later, ozone alone will probably not be tried.

A complicating factor in the treatment of Lakehurst water is the presence of 2 mM ferrous iron (about 100 ppm) in the water. This low oxidation state iron consumes an equivalent amount of oxidant, which will raise the treatment cost significantly. Therefore, unless the presence of the iron was to be chemically utilized in some manner during treatment experiments, the iron was oxidized by pH adjustment to 8-9 and oxygen sparging.

Experiments LH-1 to LH-5 were preliminary runs that set-up the conditions for LH-6 through LH-8. The latter are described below:

LH-6 Ozone/UV at low pH

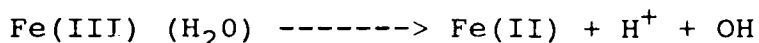
Previous experiments had indicated that the presence of the inorganic carbon (carbonate/bicarbonate; denoted IC), present naturally in the water as well as that resulting from the mineralization of organic contaminants, was detrimental to the efficiency of the Advanced Oxidation Processes (AOPs). During the later stages of treatment, organic acids accumulate that are not capable of reacting as quickly with hydroxyl as is IC. A typical product which occurs in the later stages of may ozonation and AOP reactions is oxalic acid. Since there is gas flow through the reactor during all AOP experiments, lowering the pH should allow the IC to be sparged as carbon dioxide from the reactor both initially, and as more is formed, maintaining the IC concentration in the reactor at a much lower level than would be possible at higher pH.

In addition, a kinetic calculation showed that oxalic acid is in its most reactive form with respect to hydroxyl radical when the pH is in the range 2.0-3.5. Thus experiment LH-6 was run at a pH of 2.4 after the filtration of the preoxidized iron.

LH-7 UV only

At first, the idea of UV photolysis being an effective water treatment process was discounted, since 1) the types of compounds thought to be present would not be susceptible to photolysis, and 2) because photolysis rarely leads to the complete destruction of organic compounds. However, when it was discovered that 2mM iron was already present in the water, we decided to try

to take advantage of the well-known photochemistry of the dissolved iron aquo species. Photolysis of the hydrated iron is known to result in ligand-to-metal charge transfer, which produces a hydroxyl radical. The iron species that participates in the photolysis is denoted here by Fe (III) (H²O), although there are undoubtedly other ligands in the coordination/solvation sphere:



If successful this process could be carried out much less expensively than could ozone generation and contacting. The pH of the solution was lowered to help keep the iron(III) in solution, as well as for the reasons described previously.

LH-8 H₂O₂/UV

This is a commercially-available AOP which can in some instances be less expensive than ozonation processes, but which is very sensitive to the presence of IC. A potential bonus when using this process is that in some cases, peroxide can be regenerated by reactions subsequent to OH attack of the organic molecule. One disadvantage of the process is that it is more adversely affected by the presence of bicarbonate alkalinity than are the ozonation at low pH.

ANALYTICAL METHODS

In any treatment project of this type, the choice of appropriate analytical parameters can be among the most difficult decisions to be made. Analytical parameters, detection limits, and treatment criteria all intimately linked. Previous analyses of samples from this well (BJ) have indicated that little or no significant "priority pollutants" are present, yet the water has a bad odor and is obviously unsuitable for discharge back to the aquifer. As of our last communication with NJDEP, contaminants to be cleaned up and monitored had not yet been selected by the regulatory agencies. Suggested parameters were TOC, petroleum hydrocarbons, surfactants, and ethylene glycol. The last two parameters were suggested because of their possible presence in some AFFF formulations. Problems involving the analytical methods have been discussed in previous reports. In addition to interference problems, most of which have been identified, there is the perhaps bigger issue of appropriateness. The following briefly summarizes the present situation.

Total Organic Carbon (TOC) - TOC is presently being used as an

indicator parameter. It is important from a mass balance point of view, for comparing efficiencies of various processes. In the long run, it may be the most important analytical parameter to be monitored. It is common to hear the statement that in remediation to remove regulated contaminants, one does not have to remove all of the TOC. That may be true of natural organic material which is present, although it is a topic of much current research whether oxidation by-products represent any threat to the public health or the environment. In the present case, however, the majority of the 48mg/L of TOC is anthropogenic material which appears to be largely weathered/oxidized hydrocarbons (i.e., carbonyl compounds and carboxylic acids) and perhaps some partially degraded AFFF components. These components should be removed before the water is discharged to the aquifer, as evidenced by the petroleum/solvent smell of the water before treatment. Thus, we have used TOC as our primary indicator parameter.

Organics Acids - Organic acids are important products in the mineralization of all organic compounds, and are therefore important indicators of the progress of the treatment reactions. It was our determination that the products of treatment were organic acids which allowed us to identify IC as the problem in the final stages of LH-2, -3, and -5. These acids are quantified by titration and Gran plot analysis.

Carbonyl Compounds - Previous studies in this laboratory have shown that carbonyl compounds represent the most predominant class of intermediate by-products which occur in the AOPs. Carbonyl compounds are determined by reaction with 2,4-dinitrophenylhydrazine, followed by extraction and HPLC analysis. In addition to quantification of total carbonyls as a surrogate parameter, the retention time of the various products gives reasonable estimate of the chain length, and therefore of the progression of the fragmentation of the longer hydrocarbon and fatty acid molecules.

RESULTS AND DISCUSSION

TOC Destruction

The destruction of TOC is shown in Figure 1 for experiments LH-2 to LH-8. The UV only (LH-7) and peroxide-only (LH-4) treatments were found to be ineffective at removing organic carbon from the water. Peroxide treatment did selectively remove approximately 2/3 of the organic acids which were initially present (data not shown).

Of the ozone/peroxide experiments, run LH-3 was slightly more effective than LH-2 at destroying TOC. There were two differ-

ences between these two experiments. One was that the iron precipitate was left in the reaction mixture in LH-2 but removed in LH-3. The other difference was that the peroxide was continuously metered into the reaction mixture in LH-3, but was added in increments in LH-2. Total peroxide dose was actually higher in the poorer-performing LH-2 than in LH-3.

In the first ozone/UV run, LH-5, TOC was destroyed at a rate that was very similar to that in the ozone/peroxide experiment LH-3. Peroxide accumulation and destruction curves were also almost identical. However, as will be seen later, more ozone was required in LH-5 for the same amount of TOC removal as was observed in LH-3.

In contrast to LH-2, -3, and -5, the pH was lowered to 2.4 before the second ozone/UV experiment (LH-6) was begun. Although there appears to be an initiation period for LH-6, the overall removal of TOC was seen to be much faster in LH-6 than in previous runs, as predicted above. The greater accumulation of peroxide in LH-6 indicates that the lower the pH, the more time was required to establish the free-radical chain reaction, during which time more ozone photolysis/peroxide accumulation took place. The photolysis of ozone in aqueous solution produces hydrogen peroxide.

The plots in Figure 1 do not account for the fact that ozone is used up more rapidly in ozone/UV experiments than in ozone/peroxide treatment. It is revealing to plot the percent of TOC mineralization as a function of the utilized ozone dose, which is the amount of ozone actually consumed in the reaction. On the basis of ozone consumed, TOC is mineralized more efficiently in the early stages of the reaction, by ozone/peroxide treatment. The fact that considerable ozone is being converted to hydrogen peroxide in the ozone/UV system does not entirely account for that difference. However, in the later stages of reaction, low pH ozone/UV treatment is clearly the most efficient, due primarily to the competition by IC at the higher pH values. It is interesting that LH-2, -3, and -5 all seem to converge to the same curve at higher ozone doses.

Another revealing manner in which to plot the data is shown in Figure 2, which shows the efficiency is represented as the number of moles of TOC removed per mole of oxidant (ozone plus peroxide) used. Again, it is seen that peroxide/UV (LH-3) is much more efficient at the beginning of the treatment, but that ozone/UV is more efficient in the later stages. The efficiencies shown in Figure 2 are cumulative, that is, the efficiency at a given conversion is calculated from total carbon removed and total ozone consumed up to that point in the reaction. Therefore, the difference between the instantaneous efficiencies at a given conversion is even greater than that indicated by the figure. All efficiency curves in Figure 2 should pass through the origin, and all should extrapolate to zero at 100% conversion. The first

statement is due to the fact that ozone must be removed from the gas phase before it can react to remove TOC; thus, D is nonzero while TOC is still zero. The second characteristic is due to the fact that toward the end of treatment, remaining TOC finds it more and more difficult to compete for hydroxyl radicals as the TOC concentration continues to decrease.

PHC Destruction

Another means by which to judge the success of treatment is by the removal of Petroleum Hydrocarbons (PHCs). Interpretation of our data is complicated by the fact that we discovered the fatty acid contribution to the PHC determination and modified our PHC analysis, beginning with LH-5. However, the data shown in the lower left-hand corner of Figure 1 is typical of runs LH-3, -5, and -6, where PHCs are destroyed to less than 2% of the starting concentration (which is typically 3 mg/L) in about 10 minutes. Figure 13 emphasizes the fact that the other organic material present is liable to be of considerably greater environmental significance than are the PHCs.

SUMMARY

Neither hydrogen peroxide nor UV alone was effective in destroying the majority of organic compounds which are present in the Lakehurst ground water sample. Ozone/peroxide treatment at a pH of approximately 8-9 was quite efficient in the early stages of the reaction, but competition from carbonate/bicarbonate drastically decreased the efficiency of treatment in the later stages when the majority of the remaining by-products were more refractory organic acids. Only 80-90% of the TOC was removed in three hours of treatment, although the first 50% was destroyed in the first 30 minutes. Ozone/UV at pH 8 was slightly faster than ozone/peroxide, but required a larger ozone dose for the same amount of TOC removal.

Ozone/UV at pH 2.4 was less effective in the early stages of the reaction, but was very effective in the later stages. The TOC of the water was completely destroyed in one hour under the conditions employed despite the lower initial efficiency.

PROJECTED WORK

The promising results obtained using ozone/UV at low pH indicate that this is the method of choice for the final stages of the reaction. These results might seem to suggest that ozone/peroxide at low pH might perform even better. However, ozone/peroxide cannot achieve the desired results at low pH since that system depends on the dissociation of hydrogen peroxide ($pK=11.6$) to initiate the chain reaction. The initiation reaction is expected to be five orders of magnitude slower at pH 3 than at pH 8.

Nonetheless, the ozone/peroxide system may be tested at low pH in order to confirm that hypothesis, if time and resources permit.

Similarly, generation of hydroxyl radicals from ozone in the absence of UV or peroxide generally requires basic conditions, under which the bicarbonate will accumulate and be detrimental to reaction efficiency. Ozonation under basic conditions will be tried as an alternative to ozone/peroxide in the early parts of treatment, but is not expected to yield any appreciable advantage over ozone/peroxide.

A promising alternative seems to be a two stage reactor system in which ozone/peroxide is used at basic pH in the first stage, followed by pH adjustment to approximately 3, and ozone/UV treatment in the second stage. In this manner, we would take advantage of the high efficiency portions of each process.

We will also separately investigate one of the reasons that the ozone/UV process may be so effective in the latter stages. Small quantities of iron (III) are still present in the reaction mixture, despite preoxidation. Oxalate, complexes with iron (III) to form a photochemically labile species, which decomposes to carbon dioxide upon irradiation with UV. It may be possible to incorporate this reaction into the treatment process to a greater extent.

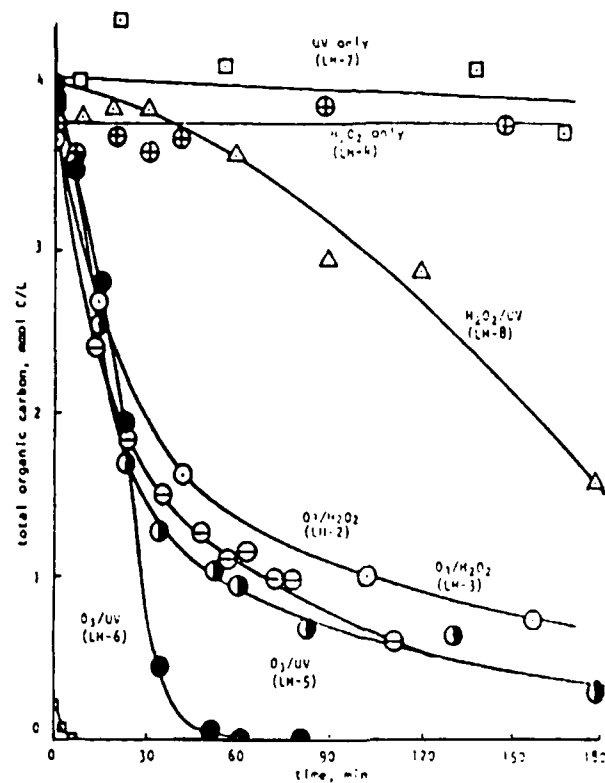


Figure 1 TOC disappearance curves for AOP treatment of Lakehurst water

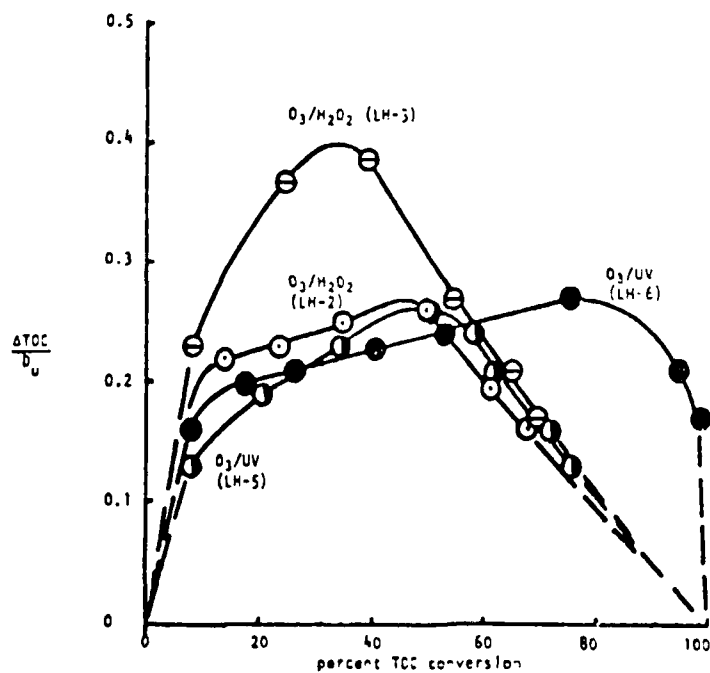


Figure 2 Destruction efficiency of TDC throughout AOP treatment of Lakehurst ground water

DECONTAMINATION OF PCB LADEN SOILS USING KPEG

D. B. Chan, NCEL

The Naval Civil Engineering Laboratory(NCEL) completed a joint pilot study with the U. S. EPA Risk Reduction Engineering Laboratory (RREL) in Cincinnati, Ohio to decontaminate PCB contaminated soils at the Navy's Public Works Center in Guam.

The PCB contamination resulted from long term spills from a storage tank at a transformer maintenance/services shop in Building 3009. The spilled PCBs had migrated into a storm drainage ditch. Approximately 5,000 cubic yards of soil were subsequently contaminated. Contamination penetrated as deep as 8 feet at some places along the drainage area. Concentration levels reached as high as 50,000 parts per million(ppm) with an average reading of 2500 ppm.

A chemical reaction process, Potassium Polyethylene Glycol(KPEG), was chosen from other alternatives for treatment of the soils. The KPEG process is capable of dechlorinating a wide variety of halogenated organic compounds including PCBs, dioxins, and dibenzofurans. A 1.5 ton batch system was fabricated for the pilot study. The hardware consisted of a mixer cum reactor, a steam generator, a steam condenser with a carbon adsorber and auxiliary equipment.

PCB contaminated soils were fed into the mixer and heated (via a steam jacket) to the reaction temperature of 300° F. At this temperature reaction times of four hours were needed to complete the destruction. Steam generated from the mixer was processed through a condenser and a carbon adsorber to remove any PCB residues. Upon cooling, treated soil samples were measured to determine if PCB cogener peaks of 2ppm or less were attained.

The KPEG process demonstrated its effectiveness in reducing PCB concentration from about 3000 ppm to below 2 ppm. This reaction efficiency met the EPA permit standards. During the test runs some material spilled when there was a failure in the ventilation system. This particular material was also treated during Batch Run #10 and treatment effectiveness again met standards. The chemical concentrations were added at a ratio of 50% Polyethylene Glycol to 10% Potassium Hydroxide by weight with the soil charge. This chemical dosage was stoichiometrically much greater than the laboratory studies indicated.

Recent laboratory studies indicate that the chemical dosages could be reduced to approximately 1% by weight for both chemicals. PCB concentrations from soil samples (range 500-800 ppm)

were reduced to less than 1 ppm in series of laboratory experiments. This low chemical dosage requirement indicates that the KPEG process can be made even more cost effective.

Fifteen tons of PCB contaminated soil, containing approximately 3,000 ppm of Aroclor 1260 were treated in thirteen batches at Public Works Center Guam. All batches met the permit requirements. Carbon from the adsorber along with protective coveralls, gloves, boots were treated in the last batch.

Comparative cost analysis with incineration indicates a five fold cost reduction potential from the use of the KPEG process. Continued laboratory evaluation of the process has led to significant process improvements. Substitution of sodium for potassium in the form of sodium hydroxide reduces reaction times from 4 hours down to 1 hour. These improvements would make the process more cost effective. Work has begun on the design and fabrication of a 1.5 ton/hour continuously operated unit. This will be tested in Guam next summer.

APEG PROCESS

APEG Processes	Chemicals/Dosage (by Wt.)	Reaction Temp (F)	Reaction Time (hr)	Product
KPEG (old)	PEG 400/50% KOH/10%	300	4	Non-Toxic PCB-PEG
NaPEG (new)	PEG 400/1% NaOH/1%	600	1	Non-Toxic Aliphatic HC

KPEG MILESTONES - GUAM

ADMINISTRATIVE TECHNICAL

FY 86

Prelim On Site

FY 87

IAG w/EPA

Soil Shipment Permit

Tech Assess

Houston Biodeg Study

Guam Soil Samples

Pilot Studies

Soil Exc/Screening

Pilot Design

FY 88

R&D Permit(EPA HQ)

Pilot QA/QC Plan

Pilot Safety Plan

EPA Region IX Permit

Pilot Study

Biological Exam

KPEG MILESTONES - GUAM

ADMINISTRATIVE

FY 89

REMOVAL ACTION

TRC Meetings

TRC Doc. Reviews

FY 90 - 92

Public Hearings

Demo Operation Permit

RA - Site Clean-up

TECHNICAL

Scale Up Design

Engr. Eval. Report

Cost Analysis

FY 90

FFR

System build

FY 91 - 92

System Demo

Clean-up

Final Report

ORDNANCE BIODEGRADATION

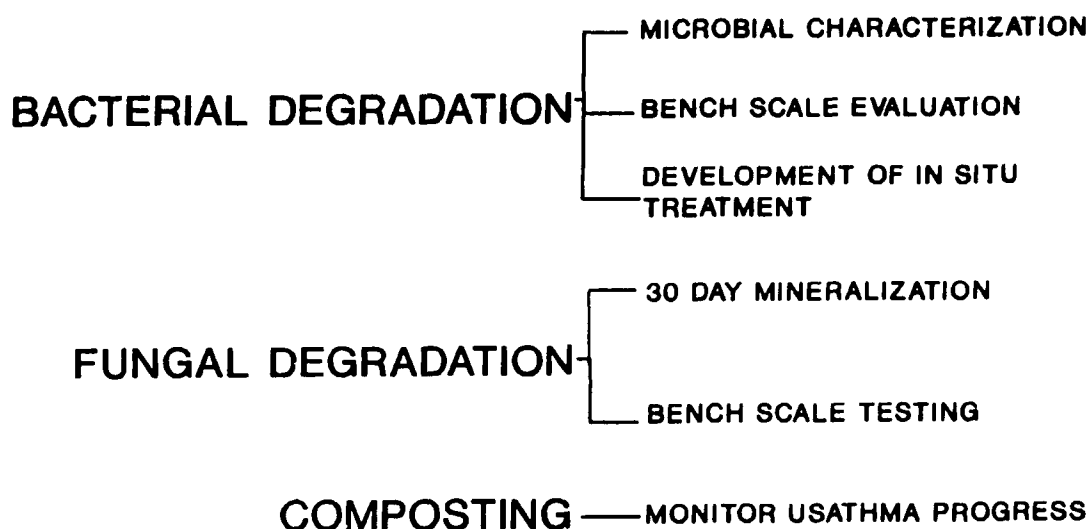
C. A. Lebron, NCEL

OBJECTIVE: To bioremediate soil contaminated with ordnance compounds (TNT and RDX) utilizing native bacterial populations or fungi

SITE D, SUBASE Bangor, Washington

- **Former ordnance burning ground (1946 through 1963)**
- **Elevated concentrations of TNT and RDX**
- **Variable soils (glacial till and underlying clayey subsoil)**

APPROACH



RESULTS OF MICROBIAL CHARACTERIZATION

- HEALTHY ASSEMBLAGES OF MICROFAUNA
- ONE COLOCNY CAPABLE OF DEGRADING TNT TO CO₂
- LOWER CONCENTRATIONS OF TNT THAN PREVIOUSLY DETECTED 7,560 ug/Kg v. 6,000,000 ug/Kg
- RDX NOT DETECTED v.758,00 ug/Kg
- HIGH CONCENTRRATIONS OF DNT (THE EXPECTED INITIAL DEGRADATION PRODUCT)

PRELIMINARY RESULTS OF BENCH SCALE TESTING

- **WELL OXYGENATED SOIL**
- **HIGH CONCENTRATIONS OF DNT**
- **NO RDX DETECTED**
- **BEST POTENTIAL FOR RING CLEAVAGE
IS UNDER DENITRIFICATION CONDITIONS**

RESULTS OF FUNGAL TREATIBILITY TEST:

- **COMPLETE DEGRADATION TO CO₂ IN 30 DAYS
IN NITROGEN LIMITED CULTURES**
- **MASS BALANCE ANALYSIS SHOWED THAT
LESS THAN 5% OF THE RADIOACTIVITY
REMANIDE AS UNDERGRADED ¹⁴C-TNT**

COMPOSTING

- MONITOR USATHAMA'S PROGRESS
- RAPID TNT AND RDX REDUCTION
 - 83.6% Reduction for TNT
 - 78.3% Reduction for RDX
- NO RING CLEAVAGE HAS BEEN DEMONSTRATED AS EVIDENCED BY THE INSIGNIFICANT QUANTITY OF $^{14}\text{CO}_2$ EVOLVED

IN SITU BIOREMEDIATION OF NAS PATUXENT RIVER FUEL FARM
R. Hoeppel, NCEL

SUMMARY

Subsoil, groundwater and surface water that were contaminated with jet fuel leakage from the fuel farm are being reclaimed by combined in situ technologies. Pilot studies will be conducted that compare cost and effectiveness of both a groundwater treatment scheme (Enhanced In Situ Bioreclamation) and an unsaturated soil treatment that combines soil vapor extraction with biodegradation (Bioventing). "Remedial investigations" at the field site were completed in Oct 89, which included: soil gas analysis, geophysical evaluations, and soil/water chemical and biological analyses from 38 new and 7 preexisting wells. The findings indicate multiple contamination plumes from more than one source and fuel type. The plumes underly an area of up to 30 acres, at an average depth of about 15 ft. Laboratory data indicate that jet fuel-saturated sand will not allow for rapid biodegradation because of a low surface area of water insoluble fuel components in contact with viable microorganisms. Jet fuel concentrations in soil of less than 0.1% appear to degrade at a rapid rate. The more soluble and toxic aromatic fraction is rapidly biodegraded by the indigenous soil microorganisms. Laboratory studies also indicate that "bioventing" should be an effective remediation method that is only a third to a tenth the cost of other remediation options.

