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Bench-Scale Investigation of Composting for Remediation of Explosives-Contaminated Soils from Naval Surface Warfare Center, Crane, Indiana

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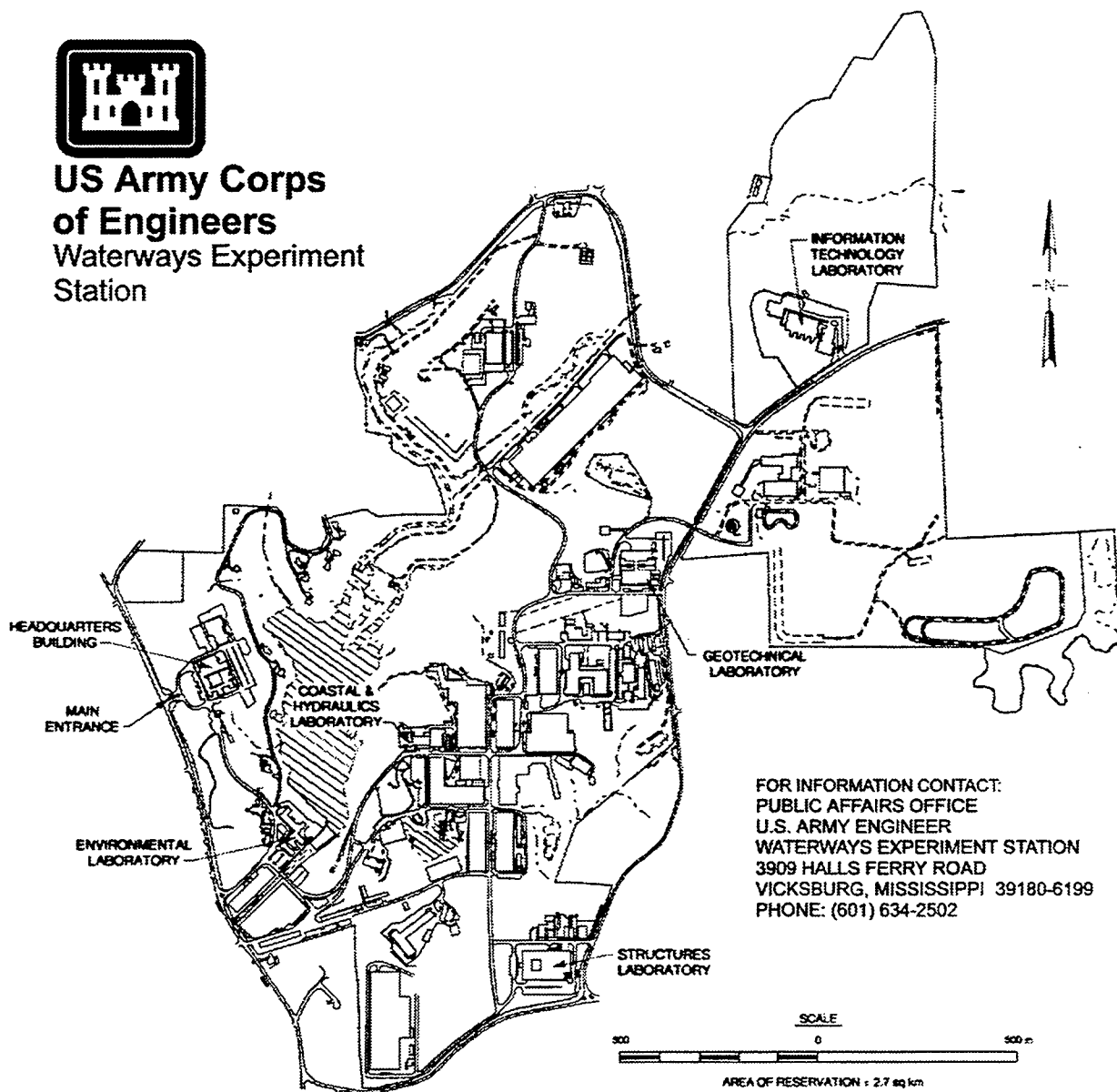
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Preface

This report was prepared by the U.S. Army Engineer Waterways Experiment Station (WES) in cooperation with the U.S. Navy, Naval Surface Warfare Center, Crane (NSWCC), Indiana, and the Department of the Navy, Southern Division, Naval Facilities Engineering Command (NFEC), Charleston, South Carolina. Program Manager for NFEC was Ms. Adrienne P. Townsel-Wilson. Project Manager for NSWCC was Mr. Thomas J. Brent. Project Managers for WES were Dr. Kurt T. Preston and Mr. Roy Wade.

The bench-scale and toxicology studies were conducted between October 1994 and July 1996 in the WES Environmental Laboratory (EL). This report was written by Dr. Kurt T. Preston and Mr. Roy Wade, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), EL, Dr. Kyoung S. Ro, Louisiana State University, and Mr. Steve Seiden, North Carolina State University. Laboratory support was provided by Mr. James Davis. The toxicity study was conducted by Mr. Michael E. Honeycutt, Dr. Victor A. McFarland, and Ms. A. Susan Jarvis of Fate and Effects Branch, Environmental Processes and Effects Division (EPED), EL.

The report was prepared under the direct supervision of Mr. Danny Averett, Chief, ERB, and under the general supervision of Mr. Norman R. Francingues, Jr., Chief, EED, and Dr. John Harrison, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Robin R. Cababa, EN.

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1 Introduction

The production and handling of conventional munitions have resulted in the generation of explosives-contaminated soils at various military installations. The principal explosive contaminants are 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). The Naval Surface Warfare Center (NSWC), Crane, Indiana, provides material and logistic support to the Navy's weapon systems, including expendable and nonexpendable ordnance items. As the complexity of weapons increased, the facility became more involved in the technical aspects of weaponry through the development of test methods, procedures, and equipment, while the facility's basic mission remained the same.

Because of the potential for groundwater contamination, and the subsequent migration of explosives, treatment of the explosive-contaminated soils at several sites at the NSWC is necessary to protect the environment and avoid costly actions in the future. Incineration and composting are demonstrated technologies for the remediation of explosives-contaminated soils. However, incineration is publicly undesirable and economically infeasible for remediation of small sites. Composting was the selected technology to be evaluated for the remediation of the explosives-contaminated soils at NSWC. The results of a bench-scale study supporting the implementation of composting at NSWC are presented.

Background of NSWC

The NSWC is located 20 miles southwest of Bloomington, Indiana, approximately 75 miles southwest of Indianapolis, and 71 miles northwest of Louisville, Kentucky (Figure 1). The NSWC occupies 62,463 acres (approximately 96 square miles) in north Martin County and neighboring Greene, Daviess, and Lawrence Counties. NSWC provides material, technical, and logistic support to the Navy for equipment, weapon systems, and expendable and nonexpendable ordnance items. The facility was opened in 1941 as the Naval Ammunition Depot, Burns City, Indiana, and renamed as the U.S. Naval Ammunition Depot Crane, Burns City, Indiana, in 1943. Its mission was to serve as an inland munitions production and storage center for all types of ammunition, including pyrotechnics and illuminating projectiles. The facility was renamed as the Naval

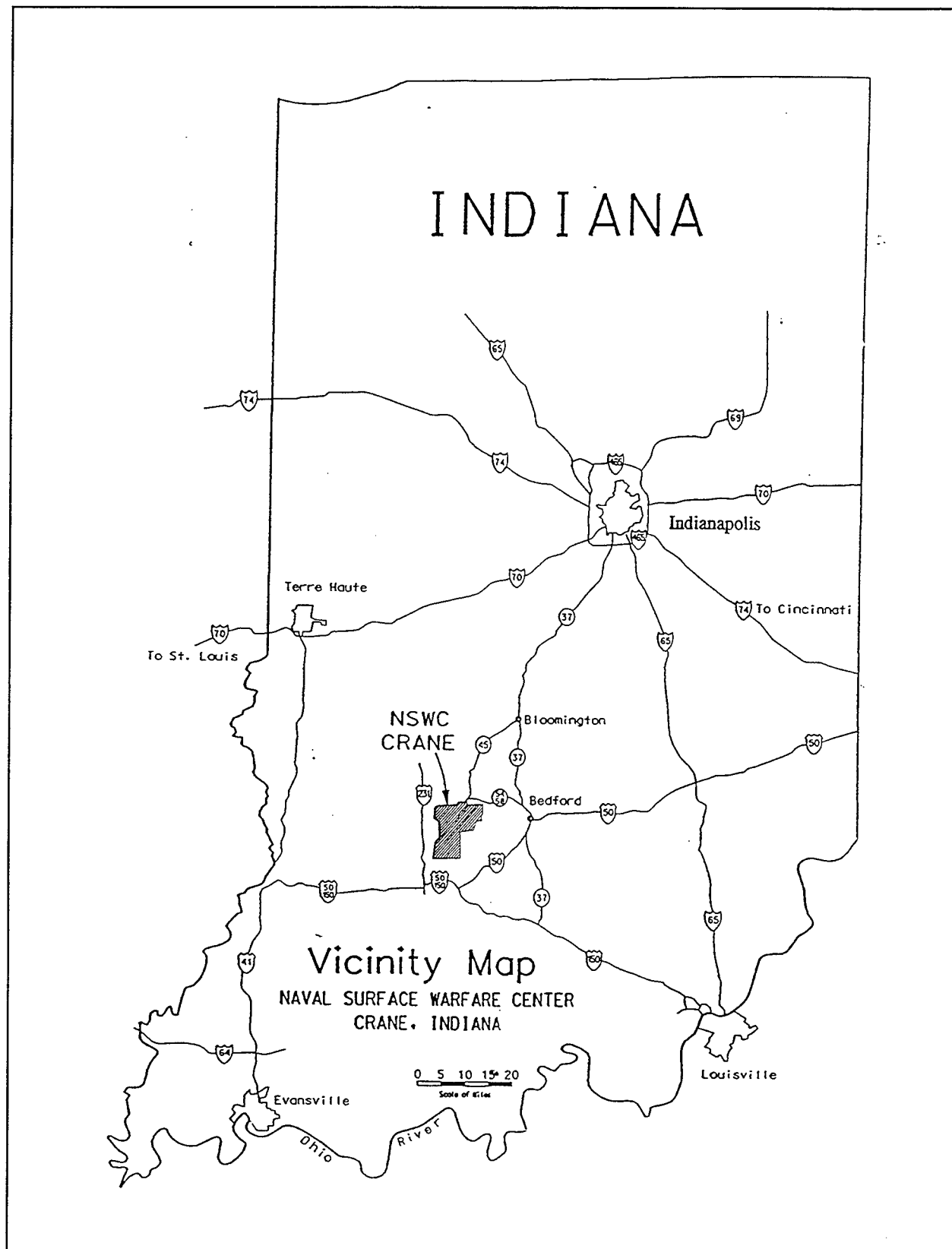


Figure 1. Location of NSWC, Crane, Indiana

Weapons Support Center in 1975 and was changed to Naval Surface Warfare Center, Crane Division, in 1991. The Department of Defense (DoD) ammunition procurement responsibility was transferred to the Army in 1977. The Army has assumed ordnance production, storage, and related responsibilities under the single service management directive. All environmental activities on the installation, including permitting activities, remain the responsibility of the Navy.

Synopsis of Former Studies

In early 1981, a potentially hazardous substance release from the NSWC was discovered. An Initial Assessment Study (IAS) for the NSWC was begun in April 1981 and completed in May 1983 by the Naval Energy and Environmental Support Agency (NEESA). A Solid Waste Management Unit (SWMU) report submitted to the U.S. Environmental Protection Agency (USEPA) in January 1985 listed all of the hazardous waste sites identified in the IAS. The Navy decided in the summer of 1993 to implement remedial action at those SWMU's for which sufficient site assessment and characterization data were available. Bench-scale testing to evaluate and design composting of explosives-contaminated soils from SWMU 03 Ammunition Burning Ground (ABG) site and SWMU 10 Rockeye site was assigned to the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. In the fall of 1994, the WES initiated a study of composting as a remediation method for explosives-contaminated soils.

Site History

ABG site (SWMU 03)

The ABG is located near the eastern boundary of the NSWC (Figure 2) and occupies approximately 202,344 m² (50 acres). The ABG lies near the head of the valley of Little Sulfur Creek. The site is approximately 610 m (2,000 ft) long by 305 m (1,000 ft) wide with the long axis oriented east-west. The ABG has been used extensively since the 1940's for the destruction of materials contaminated with explosives, rocket motors, candles, flares, solvents, red phosphorus, small detonators, and fuse materials. The largest quantities were destroyed between 1956 and 1960 when approximately 6,804 kg (15,000 lb) per day of smokeless powder and approximately 21,772 kg (48,000 lb) per day of high explosives (H-6 and Composition B) were burned. The area also is used for flashing (burning) of the residue from bombs and projectiles after they have been subjected to melt-out or drill-out operations removing the bulk of the explosives. From 1970 to 1981, at least 10,000 major weapons were destroyed.

Solid explosives residues not in containers or bombs were formerly spread out on burning pads or in flash pits and ignited, or flashed. Flashing today is done in clay-lined steel pans. There are 29 pans currently in operation at the ABG.