INTRODUCTION

More than a third of the Navy's 813 known disposal and spill sites that require attention are contaminated by fuels and oils. In most instances large quantities of soil and subsoil are contaminated to the groundwater table, often at depths that preclude excavation. Often the contamination migrates under buildings, creating explosive or unhealthful conditions. Besides the costs to replace lost structures, soil removal and disposal in approved landfills can exceed \$400 per cubic yard, and the price continues to skyrocket. Treatment of fuel-contaminated groundwater alone is also not cost-effective or desirable because low levels of potentially toxic and foul-tasting fuel components can be continually released to groundwater from overlying contaminated soil for many years.

The most cost-effective and acceptable methods for destroying or detoxifying wastes are by treating them on-site, preferably in-place (in situ). For fuels, several in situ methods have been used successfully in pilot field testing and, based on limited data, appear to be far superior in cost to removal and disposal or treatment off-site, or on-site incineration. Two of the most promising are:

- * enhanced in situ bioreclamation; and
- * soil venting (soil vapor extraction).

"Enhanced In Situ Bioreclamation" is a process that uses the catalytic/metabolic machinery of microorganisms to degrade or detoxify primarily organic contaminants where they lie in soils and groundwater; the mechanism in the recent past for promoting in situ biotransformation has been by treating pumped groundwater with nutrients and a free oxygen source and reinjecting this water into the contaminated unsaturated zone upgradient from the pumping wells. Metal contaminants can also be immobilized/mobilized by microbial interactions but this is not usually referred to as biodegradation. The ultimate products of biodegradation are carbon dioxide (or methane) and water. Although most of the microbiological treatment occurs in the subsurface, part of the contamination may be transported to the surface, where it is treated above-ground.

A typical in situ bioreclamation is depicted in Figure 1. This portrays in-place simultaneous treatment of fuel/oil contaminants in both the unsaturated soil and groundwater by stimulating the growth and metabolic activity of natural hydrocarbon-degrading microorganisms in the soil and water. Since most refined petroleum products are biodegraded at accelerated rates under aerobic conditions, free oxygen is usually injected into the subsurface (either as air, pure oxygen gas, or in the form of stabilized hydrogen peroxide). Nutrients, especially bioavailable forms of nitrogen (usually ammonium) and phosphorus (soluble phosphates), are also added to the contamination zone since petroleum products are deficient in proper nutrient balances. Most bioreclamations performed up to the present have operated by pumping groundwater from wells downgradient or peripheral to the contaminated area to wells or ditches emplaced upgradient or within the contaminated zone (usually within the unsaturated soil profile). This pumping and reinjection of groundwater drastically increases the groundwater flow velocity within the treatment area, and is supposed to increase the horizontal movement of oxygen and nutrients through the contaminated area. In-place bioreclamation works most efficiently where soils have high permeabilities, such as in sandy profiles. Since most fuel components are insoluble in and lighter than water, they tend to remain mainly in the unsaturated soil profile and, upon reaching the saturated zone, float as a free product layer on the water table. The more water soluble (and often more toxic) fuel components, such as the simple aromatics (benzene, ethyl benzene, toluene, xylenes), will slowly dissolve into groundwater over long time periods. All contaminant phases (soil-sorbed, free product, dissolved) can contribute to the soil vapor phase.

LABORATORY STUDIES

Two major problems often encountered in field-scale in situ bioreclamations of fuels are: difficulty in transporting free oxygen into the contamination zone and inability of micro-

In-SITU Bioreclamation of Fuel Oil Contaminated Soil and Groundwater

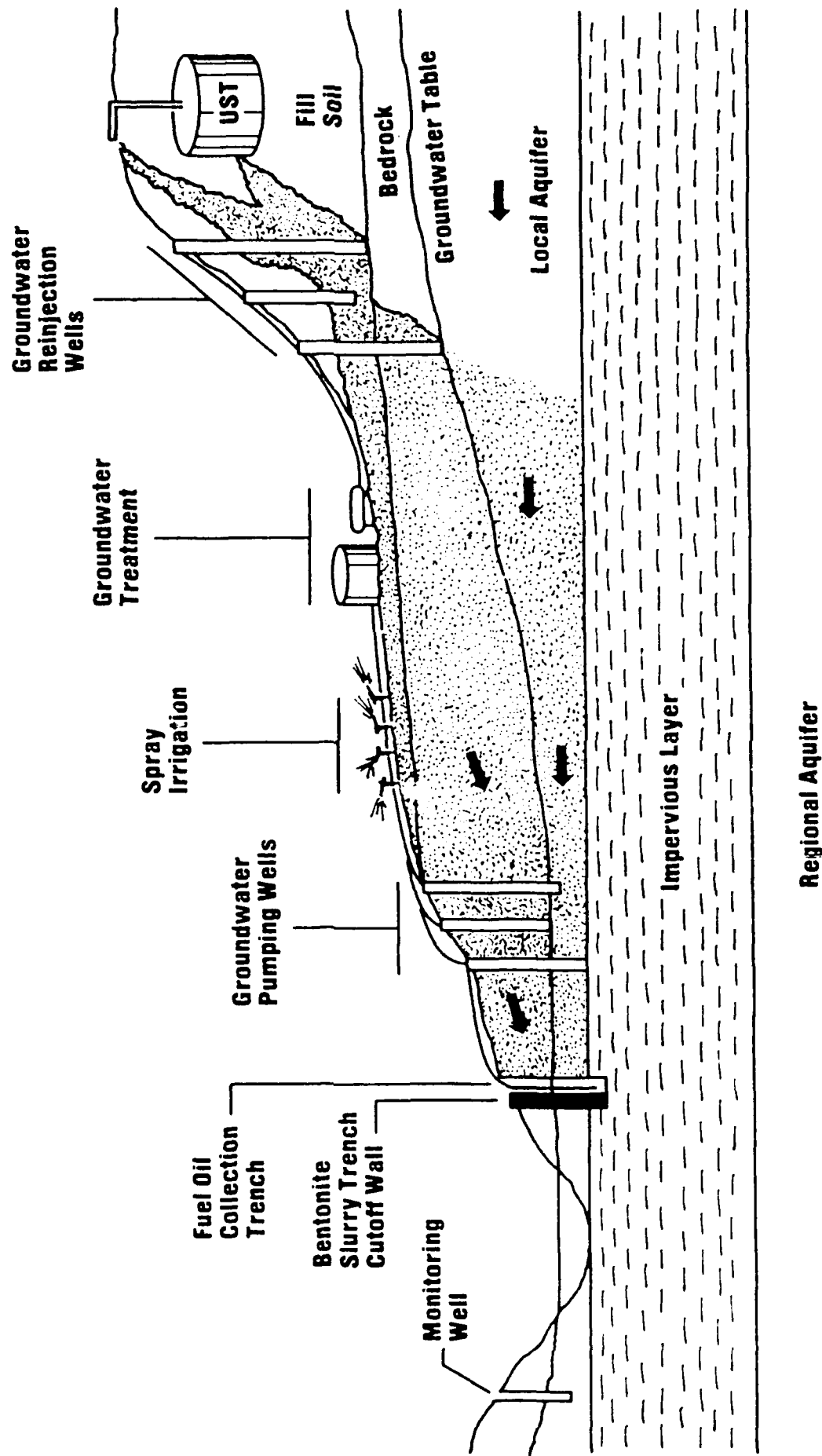


Figure 1. Saturated Zone In Situ Bioreclamation

organisms to achieve intimate contact with the predominantly water-insoluble fuel components. Water has a poor oxygen carrying capacity and hydrogen peroxide (a commonly used source for free oxygen) has been observed to be rapidly broken down into free oxygen and water by reduced iron and microbial enzymes in the soil. Free oxygen, being lighter than most other common soil gases, rapidly migrates vertically to the soil surface. The large quantities of fuel sorbed by unsaturated soils tend to prevent water infiltration; thus microbial growth and fuel biodegradation are often limited by the small surface area of fuel in contact with water (which is where microorganisms can proliferate). Thus insoluble hydrocarbons are seldom rapidly degraded, even after removal of free product from the water table. While our laboratory studies showed that the more water soluble aromatic compounds are degraded within days or weeks, using jet fuel-contaminated soil from the NAS Patuxent River fuel farm, degradation of the water insoluble fraction (mostly branched-chain aliphatic compounds) occurred only at very slow rates when concentrations exceeded 500 to 1000 parts per million (0.1%) by weight (Figure 2). Laboratory soil column and microcosm studies also showed that many of the hydrocarbon degrading bacteria in the contaminated fuel farm soils were negatively impacted by even low concentrations of hydrogen peroxide and fuel biodegradation was inhibited. Soil aeration proved to be as good as hydrogen peroxide for oxidizing the soil profile and forced aeration removed over 80% of JP-5 jet fuel when large volumes of air were used. Although the laboratory soil venting study was not real world, it strongly suggested that soil venting could remove the more volatile components in JP-5 jet fuel. Field studies have verified that gasoline grades of fuel can be removed from dry sandy soils to below detectable levels by soil venting.

SOLUTIONS FOR IN SITU BIODEGRADATION PROBLEMS

Theory and recent studies indicate that free oxygen (e.g., in air) can move thousands of times faster through the unsaturated soil above the water table than it can in the groundwater. The maximum free oxygen content of water in intimate contact with air is about 10 parts per million (ppm) whereas gas-phase air can transport over 200,000 ppm of free oxygen; air diffusion through unsaturated soils is also many times more rapid than water diffusion and air penetrates more readily through water insoluble materials. Air has been observed to move rapidly into and through unsaturated porous soils when a small vacuum is pulled on a well or covered ditch emplaced in the unsaturated zone, a process that is termed "soil vapor extraction" or "soil venting".

Soil venting not only has the capability of moving large quantities of free oxygen into subsurface contaminated soils (thus alleviating the high oxygen demand), but also for

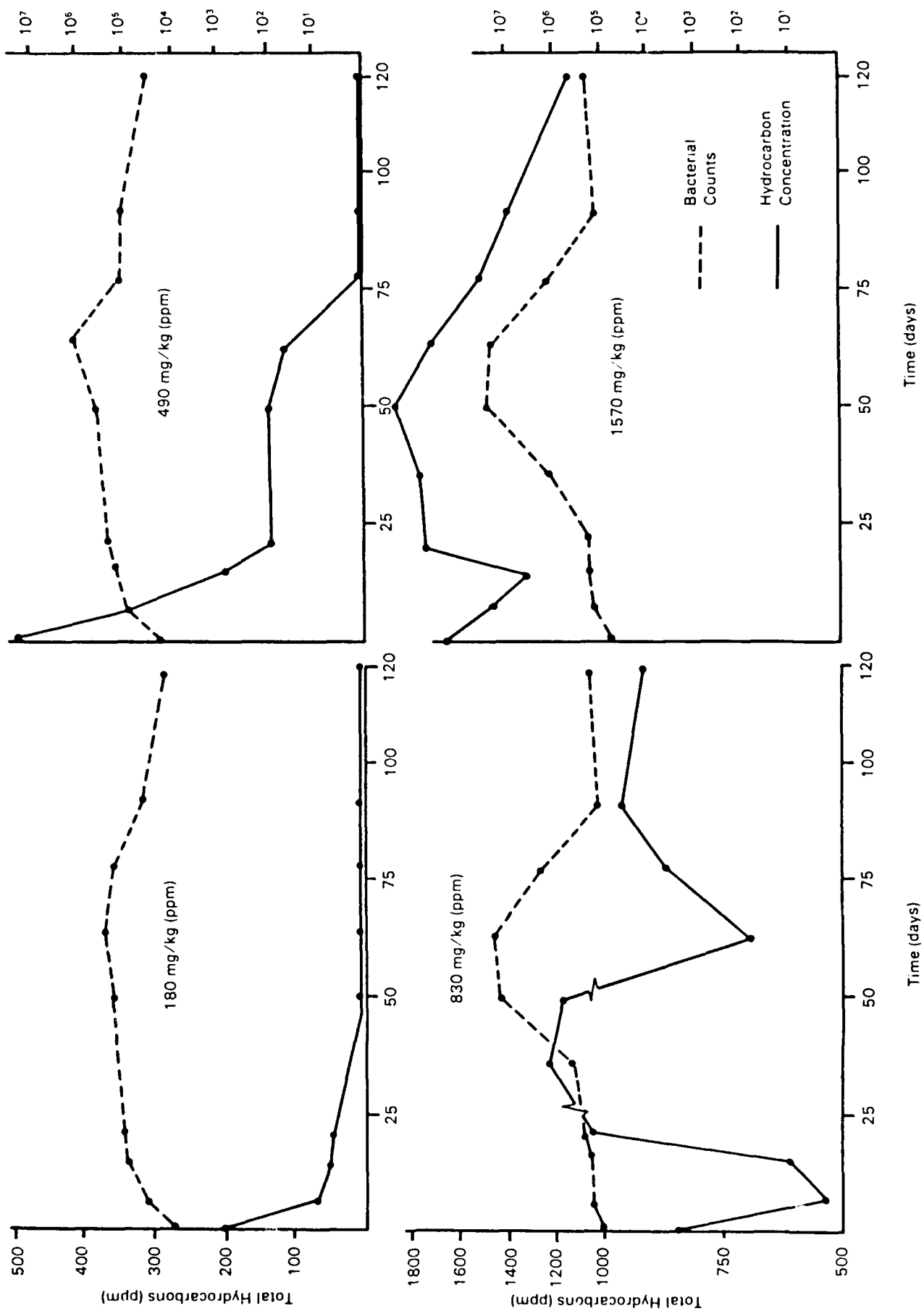


Figure 2. Effects of hydrocarbon and bacteria concentrations in sand on hydrocarbon degradation rates.

greatly increasing the rate of removal of volatile organics (VOCs) from the unsaturated soil and groundwater table. If fuels such as JP-4, JP-5, diesel, or mixed hydrocarbon wastes (POL) are involved in subsoil contamination, a combination of soil venting and enhanced in situ bioreclamation should prove to be a logical and cost-effective method, since each individual method has already been shown to be cost-effective for in situ cleanups. This combination has recently been coined "Bioventing".

Figure 3 depicts a "bioventing" scenario. The methodology involves installation of a subsoil dewatering system that requires installation of multiple dewatering points (to just below the lowest zone of contamination) that encircle the subsurface contaminant plume. Additional larger diameter "vapor extraction wells" are emplaced within the dewatering system boundary to various depths above the newly established water table. A vacuum placed on the interconnected dewatering points will remove contaminated groundwater, free fuel on the water table, and some vapor phase fuel in the soil gas. A vacuum placed on the vapor extraction wells will initially remove the most volatile components in the fuel, with the vapor extraction rate declining over time. The process moves both air into and fuel vapor out of the soil profile at a highly accelerated rate. Many of the VOCs removed during soil venting are water insoluble hydrocarbons that are difficult to biodegrade rapidly, as well as those that are most toxic to microorganisms if in liquid form. The combined effect of decreased fuel concentrations and increased free oxygen in the subsurface create ideal conditions for aerobic biodegradation. The only limiting factor should be the nutrient imbalance. Nutrients must thus be added to the soil, which would require periodic spray irrigation of the soil surface or use of infiltration galleries. Soil venting is impeded by the presence of water in soil due to partitioning of contaminants into the water phase and covering of soil-sorbed fuel by a water layer. However, soil venting is very efficient in evaporating water from soil. Thus the trick is to properly pulse water/nutrient addition with soil venting and being careful not to dry the soil to the point of impeding microbiological activity. Preliminary laboratory studies and field pilot studies initiated last year at other DoD sites look promising and "bioventing" may soon prove to be a cost-effective tool for destroying less volatile fuels in-place.

Additionally, biodegradation may prove to be a relatively cheap method for destroying the vapors that are removed from the soil during soil venting, which includes the more volatile gasoline grades that may be removed exclusively by soil venting. High rate above-ground (on-site) bioreactors are presently on the market and new bioreactor designs are continually being developed that should rapidly destroy (through microbial degradation) fuel vapors. A less costly

BIOVENTING

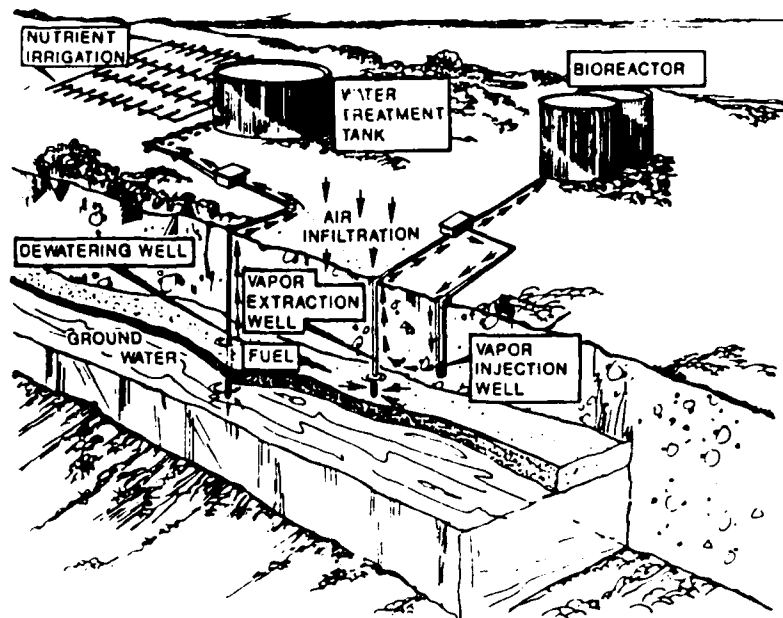


Figure 3. Unsaturated Zone *In Situ* Bioreclamation (Combined Soil Venting and Biodegradation)