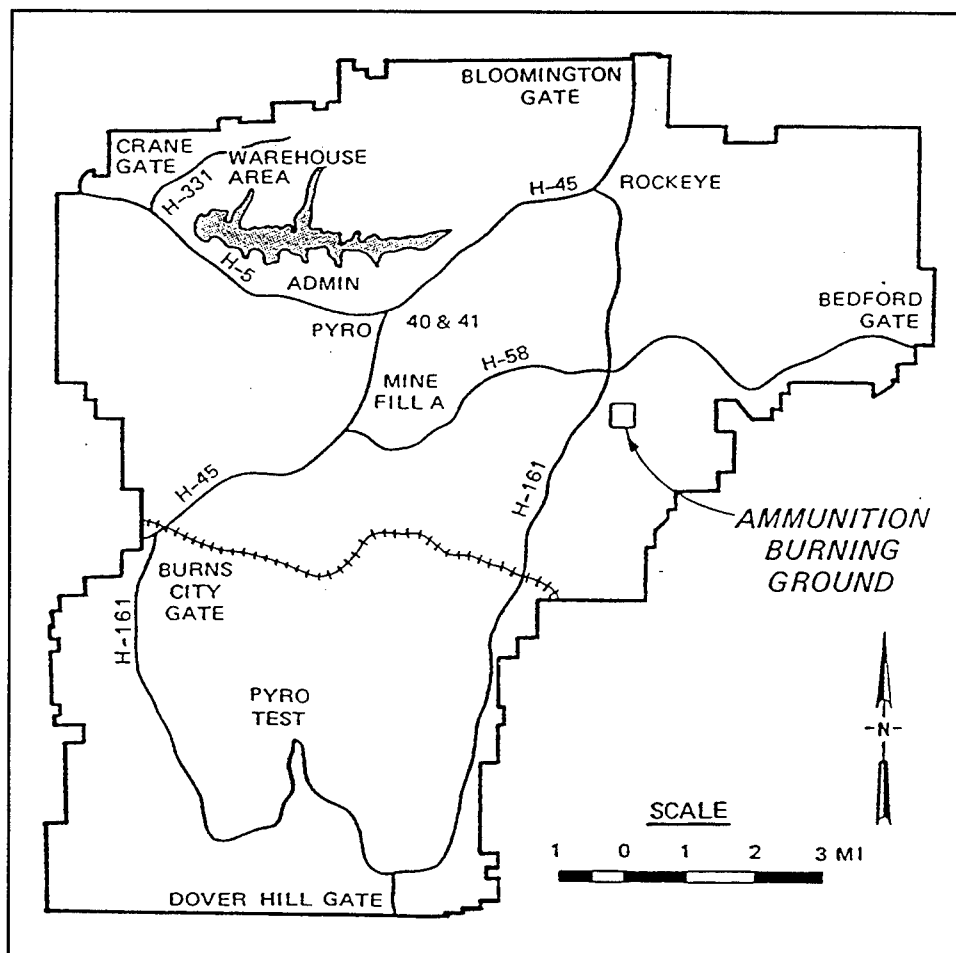


Figure 2. Location of ABG and Rockeye sites

Bulk propellants typically are poured into burning pans to a depth of a few inches, primed, and remotely initiated. An ash pile consisting of approximately 5,575 kg (12,290 lb) of burn residue accumulated near the incinerator pit. The ash pile was removed between July 1986 and February 1987. Hazardous waste ash from the burning operations is now stored in two large roll-off boxes. The ash is stored until sent off-site to a hazardous waste landfill.

Three surface impoundments (ponds) were constructed for the purpose of removing liquids from otherwise combustible sludges resulting from the blending and loading of munitions. In 1982 the impoundments were modified to include a liner and leachate collection system for each one. Each of the impoundments is approximately 12 m (40 ft) in diameter. Two ponds held TNT, RDX, and break-down compounds in water from the Rockeye facility and other locations within the NSWC. The third pond held phosphorus compounds. The three ponds have been replaced by sludge dewatering units. The ponds are now empty and scheduled for closure. Another tank holds explosives wastes contaminated with pink water. Two empty underground storage tanks (UST's), scheduled for closure, were used

to store runoff and leachate from the three ponds. The UST's are near the pink-water tanks.

Rockeye site (SWMU 10)

The Rockeye site is a 161,875-m² (40-acre) tract located in the north-central portion of the NSWC (Figure 2). The Rockeye facility began operation in the mid-1950's as a press loading operation for 76.2-mm (3-in.) projectiles using Composition A-3 explosive (RDX and wax). In 1967-68, the Rockeye facility was converted to a case-filling operation and produced the MK20 series anti-tank Rockeye cluster bomb. The explosive material in Rockeye bombs is Octal Compound B (RDX, HMX, TNT, and wax) high explosive. As part of the loading operation, the system generates a large volume of wastewater, primarily from bomblet and tray washdown and from melt and pour operations in Buildings 2731 and 2734. The wastewater was collected in four sumps which were periodically pumped. After pumping, the remaining residue was sent to the ABG for disposal. Prior to 1978, explosives-contaminated waters were discharged, from full sumps, directly into local surface drainage pathways. Red-colored "pink water" from washdown operations was observed in drainage way surface waters in 1977, prior to installation of a treatment facility. On the north side of the facility, the waters were released to a headwater branch of Sulfur Creek. On the south side of the facility, the waters were released to a headwater branch of Turkey Creek. TNT concentrations as high as 50 parts per million (ppm) were detected in surface water discharges.

In the spring of 1978, an activated carbon water treatment facility, located in Building 3044, was brought into operation to treat the wastewater for recycled usage. A scrubber system was designed and installed to remove contaminated particles in the steam-fed tray wash area. In the tray wash area, explosives-contaminated trays were steam cleaned. Since the installation of the pollution abatement equipment, the release of explosives-contaminated waters ceased.

Site Contamination

Soil borings at the ABG and Rockeye sites were drilled and soil samples collected during the early 1990's by the Geotechnical Laboratory at WES during a Resource Conservation Recovery Act Feasibility Investigation (RFI). These soil borings were analyzed for explosives, other organic contaminants, and metals.

ABG site

Results from RFI show soil at ABG was contaminated with explosives, metals, and other organic analytes. Ammunition burning and thermal treatment activities at the ABG have released residues of antimony, cadmium, chromium, copper, lead, mercury, nickel, silver, zinc, aluminum, barium, magnesium, manganese, tin,

sodium, and phosphorus to the soils. Soils south and east of the former ash pile (Borings 7, 9, and 12 shown on Figure 3) had particularly high concentrations of metal constituents when compared to background soils, as well as when compared to soils from the other test borings. Soils from borings around the burn pads (Borings 4, 5, 6, 8, 10, and 11 shown on Figure 3) also produced soil samples with metals concentrations that were higher than those determined for the background borings, but generally not as high as those reported for Borings 7, 9, and 12. These inorganics are common constituents of material burned at the ABG site.

Explosive compounds were found in soils from all the ABG borings except the background borings. Borings 4 and 5 had maximum total explosives concentrations exceeding 1,000 mg/kg. A TNT concentration of 1,640 mg/kg was detected in Boring 4, which was the highest explosives concentration detected in the soil samples. An RDX concentration of 1,070 mg/kg was detected in Boring 5. Explosives contamination was also detected in deeper soil samples within the borings, but not always.

Several volatile organic compounds (VOC) were found in the ABG soils. The maximum measured concentration of trichloroethane was 2.9 µg/kg and 1.3 µg/kg for tetrachloroethene. Semivolatile organics, pesticides, herbicides, and polychlorinated biphenyls were below detection limits.

In general, the most significant soil contamination at the ABG can be defined by the metals and explosives compounds listed earlier. Other contaminants, including other inorganics, polycyclic aromatic hydrocarbons, VOC's, pesticides, and herbicides, were present but at concentrations that were orders of magnitude lower than explosives and metal concentrations.

Rockeye site

Groundwater and soil contaminant release characterization studies indicate explosives contamination of groundwater in several groundwater monitoring wells in the northeast drainage ways of the site and in surface soils located in the central and northeast quarter of the site.

During RFI phases, explosive analytes were detected in soil samples collected from the borings around the sumps, in the surface drainage ways, and in the surface soil sampling (Figure 4). Soil borings are indicated in Figure 4 by numbers 1-13 and surface soil scrapes are indicated by letters A-H. Locations marked BN1-BN3 were "background north" surface soil samples. The explosives 1,3-dinitrobenzene (DNB), dinitrotoluene (DNT), RDX, and HMX were detected. HMX was detected in more soil samples and in greater concentrations than any other explosive analyte. HMX concentration of 1,960 mg/kg was detected in one soil sample from Area G (Figure 4) and 42.7 mg/kg in the soil from Boring 12. Area E had the greatest number of explosives-contaminated soil samples of all sampling areas. Area H, behind Building 2734 near the center of the facility, had

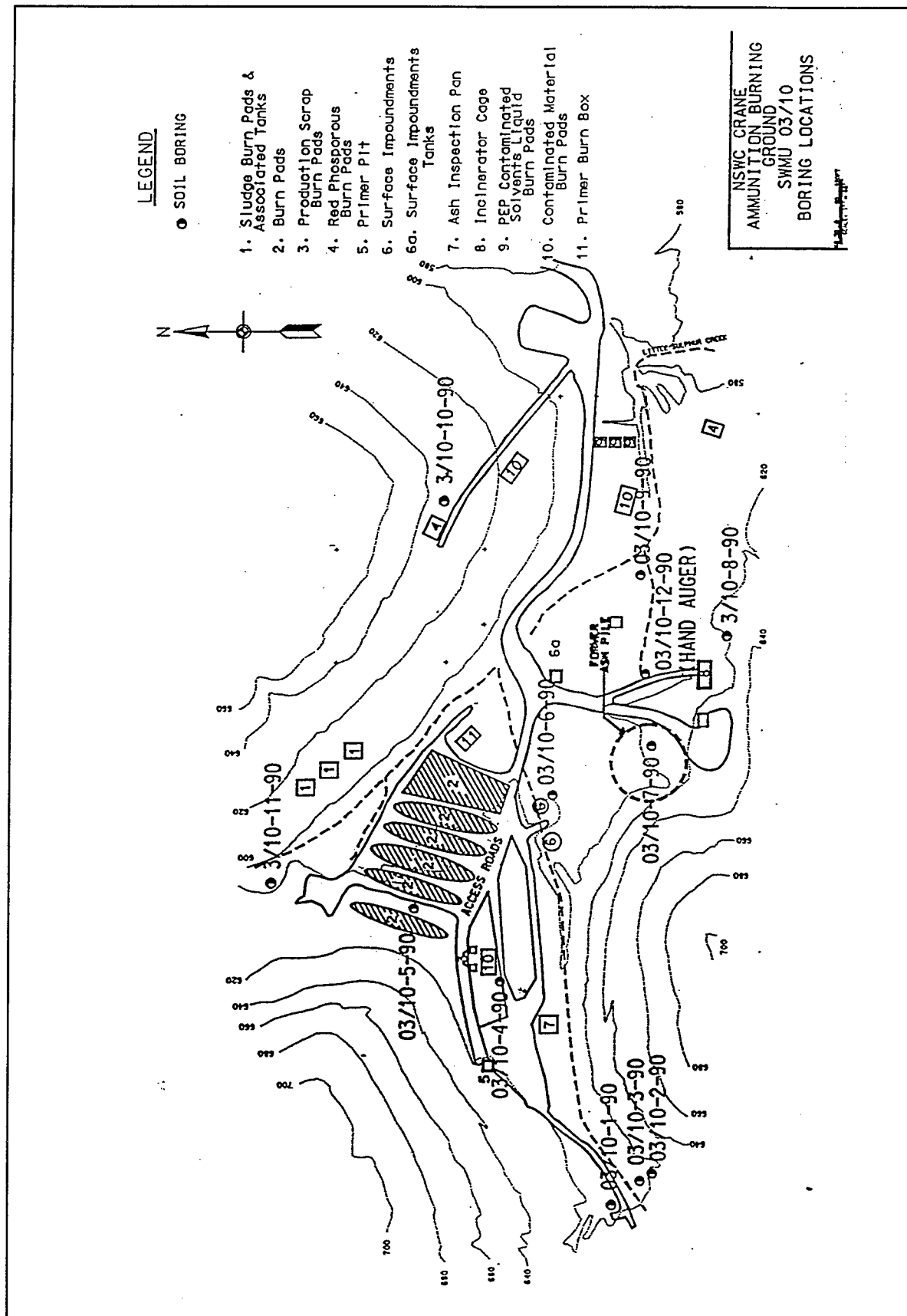


Figure 3. ABG site soil boring locations

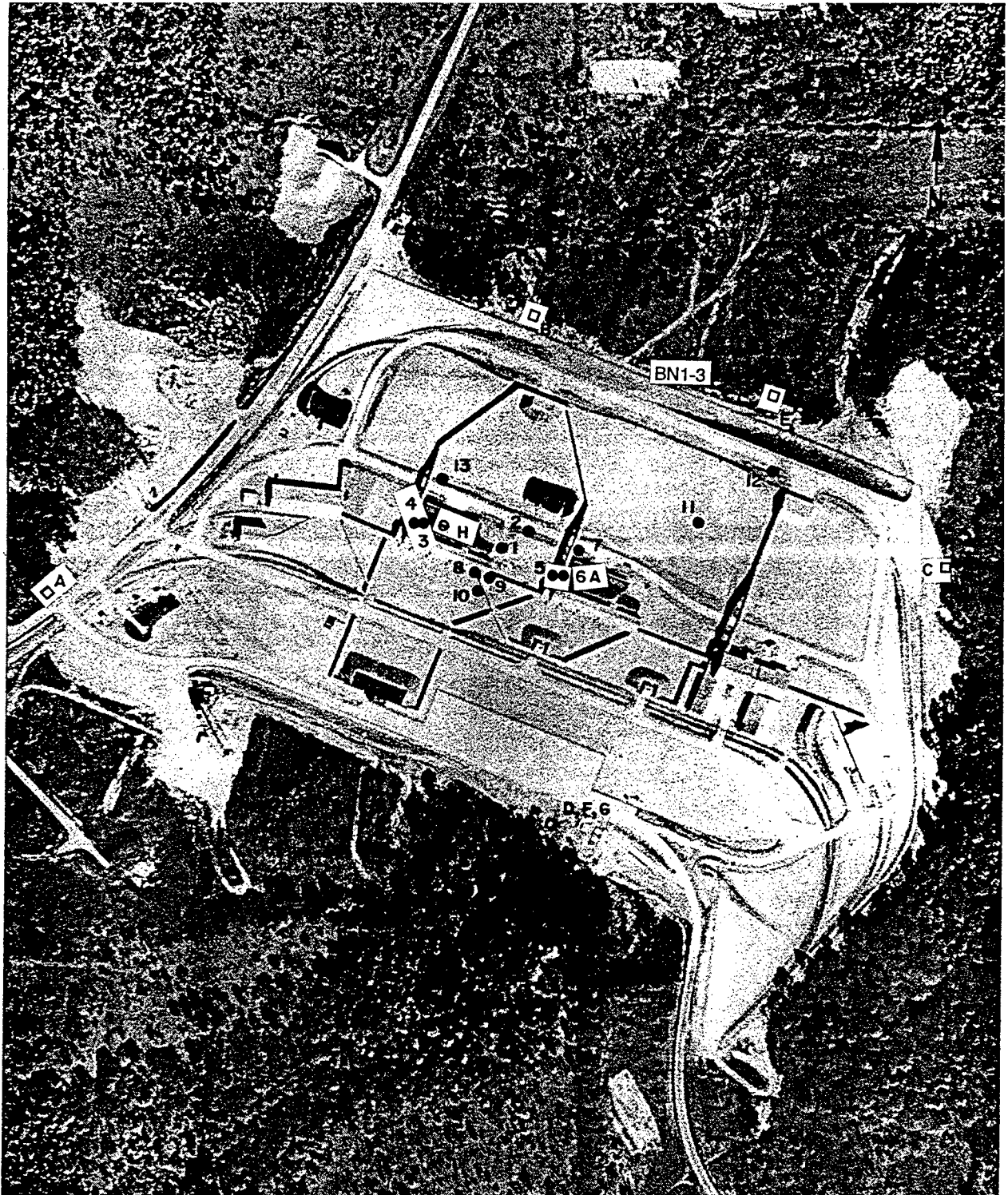


Figure 4. Rocky site locations for soil borings (1-13), surface sample areas (A-H), and "background north" surface sample areas (BN1-BN3)

concentrations of TNT, RDX, and HMX of 295, 3,350, and 10,400 mg/kg, respectively. Area H is bare earth on an otherwise grassy berm, near an exhaust vent of Building 2734.

Because inorganic compounds are naturally occurring compounds at the Rockeye site, the inorganic analytical data had to be compared with established background samples. The maximum metal concentration was detected in the surface soil samples, except for antimony and aluminum. Additionally, the maximum concentrations of all inorganic parameters, except copper and tin, were detected in the northeast and south streams. The lack of pattern in the inorganic concentrations was not determined with certainty from the available data. There was insufficient information to link the inorganic concentrations detected in the surface drainage to the possible contaminant sources (i.e., the sumps). It is possible that inorganic contaminants were carried by the surface drainage away from the sumps and deposited along the Rockeye perimeter. This would explain the higher metal concentration in the surface soil samples than in the boring samples near the sumps.

Purpose

The purpose of this report is to document and present the results of the respirometric, toxicity, and bench-scale composting tests performed as part of a comprehensive remediation composting study. The results of this study will be provided to assist with design of pilot-/field-scale remediation compost systems at NSWC.

Testing Objective

The objective of this study was to evaluate and select the best combination of amendments, contaminated soils, and bulking agents to be used in the composting technology for remediating soils contaminated with TNT, HMX, and RDX. The objective of the respirometric test was to provide a general indication of biological activity within each compost mixture. The respirometry was also used as a tool for the specific screening of compost mixtures for the NSWC soil. The objective of the bench-scale compost reactor test was to extend the respirometric study by evaluating the applicability of the screened compost mixtures for the degradation of explosives compounds under actual composting environments prior to the pilot-/field-scale implementation. Another objective of the bench-scale test was to determine the leachability of lead (Pb), mercury (Hg), and cadmium (Cd) from the best compost mix. The objective of the toxicity test was to evaluate the toxicity of the composted soils.

Scope of Work

The scope of work included a survey of locally available sources of amendments and bulking agents to be used for testing on the ABG and Rockeye soils and collection of soil samples at these sites. An initial screening of eight compost mixtures was performed using a respirometer to determine if biological activity was present in the mixtures and if a reduction in explosives concentration occurred. An optimum compost mixture was selected for further evaluation. The bench-scale composting test was performed to further validate the respirometric test results under actual composting environments. The Toxicity Characteristic Leaching Procedure (TCLP) was used to determine the leachability of Pb and Cd. The acute toxicity and genotoxicity testings used earthworms and compost mixtures to characterize the toxicity reduction of the composted soils.

2 Remediation Composting Process Parameters

Successful design and operation of the remediation composting require careful consideration of numerous factors affecting the process. The factors can be divided into three classes: physical, chemical, and biological. Physical factors define the structure of the compost matrix. Chemical factors consider the adequacy of substrates and the toxic effects of contaminants on the compost biomass. Biological factors define biodegradability and the biodegradation rate. Careful choice of a composting system with proper thermodynamic properties ensures the optimal thermophilic conditions.

Physical Factors

Porosity

Porosity is a measure of pore, or void, space between solid particles in a bed and is defined as the ratio of void volume to the total bed volume in a system. It may be represented as a fraction or on a percentage basis. Porosity is important in compost systems for a number of reasons. The pore space provides a conduit for nutrient movement through the compost pile, space for the growth of microbial communities, and a reservoir for moisture held in the compost mixture.

The gas/liquid ratio has a profound impact on the efficiency of the compost operations and the efficacy of the treatment process. When the pore space is completely filled with water, oxygen within the system may become limited, and the compost system would become anaerobic. Also, the physical strength of the compost matrix will be undermined. Although this example is extreme, it highlights the importance of the interaction of solid particles, pore space, and the free air-space (FAS) in the definition of the physical nature of the compost matrix.

Free airspace

The FAS is the ratio of the empty pore space (V_a), or void volume not occupied by water, to the total volume. FAS is that portion of the pore space occupied by gas phase. Research indicates that the optimal biological activity occurs with an FAS ranging from 0.20 to 0.35 (Haug 1993). FAS is critical for the movement of oxygen and other gases into and through the compost matrix by diffusion, convection, or forced ventilation.

The FAS may be managed by selection of the amendments and bulking agents, which are perhaps two of the most critical design selections. The selection of these influence the nature of the compost, the efficiency of the operation, and the economics of the system.

In general, FAS begins to become available within the pore space in most compost systems at approximately 40 percent solids (Haug 1993; Golueke 1991). Thus, 40-percent solid content is generally considered as the maximum for most compost systems without augmentation by forced aeration.

Moisture content

An understanding of the role of water in compost design is of paramount importance. Beyond the role of water as a biochemical solvent, water in compost systems has an even larger multifaceted role. Water plays a key role in the cooling of compost systems. Also, moisture content influences the nutrient movement and the compost matrix structure.

As biochemical solvents, aqueous solutions are theoretically the ideal media for biological activity. In a completely mixed aqueous system, substrate is instantly available to the microbial community in equal concentrations. When nutrients are added to the system, the biomass will be very active and immediately utilize the available substrate. However, in aqueous aerobic systems, oxygen is often the limiting substrate due to its low solubility in aqueous solutions. Aqueous bacterial reactor systems generally attempt to improve oxygen transfer into a solution by physical agitation or sparging of air.

Compost, a highly active aerobic system, can also suffer from oxygen limitation. As a result, proper management of the air and water within the compost pore volume is critical.

The optimal moisture content reported by researchers varied from 45 to 90 percent (Biddlestone et al. 1987; Haug 1993). The reported optimal moisture content varied because of widely varying water absorption capacity of soil particles and composting materials used in research. Generally, a moisture content of about 45 to 65 percent is used. Above this range, the pore space will be filled with water or, at the very least, water tension in the pore space will hinder the movement of gases between pores so that oxygen in the pore space becomes depleted. Below

this range, moisture is not available to the microbial communities. The water remaining becomes associated with the solid particles due to the matrix potential arising from the capillary forces and adsorption. This water is held so tightly that it may be unavailable for utilization by microbes. Consequently, moisture may be present in the matrix, but the lack of moisture available to the microbial communities results in growth-rate limitations and a loss of process efficiency.

Particle size

Various shredders and other mixing devices are used to break down and homogenize the compost materials into smaller, more manageable sizes. Since most of the composting microbial activities occur on the surface of the substrate particles, smaller size particles, which offer larger surface area, appear to enhance the microbial reactions. However, the movement of oxygen and water may be hindered in narrow interstitial spaces between the small particles packed tightly together. Generally, particle sizes between 12.9 and 49.5 mm are used for composting (Forster and Wase 1987). Small particles are used for forced aeration compost systems; large particle sizes are appropriate for windrow systems.

Temperature

Temperature is an important indicator in composting. Heat is generated as a byproduct of microbial breakdown of the organic substrate, raising the compost temperature to the desired thermophilic conditions. Microbial activities and chemical reactions are usually faster at higher temperatures. For municipal solid wastes (MSW), retention of heat is also necessary in order to sanitize the wastes. The retention and continual generation of heat are dependent upon the configuration, size, and insulating property of composting systems, the ambient temperature, and the heat values of substrates. Although beneficial in many ways, higher temperature causes the microorganisms and enzymes to become inactive, and the composting process will stop beyond 70 °C. Above 60 °C, most mesophiles, including fungi, will be destroyed or inactivated, and the decomposing activity is carried out mainly by actinomycetes. After readily available substrates such as starches, sugars, lipids, and proteins have been consumed, the compost temperature will fall below 60 °C, allowing fungi and actinomycetes to attack cellulose and lignin portions of the substrates. Recently, researchers agreed that 55 to 60 °C is the optimal temperature range (Bollen 1985; Finstein and Miller 1985).

Electrical conductivity

Avinmelech et al. (1996) suggested that electrical conductivity (EC) could be used as a quick stability index for compost derived from MSW. Their stabilized compost EC values decreased to approximately 50 percent of the initial values. This phenomenon was also observed by Iannotti et al. (1993). The EC usually decreases as compost ages due to destruction of organic volatile acids. However,

the opposite trend of EC for grass clippings and yard trimmings has been observed. Their ingredients contained a relatively large fraction of nitrogen with the ammonium concentration increased with composting time. Because of the varying EC values among researchers, more research is required to clearly understand the relationship between EC and compost stability.

Chemical Factors

Contaminated soil loading

The economics of composting systems is primarily based on the amount of contaminated soil processed during a given time period. The higher the ratio of contaminated soil in a unit volume of compost given an equivalent microbial activity, the lower the overall cost of the system on a unit basis. However, this economic incentive must be carefully balanced with the possible inhibition by the contaminants on the compost of microbial activities and for the decrease in compost temperature simply due to replacing organic substrates with mostly inert soil. Loading the system with an excess of inhibitory contaminant slows microbial activity and results in an increase of composting time or may cause a total process upset. As a result, the composting process may not be able to reach or maintain a stable thermophilic state for the desired reaction time due to lack of organic substrates.

Carbon to nitrogen ratio (C/N)

Compost microorganisms require adequate levels of carbon (C) sources and nutrients including nitrogen (N), phosphorus, sulfur, and other trace minerals and growth factors. Among these, C and N are usually the limiting substrates, while other elements and nutrients are abundant in composting processes. Chemical elemental analysis of soil microorganisms revealed that the cells in general contain about 50 percent C, 5 percent N, and 0.25 to 1 percent phosphorus on a dry weight basis (Alexander 1977). Assuming about 1/2 to 2/3 of the carbon is converted to carbon dioxide (CO₂) and the rest to cell mass, the required C/N ratio would be about 23 to 35. The optimal C/N ratios for different composting materials range from 20 to 35 (Haug 1993).

If the initial C/N ratio is too high (i.e., low nitrogen level), the microorganisms pass through many life cycles to achieve a stable state (i.e., C/N of about 10). This may not be desirable for conventional MSW composting because it reduces the substrate stabilization rate. It may, however, be beneficial for remediation composting because dead microorganisms themselves are organic substrates and support endogenous activities for long periods. If the C/N ratio is too low, nitrogen will be lost as ammonia, which may reach toxic levels and raise the pH of the compost mix. For a compost mix with high C/N ratio, ammonia-releasing substrates such as blood, urine, or urea can be added. If phosphorus and other nutrient concentrations are low, as in cases using industrial solid wastes as substrates,

these elements need to be supplemented in order to avoid unnecessary rate limitations.

pH

pH of the compost matrix must be near neutral (i.e., pH of 7). For all practical purposes, microbial growth is severely limited at pH values less than 3 or greater than 11. The optimum pH of composting has been reported to be between 6.0 and 8.5 (Fitzpatrick 1993). At higher pH (strongly basic), ammonium ions (nitrogen source) are lost as ammonia, and essential elements such as calcium and magnesium may not be available to microorganisms due to precipitation as insoluble metal hydroxides or carbonates. At lower pH (strongly acidic), toxic metals, aluminum, copper, zinc, etc. leach from minerals and substrates and may stop the composting process.

Overall, compost mix pH may be adjusted with co-substrates or other pH adjusting chemicals such as lime and baking soda if the initial pH falls outside the optimum range. For instance, wood wastes and sludges from pulp and paper mills may have a low pH of 5 to 6 and high C/N. Addition of ammonia-releasing substrates such as urine or urea will neutralize the acidity and provide necessary nitrogen to microorganisms. Fortunately, composting has the unique ability to buffer both high and low pH to a neutral range as composting proceeds. This phenomenon may be explained by the release of CO₂ and ammonia (NH₃) as a result of organic decomposition. Therefore, pH adjustment is not usually required and is not a common practice in composting systems.

Biological Factors

Biodegradability and biodegradation rate

Substrate biodegradability determines the amount of substrate energy available to drive the composting process, the requirement for additional energy amendments, the stoichiometric oxygen demand, the air demand to remove heat from the process, and the final product mass. Literature values for biodegradability of substrates vary widely, for instance, 28 percent for steer manure to 68 percent for chicken manure (Klein 1972) or 21.7 percent for newsprint to 81.9 percent for food wastes (Kayhanian and Tchobanoglous 1992). Chandler et al. (1980) reported that the lignin content was the single most important factor influencing the biodegradability of a compost system.

In contrast to MSW which requires a long retention time (typically more than 90 days of composting) to achieve adequate stabilization, long retention time may not be required nor desired for remediation of soils contaminated with explosive compounds. Most of the previous remediation composting studies indicated that less than 30 days were required to substantially degrade or transform TNT, RDX,

and other explosive compounds by aerobic composting (Doyle and Isbister 1982; USATHAMA 1988; Garg, Grasso, and Hoag 1991; Pennington et al. 1995).