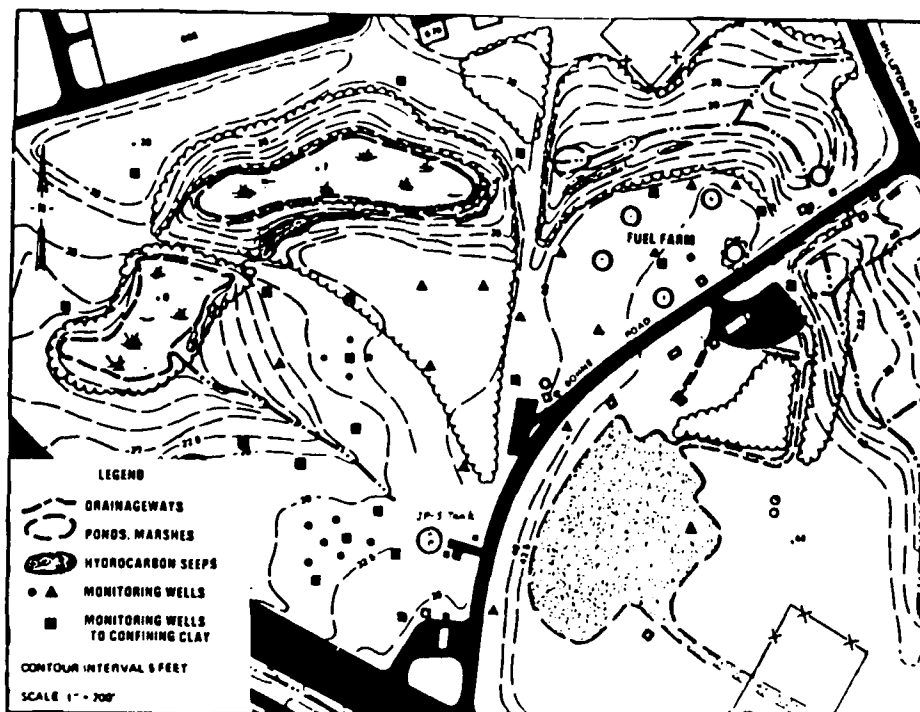


Figure 4. Monitoring Well Locations at Fuel Farm

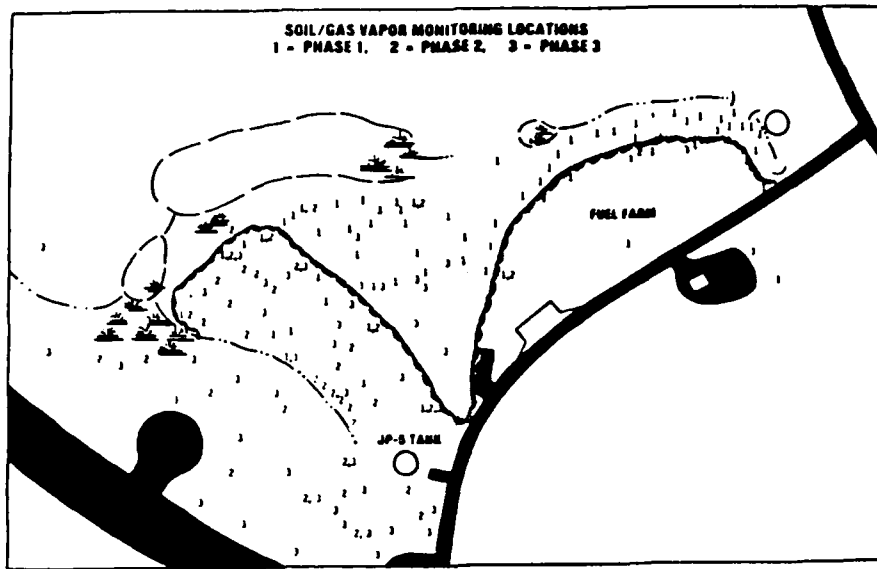


Figure 5. Soil Gas/Vapor Sampling Locations at Fuel Farm

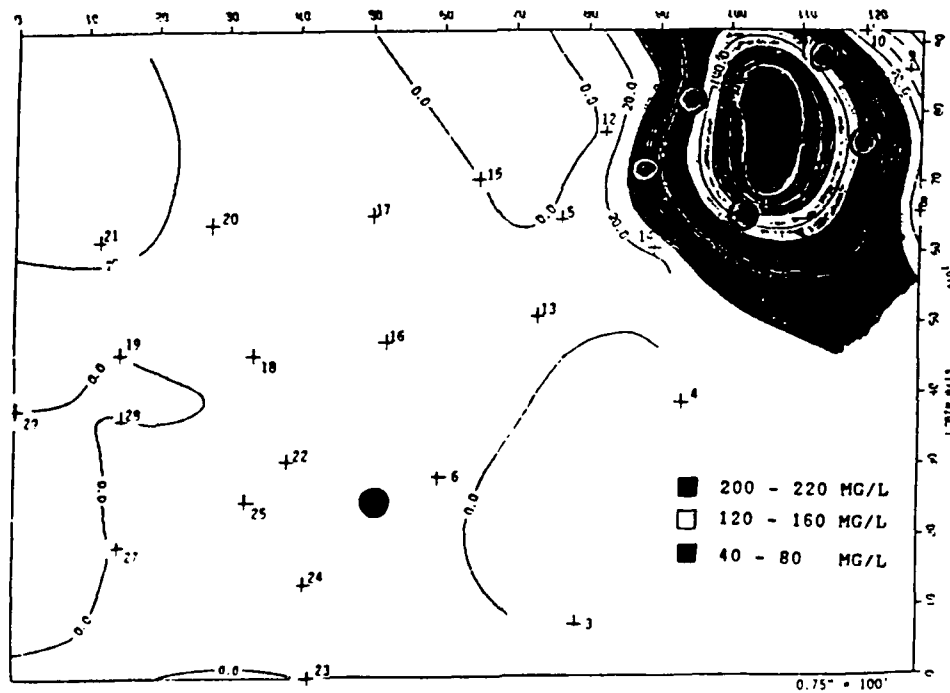


Figure 6. TOTAL PETROLEUM HYDROCARBONS (PPM) IN GROUNDWATER

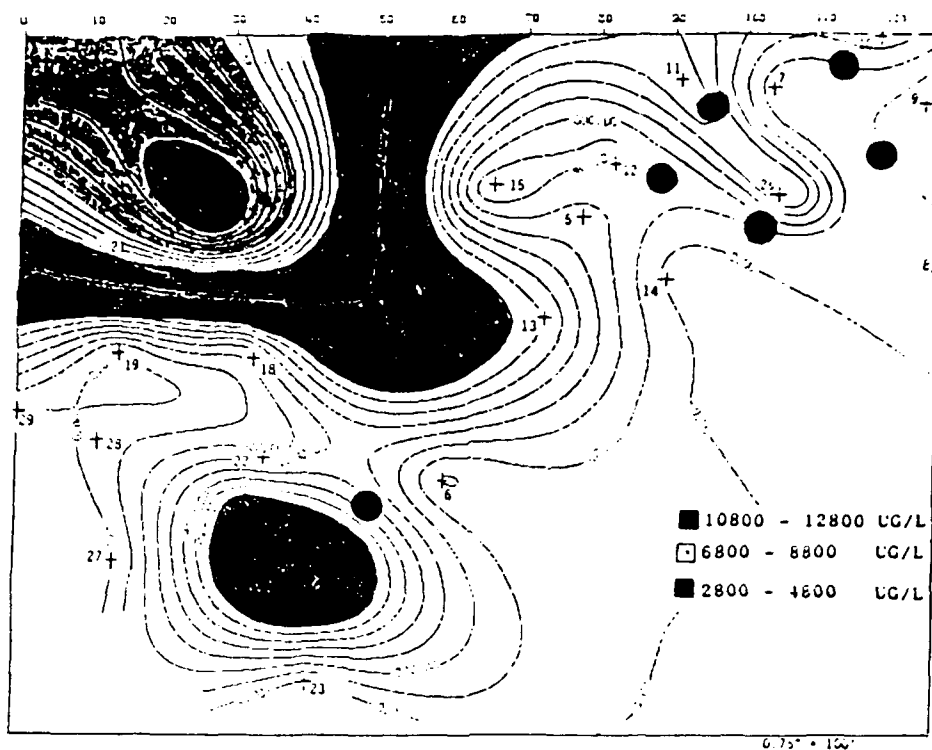


Figure 7. TOTAL VOC'S (PPB) IN GROUNDWATER

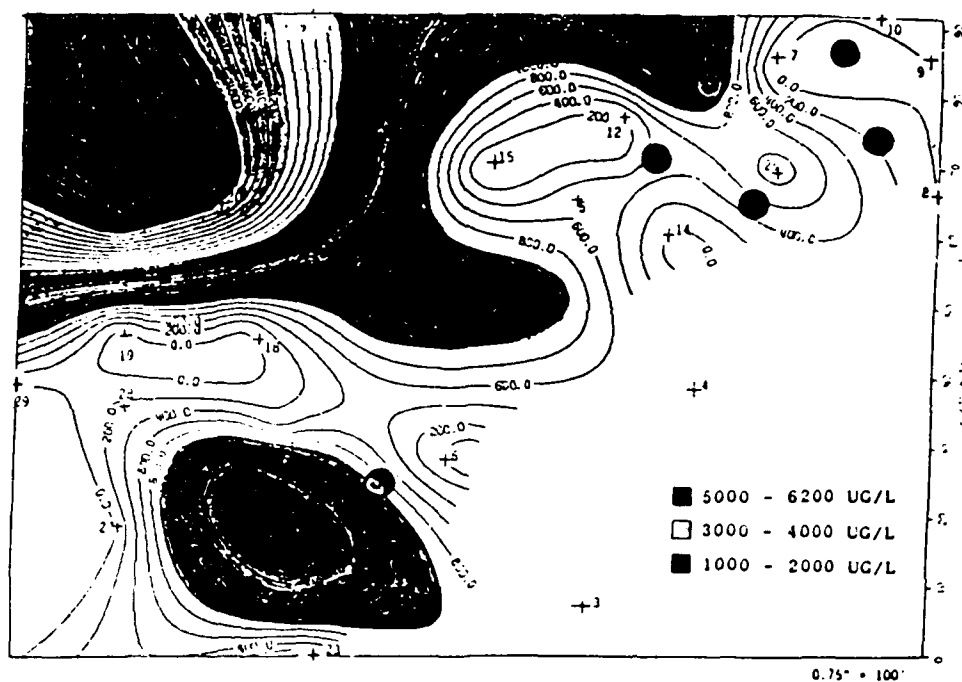


Figure 8. TOTAL AROMATICS (PPB) IN GROUNDWATER

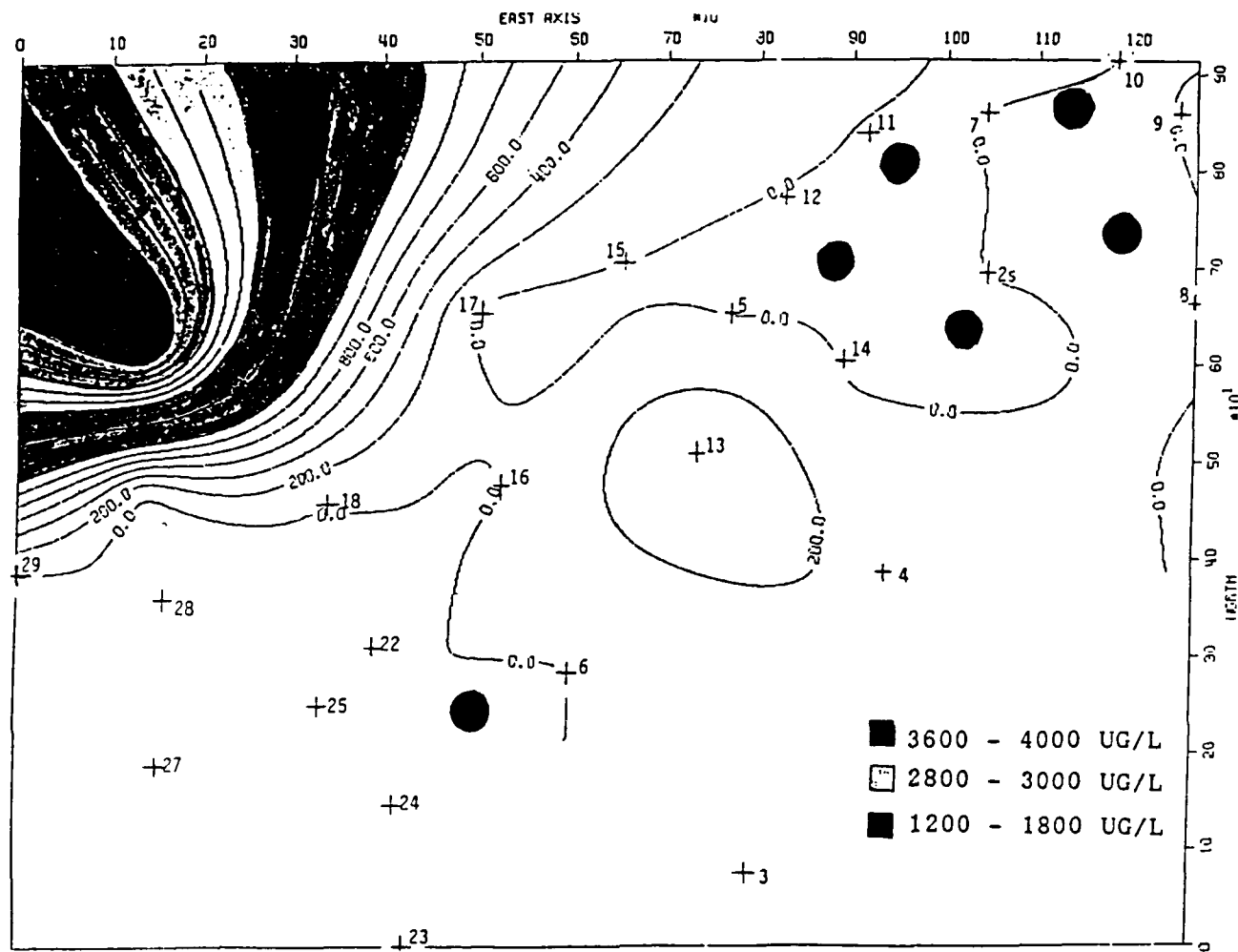


Figure 9. TOLUENE (PPB) IN GROUNDWATER

B I O R E M E D I A T I O N T E C H N O L O G Y

Principal Investigator: S. Yamamoto

Associate Investigators: C. Hui, G. Pickwell

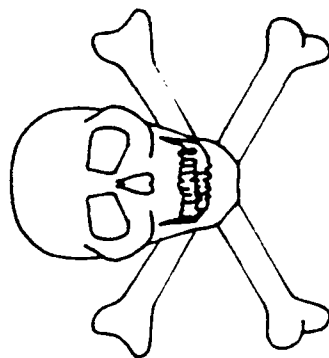
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Bioremediation is the use of biological processes to return a given site, which has been contaminated with hazardous substances, to a relatively uncontaminated condition. The use of biological processes for reclamation has potentially great advantages: it can be thorough, permanent and relatively inexpensive. Biological processes use the metabolic efforts of living organisms to transform hazardous substances to non-hazardous substances (Fig. 1). These organisms are primarily bacteria, although some fungi and algae may also perform these transformations. The transformation will continue as long as the organism, the degradable substrate, and the appropriate microenvironment are all present; albeit the rate of transformation slows when the substrate becomes much less concentrated and/or the microenvironment becomes filled with microbiological waste. Transformation of the substance from hazardous to non-hazardous categories eliminates the necessity to ship and/or store hazardous material: it has been rendered non-hazardous. The utilization of biological processes usually requires lower levels of labor and equipment than

BIOREMEDIATION TECHNOLOGY

Biological processes to reclaim sites contaminated with hazardous wastes.



BACTERIA
ALGAE
FUNGI



NO SHIPPING
NO STORAGE

PERMANENT
THOROUGH
INEXPENSIVE

FIGURE 1

other means of hazardous substance clean-up, making total costs relatively low.

Biological processes may include in-situ treatments, land farming, composting, and bioreactors. In-situ methods consists primarily of providing nutrients and oxygen to the organisms in the ground at the contaminated site to enhance their metabolic activity. Land farming requires removal of contaminated soil to a near-by location where it can be treated with microbes and/or microbe nutrients and then tilled or moistened ("farmed") to optimize microbial activity. When the concentration of the hazardous substance has reached acceptable levels, the soil is returned to the original site. Composting is similar to land farming except that organic matter (compost) is added to the contaminated material and ventilation is more critical (probably because the thickness of the compost pile is greater than the layer of dirt in land farming and organic decomposition depletes oxygen). Bioreactors utilize a container to hold a solution or slurry of the hazardous substance which is then biologically treated. If it is groundwater which is being treated, the hazardous substance is already in solution and a fixed-film reactor is appropriate. If the hazardous substance is in the soil, the substance must be transferred to an aqueous solution, which may or may not be subsequently separated from the soil before treatment; If the soil and water are to be treated together with ventilation, a three-phase reactor is appropriate (Fig. 2).

BIOREMEDIATION TECHNOLOGY **BIOREACTOR SCHEMATICS**

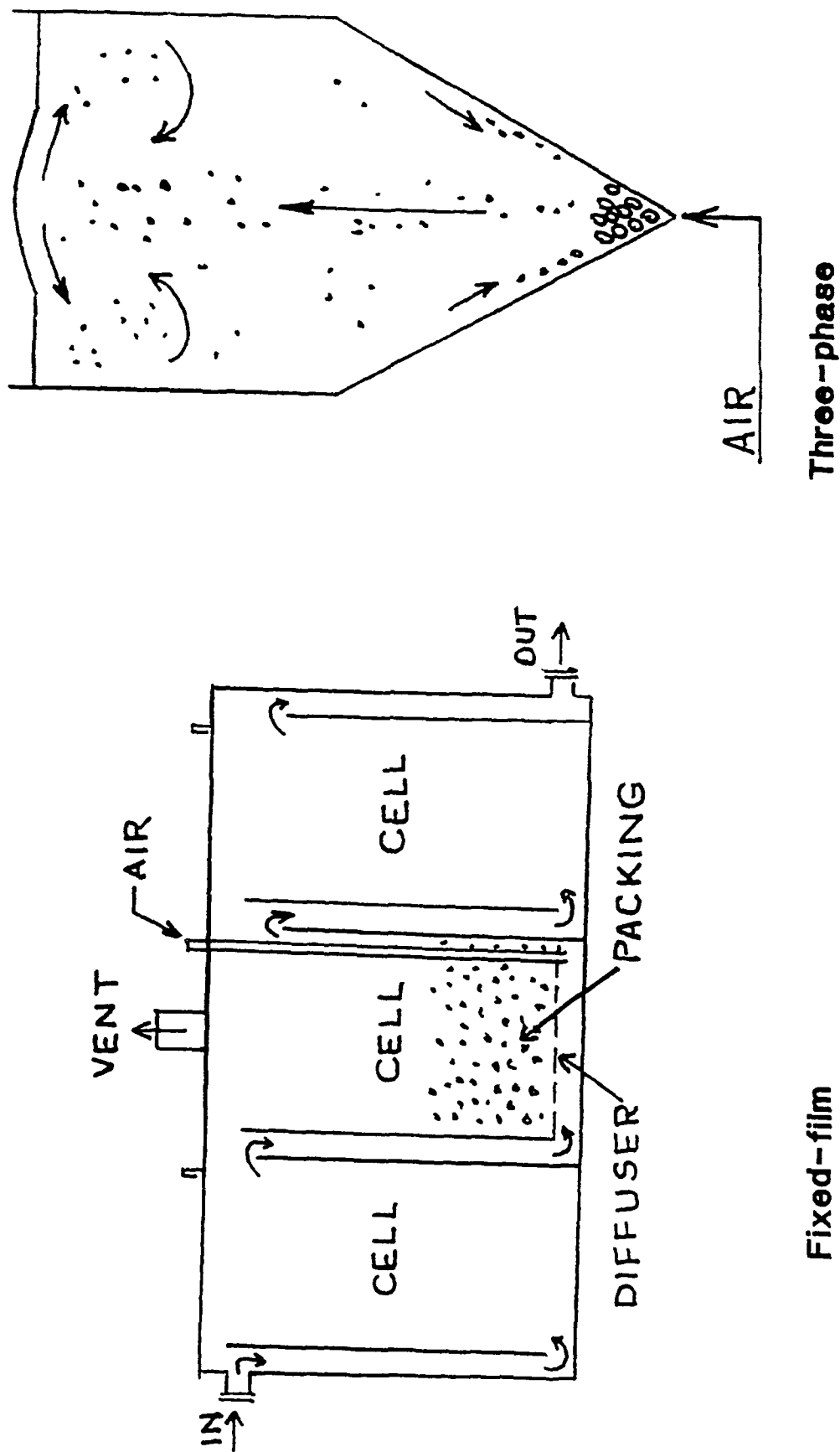
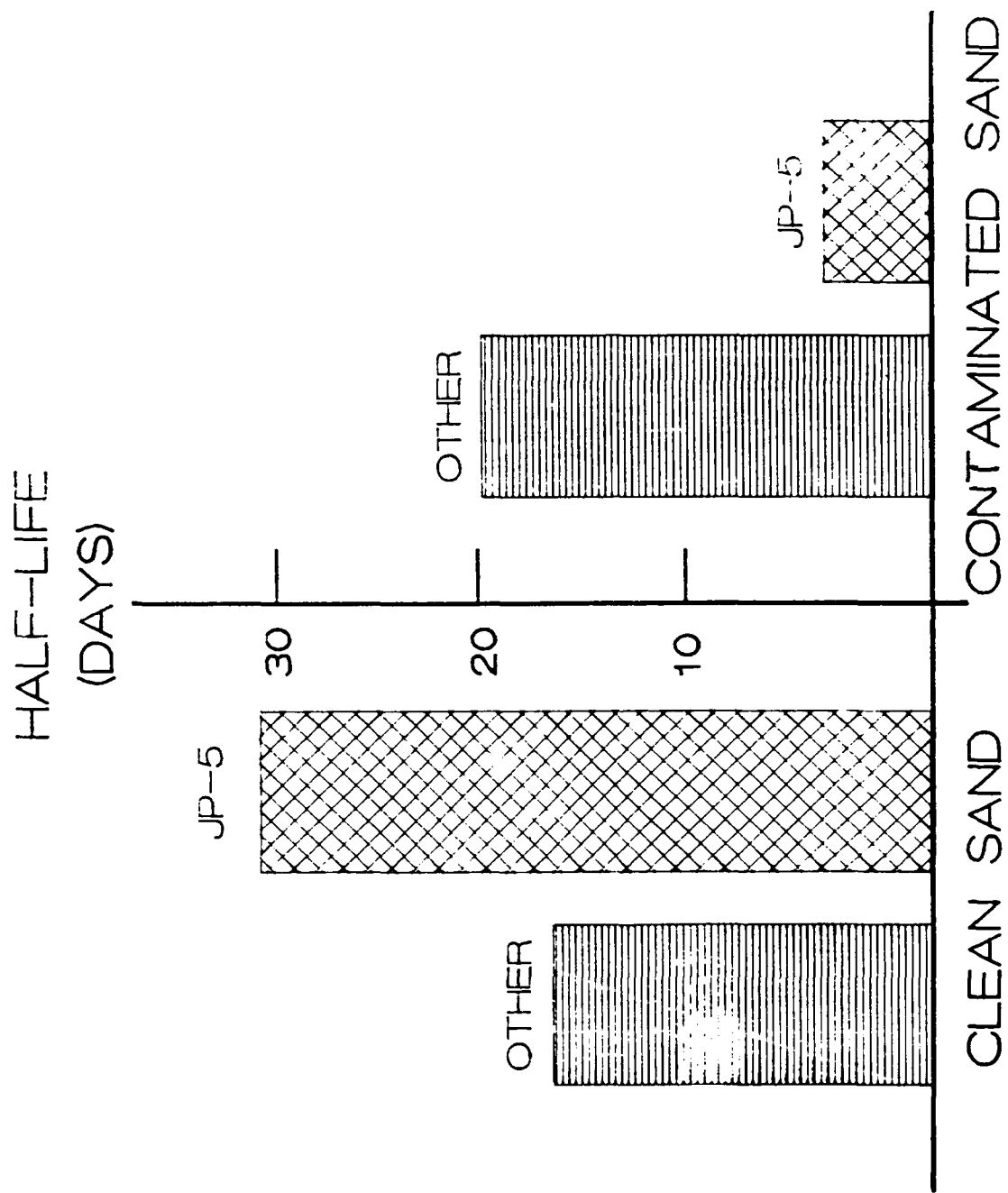


FIGURE 2

The Air Force has successfully directed its bioremediation efforts toward trichloroethene in bioreactors and toward fuels. However, its efforts at in-situ remediation of fuel spills have been unsuccessful. The Army has successfully pursued compost remediation of explosives. The Navy, through its work at the Naval Air Station at the Patuxent River, has shown that degradation of jet fuel (JP-5) occurs faster in sand which has been previously contaminated with JP-5 than in clean sand (Fig. 3) although degradation takes place in both. The interpretation of these Navy data is that the naturally-occurring organisms (or the organismal mixture) adapt to the JP-5 environment, degrading it in the process. Bioremediation enhances this natural process.

Maximizing the benefits to the entire Department of Defense requires that this program investigate remediation of a hazardous waste problem common to all the services. This program will direct its remediation efforts towards soil contaminated with mixed petroleum hydrocarbons: gasoline, motor oil, lubricants, jet fuels, or diesel fuels. Each military service uses these substances. This program will be the first effort in the comparison of techniques for bioremediation of soil. These comparisons will determine what parameters are most important to minimize cost for an equivalent level of remediation.