Aeration

Aeration is important in two aspects: oxygen supply to aerobic microorganisms and cooling/drying of the compost by evaporation of water. For nonmechanical aeration systems, oxygen may be transported via molecular diffusion and free convection of air movement due to temperature gradients. Oxygen may also be supplied by forcing air through the compost matrix or mechanically mixing the compost intermittently to enhance oxygen transfer. Aeration is also used to dry, and subsequently cool, the compost by promoting evaporation of water. Approximately 10 to 30 times more aeration is required for drying of 20 percent solids than for biological oxidation (Haug 1993). Composters typically use about 1 m³ air/kg volatile solids per day (VS-d).

3 **Respirometric Study**

Introduction

Respirometry is a technique for determining oxygen consumption in an aerobic environment (Mahendraker and Viraraghavan 1995) under conditions that avoid rate limitations from lack of nutrients, oxygen, moisture, imbalanced pH, or inadequate seed microbes. During aerobic respiration, microbial activity results in mineralization of organic matter into CO₂ and water, as well as utilization of the substrate as a carbon and energy source for cell growth and maintenance. Monitoring of respiration rates in microbial populations or biomass is a very useful tool which has been applied to wastewater treatment, composting, and bioremediation, for measuring the biodegradation of organic matter.

Respirometry, as mentioned earlier, provides biodegradation rate, the rate at which microorganisms degrade different organic substrates (Flathman and Nowakowski 1995; Carlsson 1993; Vanrolleghem and Verstraete 1993; Kappeler and Gujer 1992; Grady et al. 1989). Respirometric data can be used to approximate the short-term biochemical oxygen demand (SBOD) and the oxygen uptake rate (OUR) and to estimate the standard biochemical oxygen demand (BOD) (Spanjers, Olsson, and Klapwijk 1994; Vanrolleghem and Spanjers 1994; Jacobi and Fussa 1993). In addition, respirometry helps to identify the toxic and inhibitory effects that the organic analysis may have on the microorganisms (Boening, Hendricks, and Rossignol 1995; Spanjers, Temmink, and Klapwijk 1994; Herricks et al. 1991).

Finally, respirometry can be used as a tool for determining treatment plant design parameters for sizing blowers, aerators, and composting piles (Hunter, Johnson, and Carns 1995; Brouwer, Klapwijk, and Keesman 1994; Arthur and Meredith 1993; Klapwijk, Spangers, and Temmink 1993; Watts and Garber 1993; Rozich and Guady 1992). Several reviews that discuss different techniques and applications for respirometry are available (Mahendraker and Viraraghavan 1995; Arthur and Meredith 1993). To date, no significant research has been conducted on using respirometry to provide insight on contaminated soils, in particular, soils contaminated with explosives (Mahendraker and Viraraghavan 1995).

In this study, a respirometric technique was used as a first step to determine the optimal compost mix for treating explosives-contaminated soils from the Rockeye site. Eight compost mixtures were evaluated for their total oxygen utilization and uptake rates, as well as for the degradation of TNT, HMX, RDX, 4A-DNT, and 2A-DNT.

Materials and Methods

Soil samples

Several cubic yards of contaminated soil were collected during March-October 1994 by WES from an area near the center of the ABG burn pit (latitude 32°12.78'N and longitude 90°53.20'W) and from the Rockeye site vicinity (latitude 38°50.74'N and longitude 86°45.28'W). These sample locations were selected because previous soil borings indicated explosives contamination (Site Contamination, Chapter 1). Grab samples were collected to a depth of about .46 m (18 in.) because soil borings showed little contamination beyond that depth. Upon delivery at the WES, the soil samples were stored at 4 °C until experimentation. Soil collected from the Rockeye site was used throughout this study, since the ABG soil analytical result showed insufficient explosives-concentration for this study. Physical characteristics of the Rockeye soil are shown in Table 1.

Compost mixtures

Eight different composting mixtures were evaluated; ingredients for these mixes are shown in Table 2. Each compost mixture contained 20 percent by volume (v/v) soil, 40 percent (v/v) amendments, and 40 percent (v/v) bulking agents. The amendments were cow, pig, and turkey manures and publicly owned treatment works (POTW) sludge, while the bulking agents included recycled paper, sawdust, and alfalfa. The compost mixtures had C/N ratios ranging from 16 to 93 (except for one with a C/N ratio of 414), moisture contents of 53-64 percent, and pH of 6.2-8.2.

Respirometer procedure

A BI-1000 Electrolytic Respirometer (Bioscience, Inc., Bethlehem, PA) was used to collect oxygen utilization data. This respirometer consisted of eight 1-L reactor bottles, a reactor module, a water bath (40 °C), a temperature controller, a personal computer, and control software. Approximately 200 ml of each mix was placed into a flask. The initial amounts of total volatile solids (TVS), total Kjeldahl nitrogen (TKN), TNT, RDX, HMX, 4A-DNT, and 2A-DNT for each treatment were determined by analyzing a portion of the remaining mix.

Table 1
Physical Characteristics Of Rockeye Soil

Physical Properties					
Color (Munsell Soil Color Chart)			7.5YR 4/3, Strong Brown		
pH			7.43		
Average Densities of Fractions (oven dried at 60°C)					
Sample Description			Average Density, g/cc		
Bulk < 2.00 mm, dry sieved			2.63		
Bulk < 0.85 mm, dry sieved			2.63		
Bulk < 0.85 mm, wet sieved			2.63		
Sample Fractions					
Dry-Sieve Analysis (2,830.76 g as-is and 2,596.68 g Dry Wt.)					
Sieve Fraction	Raw Wt., g	Solids per 1-g Sample	Oven-Dried Wt., g (Moisture Test)	Percent Dry Fraction	
> 2.00 mm	341.40	0.9615	328.26	12.64	
0.063 - 2.00 mm	2,417.12	0.9227	2,230.36	85.89	
< 0.063 mm	43.59	0.9423	41.08	1.58	
Gain (Loss)	(28.65)	---	3.01	0.11	
Wet-Sieve Analysis (2,832.39 g as-is, 2,598.17 g Dry Wt., 19.0 L rinse water)					
> 2.00 mm	279.79	0.9096	254.51	9.80	
0.063 - 2.00 mm	833.99	0.7737	645.24	24.83	
0.0027 - 0.063 mm	---	58 g/L	1,102	42.41	
< 0.0027 mm	---	---	---	---	
Loss	---	---	---	22.96	
Moisture Tests (oven-dried at 60 °C)					
Sample	Initial Wt., g	Dry Wt., g	Percent Moisture	Percent Solids	
Bulk < 2.00 mm dry sieved	15.60	15.03	8.27	91.73	
Bulk < 0.85 mm dry sieved	66.79	61.62	7.74	92.26	
Bulk < 0.85 mm wet sieved	535.47	74.67	86.06	13.94	
Hydrometer Procedure					
Time	Temp., °F	Hydrometer Reading		Reading Correction	
0 hr	77.0	---		---	
40 sec	77.0	32		33.80	
2 hr	71.6	11		11.72	
24 hr	69.8	7		7.36	
Silt + Clay, %	Sand, %	Silt, %	Colloidal & Noncolloidal Clay, %	Colloidal Clay, %	Noncolloidal Clay, %
67.6	32.4	44.2	23.4	14.7	8.72
Note: USDA Classification; Loam					

Table 2 Respirometric Result-Composition and Physicochemical Properties of the Compost Mixtures				
Mixture Number	Amendments and Bulking Agents	pH	Moisture, %	C/N Ratio
1	Turkey Manure and Sawdust	8.2	55.1	23
2	Turkey Manure and Recycled Paper	7.5	61.5	16
3	Swine Manure and Sawdust	7.2	55.7	39
4	Swine Manure and Recycled Paper	6.2	55.8	30
5	POTW Sludge and Sawdust	7.9	53.1	28
6	POTW Sludge, Recycled Paper, and Sawdust	7.2	63.8	414
7	Cow Manure and Alfalfa	7.7	63.9	70
8	Swine Manure, POTW Sludge, Sawdust, and Recycled Paper	6.3	55.0	93
Note: All mixtures contain 20% soil (vol/vol).				

After 10 days, the compost was removed from each bottle and analyzed for final amounts of explosive, TVS, TKN, pH, and moisture content. The half-life of each mix was calculated to determine which mix most effectively removed the explosives from the soil. In addition, the final respiration data were used to estimate the amount of oxidized carbon, which was later used to determine the substrate degradation rate and the specific biodegradation rate (SBR) of each mix (Table 3).

Physicochemical parameters

- a. *Oxygen utilization.* The BI-1000 was programmed to record data every 30 min. This respirometer incorporates a potassium hydroxide trap to remove the CO₂ respired by the biomass, resulting in the change of the pressure inside the flask. The change in pressure is proportional to oxygen utilization. The oxygen utilized was replaced with oxygen produced by electrolysis of water at 100 mg/hr. The oxygen replacement was computer controlled.
- b. *Oxygen uptake rate.* OUR's were determined from the oxygen utilization data collected by the BI-1000 respirometer. OUR's were calculated by dividing the change in oxygen by the time interval for a specific change.
- c. *Moisture content.* The moisture content was determined by oven-drying the compost at 104 °C for 24 hr, subtracting the final weight from the initial weight, and dividing the result by the initial weight (Greenburg et. al. 1992).

Table 3
Respirometric Biodegradation Kinetic Coefficients of the Compost Mixtures

Mixture Number	Total Oxygen Consumed, g	Maximum OUR, g/day	Degraded Organic-C, g	Initial Organic-C, g	Substrate Degradation Rate Coefficient, days ⁻¹	SBR, days ⁻¹
1	4.75	1.50	1.73	9.37	0.020	0.018
2	4.20	6.03	1.53	7.20	0.024	0.021
3	5.87	2.87	2.13	11.95	0.020	0.018
4	4.04	2.02	1.47	12.31	0.013	0.012
5	10.03	6.68	3.65	12.63	0.034	0.029
6	6.17	3.42	2.24	9.54	0.027	0.023
7	5.71	5.22	2.08	8.07	0.030	0.026
8	5.33	2.15	1.94	12.61	0.017	0.015

d. *Total volatile solid.* The TVS's were determined by placing the compost sample into a furnace at 550 °C, subtracting the final weight from the initial weight, and dividing the result by the initial weight (Method 2540G Total, Fixed, and Volatile Solids and Semi-solid Samples; Greenburg et al. 1992).

e. *Total Kjeldahl nitrogen.* Compost, 3-5g, was mixed together with 5 ml of sulfuric acid in a 250 ml polyethylene bottle. After agitating the bottle for 3 min, 245 ml of double-distilled water was added. Twenty milliliters of sample was digested using a BD-46 Digestor. After digestion, the TKN values were measured on a Lachat instrument using QuikChem method 10-107-06-02-D.

f. *Specific biodegradation rate.* The SBR was calculated by dividing the grams of degraded carbon as CO₂ by the grams of initially available carbon in dry weight and by the days of incubation. The total amount of dry weight carbon can be estimated as follows (Haug 1993):

$$\text{Dry Weight C} = (\text{TVS}/1.8) * \text{Dry Weight} \quad (1)$$

The mole ratio of O₂ consumed to CO₂ generated was about 16.5/16 and this ratio was used to estimate CO₂ generation based on O₂ consumption data.

g. *pH.* Approximately 5 g of compost was mixed into a slurry using 2 to 3 times the amount of distilled deionized (DDI) water. The mixture was stirred twice before measuring it with a pH meter.

h. *Carbon to nitrogen ratio.* The C/N ratio was calculated using the following equation:

$$\text{C/N} = \text{biodegradability factor} * (\text{TVS}/1.8)/(\text{TKN} * 10^{-4}) \quad (2)$$

The biodegradability factor is assumed to be 0.5 (Haug 1993). The percent available nitrogen is the TKN value divided by 10,000.

Explosives analysis

Explosives were determined by SW846 Method 8330: Nitroaromatics and Nitroamines by High Performance Liquid Chromatography (HPLC) (USEPA 1992). Samples were homogenized by stirring and extracted without drying. Chromatographic analysis was performed with a Perkin Elmer Integral 4000 HPLC using a C-18 Reverse Phase HPLC column (Supelco LC-18), 247.7 by 4.6 mm (5 μ m). Extraction was performed using acetonitrile.

Half-life estimations for explosives

The half-life estimations were determined by assuming the first-order equation,

$$k = \ln(C_o/C_t)/t \quad (3)$$

where

k = first-order rate coefficient, day⁻¹

$\ln$ = natural log

C_o = initial contaminant concentration, mg/kg

C_t = contaminant concentration at time t , mg/kg

t = composting time, days

Equation 3 was solved for k . The half-life (days) was then estimated from Equation 4.

$$t_{1/2} = 0.693/k \quad (4)$$

where $t_{1/2}$ = half-life, days.

Results and Discussion

The respirometric study ran for 10 days. The TVS remained constant during the 10 days of incubation. Due to the relatively large sample volume required for explosive analysis, an insufficient amount of composting material was available to run final pH, TVS, and moisture content analyses on each mixture.

Table 3 shows the substrate degradation rate coefficients, the maximum OUR, and the first-order SBR. The SBR for each mix was determined from accumulated oxygen data from the respirometer. Mix 5 had the highest SBR of 0.029 day^{-1} and the Mix 4 had the lowest at 0.012 day^{-1} . If the explosives degradation rates increase with increasing SBR's, the first choice would be Mixes 5, 6, and 7. The maximum OUR varied from 1.50 to $6.68 \text{ g O}_2/\text{day}$. Mixes 5 and 7 exerted high OUR values.

The substrate degradation rate coefficients ranged from 0.013 to 0.034 day^{-1} (see Equation 6; Table 3). Haug (1993) reworked a correlation for substrate degradation rate coefficient at various temperatures for composting a mixture of garbage and dewatered, digested sludge cake as:

$$k_T = 0.00632 * (1.066)^{T-20} \quad (5)$$

$$k_d = \ln(C_i/C_f)/t \quad (6)$$

where

k_T = substrate degradation rate coefficient at T , (day^{-1})

T = temperature, $^{\circ}\text{C}$

k_d = substrate degradation rate coefficient, day^{-1}

C_i = initial organic carbon, g

C_f = final organic carbon, g

Equation 5, using 40°C as the respirometric test temperature, predicts a k_T of 0.023 day^{-1} , which is within the substrate degradation rate coefficient range observed during this study.