ENHANCEMENT OF BIODEGRADATION

FIGURE 3

POLLUTION ABATEMENT: RUNOFF CONTROL AND ASSESSMENT

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Assessment and Management of Runoff Pollution

Laurence E. Gadbois, NOSC

ABSTRACT

Four aspects of the pollution content in runoff from Navy bases are poorly quantified: (1) the concentration of chemicals present, (2) the chemical form (dissolved, particulate, globules), (3) the chemical content variability within and between storms, and (4) the environmental impact in receiving water. Initial data collection leading to protocols to address these four issues are being performed. Items 1-3 can be assessed via field sampling of a variety of Navy activities under various storm conditions. Protocol for bioassays or extrapolation of chemical data to environmental impact needs much more research. Data from item (4) will tell if there is a problem which needs remediation. Data from items (1-3) will guide the decision as to the appropriate remediation technique to implement, and how to document the effectiveness of that technique.

INTRODUCTION

Water quality continues to decline in many waterways and bays despite reductions in point source discharges. Historically point source discharges have been scrutinized extensively because generally (1) they represent clearly identified problem sites, (2) the responsible party is known, (3) valid collection sites are easily recognizable, and (4) presampling knowledge of which toxicants to look for in the discharge is available. Runoff pollution often possesses few or none of these traits. This elusive aspect has caused runoff discharges to go relatively unmonitored and unregulated.

Figure 1 is a conceptual sketch of the factors to consider when quantifying runoff from the four perspectives outlined in the purpose section. The highlighted areas of figure 1 (shaded ovals and heavy arrow) are the research foci of the author. The concepts behind these factors form the content of this chapter. All the areas mentioned in figure 1 have been reasonably well researched or are in the process of being researched. The author's research when pooled with the collective results of many others will provide a scientifically valid basis for a feasible effective runoff initiative suitable for Navy-wide implementation.

PURPOSE

This chapter describes the author's research of runoff pollution which stresses four facets: (1) Identification and quantification of chemicals present, and their form. These factors are important for the selection of remediation method. (2) Temporal variability in pollutant content. (Concentration profile during a storm, effects of storm intensity and interval between storms.) This information will identify how much of the runoff volume needs remediation. (3) Monitoring methods. This is needed to assess the magnitude of the problem, and document effectiveness of remediation. (4) Risk assessment methods to determine the biological/environmental impact of the runoff pollution.

DISCUSSION

Which chemical pollutants are present in runoff can in large part be surmised by a review of the land use in the drainage basin. Anthropogenic chemical history tempered by natural alterations and additions will indicate which chemicals should be investigated.

Physical and biological pollutants may occur in addition to the chemicals. Runoff from a large hot asphalt slab can produce a thermal plume. Otherwise biologically inert material (such as suspended solids, pigments) may cloud receiving water, hamper vision and photosynthesis, and overwhelm filter-feeders. The rapid drainage rate of paved areas -- as opposed to dirt and vegetated areas -- causes high water velocities with scour and turbidity in a receiving stream. Runoff may also be the vector for bacterial and viral input to receiving waters.

When the diversity of activity, land use, terrain, and climate at Navy bases is considered it is intuitive

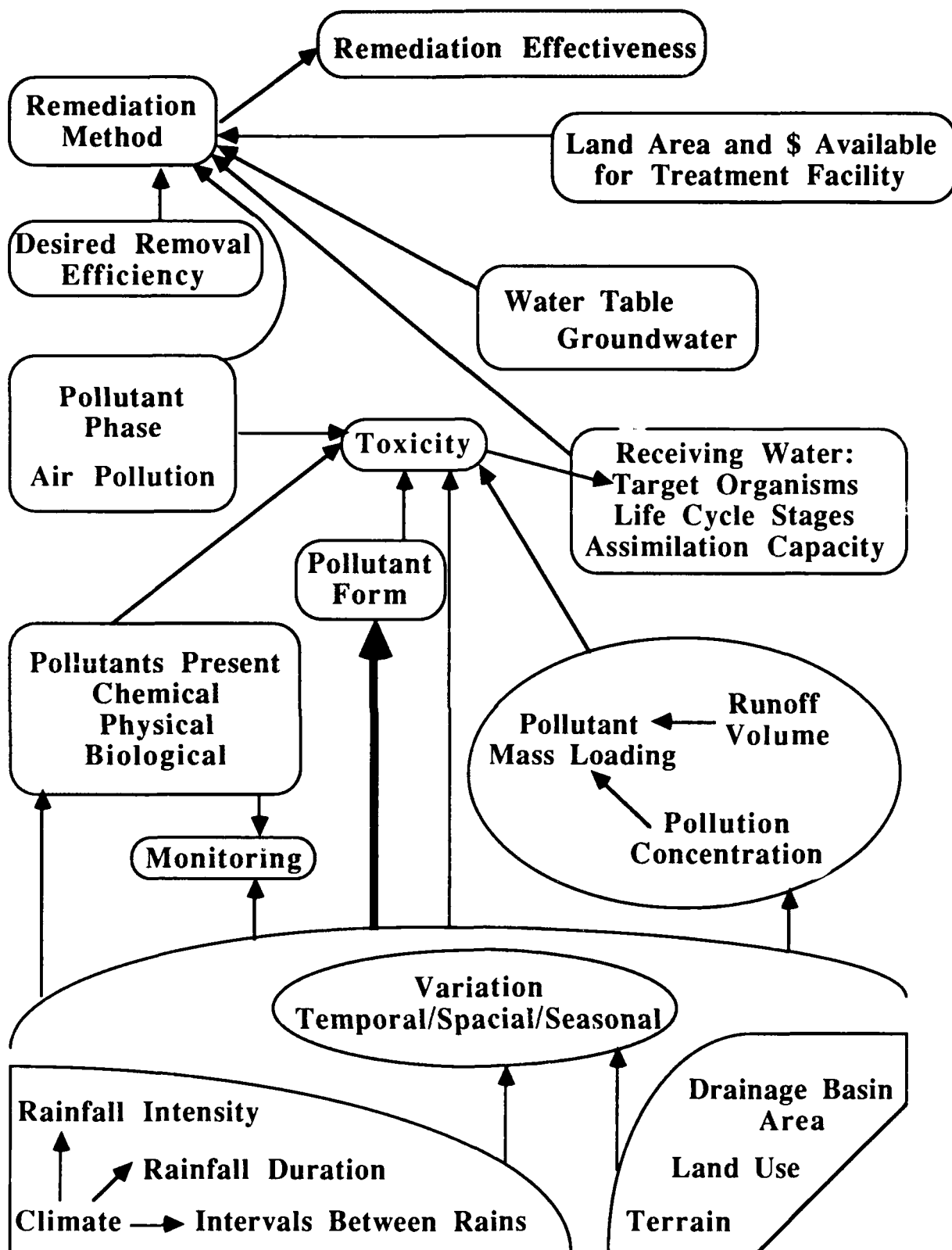


Figure 1. Assessment and Remediation of Runoff

that pollution profiles would be highly variable. What to measure and when to measure it are highly site specific. Even at a single site the concentration profile changes during a storm, total loading is a function of rain intensity, duration, and interval since the last rain, and whether the precipitation is frozen or not.

Where to measure is also at issue. At some sites sheet flow is collected in ditches or storm drains and discharged at an easily accessible outfall. At other sites the outfall discharges below the surface of the receiving water, causing dilution and a hard-to-sample situation. At still other sites the sheet flow is not collected - rather it discharges into the receiving water at a multitude of points.

Variation on temporal, spacial and seasonal scales must be accounted for in a monitoring program. Because variation may arise from so many factors, a diverse sampling is needed to quantify the variability due to each factor. Only then can appropriate guidelines for monitoring be drafted.

Chemical concentration by itself is useful for hazardous waste minimization planning. It also provides some insight to appropriate management measures and potential environmental impact. Useful additional knowledge is the partitioning of the pollutant into the dissolved, particulate, and globule(or colloid) form. Figure 2 shows an example of the heavy metal lead which tends to be associated with the suspended solid phase. The figure shows how lead and suspended solids are co-removed as contaminated water traverses a grassed channel. Figure 3 shows how suspended solids removal can be efficiently achieved merely by a short term detention of the runoff flow.

Many management measures for runoff pollution are available. Figures 2 and 3 alluded to grassed channels and overland flow. Figure 4 shows 14 methods and their effectiveness on different categories of pollutants. Non-use of potentially polluting material is of course the preferable management method. A review of figure 4 shows three basic approaches to management: (1) Reduction at the source - the hazardous waste minimization concept. (2) Dispersion and treatment at the source site. (3) End-of-the-pipe methods.

Many simple methods target particulates and associated toxicants (figures 2,5). A more elaborate method, such as a wetlands (figure 5), traps not only the particulates but may retain and remediate dissolved pollutants. Figure 5 lists six categories of pollutants, and the wetland processes which remediate that pollutant. Figure 6 lists parameters for a wetland to provide peak remediation. These design parameters maximize the effectiveness of the biological component of the wetland.

SUMMARY

Adequate data exists to indicate that Naval facilities produce runoff sufficiently polluted to warrant implementation of low cost moderately effective remediation procedures. Monitoring protocols and risk assessment methods need development in order to better assess the scope of the problem, guide remediation efforts, and assess the effectiveness of the remediation. Better quantitative understanding of the concentration and form of chemicals present, the variability, and the environmental impact will allow determination of the necessary level of remediation.

RECOMMENDATIONS

- (1) Begin installation of low cost moderately effective remediation programs of a variety of designs. To meet zero-discharge longer range goals, these intermediate techniques should be those which work in-line with more effective techniques which may be used in the future.
- (2) Initiate a Navy-wide survey of the runoff problem.
- (3) Monitor the effectiveness of the remediation techniques implemented. Conduct cost analysis of the pollution remediation effectiveness.

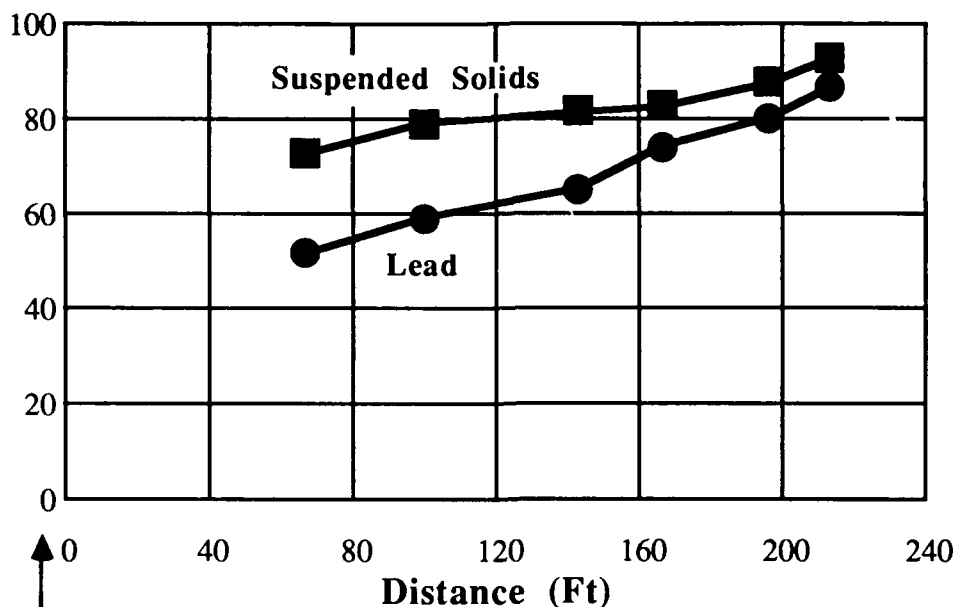


Figure 2. Suspended Solids and Lead Removal vs Channel Length for Grassed Channels

(Adapted from Wang, et al., 1981; and Mar, et al., 1982)

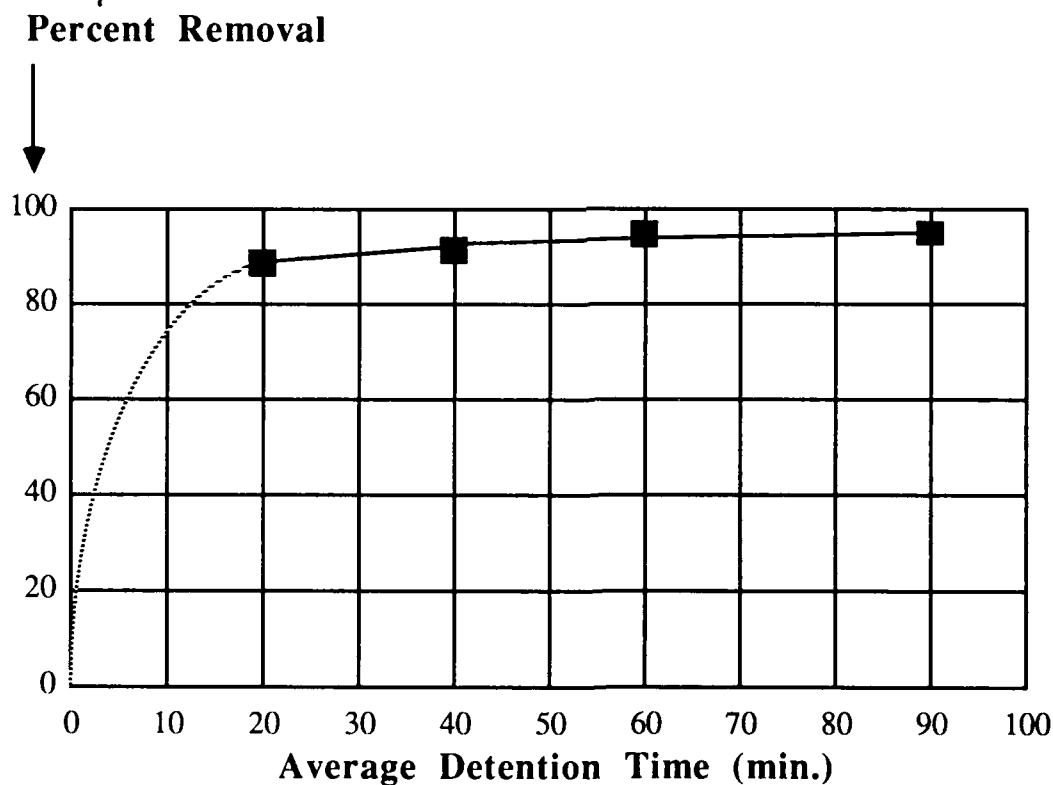


Figure 3. Suspended Solids Removal vs Detention Time for Overland Flow Systems

(Adapted from U.S. EPA, 1980, using municipal wastewater)

<u>Heavy Metals</u>	Adsorption Settling
<u>Toxic Organics</u>	Adsorption Settling Biodegradation
<u>Solids</u>	Adsorption Settling
<u>Nutrients</u>	Bioassimilation
<u>Oil & Grease</u>	Adsorption Settling Biodegradation
<u>BOD</u>	Biodegradation

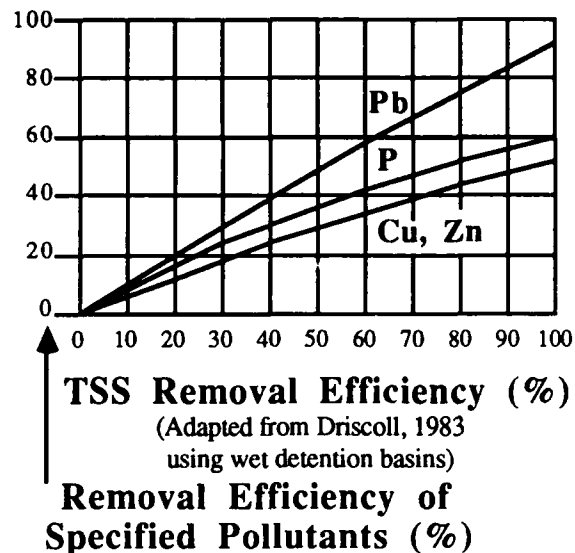


Figure 4. Wetland Treatment by Category of Pollutant

-
- Relatively long retention time of runoff inflow.
 - Shallow water with a low basin gradient resulting in slow-moving, well-spread sheet flow.
 - Minimal direct open channels. (Where open channels exist, circuitous flow routes preferred.)
 - Maximum contact between runoff inflows and wetland soils and vegetation.
 - Irregular bottom morphology and bank edges.
 - Constricted outlet or no surface outlet.
 - Persistent emergent and/or floating vegetation.
 - Sufficient storage volume for runoff.

Figure 5. Wetland Design Parameters

Management Measure	Particulates	Heavy Metals	Pesticides	Organics
Curb Elimination	H	H	N/A	H
Litter Control	L to H	L to H	L to H	L to H
Controlled use of Deicing Chemicals	N/A	H	H	H
Controlled use of Pesticides/Herbicides	N/A	H	H	H
Grassed Channels	H	H	M	H
Overland Flow	H	H	M	H
Dry Detention Basins	L to H	L to H	L to M	L to M
Wet Detention Basins	H	H	H	H
Infiltration Systems	H	H	H	H
Wetlands	H	H	M to H	M to H
Street Cleaning	L to H	L	L	L
Catchbasins	L	L	L	L
Porous Pavements	H	H	N/A	H
Filtration Systems	L to M	L	L	L

Figure 6. Effectiveness Ratings of Management Measures

(Source Dorman et al. 1988)

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WETLANDS TREATMENT SYSTEM FOR NONPOINT SOURCE POLLUTION
L. A. Karr, NCEL

1. Purpose: Create wetlands that offer an effective means of reducing nonpoint source (NPS) pollutants in storm run-off discharged from Navy bases.

2. Background: The water quality in waterways and bays has declined or not improved as point source discharges of pollutants are eliminated. The cause is due to both point source discharges regulated under NPDES permits and NPS source discharges. NPS contributes twice the amount of pollutants to estuaries than point sources. Characteristics of urban NPS are included as Tab A.

3. Discussion: Traditional Storm Water Treatment: Many techniques have been developed to improve the quality of wastewaters discharged into natural receiving bodies of water including activated sludge, trickling filters, oil/water separators, and chemical/physical processes (Tab B). These techniques were designed to treat sewage and industrial wastewaters generated by specific point sources at a constant flow rate. Problems with using traditional treatment are:

1. Due to highly variable influent flows, ineffective in removing all NPS pollutants during the rainy season.
2. Need several methods to remove the diversity of components found in urban NPS discharges, which increases construction costs.
3. Requires large amounts of dry land.
4. Expensive to operate and maintain.
5. Creates a sludge disposal problem.

Wetland Treatment System. Removing pollutants from storm water with this system combines physical, chemical, and biological mechanisms. These natural mechanisms are complex and highly interactive. Advantages with using the wetland treatment system are:

1. Does not require any dry land.
2. Requires no operator to check and adjust sensors, repair and service equipment.
3. Traps pollutants or converts them to useful nutrients.
4. Controls shoreline erosion.
5. Creates wildlife habitats.
6. Provides improved natural resources and environmental education.
7. Supplies recreational opportunities.

4. Conclusions: EPA considers urban run-off to be an NPS pollutant. Most urban run-off is discharged through storm sewers, but new regulations are being issued that will regulate storm sewer discharges. Urban run-off was managed at the local level through land management, but these controls have not been effective -- our waterways' and bays' water quality is still declining. Treating these discharges is necessary to reverse this trend and improve water quality.

Research into the wetlands treatment system will increase the value of the Navy's environmental dollar. Results of NCEL's research will be useful for not only the NPS program, but also the Navy's policy to increase wetlands.

5. Recommendations: The proposed wetland treatment system (Tab C) is ideally suited for EPA's recommended themes for NPS action: Public awareness; successful solution; financial forces and incentives; regulatory programs and good science. This system will also fill the Navy's policy of no overall net loss of Navy and Marine Corps wetlands, and by the year 2000 increase the quality and quantity wetlands.

Tab A - Storm water discharge characteristics

Tab B - Wastewater treatment technologies

Tab C - Conceptual design of a wetland treatment system

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Tab A

Characteristics of Urban Stormwater 1,2
Range low to high

	<u>Low</u>	<u>High</u>
BOD	1	700 mg/l
TOC	1	150 mg/l
COD	5	3,100 mg/l
SS	2	11,300 mg/l
Total Solids	200	14,600 mg/l
Volatile Solids	12	1,600 mg/l
Settleable Solids	0.5	5,400 mg/l
Organic N	0.01	16 mg/l
TKN	0.01	4.5 mg/l
NH ₃ N	0.1	2.5 mg/l
NO ₃ N	0.01	1.2 mg/l
Soluble PO ₄	0.1	10 mg/l
Total PO ₄	0.01	125 mg/l
Chlorides	2	25,000 mg/l ^a
Oils	0	110 mg/l
Phenols	0	0.2 mg/l
Lead	0	1.9 mg/l
Total Coliforms	200	146 x 10 ⁶ /100 ml
Fecal Coliforms	55	112 x 10 ⁶ /100 ml
Fecal Streptococci	200	1.2 x 10 ⁶ /100 ml

^a With highway deicing

Tab B

TYPICAL RESULTS -- ADVANCED WASTEWATER TREATMENT PROCESSES^a

Process	BOD ₅ (mg/l)	COD (mg/l)	SS (mg/l)	PO ₄ (mg/l)	NH ₃ (mg/l)	TDS (mg/l)
Preliminary^b						
Coagulation and sedimentation	67-83	62-83	87-96	67-83		
Plus mixed media filtration	77-90	69-90	98-99	83-96		
Plus activated carbon adsorption	97-98	91-95	98-99	83-96		
Plus ammonia stripping	97-98	91-95	98-99	83-96	47-95	
Primary						
Coagulation and sedimentation	67-83	62-83	89-96	67-83		
Plus mixed media filtration	77-90	69-90	98-99	83-96		
Plus activated carbon adsorption	97-98	91-95	98-99	83-96		
Plus ammonia stripping	97-98	91-95	98-99	83-96	47-95	
High-rate tricking filter						
Plus mixed media filtration	93-99	88-93	91-96			
Coagulation and sedimentation	95-97	89-93	95-98	75-92		
Plus mixed media filtration	96-98	90-94	99.6-100	92-99		
Plus activated carbon adsorption	99-99.7	95-98	99.6-100	92-99		
Plus ammonia stripping	99-99.7	95-98	99.6-100	92-99	47-95	
Conventional activated sludge						
Plus mixed media filtration	98-99	90-94	95-99	10-30	30-50	
Coagulation and sedimentation	98-99	90-94	96-99	75-92		
Plus mixed media filtration	99-99.7	91-95	99.6-100	92-99		
Plus activated carbon adsorption	99.7-100	97.99	99.6-100	92-99		
Plus ammonia stripping	99.7-100	97-99	99.6-100	92-99	47-95	
Algae harvesting	50-75	40-60		50	50-90	
Ammonia stripping					80-98	
Anaerobic denitrification					65-95	
Bacterial assimilation	75-95	60-80	80-95	10-20	30-40	
Carbon adsorption	70-90	60-75	80-90			
Chemical precipitation	70-90	75-95	60-80	88-95	5-15	20
Plus activated sludge	90-95	85-90	80-95	30-40	30-40	10
Plus filtration				95-98		
Electrochemical treatment	50-60	40-50	80-90	80-95	80-85	
Electrodialysis				30-50	30-50	40
Filtration						
Multimedia	50-70	40-60	80-90			
Diatomite bed			95-99			
Microstrainer	40-70	30-60	50-80			95-99
Flotation						
Foam fractionation	70	60-70	75-90			
Freezing	99-99	90-99	95-98			95-99
Gas phase separation						
Ion exchange	40-50	30-50		85-98	80-92	
Land application	90-95	80-90	95-98	60-90	60-80	
Modified activated sludge						
Oxidation (chlorine)	80-90	65-70			50-80	
Reverse osmosis	95-99	90-95	95	95-99	65-99	95-99
Sorption	50	40		90-99		10
Distillation	98-99	95-98	99	99	90-98	95-99

^a Based on raw wastewater values of 300mg/l BOD₅; 480mg/l SS 12 mg/l PO₄; and 19 mg/l NH₃-N²

^b Preliminary treatment - grit removal, screen chamber, Parshall flume, overflow.