The initial explosives concentration of soils prior to mixing of the compost material and the initial and final concentrations of TNT, RDX, HMX, 4A-DNT, and 2A-DNT as well as the average half-lives for each compost mix, assuming a first-order decay reaction, are shown in Table 4. In the soil, the concentration was much higher than the initial compost mixes concentration. For compost Mix 7, TNT, RDX, and HMX concentrations were reduced 85, 53, and 50 percent, respectively. The transformation product 2A-DNT concentration increased while the 4A-DNT concentration was below detection limits. For each compost mix, the initial explosives concentrations were analyzed in triplicate; however, the final concentrations were determined from single samples due to the limited amount of compost mix in the respirometer tubes. The average half-life ranges are presented in Table 4. The half-lives of TNT from this study are similar to those from static tank composting of the contaminated soils at the Umatilla Depot Activity, Hermiston, Oregon (i.e., 0.55 to 1.24 days) (U.S. Army Environmental Center (USAEC) 1993).

Table 4 Respirometric Explosive Analysis, Half-Lives, and Degradation Ranking for the Compost Mixtures																					
Mixture Number		Explosive Results																			
		TNT				RDX				HMX				4A-DNT				2A-DNT			Overall Ranking
		* Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Half-Lives (day)		* Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Half-Lives (day)		* Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Half-Lives (day)		* Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Half-Lives (day)		* Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Half-Lives (day)	
1	1,054	0.2	0.83		121	2.8	1.84		3,913	1,180	5.78		146	5.3	2.09		45	5.7	3.35	4.0	
2	1,140	1.6	1.05		163	1.6	1.49		5,797	3,880	17.26		168	7.5	2.23		57	1.8	2.00	5.0	
3	2,747	10.7	1.25		184	0.3	1.05		5,620	3,320	13.17		33	6.1	4.09		18	2.2	3.28	5.0	
4	1,897	0.9	0.91		164	0.3	1.07		5,420	3,260	13.63		153	2.5	1.69		94	1.6	1.71	2.8	
5	828	0.4	0.90		121	0.3	1.12		3,743	2,310	14.36		194	3.0	1.66		54	7.0	3.39	4.2	
6	925	1.6	1.09		152	8.7	2.43		5,607	4,700	39.29		124	18.3	3.63		50	6.3	3.35	7.0	
7	975	0.8	0.97		186	0.3	1.05		6,227	3,710	13.38		230	2.6	1.55		57	2.1	2.09	2.8	
8	996	0.5	0.92		99	2.2	1.82		3,510	3,250	90.05		67	6.1	2.89		29	0.6	1.82	5.2	
Soil	6,490	---	---		395	---	---		12,500	---	---		BDL	---	---		10.4	---	---	---	

Note: * - average concentrations; BDL - below detection limit

Note: * - average concentrations; BDL - below detection limit

To determine the optimum mix for explosives degradation, each explosive compound was ranked from the shortest half-life to the longest. The shortest half-life was given a ranking of 1, while the longest had a ranking of 8. The ranks for each compound in a mix were added, then divided by the number of explosive compounds (5) in order to determine the average overall effective ranking (Table 4) for all five explosives. Mixes 4 and 7 had the lowest overall ranking score (i.e., the fastest degradation potential for each explosive compound and transformation product). The rankings do not consider the toxicity effects to humans.

Eight compost mixtures were evaluated for their substrate utilization rates and degradation rates of explosive analyte and transformation products found in the Rockeye soils. Three selection criteria were used to select the two best mixes for bench-scale testing: explosive analyte degradation rate, system efficiency, and system simplicity. Mixtures with high explosive or transformation product degradation half-lives were not considered for bench-scale testing. Mixtures with low system efficiency were not considered for bench-scale testing. The system efficiency was based on comparing measured carbon utilization with the estimated carbon availability. The system simplicity was based on the number of components required for the compost mix. Mixtures with fewer components were considered to be better from coordination, implementation, and cost perspectives.

Compost Mixes 6 and 8 appeared to have a significantly higher HMX degradation half-life, while 2A-DNT degradation half-life was high for Mixes 1, 3, 5, and 6. Compost Mix 7B was eliminated due to the lowest system efficiency. Compost Mix 6 was rated high in system efficiency but low in system simplicity. Therefore, compost Mixes 1, 2, 3, 5, 6, and 8 were not considered for further testing.

Compost Mixes 4 (swine manure, recycled paper, and soil) and 7 (cow manure, alfalfa, and soil) showed the fastest explosives degradation potential. Although Mix 7 was among the highest in terms of substrate degradation rate, Mix 4 was the lowest in that category. The low substrate utilization rate of the Mix 4 may not heat the compost piles due to low energy generation rate. This insufficiently heated compost poses a threat to public health because of improper sanitization at low temperatures. Furthermore, compost Mix 4 was a slurry mixture and appeared not to possess the structural integrity of normal compost with sufficient FAS. Unfortunately, until mixing the larger volume of compost mix using the recycled paper, the structural integrity failure was not noticeable because of the smaller volume required for the respirometric study. Therefore, compost Mix 4 was not recommended for subsequent bench-scale composting experiments.

Although, compost Mixes 1 (turkey manure and sawdust) and 5 (POTW sludge and sawdust) were not selected for bench-scale testing, these mixes may be effective in treating the explosives-contaminated soils. Both mixes ranked high in system efficiency and simplicity. Because of the high 2A-DNT half-lives, it may require a longer composting period. Having the highest SBR, the compost temperature of Mix 5 is expected to be high enough to achieve proper sanitation and thermophilic conditions in which explosives may be degraded more effectively. The overall explosives degradation effectiveness rankings for Mixes 1 and 5 are

4.0 and 4.2, respectively, which is slightly below that of compost Mixes 4 and 7. However, compost Mix 7 was recommended for subsequent bench-scale composting experiments.

4 Bench-Scale Composting Study

Introduction

The standard composting method of the American Society for Testing and Materials (ASTM) D5338 (ASTM 1992) uses incubators in order to externally control the compost reactors at predefined temperatures (35 °C for the first 16 days and 55 °C for 28 days). With this externally predefined temperature control, reproducibility of data may be improved; however, many leading experts argue that it may not adequately represent the actual composting process in which self-heating is induced. A relatively high surface area to volume ratio compared with field or pilot compost piles results in high conductive and convective heat loss. In some systems, the heat generated from degrading organic substrates may not be enough to raise and maintain the thermophilic compost temperatures. It has been a common perception among composting researchers and practitioners that the minimum size of a pilot compost pile must be at least 19 to 38 m³ (25 to 50 yd³) in order to retain the heat (Hanif 1995).

Several researchers used feedback temperature control and heating systems in order to minimize the heat loss and were able to maintain self-heating induced thermophilic conditions (Cook, Bloom, and Halback 1994; Hogan, Miller, and Finstein 1989; Magalhaes et al. 1993). Small bench-scale remediation composting systems require much more precise design and operational control in order to be successful, compared with rather insensitive, but more stable, pilot-scale compost piles.

The WES Adiabatic Composting System (WACS) II is a composting reactor with a sophisticated feedback temperature control and heating system. Compost Mix 7 was evaluated for the feasibility of treating soils contaminated with the explosives in actual composting environments using the WACS II system.

Objectives

The preliminary success of the compost Mix 7 from the respirometric experiment was evaluated in bench-scale studies. A bench-scale remediation composting system, designed to simulate field composting conditions, was used to extend the respirometric study. The bench-scale study was designed to provide preliminary feasibility data, the fate of the contaminants, and the toxicity of the composted product.

Materials and Methods

Bench-scale reactor system

The WACS II is a pseudo-adiabatic composter combined with instrumentation and automatic data collection, as shown in Figure 5. The composting reactor is a 14-L polyvinyl chloride (PVC) cylinder insulated to reduce conductive heat transfer. This reactor was placed into a Styrofoam box to further isolate the composter from ambient temperatures. This isolation eliminates heat loss so that heat can accumulate inside the reactor, raising the composting temperature. The resistance temperature probes (RTD's) were inserted into the center of the composting reactor as well as against the inside and outside of the cylinder wall. A proportional-integral-derivative (PID) feedback temperature control system used the two reactor wall RTD measurements to track the temperature differences. The temperature of air in the Styrofoam box was maintained at the same temperature of the inside reactor wall by passing preheated or cooled water through a radiator inside the box while a fan circulated the temperature-controlled air.

Finally, preconditioned air was supplied to the reactor to maintain aerobic respiration and to reduce convective heat loss from the composting pile through the latent heat of vaporization. Air temperature was dynamically adjusted to the temperature at the core of the composting pile. Air was also humidified before entering the reactor. Aeration events occur every one in ten minutes if the composting temperature is less than 55 °C or continuously if the temperature is above 55 °C. Temperature readings were recorded every 2 min as well as total elapsed time for aeration events.

Pilot-scale reactor system

To simulate field-scale operations, the composting Mix 7 was used in a 40-L adiabatic composter (Oxymax) developed by Columbus Instruments (Figure 6). This pilot-scale system provided enough composting material to conduct metal leachability, toxicological, and mutagenic experiments. Similar to the WACS II system, the Oxymax composter uses a temperature control feedback system to minimize heat transfer effects. The reactor tracks temperature as well as microbial activity through O₂ and CO₂ sensors in the exit air stream. Filtered

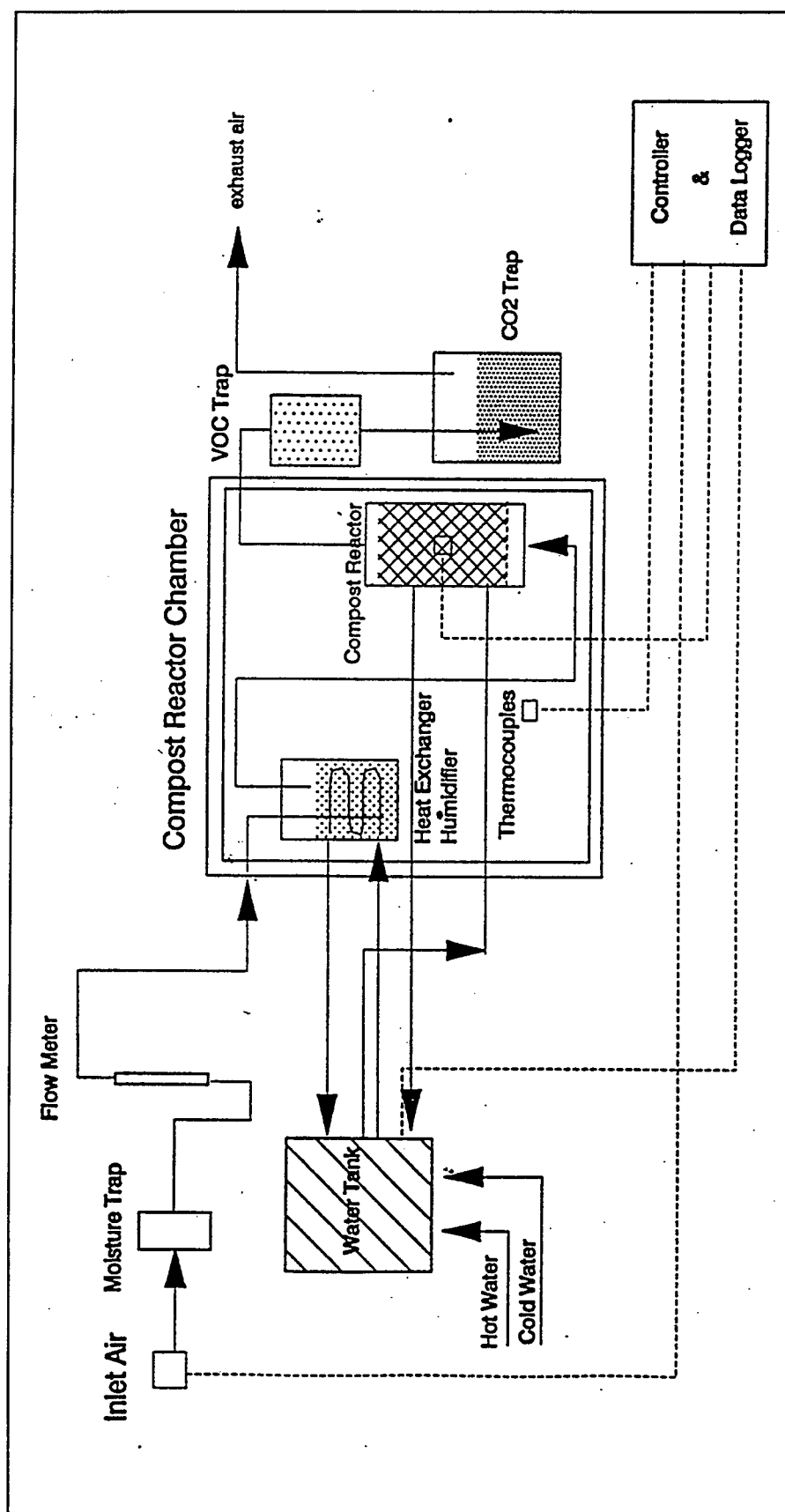


Figure 5. Schematic diagram of bench-scale batch compost reactor system

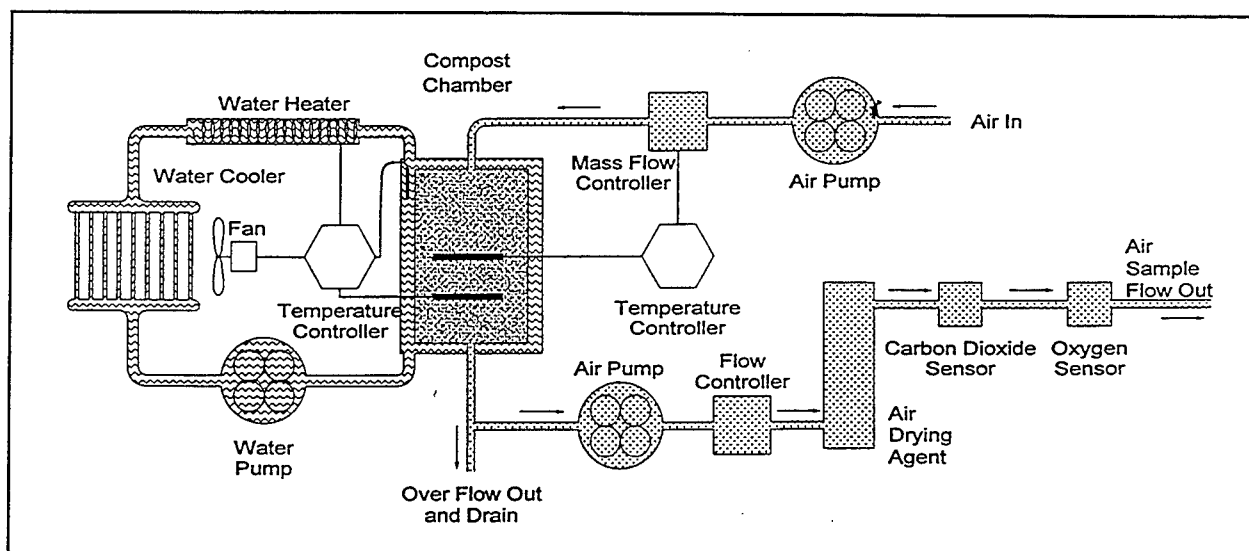


Figure 6. Schematic of Oxymax system with an adiabatic chamber

air was passed through the compost reactor with a known flowrate. The temperature, inlet air flowrate, and exit gas O_2 and CO_2 concentrations were automatically logged every 20 min in a personal computer.

Compost mixing procedure

The ingredients for Mix 7 (40 percent cow manure, 40 percent alfalfa, and 20 percent soil) were measured by volume, weighed, and mixed together in a 15-gal twin-shell mixer. Table 5 shows the composition of Mix 7 used in the bench-scale system. The ingredients were homogenized for at least 2 hr. Compost mix samples were collected in triplicate. Each sample was analyzed for pH, moisture content, TVS, TKN, EC, Pb, Cd, Hg, and explosives (TNT, RDX, HMX, 2A-DNT, and 4A-DNT). Other samples were collected on day 15 and day 30.

TCLP leaching procedure

The compost sample of Mix 7 from the Oxymax system was subjected to the TCLP extraction procedure to determine the contaminant mobility as defined by the USEPA (1986). The samples were placed either in a 0.5N acetic acid or an acetate buffer extract, depending on the buffering capacity of the compost as determined by pH adjustment, at a 20:1 liquid-to-solids ratio. The mixture and extract were tumbled for 18 hr, after which the samples were filtered using a Whatman GF/F 0.75- μ m filter. The filtered extracts were placed in precleaned bottles and stored at 4 °C prior to analysis. Each extract was analyzed in triplicate for Pb and Cd at days 0, 15, and 28. The total metals analysis was

Table 5 Bench Scale - Compost Composition of Mixture 7							
Ingredients	Volume, %	Wet Weight, g	Wet Weight, %	Moisture, %	Dry Weight, g	Dry Weight, %	FAS, %
Cow Manure	40	4,343.7	53	75	1,085.9	24	
Alfalfa	40	780.4	10	4	747.6	16	
Soil	20	3,068	37	9	2,782.7	60	
Total		8,192.1	100		4,616.2	100	65

performed using SW846 Method 6010A for total lead determination and Method 7131A for total cadmium determination (USEPA 1994 a, b).

Results and Discussion

Figure 7 displays the average, maximum, and minimum core compost temperature profile in WACS II bench-scale compost reactor for 30 days. The compost reached a thermophilic temperature range within the first 24 hr and remained thermophilic for approximately 4 days. The compost achieved the maximum temperature of 55 °C during days 3, 4, and 5. The compost temperature dropped to room temperature after 10 days of composting. This core compost temperature profile indicated that the WACS II system closely simulated actual field-scale compost piles.

The composting temperature profiles of the core, inside wall, outside wall, and air temperatures are shown in Figure 8. The core compost temperature was slightly higher than the wall temperature, showing radial heat loss through the reactor. This ensured self-heating of the compost and no external heat input as in the real field compost piles. The air temperature was maintained approximately 10-15 °C below the core temperature to allow heat removal from the system and achieve the optimal composting temperature of 55 °C.

Figure 9 displays the daily aeration and cumulative aeration minutes for 35 days. Day 3 had the highest aeration of 235 min of air at a rate of 3.78 L/min. The number of aeration minutes corresponded well with the temperature profile, increasing from days 0-3, declining from days 3-5, and remaining constant to day 35. The overall accumulated air was 4,959 min. Air was exchanged 1,339 times throughout this run. Haug (1993) estimated that a yard waste composting pile with 80 percent TVS and 50 percent degradability would require 1,510 exchanges of air. The overall aeration for this composting run was 0.43 m³/kg VS-d.

Physicochemical properties of the compost mix at days 0, 15, and 30 are shown in Table 6 and Figure 10. The moisture content decreased slightly but stayed in the optimal ranges (44.9-49.0 percent) during the 30 days of composting.