PROBLEM

VISTA PT., NORFOLK

- SURFACE RUNOFF PASSES THROUGH OIL/WATER SEPARATOR PRIOR TO DISCHARGE INTO WILLOUGHBY BAY
- DISCHARGE WATER QUALITY CAN POTENTIALLY IMPACT THE BAY
- SHORELINE EROSION

POTENTIAL CONTAMINANTS OF CONCERN

VISTA POINT, NORFOLK, VA

PARAMETER	O/W SEPARATOR SLUDGE	WATER
PETROLEUM HYDROCARBON	52,000 UG/L	7,400 UG/L
LEAD	22,300 MG/KG	166 UG/L
COPPER	83 MG/KG	153 UG/L
ZINC	196 MG/KG	43 UG/L
TKN	66,000 MG/KG	10 UG/L
TOTAL PHOSPHORUS	10,000 UG/L	548 UG/L
COD	22,000 MG/KG	34 MG/L
BOD 5	(>55 MG/L)	(42 MG/L)

MAY 1989

POTENTIAL CONTAMINANTS OF CONCERN
VISTA POINT, NORFOLK, VA

PARAMETER	BAY	
	SAND	WATER
PETROLEUM HYDROCARBONS	210 MG/KG	2340 UG/L
LEAD	95 MG/KG	<100 UG/L
COPPER	19 MG/KG	<25 UG/L
ZINC	173 MG/KG	<20 UG/L
TFH	400 MG/KG	9 MG .
TOTAL PHOSPHORUS	295 MG/KG	<100 UG/L
COD	8070 MG/KG	255 MG/L
BOD	(0.381 PPM/GM)	(3.1 MG/L)

5

MAY

DEMONSTRATION ALTERNATIVE	COST FACTOR
1. BREAK WATER WITH CREATED WETLAND	1.0
2. RETAINED FILL MATERIAL WITH CREATED WETLAND	2.5
3. RETAINED FILL MATERIAL, BREAKWATER, WITH CREATED WETLAND	4.0

COORDINATION

- NCEL
- COMNAVBASE NORFOLK
- NOBU-11
- LANTDIV
- CHESDIV
- NAVFAC
- NOSO
- NEESA
- EPA
- USAE WES
- VIMS
- ANNE ARUNDEL CO
- ACOF NORFOLK
- VMRC

METAL CONTAMINATION
AND
SMALL ARMS RANGES

STUDY AREAS

QUANTICO MCB, VA

- SHARPSHOOTER RANGE 4
- HORIZON A
- YELLOWISH BROWN SANDY CLAY
- HORIZON B
- RED, FINE GRAINED, WELL SORTED SAND

LITTLE CREEK AMPHIBASE, VA

- RIFLE RANGE
- UNCONSOLIDATED SAND, CLAY AND SOME GRAVEL

SAMPLE COLLECTION AND ANALYSES

SOIL (pH AND METAL SCAN)

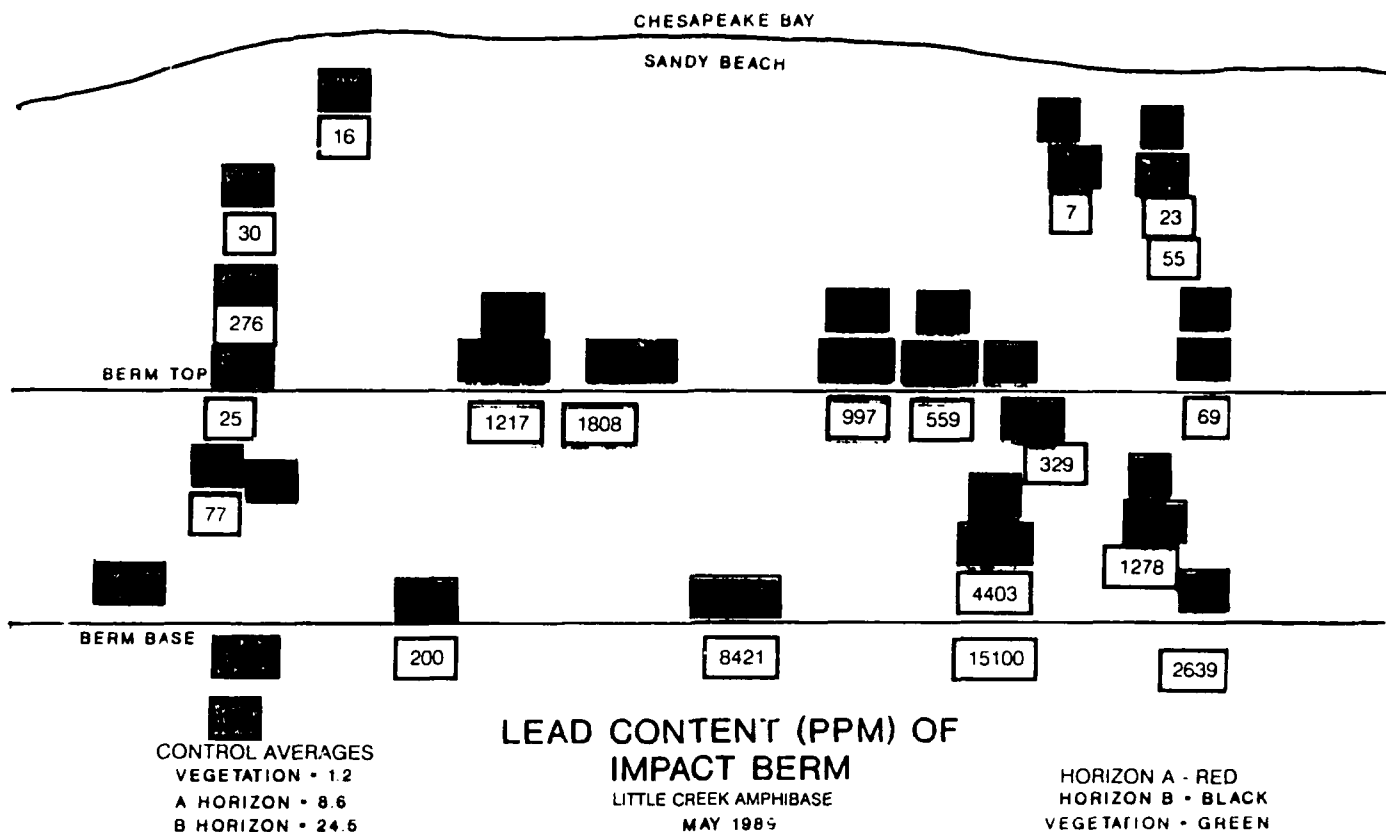
- HORIZON A: 5 - 10 CM
- HORIZON B: 15 - 20 CM

LEAF LITTER (METAL SCAN)

- SURFACE NEEDLES

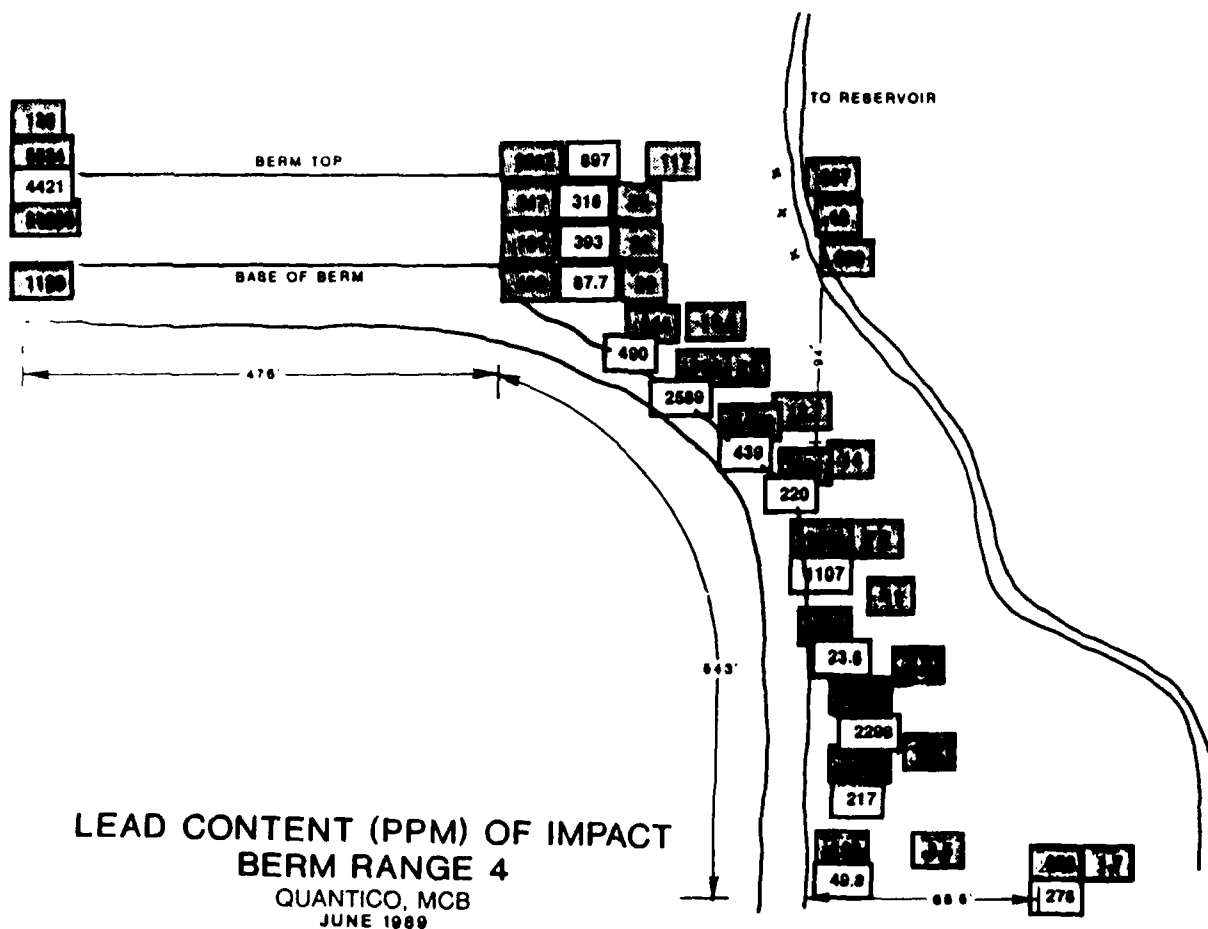
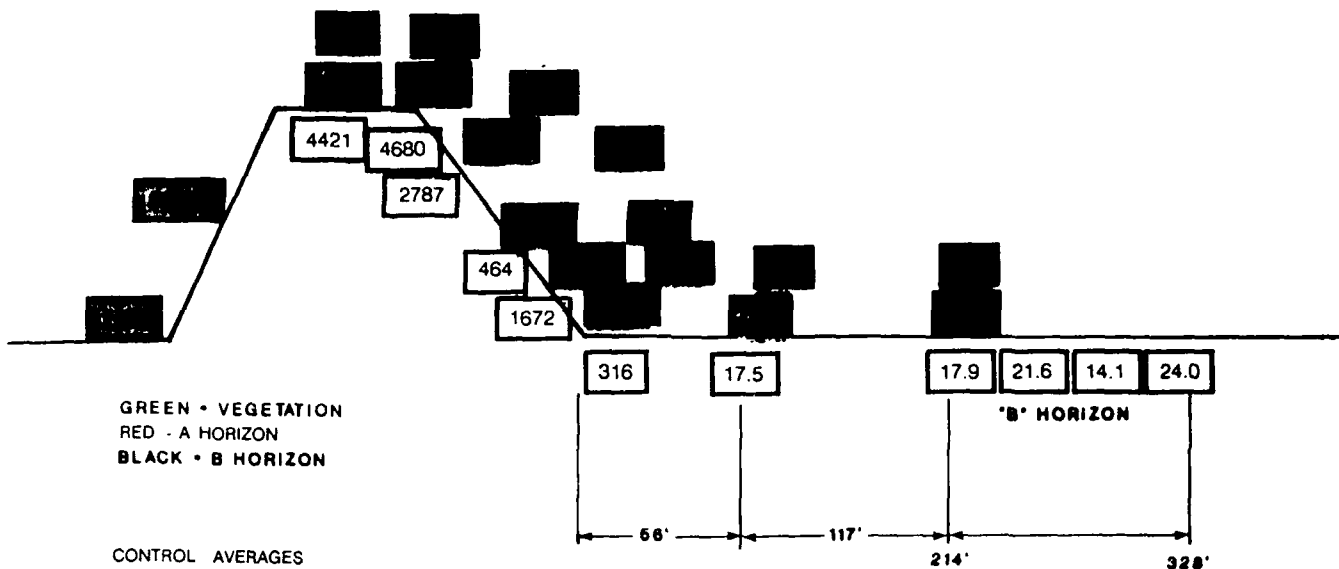
VEGETATION (METAL SCAN)

- VIRGINIA PINE
- WILD CHERRY
- OAK



**LITTLE CREEK RIFLE RANGE AND CONTROL
MAY 9, 1989
SUMMARY TABLE**

ppm			ppm		
Pb	Cu	Zn	Pb	Cu	Zn
RIFLE RANGE			CONTROL		
SOIL-HORIZON A			SOIL-HORIZON A		
NO. OF SAMPLES	21	21	NO. OF SAMPLES	7	7
MINIMUM	15.1	1.9	MINIMUM	4.8	2.9
MAXIMUM	15100.0	957.0	MAXIMUM	18.2	5.5
MEAN	2954.3	137.0	MEAN	8.6	3.8
RIFLE RANGE			CONTROL		
SOIL-HORIZON B			SOIL-HORIZON B		
NO. OF SAMPLES	18	18	NO. OF SAMPLES	8	8
MINIMUM	7.2	2.0	MINIMUM	5.0	2.2
MAXIMUM	8421.0	416.0	MAXIMUM	61.2	121.0
MEAN	1243.0	82.4	MEAN	24.5	40.8
RIFLE RANGE			CONTROL		
VEGETATION-AVG.			VEGETATION-AVG.		
NO. OF SAMPLES	25	25	NO. OF SAMPLES	7	17
MINIMUM	2.5	6.7	MINIMUM	0.8	7.9
MAXIMUM	265.0	26.1	MAXIMUM	2.0	20.4
MEAN	57.9	14.1	MEAN	1.2	13.2



COMMENTS NOTED DURING RESEARCH AND DEVELOPMENT TECHNICAL REVIEW
SESSION ON SAMPLING NETWORKS MONITORING AND ASSESSMENT

THURSDAY, NOVEMBER 9, 1989

Moderator - LCDR William J. Wild

#1 Overview of the Navy's Underground Storage Tank Program.
Mr. Ned Pryor, NAVFAC 181E

This discussion was based on the Requirements of the Resource Recovery and Conservation Act (RCRA) which regulates the management of Underground Storage Tanks (USTs). The general statement was made that in effect, the EPA has turned over the regulation of USTs to the states, and that the coverage was targeted against storage tanks which contain or contained hazardous wastes or petroleum products. The only exemptions were in the general categories of Bulk Tanks (25,000 gal or more) or those that contain Avgas. It does provide coverage for all new tanks and specifies that they shall: (1) be non-corroding (2) have spill protection (3) have leak detection (4) be certified and (5) have double wall construction. Old tanks which are to be kept in service must also be retrofitted with these capabilities. For those existing tanks which will be kept in use, removal is specified, as well as specific recordkeeping requirements for documentation of compliance.

There are about 8450 tanks Navy wide which currently fall under the provisions of this regulatory action. Approximately 25% of these are abandoned, and only 11% of the total have had successful closure actions. Funding for compliance comes primarily from the Navy's Pollution Abatement Account with the remainder (historical sites only) funded with the Defense Environmental Restoration Account (DERA) monies. The long-term intention is to program future compliance with OM&N funding at the facility level. No long term (centrally funded program) will exist to replace old tanks.

#2 Underground Storage Tank Leak Detection

Mr. Nick Olah - NCEL

The second presentation was directed toward the ability to detect leaks from tanks using sensors in both the vadose and saturated zones. Essentially, the technology exists to instrument existing tanks up to 25,000 gal and less. However, those tanks which exceed that capacity (bulk tanks) cannot be adequately monitored for leaks. The Navy has approximately 650 tanks which fall into the bulk tank category.

The Navy Civil Engineering Laboratory has developed a Metal Oxide Semi-Conductor (MOS) sensor which can be used in either the vadose or saturated zones to detect leaking tanks. The response for the MOS is essentially near-real-time and offers a technological breakthrough in this area. Field testing will be conducted at NAS Lemoore on an operational JP-5 transfer facility in FY 90.

#3 Marine Environmental Survey Technology

Mr. Bart Chadwick - NOSC

The third presentation was a discussion of the Marine Environmental Survey Capability (MESC) resident at the Naval Ocean Systems Center (NOSC). This is a 40 ft. Environmental Survey Craft which was developed to provide a water-quality monitoring and mapping system that can be used to survey chemical, biological and hydrographic parameters in harbors, bays and other near-shore environments. This system will provide a method of collecting high resolution spatial and temporal environmental data in order to (1) discriminate Navy from non-Navy pollution sources, (2) locate point and non-point sources of pollution, (3) map the extent of accidental discharges, (4) verify hydrodynamic and ecological models used to assess environmental consequences of Navy operational activities and to support risk evaluation at Hazardous waste sites. This capability is operational and transportable and can be on site within two weeks anywhere in CONUS.

#4 Prediction of Toxicant Dispersion and Environmental Fate

Dr. Ken Richter - NOSC

The final presentation was a description of a project to validate a computer-based hydrodynamic/toxicological model of San Diego Bay so that it might be used to predict impact on that body of water resulting from any plume (toxic or sediment) released into the bay from a hazardous waste site, dredging activity or spill. (Generic models of other Navy harbors have been developed by David Taylor Research Center). The hydrodynamics submodel predicts wind and tidally driven transport within a body of water, and the toxicant submodel predicts toxicant dispersal and partitioning into the water column, sediment and biological fractions. Uptake by hydrolysis, adsorption, biological processes, and subsequent degradation can also be entered. Application of this project will be initially directed toward dredging activities at NAS North Island followed with work at another site to be determined involving heavy metal leaching into the water from a hazardous waste site.