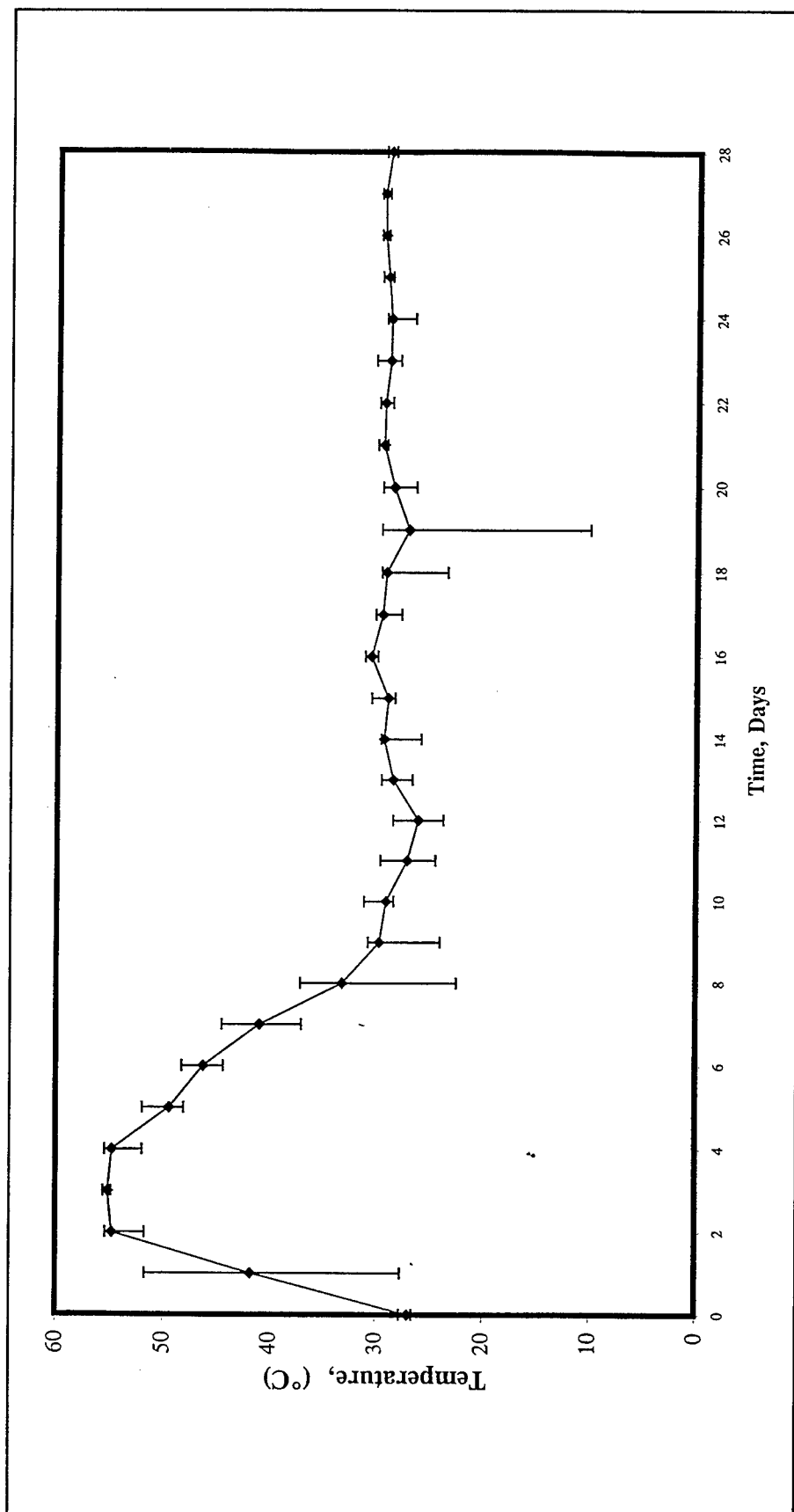


Figure 7. Mixture 7 maximum and minimum compost core temperature profile

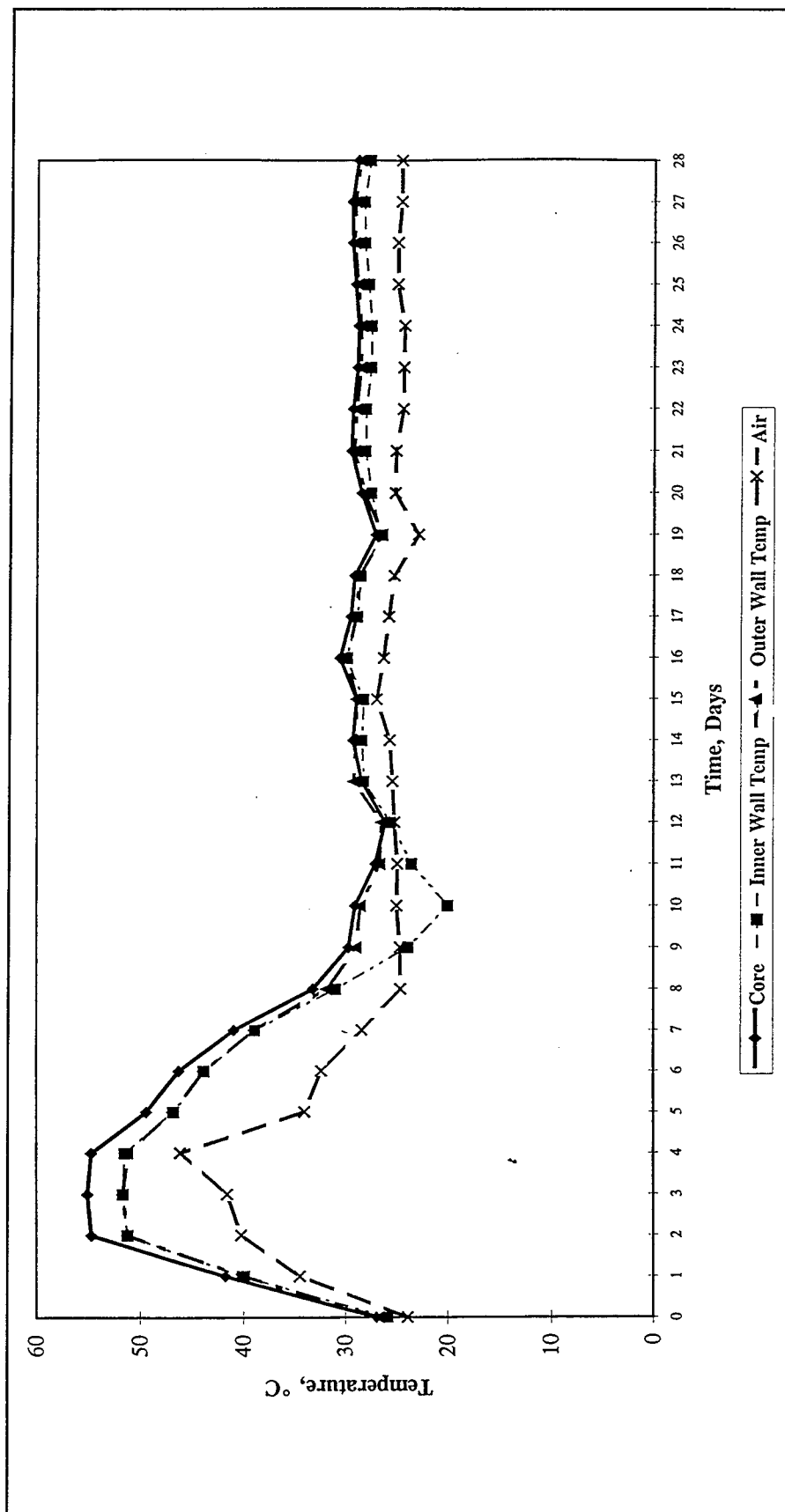


Figure 8. Mixture 7 temperature profile of various WACS II components

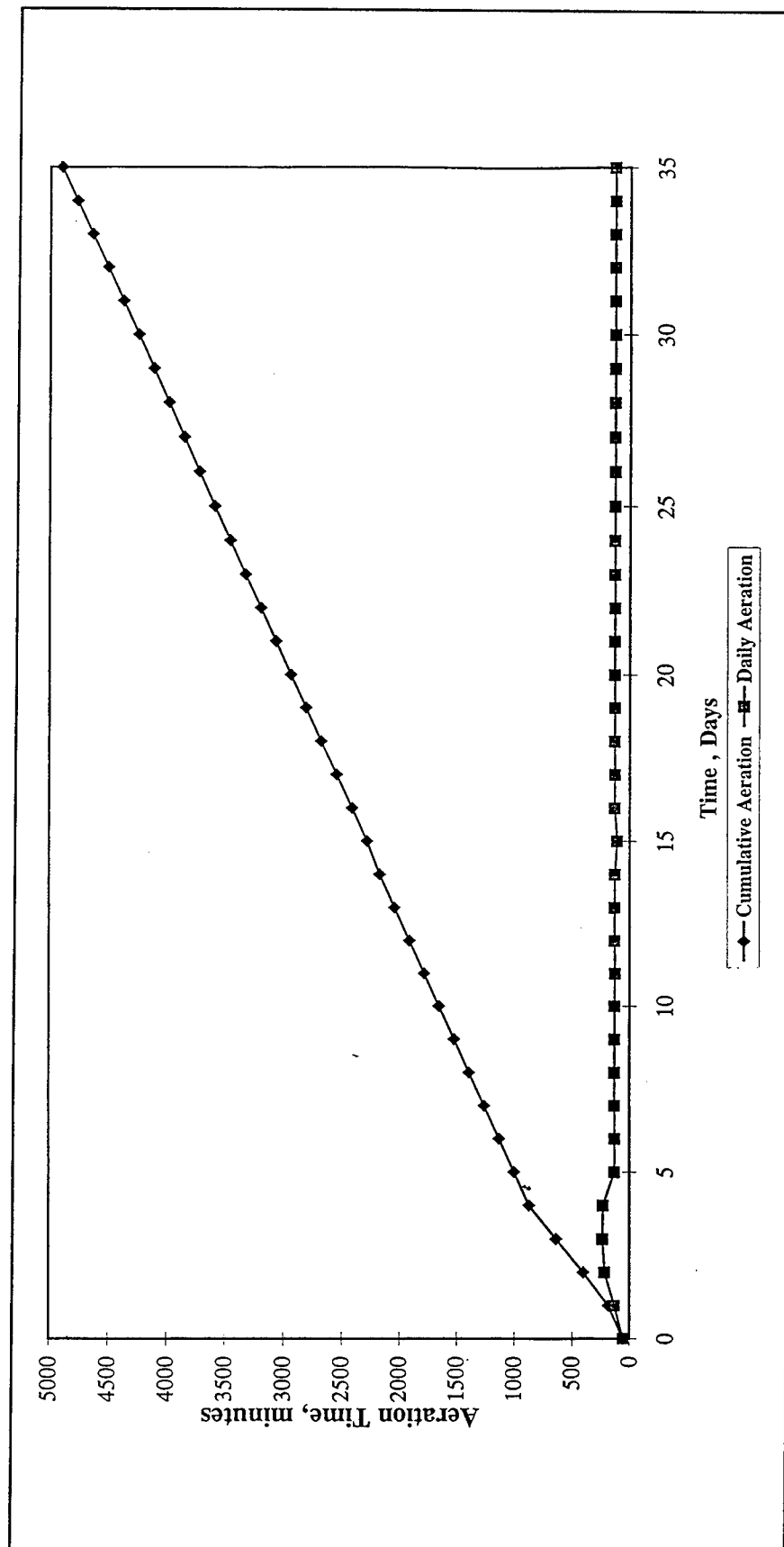


Figure 9. WACS II aeration times for Mixture 7

Table 6 Bench Scale - Physicochemical Properties for Mixture 7						
Sample Number	Moisture, %	TVS, %	pH	C/N Ratio	TKN ¹ , mg/kg	EC ¹ , mmho/cm
Day 0	49.0	30.0	6.73	36	2,325	3,227
Day 15	47.2	21.8	8.74	31	1,977	2,397
Day 30	44.9	21.1	7.78	35	1,586	2,787
¹ average of triplicates						

The initial pH, 6.73, increased to 8.74 at day 15, then decreased to 7.78 at day 30. The values and trend of pH during composting in this study compare well with other studies (Avinmelech et al. 1996).

The TVS values decreased from 30.0 to 21.8 percent on day 15 and remained constant at 21.1 percent to day 30. This indicated a substantial reduction in organic matter during the first 15 days of composting where thermophilic conditions prevailed (Figure 7). At the later stage of composting, when the substrate utilization rate became rather insignificant due to depletion of readily available organic carbon sources, the compost temperature dropped to room temperature, resulting in practically no change in TVS.

The TKN values steadily decreased throughout the study from 2,325 to 1,586 mg/kg. Two possibilities for the decrease in TKN are ammonia-N loss through either volatilization or nitrification. The change in compost temperature did not appear to affect the TKN loss rate since a linear decrease in TKN was observed during composting. The C/N ratio decreased from 36 to 31 on day 15, but increased to 35 on day 30. In general, as compost ages, the C/N ratio decreases. In this study, the decrease in the carbon utilization rate with continual reduction of TKN during the later stage of composting resulted in an increase in C/N ratio.

The EC values decreased from 32,270 to 23,970 mmho/mm on day 15, but increased to 27,870 mmho/mm at the end of the composting run. This EC pattern was similar to that of C/N ratio. The EC values decrease with the increase in the age for many MSW composts due to destruction of organic volatile acids with time (Avinmelech 1996; Hue and Liu 1995). In addition, nitrification of ammonia may have begun during the later stage of composting when the available organic carbon was low, resulting in production of electrolytes. This may explain the fluctuation (destruction of organic volatile acids in the beginning and production of electrolytes at the later stage) pattern of the EC.

Compared with the respirometric study, no substantial HMX degradation occurred. The initial and final HMX concentrations were 4,817 and 4,658 mg/kg, respectively. The reason for the difference in HMX degradation between respirometry and composting runs is not clear at this time. The most significant difference observed between the two experiments is the temperature. In respirometry,

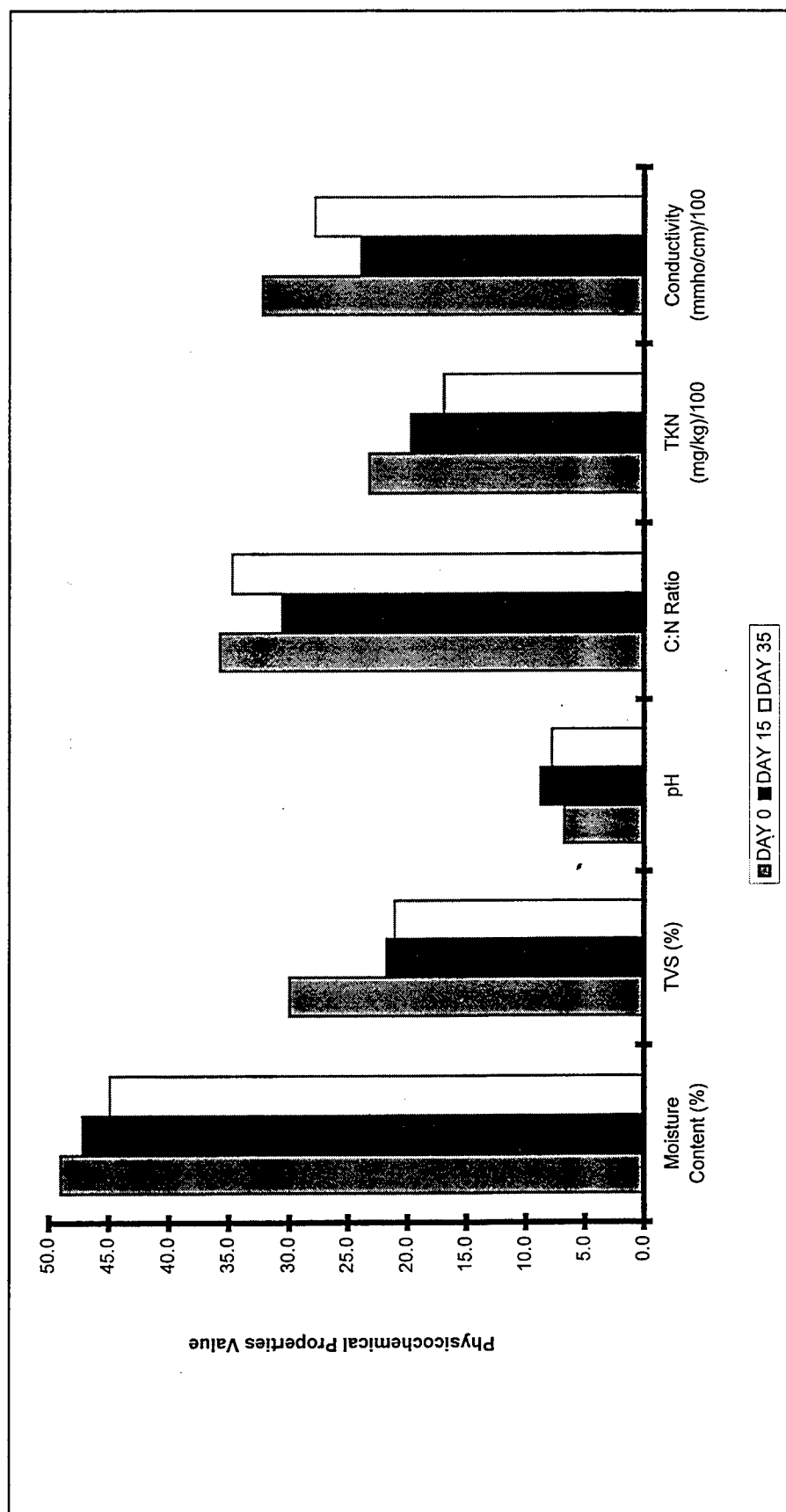


Figure 10. Physicochemical properties for Mixture 7

the mixture was maintained at 40 °C, whereas, the composting mixture heated to 55 °C and cooled down to room temperature. Different microbial populations may exist for the two studies. Figure 11 and Table 7 exhibit significant reduction for all other explosive compounds as predicted from the respirometric study. RDX, TNT, 2A-DNT, and 4A-DNT concentrations were reduced by 99.6, 99.3, 97.0, and 94.1 percent, respectively. Explosives and the transformation product concentrations were reduced within the first 15 days of composting as found in other remediation studies (USAEC, 1993).

The total metal data results were expressed on a mass-mass basis (mg/kg) and TCLP data results were expressed on a mass-volumetric basis (mg/L). Both data sets were compared by transforming each to a mass basis (mg) (Table 8). The data in Table 8 suggest that Pb and Cd may show a reduced extractability as a result of composting. When the TCLP extractability is compared with total metal content, means of 29.3 percent and 22.2 percent extractability are observed with standard deviations of 14.1 and 24.9 for Pb and Cd, respectively. The Pb data had two values that were nonsensical in that the TCLP metal concentrations were higher than the initial total metal concentrations. The reason for this observed inconsistency may be that the extractable metal concentrations, although above detectable limits, were quite low, even when using the graphite furnace methods.

Based on the metal data, no trend toward decreased extractability or increased retention time was observed. In other words, no significant differences were observed between the initial and final compost mix. Based on the data available on the reduced bioavailability of heavy metals in compost (Chaney and Ryan 1993), metal data from compost Mix 7 may not be of concern since they are below the No Observed Adverse Effect for sludge land application.

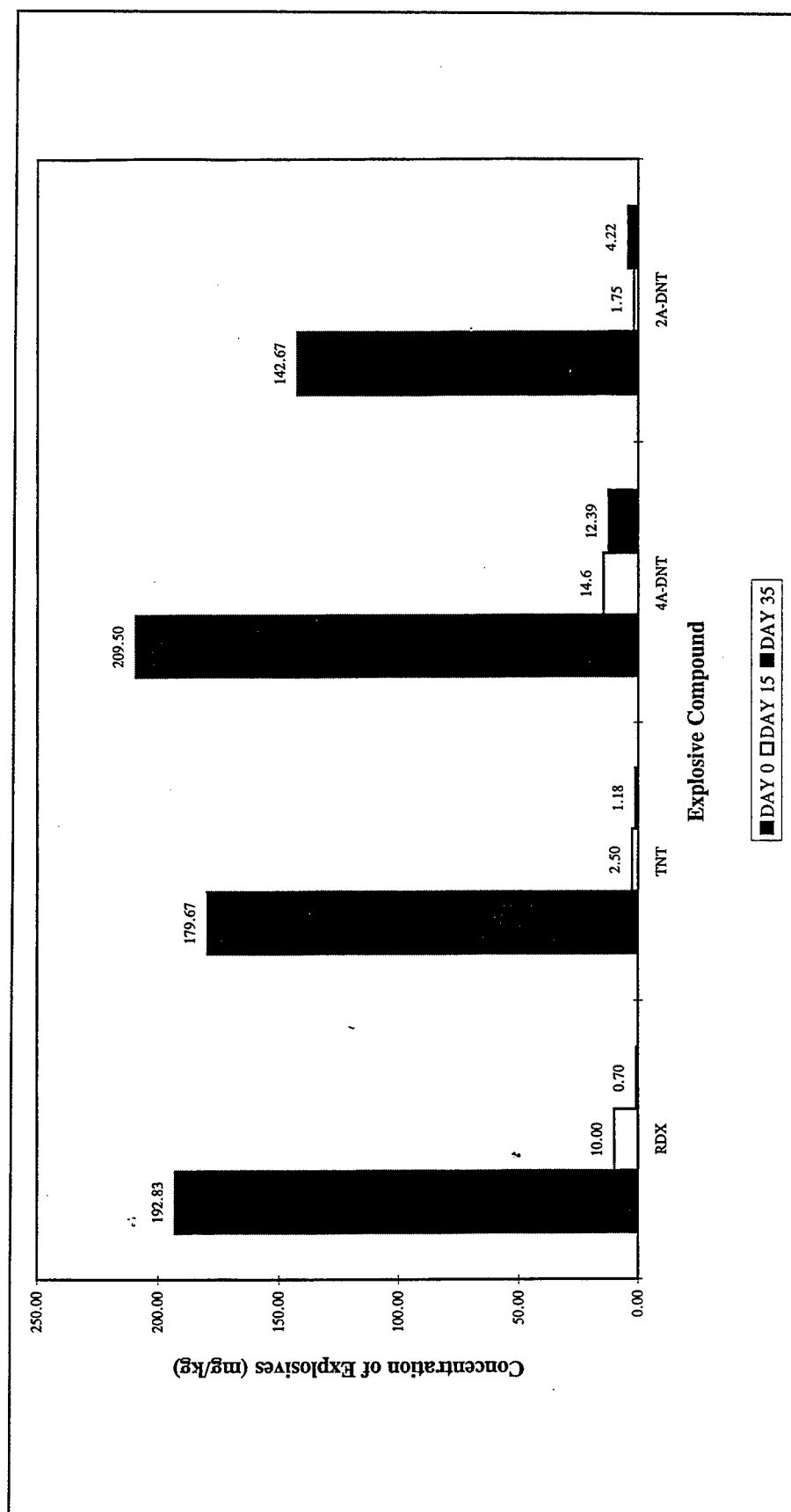


Figure 11. Explosives analysis results for Mixture 7

Table 7					
Bench Scale - Explosives Analysis for Mixture 7					
Sample Number	Explosive Concentrations, mg/kg				
	TNT	RDX	HMX	2A-DNT	4A-DNT
Day 0, Replicate 1	160	195	4,650	144	194
Day 0, Replicate 2	191	188	4,770	147	212
Day 0, Replicate 3	188	196	5,030	137	222
Average	180	193	4,817	143	210
Day 15, Replicate 1	BDL	BDL	3,520	1.61J	13.8
Day 15, Replicate 2	BDL	BDL	5,670	1.73J	16.2
Day 15, Replicate 3	BDL	BDL	5,360	1.90J	13.8
Average	BDL	BDL	4,850	1.75J	14.6
Day 30, Replicate 1	0.516J	0.551J	3,975	0.916J	10.48
Day 30, Replicate 2	0.704J	0.789J	4,350	0.930J	12.80
Day 30, Replicate 3	2.31J	0.758J	5,650	10.80	13.90
Average	1.20J	0.699J	4,658	4.22	12.4
Note: BDL - below detection limit; J - an estimated value below detection limit					