NAVY UNDERGROUND STORAGE TANK (UST) PROGRAM
N. Pryor, NAVFAC

UST REGULATIONS

- SUBTITLE I OF RESOURCE CONSERVATION RECOVERY ACT-40 CFR 280
- EPA ISSUED FINAL REGULATIONS EFFECTIVE 22 DEC 88
- PROGRAM ADMINISTERED BY STATE AND LOCAL AUTHORITIES (MAY HAVE MORE STRINGENT REGULATIONS)

UST DEFINITION

- TANK AND ASSOCIATED PIPING WITH AT LEAST 10% OF VOLUME UNDERGROUND
- PETROLEUM TANKS
- HAZARDOUS SUBSTANCE TANKS

NEW TANK INSTALLATION STANDARDS

- TANKS INSTALLED AFTER DEC 88
- PROTECTED FROM CORROSION
- EQUIPPED WITH LEAK DETECTION
- SPILL AND OVERFILL PROTECTION
- CERTIFIED INSTALLATION
- NAVY SPECS. REQUIRE DOUBLE-WALLED TANKS

EXISTING PETROLEUM UST REQUIREMENTS

- RETROFIT CORROSION PROTECTION -
DEC 98
- RETROFIT SPILL/OVERFILL PROTECTION -
DEC 98
- PHASE-IN LEAK DETECTION BASED ON
AGE OF TANK

PHASE-IN LEAK DETECTION FOR EXISTING TANKS

- INSTALLED BEFORE 1965 - DEC 89
- INSTALLED 1965-1969 - DEC 90
- INSTALLED 1970-1974 - DEC 91
- INSTALLED 1975-1979 - DEC 92
- INSTALLED 1980-DEC 1988 - DEC 93

CLOSURE REQUIREMENTS

- NON-UPGRADED TANKS OUT OF SERVICE
FOR 12+ MONTHS - PERMANENT CLOSURE
- AGENCY NOTIFICATION OF CLOSURE
- ASSESSMENT OF ANY LEAKAGE
- PROPER TANK REMOVAL AND DISPOSAL
PER API GUIDANCE
- UST SYSTEMS CLOSED PRIOR TO DEC 88
MAY NEED ADDITIONAL ASSESSMENT

RECORDKEEPING REQUIREMENTS

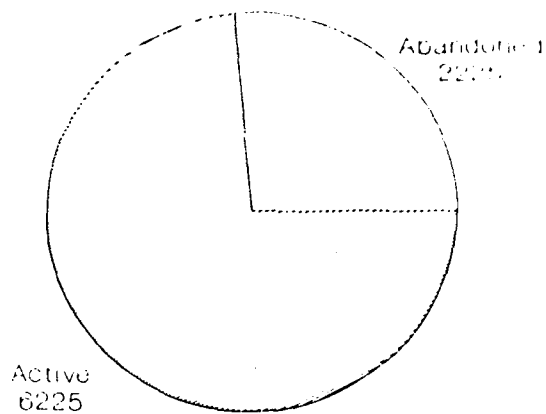
- MONITORING RESULTS
- MAINTENANCE, REPAIR, CALIBRATION RECORDS
- MANUFACTURER PERFORMANCE INFORMATION
- CLOSURE DOCUMENTATION

CORRECTIVE ACTION REQUIREMENTS

- REPORT LEAKAGE TO REGULATORY AUTHORITY
- SHORT-TERM RESPONSE - CONTAINMENT
- LONG-TERM RESPONSE - CORRECTIVE ACTION PLAN AND SITE REMEDIATION

NAVY UST UNIVERSE

8,450 USTs - 230 Activities



UST CENTRAL FUNDING

- DERA (UST Remedial Investigation/Action)
 - UP to FY 89 \$4.4M
 - FY 90+ \$45M (requested)
- PA (UST Upgrade, Leak Detection, etc.)
 - UP to FY 89 \$3.6M
 - FY 90+ \$26M (requested)

UST GUIDANCE MANUAL

- TOOL FOR EFDs
- SUMMARY OF FEDERAL UST REGULATIONS
- FUNDING GUIDANCE
- TANK MANAGEMENT PLANS
- REQUIREMENTS FOR NEW AND EXISTING TANKS
- UST REMEDIAL ACTIONS
- EXPECTED PUBLICATION DATE - OCT 89

OTHER ISSUES

- PIPELINES
- FIELD CONSTRUCTED TANKS - BULK TANKS
- HYDRANT FUELING SYSTEMS
- ABOVEGROUND TANKS

UST

IN SITU PLUME DETECTION

N.J. Olah, NCEL

- OBJECTIVE
 - Comply With Regulations for Bulk Tanks and Piping
 - Develop Early Detection Capability
- MS1
 - Sensor Network
- MS2
 - Tracers
- MS3
 - Low Level Detection
- FUELS
 - JP-5
 - DFM
 - JP-4
 - Mixtures (JP-5 & DFM)
- SENSORS EVALUATED
 - MOS
 - Adsistor
 - Aspirated MOS
 - Photoionization
 - Catalytic
- STATUS
 - Vadose Zone Lab Tests Completed
 - Liquid Zone Tests Initiated

- LOW LEVEL DETECTOR
 - Floating Hydrocarbons
 - Technology Available
 - Dissolved/Trace Contaminants
 - Technology Lacking
 - Possible Solution
 - Fiber Optics Spectroscopy
- TRACER DEVELOPMENT
 - Leak Source Confirmation
 - Fuel Components as Indicator
 - Substitute for FREON

TECHNIQUES FOR REAL-TIME ENVIRONMENTAL MAPPING AND MONITORING

S. H. Lieberman, C. Clavell and D. B. Chadwick

Naval Ocean Systems Center, San Diego, California

ABSTRACT - The characteristics of a real-time, multi-parameter measurement system for monitoring pollutants in the marine environment are described. The system couples measurements from a suite of physical, chemical and biological sensors to a positioning/navigation system through a microprocessor-based data acquisition and processing system. Environmental data can be displayed on map overlays, as it is collected, in order to track the dispersal of contaminant plumes and other dynamic features. The system can be used at a fixed location in order to document temporal variability. Recent efforts in which the system has been used in conjunction with a specially developed automated organotin analyzer are discussed.

Traditional methods of environmental sampling in which discrete samples are collected and taken back to the laboratory for later analysis are not sufficient to adequately describe highly dynamic situations in aquatic environments. In contrast to land-based sites, where it is possible to describe where a sample came from by simply documenting geographic position, in the marine environment it is also necessary to understand the local hydrography of the water in which the sample was collected. This is because in aquatic systems totally different water masses can occupy the same location at different times. Hence, to determine the source and/or fate of contaminants in marine systems it is necessary to know what the water is doing. A mechanistic understanding of complex distributions can only be achieved using a multi-parameter approach which simultaneously measures related physical, chemical and biological parameters in addition to the toxicant of interest.

To this end scientists at the Naval Ocean Systems Center have developed a real-time mapping/monitoring capability. The system integrates a suite of chemical, physical and biological sensors with a microwave positioning/navigation system [1] and a data acquisition and processing system [2]. The main components of the Marine Environmental Survey Capability (MESC) system are

shown schematically in Figure 1. The system can accommodate both *in situ* and flow-thru sensors for measuring water properties and chemical constituents. *In situ* sensors (ie., temperature, conductivity, dissolved oxygen, pH, light transmission, chlorophyll *a* fluorescence) are housed in an instrument cage (Fig. 2) that can be towed from a survey craft with the aid of a 1 m hydrodynamic depressor wing

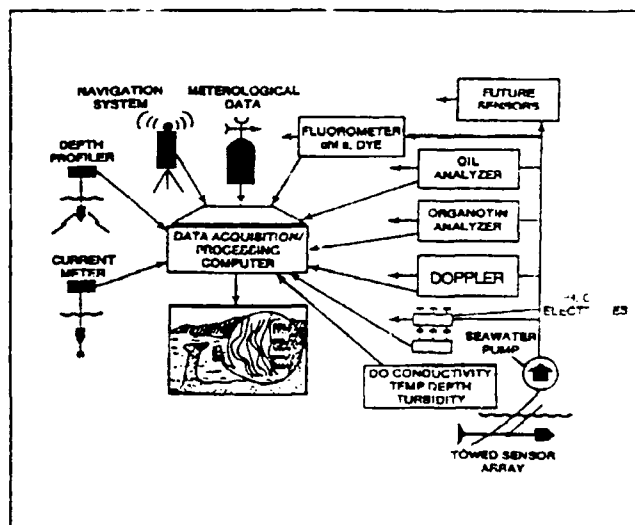


Figure 1. Schematic of Marine Environmental Survey Capability (MESC) System showing major sensor systems.

or lowered over the side to make continuous vertical measurements. For parameters for which *in situ* sensors are not presently available a high-capacity pump is used to pump water on-board the survey craft through a fared Teflon-lined hose. A manifold system distributes the flowing sample to a series of on-line instruments which include: flow-thru fluorometers for measuring petroleum hydrocarbons, fluorescent tracer dyes, etc.; a flow injection system for measuring nitrate, phosphate, silicate and ammonia; and an automated organometal analyzer. A sampling port is provided to allow on-board collection of discrete samples



Figure 2. Photograph of the MESC In Situ instrument package and oceanographic winch for deploying fared teflon sampling hose/telemetry cable.

for later analysis in the laboratory. In addition to the above sensor systems a acoustic doppler current meter, standard electro-magnetic current meters, and a meteorological data station (wind velocity and direction, relative humidity, and rainfall) are also available.

Signals from both the *in situ* and flow-thru instrumentation systems are fed into a data acquisition computer which performs analog to digital signal conversions and samples incoming digital data. Sensors can be sampled at rates up to 30 times a minute. For horizontal mapping operations conducted at a typical craft survey velocity of 5 knots this translates to a spatial resolution of approximately 5 m. For vertical profiles spatial resolution on the order of 10 cm is easily obtainable. Data from the sensors is stored as a function of time and position in IBM-compatible files. Data is also distributed in real-time to other PCs running programs for both "strip-chart" display of data and for display of selected parameters on map overlays of the study area.

In addition to the standard sensor systems that are interfaced with the MESC system, several efforts are in progress that are aimed at developing automated instrumentation for measuring selected chemical compounds that are of particular concern to the Navy. An example of such an instrument is the Automated Organometal

Analyzer (AOA) (Fig. 3) developed for the determination of tributyltin and related compounds[3]. Methods for determination of organotin compounds are of interest because they are used in antifoulant coatings that the Navy is evaluating. This instrument automatically performs a complex chemical analysis which previously required a highly trained technician to complete manually. When configured for organotin analyses the instrument can perform a complete analysis of a water sample from the flowing seawater system for tributyl-, dibutyl-, and monobutyltin at parts-per-trillion concentration levels in approximately 5 minutes. Used in conjunction with the MESC system the AOA analyzer provides near real-time information about the distribution of organotin compounds and thus helps guide monitoring efforts and ensure sampling effectiveness.

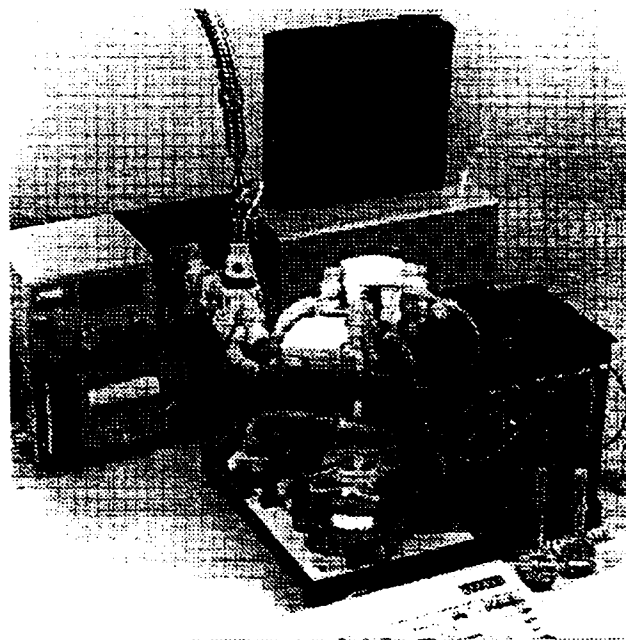


Figure 3. Photograph of the Automated Organometal Analyzer.

The MESC system has a modular design which provides a high degree of flexibility and permits the system to be easily transported and deployed from a variety of platforms. Because the objectives of each study determine the individual parameters that must be measured, the option is provided to select the appropriate sensors and instruments that will satisfy the unique requirements of each survey. Also, MESC can accommodate new sensors and/or instruments for specialized studies.

TABLE 1. RV/ ECOS SPECIFICATIONS

GENERAL SPECIFICATIONS	
Length / Beam / Draft	40 ft / 12 ft / 2 ft
Freeboard	3 ft
Transport Height	11 ft-6 in
Laboratory Space	140 sq ft (10 x 14 ft)
Wheelhouse Space	50 sq ft
Deck Space	160 sq ft
Weight	20,000 lbs
OPERATING CHARACTERISTICS	
Max Speed	20 kt
Data Taking Speed	2 to 9 kts
Range	200 miles
Positioning System Range	18 miles
AUXILLARY SYSTEMS CHARACTERISTICS	
Diesel Generator	12 KW
Hydraulic Capstan	1000 lb capacity
Davit/Hydraulic Winch	1500 lb capacity
Thru-Hull Transducer Well	12 in diameter
Oceanographic Winch	200 ft Teflon sampling hose/data telemetry cable
Radar	24 mile range
Loran C	

To insure quick response the system can be shipped by air and installed on craft of opportunity. The system is primarily intended for use aboard small vessels (suitable craft generally range from approximately 10 to 20 m in length). For environmental emergencies where a response time of 24 hours or less is required a minimum system can be transported as baggage on commercial airlines. For detailed surveys at sites where there is no suitable survey platform a custom 40 ft twin diesel support craft (R/V ECOS) is available (Fig 4). Physical and operational characteristics of the R/V ECOS are given in Table 1. This craft can be transported by truck anywhere in the continental U.S. A special cradle is also available that will permit the craft and entire MESC system to be shipped via air (C5A) when time is critical.

One of the key features of the MESC system is the automated positioning/navigation system that is interfaced with the data acquisition and processing system. The microwave positioning system uses a receiver-transmitter with an internal range processor mounted on the survey vessel to interrogate two or more shore-based reference stations to determine vessel location. A typical set up used

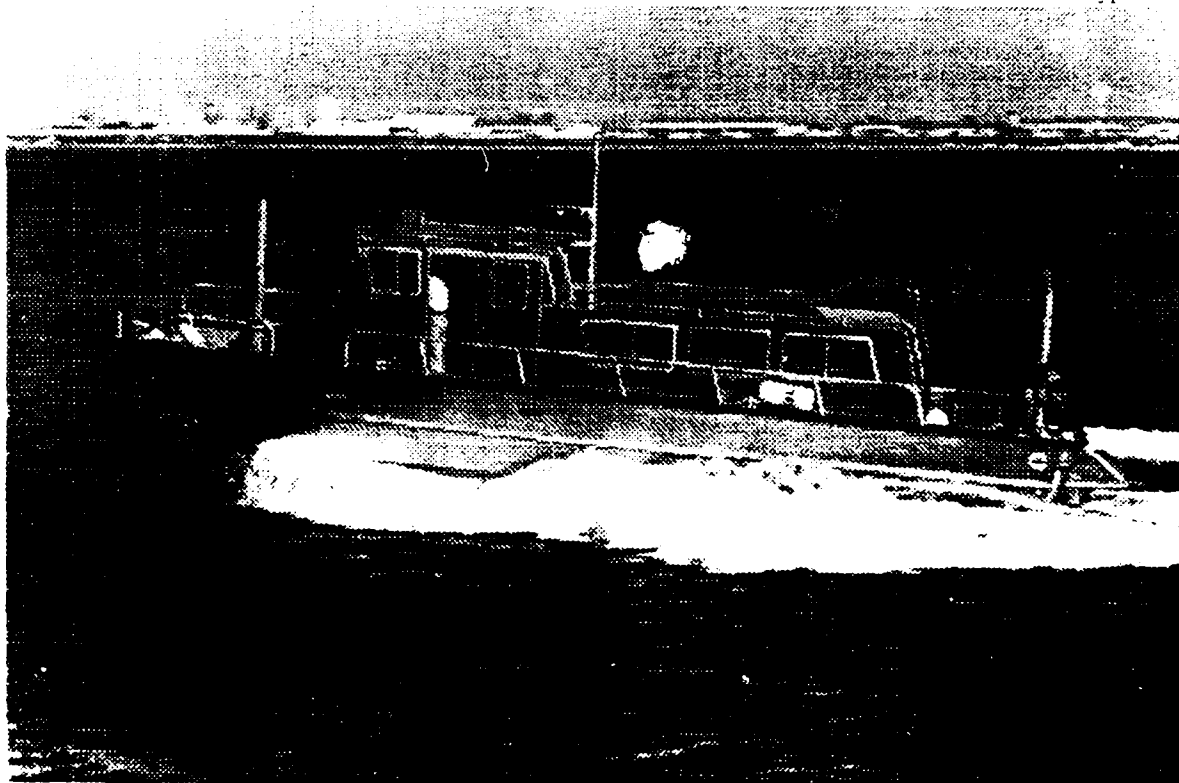


Figure 4. Photograph of MESC survey vessel R/V ECOS

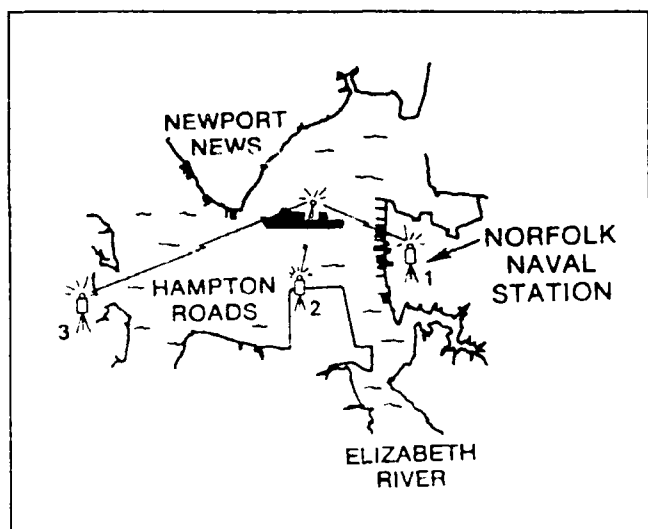


Figure 5. Schematic of the microwave positioning system setup used for a monitoring survey in the Hampton Roads area off Norfolk Naval Station.

in tests in the Norfolk area is shown schematically in Figure 5. The system provides updates of the survey craft position at rates as high as 30 times a minute with an accuracy of ± 2 m. Position information is recorded with each data record and displayed in real-time on a video monitor. For mapping surveys, track-lines can be displayed on map overlays and the progress of the survey craft along the defined pathway can be monitored by the boat operator as the survey progresses. Figure 6 shows pre-established track-lines with an overlay of the actual position of the survey craft for a survey conducted off Norfolk Naval Station.

Data collected during a survey operation can be displayed in several ways to facilitate interpretation of the observed distributions. Figure 7 is an example of a stacked three-dimensional representation showing two of the twelve parameters that were measured at a depth of approximately 1 meter during the survey shown previously in Figure 6. The flow of water from the Elizabeth River in the vicinity of the Naval Station is determined primarily by the local bathymetry. The data in Figure 7 suggests that the highest concentrations of hydrocarbons (as determined by a fluorescence method) were found mainly in the dredged channel and the immediately adjacent shallows of the Hampton Roads area. Other data showed that the source of these hydrocarbons was the Elizabeth River.

The utility of instrumentation such as the automated organotin analyzer for monitoring chemical variability as a function of time at a single sampling site is shown in Figure 8. This data shows vertical temperature structure and or-

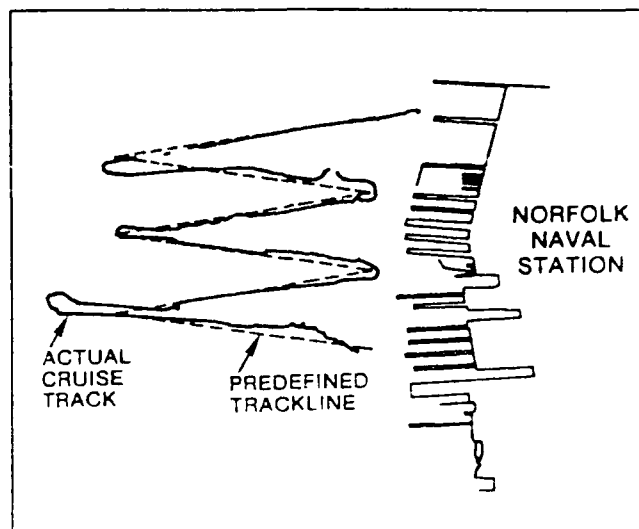


Figure 6. Map showing predefined track-lines and overlay of actual cruise track of survey craft for mapping operation conducted off Norfolk Naval Station.

ganotin concentrations measured at a distance of 1 meter off the bottom as a function of tidal height at a location in San Diego Bay. The data shows that tributyltin concentrations in near bottom waters vary by as much as a factor of seven between low tide and high tide. Comparison of the tributyltin data with the temperature and tidal data (Fig. 7) illustrates the dramatic covariability between chemical and physical properties. This type of data allows formulation of mechanistic models for the distribution of chemical toxicants.

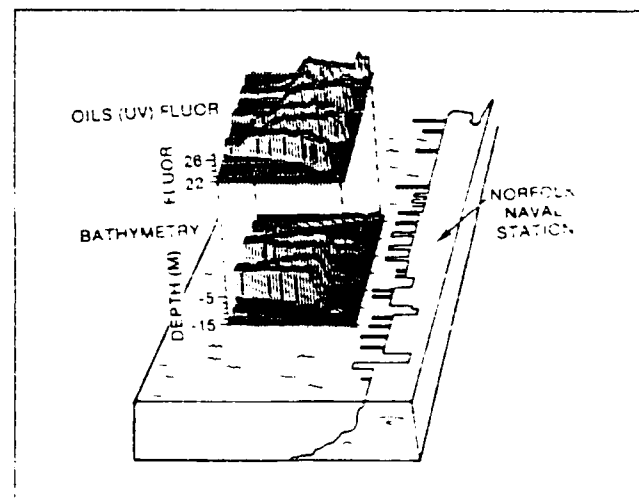


Figure 7. Map showing stacked 3-dimensional representation of hydrocarbon concentrations (as indicated by oils fluorescence) and bathymetry (bottom depth) for data collected along transect shown in Figure 6.

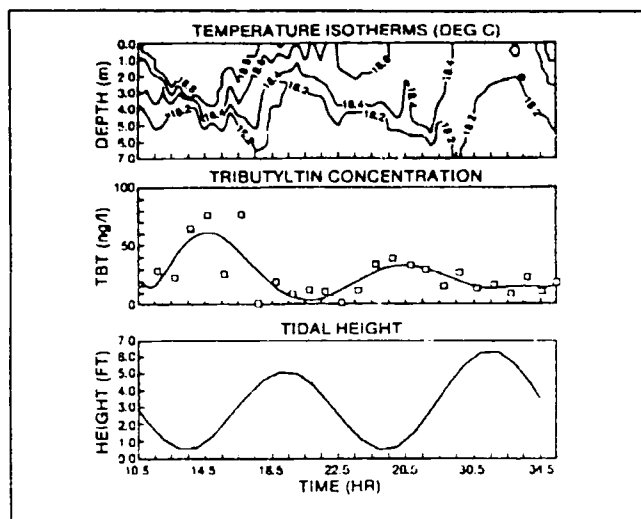


Figure 8. Time history of organotin concentrations and vertical temperature structure at a site in San Diego Bay as a function of tidal height.

With traditional methods and equipment it would not be practical, or in many cases even possible, to document this type of variability. Furthermore, there is evidence to suggest that this type of variability in the distribution of a chemical toxicant may have important biological consequences. Because an organism living on the bottom may experience significant changes in concentrations of a toxicant over time scales as short as a few hours it may not respond to the environmental insult in the same manner as it would with constant exposure. This is an important point because most toxicity tests conducted in laboratories use static levels of toxicant.

The MESC system and automated instrumentation such as the AOA are two tools that appear to have great potential for establishing a mechanistic framework for interpreting the distribution, fate and consequences of inputs of toxic chemical compounds to the aquatic environment. One of the most promising uses of these tools is for validation of computer-based models that are used to assess environmental effects from inputs to aquatic systems. At present most models lack adequate "sea-truth" data (especially in terms of chemical data) for rigorous testing of the predictions they generate. The ability of the MESC system to collect synoptic "snap shots" of contaminant distributions and related hydrographic data should provide a sound data base for validating and improving computer-based models. Use of the system for point monitoring can also provide very useful information for evaluating short term temporal variability (hours to days).

In order to function as a responsible member of the community in which it has facilities, the Navy must not only satisfy existing environmental regulations and requirements but also anticipate and attempt to predict the environmental consequences of changes in the way it operates. The development of the MESC system for real-time environmental mapping and monitoring represents an attempt to take the lead in establishing a technology base for evaluating environmental impact of its operations, in particular those resulting from activities that are largely unique to the Navy. This provides the Navy with the means to work with regulatory agencies for establishing safe and realistic regulations and criteria. Regulations based on sound scientific data, rather than political expediency or emotional perceptions, would better insure the health and safety of military and civilian personnel and at the same time promote efficient and cost effective operations.

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Title: Prediction of toxicant dispersal and environmental fate for Navy hazardous waste remediation.

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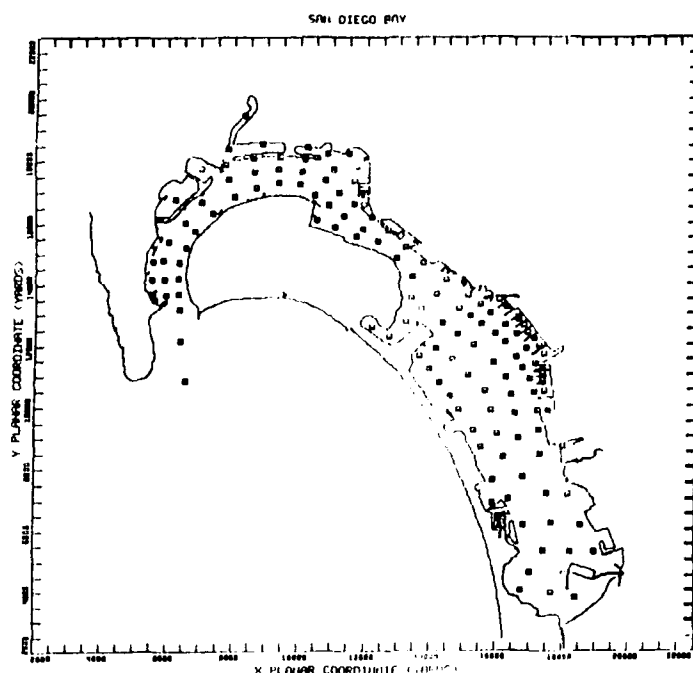
Abstract: The purpose of this project is to (1) Validate TOXIWASP, a hydrodynamic and toxicant model predicting toxicant dispersal and partitioning into water column, sediment and biological fractions in San Diego Bay. (2) Use validated model to aid Navy hazardous waste remediation in San Diego Bay, minimizing environmental impact. (3) Transport model to second Navy hazardous waste site to aid in remediation.

Introduction: Based on the National Oceanic and Atmospheric Administration status and trends program, San Diego Bay has been labeled as the most polluted on the west coast. Navy operations may have contributed to the problem here and elsewhere through chronic and acute release of various hazardous wastes. For example, shore-based landfills, ship fueling operations, and channel dredging release heavy metals, hydrocarbons, and toxic organics into the water column and sediments. Naval Facilities Engineering Command is charged by a series of local, state, and federal laws to monitor Navy wastes and minimize their impact on human health and the marine environment (e.g. CERCLA, 1986). The remedial measures Initial Decision Report has identified forty two Navy hazardous waste sites that will require remediation of contaminated sediment. In cases where dredging is required to maintain navigable waterways or to remediate contaminated areas, the impact of material resuspension is unknown or difficult to measure, due to inadequate determination of the dredge plume. Information on the dispersion and eventual fate of resuspended or accidentally released Navy wastes is needed so that future Navy operations minimize environmental risk. Inquires to David Taylor Research Center on the feasibility of applying models to support environmental restoration work have been received from NORTHDIV for NSY Portsmouth, PACDIV for Pearl Harbor and Guam, and PACNORWESBRANCH for Bremerton and Everett. In addition, sites where the application of these models will greatly enhance installation restoration, once feasibility is demonstrated, include: NCBC Davisville, RI; NAS Moffet Field, NAS Alameda, NSY Hunters Point, and NSY Mare Island, CA; NUWES Keyport and NSB Bangor, WA; MCAS Kanahoe, HI; and NSB New London, CT. Model development in San Diego Bay will directly support remedial investigation/feasibility studies for NAS North Island, NAVSTA San Diego, and the Point Loma Naval Complex. In addition, the model will support monitoring of chronic oil pollution coming from Navy, commercial, industrial, and recreational activities as well as episodic runoff. NAVSEA is funding a parallel effort at NAVOCEANSYSCEN to determine the Navy's contribution to this bay-wide problem.

Approach: A generic two-part model, TOXIWASP, was recently written for the Environmental Protection Agency for just such predictions (DiToro et al., 1981; Ambrose et al., 1986; GKY&A, 1987). The hydrodynamics submodel predicts wind and tidally driven advective transport within a body of water, given initial starting conditions at key nodal points. Specifically, the hydrodynamics submodel requires bottom depth, bottom friction, tidal height and mean water column velocity at discrete points of arbitrary spatial density (figure 1). The toxicant submodel predicts toxicant dispersal and partitioning into water column, sediment, and biological fractions, given input from the hydrodynamic submodel and uptake estimates for each of these partitions. Uptake by hydrolysis, adsorption, biological processes, and subsequent degradation can be entered (figure 2).

TOXIWASP with site specific geographical information exists for San Diego Bay, CA; Norfolk, VA; Pearl Harbor, HI; Mayport and St Johns River, FL; Bremerton and Everett, WA; and Charleston, SC. Models are being developed (FY88) for Philadelphia, PA, Long Beach, CA; and (FY89) for Portsmouth NSY, NH; and NAS Alameda in San Francisco Bay. TOXIWASP is currently resident on computer at Naval Ocean Systems Center in code 522. We propose applying the hydrodynamics submodel to San Diego Bay. A 1.2 MHz acoustic doppler current meter (Woodward and Appell; 1986), already installed on a 42 foot survey craft with high precision positioning, will provide accurate depth and current data at chosen nodal points. The survey craft "Ecos" was funded as part of NAVFACENGCOM's marine environmental quality assurance program. Ecos provides real-time measurements and mapping of physical and chemical parameters (Boer and Lieberman, 1987). Velocity data can be rapidly collected at many positions, providing good model input. In addition, acoustic backscattering from the current meter will be used to track and map dredge plumes when Navy dredge operations are monitored (Lynch, et al; 1987). Present capabilities include continuous measurements of pH, temperature, water color, oil and chlorophyll fluorescence, transmittometry, depth dependent water velocity, small particle acoustic backscatter, and organotin. On station bottle/pump and bottom sampling as well as conductivity/temperature/depth profiling are routinely made. Toxicant concentrations, other than of organotins, are usually determined in the laboratory from field samples. Past and current work (FY90) includes sediment adsorption/desorption of organics and metals on station. We are conducting monitoring surveys for petroleum-derived hydrocarbons in San Diego Bay to determine base-line levels and relative inputs of Navy and non-Navy sources. The survey craft and instrumentation is transportable by flatbed truck to other aquatic hazardous waste sites. Once the TOXIWASP model is running, water velocity, sediment plume and toxicant measurements will be used to validate output of the submodels.

Hydrodynamic validation: measure water velocity and adjust friction coefficient between links.



$$V = \frac{C}{n} \sqrt{\frac{\Delta H}{\Delta x}}$$

$$\frac{\Delta H}{\Delta t} = \frac{V \cdot \text{link cross section}}{\text{node volume}}$$

Figure 1. The location of 140 nodes in San Diego Bay. Velocity (V) is a function of the head gradient (H/X) and a bottom friction coefficient term (n). The change in head per time step is a function of the calculated velocity, the link cross section, and the volume represented by the node.

Validating toxicant distribution: measure the toxicant

TOXIMAP Segment Network

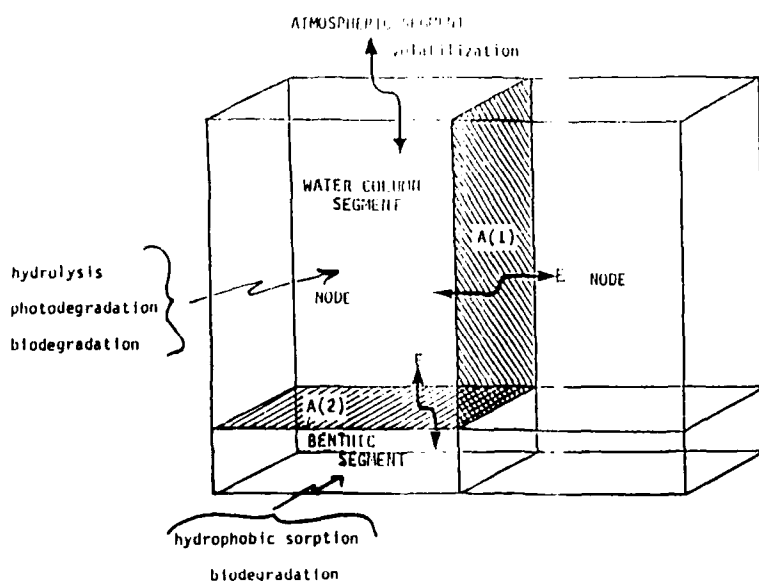


Figure 2. In the volume represented by each node, a pollutant can enter and leave advectively according to the velocity determined by the hydrodynamic submodel. Within each node, various sinks and loss rates can be modeled, depending on the nature of the pollutant.

We propose to apply the model first to San Diego Bay because of its proximity and recognized problems. We anticipate dredge cleanup at NAS North Island in the near future, identified in Navy remedial investigation and confirmation studies as a heavy metal hazardous waste site. We anticipate close scrutiny of Navy oil/water separators (donuts) which are used to handle oily, discharged, bilge water. With our oil fluorescence mapping capabilities aboard Ecos, we will be able to determine how large the Navy contribution is to the oil pollution problem. Follow on work includes modeling a second Navy site, perhaps dredge remediation of heavy metals in Pearl Harbor sediments. Pearl Harbor is particularly attractive since the specific hydrodynamic submodel is well developed (GKY&A, 1987).

Technical Work Plan: FY90: Validate the hydrodynamic submodel of TOXIWASP for San Diego Bay. This entails (1) selecting the node/link locations, (2) measuring depth and water velocities at the nodes from the survey craft, (3) running the model and validating the results with field measurements. The hydrodynamic model can be fine tuned, by iteratively adjusting several factors, such as the bottom friction coefficient, wind sheer, and fresh water input. The model is run on a vectorized super computer at NOSC and the results are down-loaded to a personal computer for graphic output and analysis. (Heath, 1988).

FY91-92: Validate the toxicant submodel for San Diego Bay. This constitutes (1) running the model with the hydrodynamic output and preselected toxicant uptake rates and (2) validating the model with field measurements. This is the more difficult aspect of the work, since relevant data will require more time-consuming measurements. Code 522 has ample experience in this field with regard to the partitioning and degradation of tributyltin (Seligman et al, 1987; Seligman et al, 1988). TOXIWASP will then be run at a second Navy site, based on experience gained in San Diego Bay.

A user data package will be developed to provide information on model construction, sampling requirements and guidelines to determine which sites are suitable for modeling. We hope to develop methodology to perform model-based risk assessments applicable to numerous hazardous waste sites to define impact on marine systems. The methodology will be useful for predicting environmental impact at other Navy sites where remediation must be undertaken.

* Richter, Johnston and Gadbios work for Naval Ocean Systems Center, code 522. Smith works for David Taylor Research Center, code 236.

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Assessment of Toxic Organics in Seawater and Waste Effluents with a Bacterial Bioassay (Microtox[®])

P. Kenis, NOSC

Toxic organic compounds are a potential hazard in the marine environment and in pretreatment discharges from Naval facilities which enter municipal waste treatment systems. Toxic organics may harm plants and animals in marine waters or be detrimental to wastewater treatment facilities by upsetting the desired microbial water treatment processes. It is therefore necessary to have an analytical capability to assess the toxicity caused by dissolved organic compounds to insure healthy marine ecosystems and optimally functional wastewater treatment facilities dependent upon microbial processes.

The assessment of toxicity caused by organic compounds is a complex problem because of the many thousands of organic compounds of potential concern that may enter the marine environment or wastewater treatment facilities. Standard chemical analytical procedures are of limited value when such a diverse and large number of potentially harmful compounds are of concern. Chemical analyses are most useful when the precise composition of organics are known and the specific analytics can be performed. Oftentimes, however, the exact organic components of a discharge are not known. And in the case of environmental monitoring for water quality, we must be able to assess potential toxicity of any harmful organic compound.

Because of this unique analytical requirement for toxic organic compounds, a rapid bioassay procedure can serve as a preliminary screening technique. If no toxicity is indicated by a bioassay of total organic components of a sample, the sample should not require further chemical analyses. If toxicity is indicated by the bioassay, then further chemical analyses may be required to identify and quantify the toxic component(s). The bioassay system to be evaluated for assessment of toxic organics is a commercially available system named MICROTOX (R) which incorporates bioluminescent bacteria as the indicator (Microbics Corp., Carlsbad, California). Toxicity is measured by a decrease in light output from the living bacteria compared to controls with no toxic material present. The advantages of this bioassay system are:

1. The instrument and reagent (freeze-dried bioluminescent bacteria) are available commercially and are simple to use with over 10 years of successful field trials.

Table 1.

MICROTOX RESPONSE
TO ORGANIC COMPOUNDS

<u>Compound</u>	<u>EC 50.ppm</u>	<u>Reference</u>
1. Benzoquinone	0.009	6
2. Hydroquinone	0.08	6
3. Methyl isobutyl ketone	0.08	6
4. Pentachlorophenol	0.08	2
5. Tetrachlorophenol	0.09	5
6. Hexachloroethane	0.14	2
7. P-tert-butylphenol	0.21	2
8. Kelthane	0.45	2
9. P-tert-pentyl phenol	0.5	6
10. P-tetra-butyl phenyl	0.5	6
11. Pentachlorophenate	0.5	5
12. Permethrin	0.56	2
13. 4-Chloro-3-methyl phenol	0.58	6
14. Acroleine	0.67	6
15. Aroclor 1242	0.7	5
16. Pydrin	0.7	6
17. pentachloroethane	0.75	2
18. Phenylazoahenol	0.77	2
19. Pentachlorophenate	0.94	1
20. Sodium Penta-chlorophenate	1.0	6
21. p-Phenol-azo-phenol	1.0	6
22. 2-Decanol	1.2	2
23. P-Cresol	1.5	5
24. Benzene	2.0	5
25. Diazinon	2.0	3
26. O-Phenylphenol	2.0	2
27. Carbaryl	2.0	3
28. 2,4,6-tribromophenol	2.7	2
29. Benzaldehyde	2.7	6
30. Formaldehyde	3.0	5
31. Malathion	3.0	5
32. Dichloran	3.0	3
33. 1-Napthol	3.3	6
34. 2,4-Dichlorophenol	4.0	2
35. 2,4-Dimethylphenol	4.0	2

<u>Compound</u>	<u>EC 50.ppm</u>	<u>Reference</u>
36. Dichloroacetone	4.1	6
37. 2,4-Dimethyl phenol	4.4	6
38. Pinacolone	5.2	6
39. Styrene	5.4	4
40. Carbon tetrachloride	5.6	6
41. 1-Napthol	5.7	2
42. 2-Decanone	6.1	6
43. 1-Octanol	6.3	2
44. 4,6-Dinitro-O-cresol	6.5	2
45. DDT	7.0	3
46. Captafol	7.0	3
47. 2,4,6-Trichlorophenol	7.2	2
48. Endrin	7.3	6
49. Glyphosate	8.0	3
50. 2-Deconone	8.8	2
51. 1,1,2,2-Tetrachloroethane	8.4	6
52. Tetrachloroethane	8.6	2
53. Tetrachloroethanol	8.7	6
54. 1-Heptanol	9.4	6
55. Formaldehyde	9.5	6
56. N-Cresol	9.5	6
57. P-Dichlorobenzene	9.7	6
58. Diazion	9.8	2
59. Malathion	10.0	3
60. 2-Allylphenol	10.0	2
61. Cyhexatin	10.0	3
62. Cyclohexanone	10.0	5
63. p-Nitrophenol	13.0	2
64. p-Dinitrophenol	13.0	6
65. O-Phenyl phenol	14.0	6
66. Octanol	14.0	6
67. n-Heptanol	14.0	1
68. Disulfaton	15.0	6
69. 2,4-Dinitrophenol	16.0	6
70. Butanal	16.0	2
71. Salicyladehyde	16.0	1
72. 6-Methyl-5-heptenone	17.0	6
73. 1,1,1,-Trichloroethane	18.0	6
74. 5-Nonanone	18.0	6
75. 6-Methyl-5-hepten-2-one	18.0	2
76. 2-Octanone	18.0	2
77. Cyclohexanone	19.0	2

<u>Compound</u>	<u>EC 50.ppm</u>	<u>Reference</u>
78. Benzonitrile	19.0	6
79. Trinitrotoluene	20.0	5
80. Allylamine	20.0	1
81. 2-Octanone	20.0	6
82. O-Cresol	21.0	1
83. O-Chlorophenol	22.0	2
84. Aceto-phenol	23.0	6
85. 1-Amino-2-propanol	27.0	2
86. Chloro-2-butanone	28.0	6
87. O-Cresol	31.0	6
88. 2-Phenoxy ethanol	32.0	6
89. Catechol	32.0	6
90. Dimethylphthalate	33.0	6
91. 2-Phenoxyethanol	33.0	2
92. Benzyl Alcohol	33.0	
93. 4-Amino-2-Nitrophenol	36.0	2
94. Benzophenol	38.0	6
95. Phenol	40.0	2
96. Hexanol	40.0	2
97. 4,4-Dimethyl-amino- 3-methyl-2-butanone	42.0	2
98. Toluene	44.0	6
99. Nitrobenzene	46.0	6
100. Hexachloroacetone	46.0	6
101. m-Methoxy phenol	55.0	6
102. N-Butyl ether	63.0	2
103. Glutaric dialdehyde	76.0	6
104. Chloroacetone	76.0	6
105. 4-methyl-2-pentanone	80.0	2
106. Trichloroethane	105.0	2
107. Cyclohexanol	115.0	2
108. Ridomil	120.0	3
109. Thiabendazole	120.0	3
110. Isoamyl alcohol	144.0	6
111. 1,2-Dichloroethane	158.0	4
112. Pyridyl carbinol	160.0	6
113. Trichloroethylene	160.0	1
114. 5-Butyl Alcohol	173.0	
115. Benzene	210.0	1
116. Methoxy acetone	240.0	6
117. Pyridine	300.0	6
118. Resorcinol	310.0	6

<u>Compound</u>	<u>EC 50.ppm</u>	<u>Reference</u>
119. 2,3-Dibromopropanol	310.0	6
120. 1,1,2-Trichloroethylene	320.0	6
121. 2,3-Dibromopropanol	320.0	2
122. n-Amyl alcohol	320.0	6
123. Ethanal	342.0	
124. Acetaldehyde	390.0	6
125. Propionaldehyde	410.0	6
126. Aniline	420.0	1
127. Chloroform	435.0	4
128. Isopropyl ether	505.0	6
129. +-Amyl alcohol	560.0	6
130. Ethylpropionate	610.0	1
131. Paraquat	780.0	3
132. 3-Pentanone	850.0	6
133. Chloroform	920.0	6
134. 4-Hydroxy-4-methyl- 2-pentone	920.0	6
135. 2-Butanone oxime	950.0	2
136. 5-Methyl-2-hexanone	980.0	2
137. Amytal	1,000.0	6
138. 2-(2-Ethoxy ethoxy) ethanol	1,000.0	6
139. 2,4 Pentaneclione	1,000.0	6
140. 2,4 Pentanedione	1,050.0	2
141. 2-(2-Ethoxyethoxy) ethanol	1,145.0	2
142. Ethyl acetate	1,200.0	6
143. Acetyl-methyl-carbnol	1,200.0	6
144. Acetal	1,500.0	6
145. 5-Methyl-2-hexanone	1,500.0	2
146. +-Butyl-methyl-ether	1,700.0	6
147. 2-methyl-1-propanol	1,700.0	2
148. 2,2,2-Trichloroethanol	1,800.0	2
149. 1-Butanol	2,200.0	6
150. 1-Butanol	2,300.0	2
151. Pyridine	2,600.0	1
152. 2-Methyl-2,4-pentanediol	2,700.0	6
153. 2-Methyl-2-4-pentanediol	3,000.0	2
154. 1-Butanol	3,300.0	5
155. Thiabenazole	3,400.0	6
156. Acrylonitrile	3,900.0	6
157. Methyl ethyl ketone	4,350.0	6
158. 2-Butanone	5,000.0	2
159. Ethylacetate	5,160.0	1
160. Diethylene Glycol	8,900.0	6

<u>Compound</u>	<u>EC 50.ppm</u>	<u>Reference</u>
161. 2-Chloroethanol	13,400.0	2
162. 2-Propanol	18,000.0	6
163. n-Propanol	18,000.0	1
164. DMF	19,000.0	6
165. Dimethylformamide	20,000.0	2
166. Acetone	21,000.0	2
167. Urea	24,000.0	5
168. Ethanol	31,000.0	5
169. Triethylene Glycol	33,000.0	2
170. 2-Propanol	35,000.0	2
171. Isopropanol	42,000.0	5
172. Ethanol	44,000.0	2
173. Propylene glycol	120,000.0	6
174. Methanol	125,000.0	2

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1. De Zwart and Slooff, 1983.
2. Curtis, et al., 1982.
3. Chang, et al., 1981.
4. Qureshi, et al., 1982
5. Bulitch and Isenberg, 1981.
6. Microbics Corp. Data Sheet.

2. Bioassays can be performed within 5 to 30 minutes.

3. There is published literature comparing this bioassay to fish and other bioassays. (Bulitch, et al., 1981; Lebsack, et al., 1981; Curds, et al., 1982; Qureshi, et al., 1982; DeZwart and Slooff, 1983)

The main disadvantage of this bioassay system is its lack of sensitivity to most organic compounds. Table 1 shows the relative toxicity of 174 compounds in order of increasing toxicity. Most organic compounds require a concentration of many ppm (mg/l) to produce an EC50 in 5 minutes (the concentration which produces a 50% reduction in light output by the bioluminescent bacteria after 5 minutes).

A discharge requirement which the Navy must meet is that the sum of some 120 priority pollutants on the EPA's list shall not exceed 2.13 ppm, whereas any single compound below a concentration of 0.010 ppm need not be included. This requirement indicates that we must be able to measure toxic organics in the range of 0.01 to 2 ppm. Currently the Microtox system cannot detect most organic compounds at these levels.

The 2.13 ppm total toxic organic requirement is incomplete since most toxic organic compounds are not on the EPA's list of priority pollutants, particularly those used by Naval rework and other facilities. Also, some organic compounds can be quite toxic below the 0.010 ppm level, such as tributyl-tin compounds used in antifouling coatings. An adequately sensitive bioassay system may be the most realistic way to assess the overall organic toxicity of a pretreatment or environmental water sample.

With greater sensitivity the Microtox system can meet these requirements. Greater sensitivity can be achieved by:

1. With a new high sensitivity reagent under development by Microbics Corp.

2. Preconcentration of dissolved organics by solvent extraction or column retention and elution.

The high sensitivity reagent under development initially showed the most promise to attain the needed extra sensitivity. Table 2 shows the sensitivity of the new high sensitivity reagent (bacteria) compared to the standard reagent (bacteria). Increased sensitivity of several orders of magnitude result with the new high sensitivity reagent.

Table 2.

MICROTOX SENSITIVITY
OF STANDARD AND HIGH SENSITIVITY REAGENT (ppm) *

<u>Compound</u>	<u>H.S. Reagent</u>	<u>Standard</u>	<u>Reagent</u>	<u>Increase In Sensitivity</u>
Systoxthione	0.0005		10	20,000
Pentachlorophenol	0.002		0.5	250
Endosulfan	0.005		27	5,400
Chlordane	0.005		3.5	700
Toxaphene	0.01		-	-
Malthion	0.05		10	200
Alderin	0.05		40	800
Diquate	0.06		100	300
Paraquate	0.3		100	300
DDT	0.5		5	10
Zinc	0.5		2	4
Cadmium	0.5		3	6
Benzene	5.0		100	6

*Concentrations are 15 minute EC50 data provided by Microbics Corp.

A direct bioassay without the need for preconcentration steps would be simple, rapid, and most readily amenable to automation. The new high sensitivity reagent appeared to meet this requirement. Initial laboratory tests were therefore conducted anticipating the availability of a high sensitivity reagent, negating the need for preconcentration steps.

A bioassay for toxic organics must eliminate toxicity caused by heavy metals. This can be done by:

1. Eliminating heavy metal toxicity by complexation with EDTA in solution, or by removing heavy metals on an ion exchange column.
2. Removing dissolved organics on an organic-affinity column after initial testing on the complete sample. A reduction in toxicity after passage through this column would be caused by toxic organics.

A simple procedure would be to render heavy metals nontoxic by the addition of EDTA solution to the test sample. For example, if a sample tested positive for toxicity, the toxic component may be toxic organics or heavy metals. EDTA should eliminate heavy metal toxicity. Toxicity resulting after EDTA addition should be caused by toxic organics.

STUDIES TO REMOVE HEAVY METAL TOXICITY BY EDTA COMPLEXATION

Table 3 summarizes the results with the standard Microtox reagent when challenged with Cu, Zn and Hg with and without EDTA. Initial tests used the 2% NaCl matrix required by the Microtox reagent with an EDTA concentration of 5×10^{-4} M (1.68 g/100 ml). EDTA at this level rendered ppm levels of copper, zinc and mercury nontoxic under 5 to 30 min. bioassay test conditions. In a seawater matrix, however, EDTA at this concentration was ineffective in eliminating heavy metal toxicity. The relatively high concentrations of magnesium and calcium in seawater likely compete for sites on the EDTA molecules, thus rendering EDTA ineffective at this concentration.

The concentration of EDTA was increased three-fold (1.5×10^{-3} M, 5.04 g/100ml) in an attempt to render ppm levels of copper, zinc, and mercury nontoxic. At this concentration EDTA reduced heavy metal toxicity about 50%, during the 5 to 30 min. bioassay.

It was concluded that EDTA added directly to seawater is not advisable as a means to separate toxicity caused by organics from heavy metal toxicity because:

Table 3.

EFFECT OF EDTA ON TOXICITY OF Cu, Zn, AND Hg
TO STANDARD MICROTOX REAGENT*

EDTA	5 x 10 M	EDTA	1.5 x 10 M
<u>2% NaCl</u> <u>Matrix</u>	<u>Seawater</u> <u>Matrix</u>	<u>2% NaCl</u> <u>Matrix</u>	<u>Seawater</u> <u>Matrix</u>
Cu, Zn, Hg all nontoxic	Cu, Zn, Hg toxic	Cu, Zn, Hg all nontoxic	50% + reduction in toxicity for Cu, Zn, Hg

*Cu, 5 ppm; Zn, 5 ppm; Hg, 1 ppm.

1. EDTA reduces heavy metal toxicity incompletely at 1.5×10^{-4} M (5.04 g/100 ml).

2. EDTA present at such high concentrations may interact with the toxic organics (antagonism or synergism) adding an unwanted variable.

From these results it appears the use of the high sensitivity reagent would require column separations to discern toxicity caused by organics from heavy metals.

CURRENT STATUS OF HIGH SENSITIVITY REAGENT

Microbics Corporation was initially optimistic that the high sensitivity reagent would soon be available for laboratory evaluation. Unfortunately, current set-backs have placed this product on an indefinite hold. Apparently, the product is quite sensitive to very high molecular weight compounds such as those shown in Table 2. Efforts have been unsuccessful to increase sensitivity to most toxic organic compounds. I have been informed by Microbics Corporation that no further development on this product is planned in the near future.

INCREASED SENSITIVITY OF STANDARD REAGENT THROUGH PRECONCENTRATION OF TOXIC ORGANICS FROM SAMPLE WATER

With no high sensitivity reagent available it is necessary to concentrate the toxic organics in environmental or pretreatment effluent samples. The standard reagent should be suitable for toxicity assessment of toxic organics after adequate preconcentration. Preconcentration can be performed by:

1. Extraction into an organic solvent such as methylene chloride, reducing to dryness or near dryness, and dissolution (or solvent exchange if methylene chloride is present) into methanol or ethanol for toxicity testing with Microtox.

2. Removal of dissolved organics on an organic-affinity column, removal with an organic solvent, and treating organic solvent as (1) above.

An organic extraction procedure should be specific for toxic organics since heavy metals and cyanide should be excluded from the organic phase. This procedure, though more time consuming than a direct analysis with a high sensitivity reagent has the advantage of its organic selectivity.

The Microtox standard reagent has been used successfully to compare the toxicity of marine sediments from several locations

(Schlewe, et al., 1985). Sediments were extracted with methylene chloride, concentrated by heating, and exchanged into ethanol for testing on Microtox.

TECHNIQUES TO INCREASE CONCENTRATION OF TOXIC ORGANICS

Dissolved toxic organic compounds can be concentrated from seawater by extraction with methylene chloride. After several methylene chloride extractions of a seawater sample, the methylene chloride is pooled and evaporated to dryness or near dryness. When evaporated to dryness the organic residue is dissolved in methanol or ethanol. When taken to near dryness, the remaining methylene chloride must be removed by exchanging into methanol or ethanol.

If 1 liter of seawater has been extracted with methylene chloride and concentrated into 1 ml of ethanol or methanol, the resulting concentration factor is 1,000. However, concentrated ethanol or methanol cannot be used with Microtox standard reagent directly since it is toxic to the bioluminescent bacteria. The Microtox standard reagent (bioluminescent bacteria) can tolerate only about 4 percent ethanol or methanol. Thus, the methanol or ethanol must be diluted by a factor of 25 to yield a final alcohol concentration of 4% tolerable to the Microtox assay. The 1,000 fold concentration of organics from the sample has now been reduced by a factor of 25, for a total concentration factor of 40.

If the methylene chloride extract is redissolved in only 0.5 ml of alcohol, the resulting concentration factor is 2,000. This value reduced by the 25 fold factor to provide the tolerable 4% alcohol concentration would yield a final concentration factor of 80.

TECHNIQUES TO INCREASE SENSITIVITY OF THE MICROTOX SYSTEM

The reported value for a Microtox assay is usually the EC50 value at 5, 15, or 30 minutes. This is the concentration of toxicant which produces a 50% reduction in light from the bioluminescent bacteria (standard reagent) after the desired time interval. Greater sensitivity can be realized by reporting a 5 to 10% reduction in light. In addition, many compounds show greater toxicity at increased time intervals beyond 5 min., such as 15 or 30 minutes. Therefore, by increasing the time of exposure to 15 or 30 minutes and measuring a 5 to 10 reduction in light compared to controls, the sensitivity is anticipated to be increased conservatively by a factor of 3 to 5.

TOTAL INCREASE IN CONCENTRATION/SENSITIVITY

An increase in concentration from 40 to 80 fold by solvent extraction combined with an increase in sensitivity from 3 to 5 by "fine tuning" should yield increased detectability by a factor of 120 to 400.

If we use a desired detectability level of 1 to 2 ppm, a 120 fold increase in detectability would yield an equivalent of 240 ppm which can be detected. A 400 fold increase in detectability would yield 800 ppm levels of toxic organics capable of detection by Microtox. From Table 1 we see that 240 ppm represents about 60 percent of the organic compounds and 800 ppm about 75 percent of the organic compounds for which Microtox toxicity data is available.

SUMMARY

The high sensitivity reagent under development by Microbics Corp. will not be available in the near future. It was anticipated that the high sensitivity reagent could detect low levels (less than 2 ppm) of most toxic organics directly in seawater without further concentration. A high sensitivity reagent would, however, require a procedure to separate toxic effects caused by heavy metals or cyanide. The high sensitivity reagent approach for measuring toxic organics will be temporarily abandoned.

The standard Microtox reagent should be useful in detecting toxic organics by preconcentrating the organics by solvent extraction and increasing the sensitivity of the Microtox procedure. We anticipate increases in concentration/sensitivity from 120 to 400 fold. This increase should allow for the detection of the majority of toxic organic compounds at ambient concentrations from 1 to 2 ppm.

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WORKSHOP COMMENTS AND EVALUATIONS

Requirements Definition Worksheet

Please fill out the following information:

Name: _____

Phone: _____ commercial

_____ autovon

Address: _____

TYPE OF ACTIVITY: _____

YOUR AREA OF COGNIZANCE: _____

The following information will be used to identify the most critical technology development required to support the Navy's Environmental Programs.

On pages 2 and 3 please rate the following Goals and Thrust Areas for level of technology development needed by placing a check mark in the appropriate space.

U=Urgent Need: Major impact on operations; no off-the-shelf technology available;

H=High Need: Could have major impact on operations; available technology too costly;

M=Moderate Need: Minor impact on operations; available technology not applicable to Navy;

L=Low Need: No impact to operations foreseen; not Navy-specific technology

N=Not Needed: Not a Problem for the Navy.

NAVY ENVIRONMENTAL R&D GOALS RANKING SHEET

U H M L N

-- -- -- -- I. Zero discharge of hazardous wastes from Navy industrial facilities.

THRUST AREAS:

- -- -- -- - Waste Stream Treatment for Industrial Processes
 - -- -- -- . Emptying/Cleaning/Derusting Bilges & Tanks
 - -- -- -- . Painting/Painting Striping Operations
 - -- -- -- . Boiler Lay-up and Cleaning Operations
- -- -- -- - Ordnance Operations and Waste Disposal
- -- -- -- - Lubricants & Other Fluids Change-outs
- -- -- -- - IWTP Reagents Use and Reuse

-- -- -- -- II. Acceptable clean up levels achieved at all Navy past hazardous waste disposal sites.

THRUST AREAS:

- -- -- -- - Remediation Technologies
 - -- -- -- . Biological (In situ/bioreactors)
 - -- -- -- . Chemical
 - -- -- -- . Physical
- -- -- -- - Risk Assessment/Risk Management Methodologies
- -- -- -- - Site Restoration and Closure Techniques

-- -- -- -- III. 100% reclamation of industrial and municipal waste water at Navy Facilities.

THRUST AREAS:

- -- -- -- - Conservation
- -- -- -- - Reuse and Reclamation of waste water
- -- -- -- - Reduction of Water Total Toxic Organics
- -- -- -- - Groundwater Protection
- -- -- -- - Monitoring and Protection of Drinking Water

NAVY ENVIRONMENTAL R&D GOALS RANKING SHEET (Cont.)

U H M L N

- - - - - IV. Zero air emissions and acceptable noise emissions from Navy shore facilities.

THRUST AREAS:

- - - - - - Air Emissions Control
- - - - - - Alternatives to VOC coatings
- - - - - - Control of new & emerging air pollutants
- - - - - - Noise reduction and control
- - - - - - Alternatives to CFC applications

- - - - - V. Nonpolluting, safe, and state-of-the-science materials and industrial processes for Navy facilities.

THRUST AREAS:

- - - - - - Improvements for Industrial Processes
 - . Emptying/Cleaning/Derusting Bilges & Tanks
 - . Painting/Stripping Operations
 - . Boiler Lay-up and Cleaning Operation
- - - - - - Substitution for Nonhazardous Materials
- - - - - - Nonpolluting Antifouling Systems

- - - - - VI. State-of-the-science methods and instrumentation for cost-effective monitoring of Navy unique pollutants and contamination.

THRUST AREAS:

- - - - - - Sensor development
 - . sensor networks
 - . real time sensors for process control and monitoring
- - - - - - Biomonitoring for Toxicity and Hazard Assessment
- - - - - - Monitoring Network Design and Implementation

- - - - - VII. Comprehensive prediction and management of environmental effects from Navy systems and operations.

THRUST AREAS:

- - - - - - Control of Nonpoint Source Pollution
- - - - - - Modeling and prediction of environmental effects
- - - - - - Remote Sensing and Remote Detection
- - - - - - Site Closure and Excess Property Procedures

EXAMPLE FORMAT FOR ENVIRONMENTAL REQUIREMENTS DEFINITION

PLEASE ANSWER THE FOLLOWING QUESTIONS:

A. HAZARDOUS WASTE MINIMIZATION

Identify Key Hazardous Waste Minimization Problems:

The 3 largest waste streams or waste problems at my facility(ies) are:

WASTE	MEDIA (solid, liquid, sludge, etc.)
1. _____	1. _____
2. _____	2. _____
3. _____	3. _____

Identify most significant HAZMIN problems.

1. Nature or description of waste disposal problem.

2. Impact or cost of problem.

3. Solution required:

B. INSTALLATION RESTORATION

List most significant clean up problems:

CONTAMINANT	MEDIA (soil, sediment, groundwater, etc.)
1. _____	1. _____
2. _____	2. _____
3. _____	3. _____

Identify installation restoration technology required.

1. Nature or description of waste clean up problem.

2. Is technology currently available? ____ yes ____ no
If yes, provide short description and estimate cost.

3. Solution or technology development required.

C. POLLUTION ABATEMENT

Identify most significant pollution abatement problems.

1. Nature or description of problem.

2. Impact of problem.

3. Solution required.

D. REGULATORY REQUIREMENT:

The Federal Regulations that most impact my Facility are:

The State Regulations that most impact my Facility are:

The Local Regulations that most impact my Facility are:

E. BONUS QUESTION:

Please describe technology development required to enhance environmental quality at your facility(ies). Provide an example if appropriate.

LIST OF ATTENDEES

ENVIRONMENTAL RESEARCH AND DEVELOPMENT TECHNICAL WORKSHOP PLENARY SESSION

TUESDAY, NOVEMBER 7, 1989

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Environmental Research and Development Technical Workshop
November 7-9, 1989
Evaluation Sheets

Based on your experience and the insight which we hope you gained from this workshop, please take a little time to provide feedback to the following questions.

Presentation of Technology Requirements:

Which of the presented technology requirements do you feel should be of highest Naval priority?

Air toxics, bioremediation, Cr, Cd, and cyanide wastewaters

In-situ treatment processes for POL contaminated soils
Methods to locate (demarcate) extent of contamination
Technology for field identification of contaminants

Ordnance disposal/reclamation
Bilgewater cleanup
VOC control

Geoprocessing for IR support
The Bulletin Board

Are there high priority requirements which were overlooked or poorly discussed?

Radon mitigation

Yes, better ways to minimize wastes; gearing up current operations at activities to meet future regulatory demands

Ordnance concerns
Efficient sampling strategies

Development of sampling plans by statistical design of experiments

Technical Presentations:

Please do not answer these following questions based on the presentation quality of the speaker. Rather compare the goals of the project with technology requirements.

List 3-4 projects which you feel are most addressing high priority requirements.

Air toxics, bioremediation, plating wastewaters

- (1) Fiber optic-based chemical sensors for in-situ measurement of metals...

- (2) Analytical methods to monitor remediation
- (3) Remote in-situ sediment toxicant release sampler
- (4) PCB remediation

Photochemical cleanup
 PCB decontamination
 Bioremediation
 Fiber optic sensors

Cone penetrometer
 Analytical methods to monitor remediation
 Organometallic (lead)

Throughout the workshop, I was impressed with the Navy's resolve to reduce their environmental impact. If the Navy is really serious though, where is the money? The development of technology as well as the application of existing technology is expensive and cannot really be expected to come from the operating budget of the activities.

For those 3-4 projects, list any technical suggestions or changes in approach you feel they should pursue.

Improve the technology for detecting other chemicals (applies to (1), above)
 Transfer the technology via U.S. EPA site programs to users (applies to (2), (3), and (4), above)

Cone penetrometer - develop standards and make field usable (prove it works to the EPA!) 6.3/6.4?
 Analytical methods to monitor remediation - develop standards and make field usable
 Organometallic (lead) - useful for drinking water programs, implement (make available) to activities

One way to stretch the budget would be to use R&D funds only for those applications with no utilization outside of the government. Development of low VOC solvents and identifying replacement plating processes do not fall in this category. Work involving ordnance and military fuels does. However, it appears that funding is being diverted away from the latter and to the former for reasons of expediency. Most of the same problems are faced by industry right now. Let's use some of their technology.

List any projects which you feel are doing little to address technology requirements.

They all seem to be in the forefront

Biological treatment

HW-89-12 - Take a good look at the data. They do not project the conclusions obtained!

Why haven't researchers working on new weapons systems been informed that they need to consider environmental demilitarization issues? Some limited work is currently being done at NWC along those lines, but it has largely been a result of the researcher's resolve, not a mandate from above.

For those projects which are "missing the boat" are they doing so because they are not addressing a valid technology need or because their technical approach is misdirected. List any technical suggestions or changes in approach you feel they should pursue.

Commercial sector has already developed many kinds of bacteria, and to me it looks like duplication of efforts and communication gaps.

There is a great deal of technical expertise within the Navy Labs for dealing with Navy/DOD specific problems. What role should we be playing in environmental research? Does it really make sense to contract out so much of the environmental research? It was my impression that as much as one third of the work performed was done by contractors. Many of the labs are struggling to survive and would welcome the opportunity to do some of this work.

General comments on the usefulness of this workshop. High and low points.

It appears more funds and research is needed. Then more application oriented effort is needed.

Lot of good ideas were exchanged; my time was spent profitably.

Suggestions:

1. Try to schedule presentations and demonstrations so that air station representatives are not left with a choice of two marine environment topics.
2. Presenters should be informed how much time they are allotted and prepare accordingly.
3. The survey results of environmental needs should have been compiled, tabulated, and presented during the open session. This would have provided greater understanding of what our focus was. The open session/panel discussion should have an agenda. They are always interesting and relevant, but I am not sure we discussed the most important issues.

Please note the previous criticisms were made as a result of occurrences during the workshop. I would not want to leave the impression there were many shortcomings; rather, the workshop was excellent and should be continued.

Also, suggest putting proceedings into a 3-ring binder so we can add our own notes and handouts.

The format of the workshop was excellent. Getting demonstrations every two hours really kept the interest up. Looking forward to next year's.

The workshop was interesting and probably useful. It can be very useful to gather researchers, sponsors, and users in the same building to try and set priorities. I came away with several ideas for research that can be performed by chemists at NWC and be useful to the Navy. However, I also have serious doubts that the work would be funded in the near future.

When funds are limited, as they currently are, workshops for determining funding policy can result in a lot of backbiting between groups competing for the same funds. Some of this was obvious at this workshop. Several investigators became very defensive when questioned about their work. Others consistently tried to end big projects before their time. I don't see any reasonable way around this problem, and only hope that the sponsors realized that it was going on and can take an objective look at the work before final decisions are made.

The question of what role researchers should take in the implementation of new technology needs to be addressed. From personal experience, I can state that we are not always welcome, even with needed technology.

There is currently too much distance between researchers and those in need of our efforts. As was pointed out during this workshop, this results in research being performed that has little utility in the real world. Meetings such as this one help, but only when the proper individuals attend. Newsletters and bulletin boards are a step in the right direction too, but it will be necessary to ensure that the researchers are included on the distribution lists; not just Public Works officers. Generation of a suitable distribution list could prove to be a major chore in itself.

One final suggestion that I have would be to include a list of attendees and affiliations in the proceedings. This would make it easier to determine who to contact for future discussions.

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1 AGENCY USE ONLY (Leave blank)

2. REPORT DATE
June 19903. REPORT TYPE AND DATES COVERED
Final

4. TITLE AND SUBTITLE

PROCEEDINGS OF THE ENVIRONMENTAL RESEARCH AND
DEVELOPMENT (R&D) TECHNICAL WORKSHOP

5. FUNDING NUMBERS

PE: OMN

6. AUTHOR(S)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Ocean Systems Center
San Diego, CA 92152-50008. PERFORMING ORGANIZATION
REPORT NUMBER

NOSC TD 1792

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Naval Facilities Engineering Command
Alexandria, VA 2233210. SPONSORING/MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This document contains the proceedings of the Environmental Research and Development Technical Workshop dated 7-9 November 1989 held at the Naval Ocean Systems Center, San Diego, CA 92152-5000.

14. SUBJECT TERMS

environmental research and development (R&D)

15. NUMBER OF PAGES

314

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

SAME AS REPORT