Table 8
Pilot Scale - Metal Analysis of Compost Mixture 7

Sample Number	Total Metals, mg/kg				Total Metals, mg				TCLP Leachate Metals, mg/L				Extractable Metals, mg				Extractable Metals, %			
	Pb	Hg	Cd	Pb	Hg	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
Day 0, Replicate 1	40.7	0.333	0.477	0.219	0.0018	0.00257	0.569	0.00201	0.1142	0.000368	52.1	14.3								
Day 0, Replicate 2	39.2	0.285	0.439	0.213	0.0015	0.00238	0.199	0.00149	0.0398	0.000298	18.7	12.5								
Day 0, Replicate 3	25.7	0.355	0.446	0.140	0.0019	0.00241	0.127	0.00260	0.0254	0.00052	18.1	21.6								
Average	35.2	0.324	0.454	0.191	0.0017	0.00245	0.298	0.00203	0.0598	0.000395	29.8	16.1								
Day 15, Replicate 1	25.7	0.753	0.512	0.134	0.0039	0.00268	0.864	0.00156	0.1728	0.000312	NS	11.6								
Day 15, Replicate 2	28.9	0.675	0.537	0.152	0.0035	0.00282	0.223	0.00120	0.0446	0.000240	29.4	8.5								
Day 15, Replicate 3	36.6	0.710	0.507	0.194	0.0037	0.00269	0.143	0.00090	0.0286	0.000180	14.7	6.7								
Average	30.4	0.713	0.519	0.160	0.0037	0.00273	0.183	0.00122	0.0820	0.000244	22.1	8.9								
Day 30, Replicate 1	27.9	0.396	0.495	0.152	0.0022	0.00208	1.74	0.00146	0.348	0.000292	NS	14.1								
Day 30, Replicate 2	26.6	0.385	0.561	0.146	0.0021	0.00212	0.208	0.00248	0.0416	0.000496	28.4	23.4								
Day 30, Replicate 3	26.1	0.425	0.587	0.102	0.0023	0.00166	0.032	0.00123	0.0448	0.001442	43.9	86.9								
Average	26.9	0.402	0.548	0.133	0.0022	0.00195	0.660	0.00172	0.1448	0.000743	36.2	41.5								

Note: NS denotes a non-sensical data point.

5 Toxicity Experiment

Introduction

Although previous composting experiments showed heat generation and significant reduction of target contaminants, in particular RDX and TNT, it is important to determine the environmental effects of remediation via composting. To quantify hazardous effects on the ecosystem, toxicological experiments were performed on the final compost mix.

Two assays were employed to evaluate the efficacy of composting in reducing the toxicity of explosives-contaminated soils, the Mutatox™ assay and the earthworm acute toxicity experiment. The Mutatox™ assay is a proprietary assay that determines the mutagenic potential of sample extracts. It utilizes a dark mutant of the bacterial strain *Photobacterium (P.) phosphoreum*, which will normally bioluminesce (similarly to fireflies). These dark mutants of *P. phosphoreum* revert to the wild type in the presence of mutagens. The mutation causes *P. phosphoreum* to bioluminesce, and the light produced is easily measured with a luminometer.

The earthworm acute toxicity experiment estimates the acute toxicity of solid wastes to the earthworm (*Eisenia sp.*) in a 14-day static test and is accepted by the USEPA (Greene et al. 1989). The responses measured include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components that adversely affect the biochemical and physiological functions of the test animal. The experiment uses soil as the exposure medium because the exposure conditions closely mimic natural conditions. The test soil is serially diluted with a noncontaminated "artificial soil" in which mature earthworms are placed for 14 days. At the end of the exposure, the live earthworms are counted and the concentration, which is expected to kill 50 percent of a test population (LC₅₀), is calculated.

The Mutatox™ assay is a quick and easy method that utilizes extracts of the sample. As such, the assay results are dependent on the ability to extract the contaminants from the sample. Conversely, Mutatox™ could "overexpress" the mutagenic potential of the sample if the contaminants are not bioavailable but are extractable. The earthworm acute toxicity assay exposes the organisms to the soil

sample and therefore assesses the toxicity of only the bioavailable contaminants. The two assays work together to provide a picture of the acute and subacute (mutagenicity) toxicity of the soil in addition to the bioavailability of soil contaminants.

Materials and Methods

Soil extraction for mutagenicity

Five soil samples (Rockeye soil, Mix 7A Initial, Mix 7B Initial, Mix 7A Final, and Mix 7B Final) were immediately stored at 4 °C until testing. Mixes 7A and 7B were replicates of compost Mixture 7. Aliquots of the samples were oven dried overnight at 130 °C for determination of moisture content. Four replicate 1-g samples of each soil sample were combined with 3 ml of pesticide-grade acetonitrile in 25-ml glass centrifuge tubes and sonicated for 18 hr in a sonicating water bath at 9 °C. The soil extracts were centrifuged for 5 min at 2,000 rpm and 14 °C for sedimentation of the soils. An aliquot of the extract was pipetted into an amber vial and solvent exchanged under a stream of ultrapure nitrogen into an equal volume of spectrophotometric grade dimethyl sulfoxide (DMSO).

Mutatox™

As per the Mutatox™ testing protocol, 10 µl of each soil extract was added to 250 µl of Mutatox™ medium and serially diluted over a wide range with extra media into cuvettes. A 10-µl portion of bacterial reagent was pipetted into cuvettes, mixed, and incubated at 27 °C for 21 hr. Phenol was used as a positive control in addition to DMSO and acetonitrile solvent controls. Each extract was measured and recorded after the incubation period using the Microbics M500 Toxicity Analyzer (Microbics Corp.). A soil extract was considered mutagenic when light levels produced were greater than two times the DMSO control for two consecutive dilutions, e.g., modified twofold rule (Chu et al. 1981).

Earthworm acute toxicity

Adult earthworms (*Eisenia sp.*) were purchased from Carolina Biological Supply Company (Burlington, NC) and held in moistened sphagnum peat on a diet of Magic Worm Food (Carolina Biological Supply Co.) for at least 3 weeks prior to testing. The acute toxicity test was conducted according to USEPA protocols (Greene et al. 1989). Test soil samples were diluted with artificial soil (70 percent industrial sand, 20 percent kaolin clay, and 10 percent sphagnum peat on a dry weight basis). The artificial soil pH was adjusted to 6.0 ± 0.5 with calcium carbonate. The dilutions were 100, 50, 25, 12.5, 6.3, and 3.1 percent sample soil to artificial soil on a dry weight/dry weight basis. Aged tap water was added, if needed, to increase the percent moisture of the soil mixtures to 25 percent. Each soil sample was split into three replicates of 100 g. The replicates were placed in

250-ml polypropylene beakers, covered with polyethylene wrap, sealed with a tight-fitting rubber band, and allowed to sit overnight.

On day 0 of the 14-day exposures, mature earthworms were removed from the peat bedding and rinsed with aged tap water, then four earthworms were placed in each beaker. The beakers were re-covered with polyethylene wrap and held under continuous illumination at room temperature (23 ± 2 °C) for 14 days. The earthworms were not fed during exposure. At the end of the exposure period, the earthworms were removed, and the numbers of live earthworms per beaker were recorded. Earthworms were considered dead if they did not respond to gentle probing with a blunt probe. A reference toxicant control was run simultaneously with the test soils by spiking artificial soil with 2-chloroacetamide. The calculated LC_{50} for 2-chloroacetamide was compared with published data for performance validation of the tests (Edwards 1984). The test data were found to be acceptable.

Results and Discussion

Compost temperature

Figures 12 and 13 show the average daily temperature profiles and the maximum and minimum temperature values for the two mixes to be used in the toxicity study. These figures show that the temperatures of both mixes did not increase to thermophilic ranges as reported in the bench-scale system within the first 24 hr. The energy content of the compost mix was probably insufficient to generate the required heat to raise the temperatures in the Oxymax system. In an attempt to rectify the situation, approximately 3 kg of molasses was added to each reactor during the incubation period. The molasses supplied enough energy for both reactors to reach thermophilic temperatures.

Respiration rate

Figures 14-16 show the average daily respiration profiles in exit air for Mix 7A, while Figures 17-19 profile Mix 7B. The error bars show the maximum and minimum O_2 and CO_2 for each system. Both mixes show significant biological activity within the first day. Figure 16 shows that as CO_2 increased to 9 percent, O_2 level was reduced to 12 percent for Mix 7A. Similar trends were observed in Mix 7B (Figure 19). However, it appears as if the energy released was not adequate to increase the temperature, even in the adiabatic reactor.

Explosives analysis

Table 9 shows the explosives profiles during composting of both reactors (Mix 7A and Mix 7B). As previously discussed, HMX concentration decreased slightly over 30 days of composting in both mixes. HMX concentration was reduced by

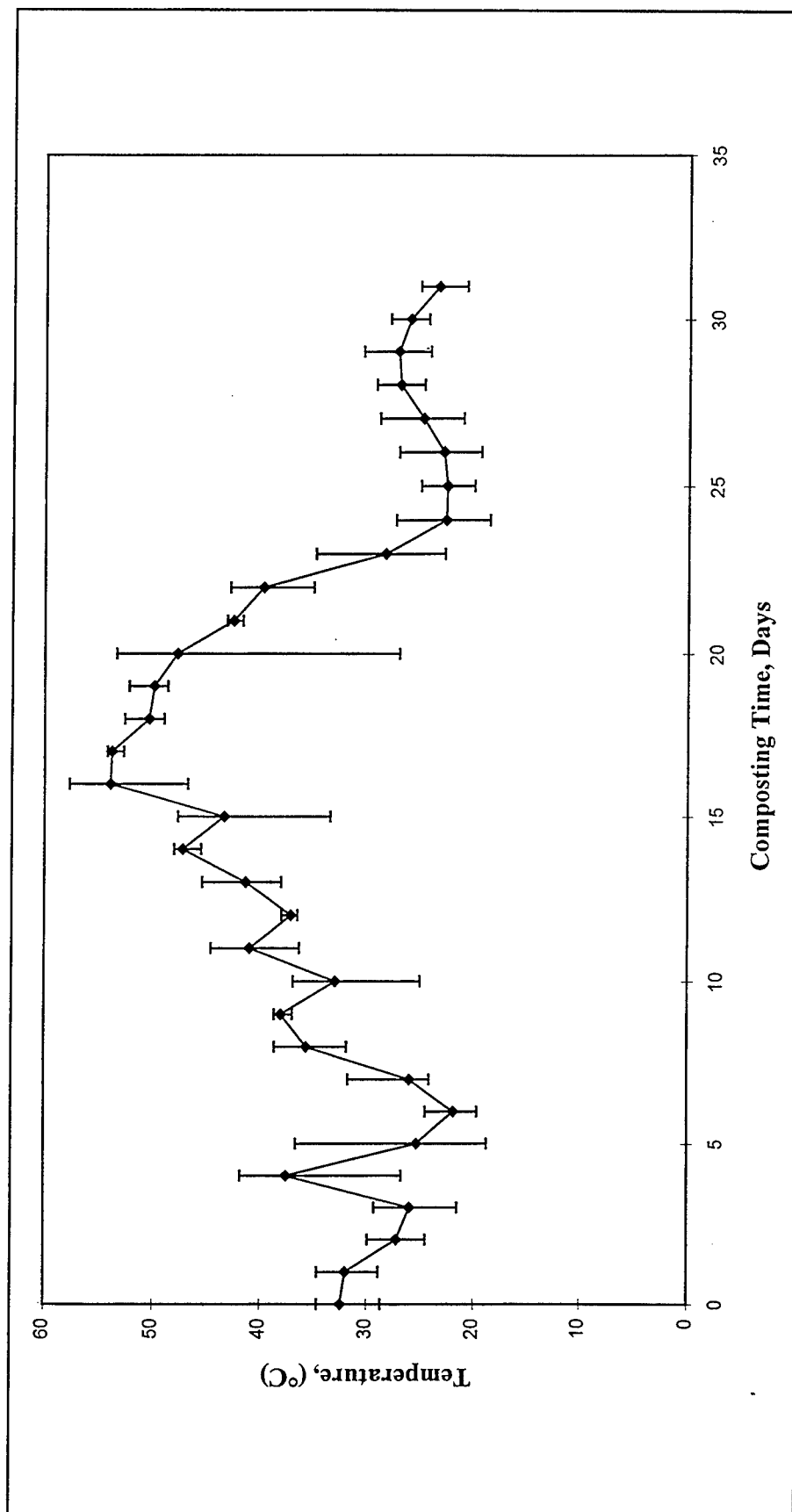


Figure 12. Mix 7A temperature profile

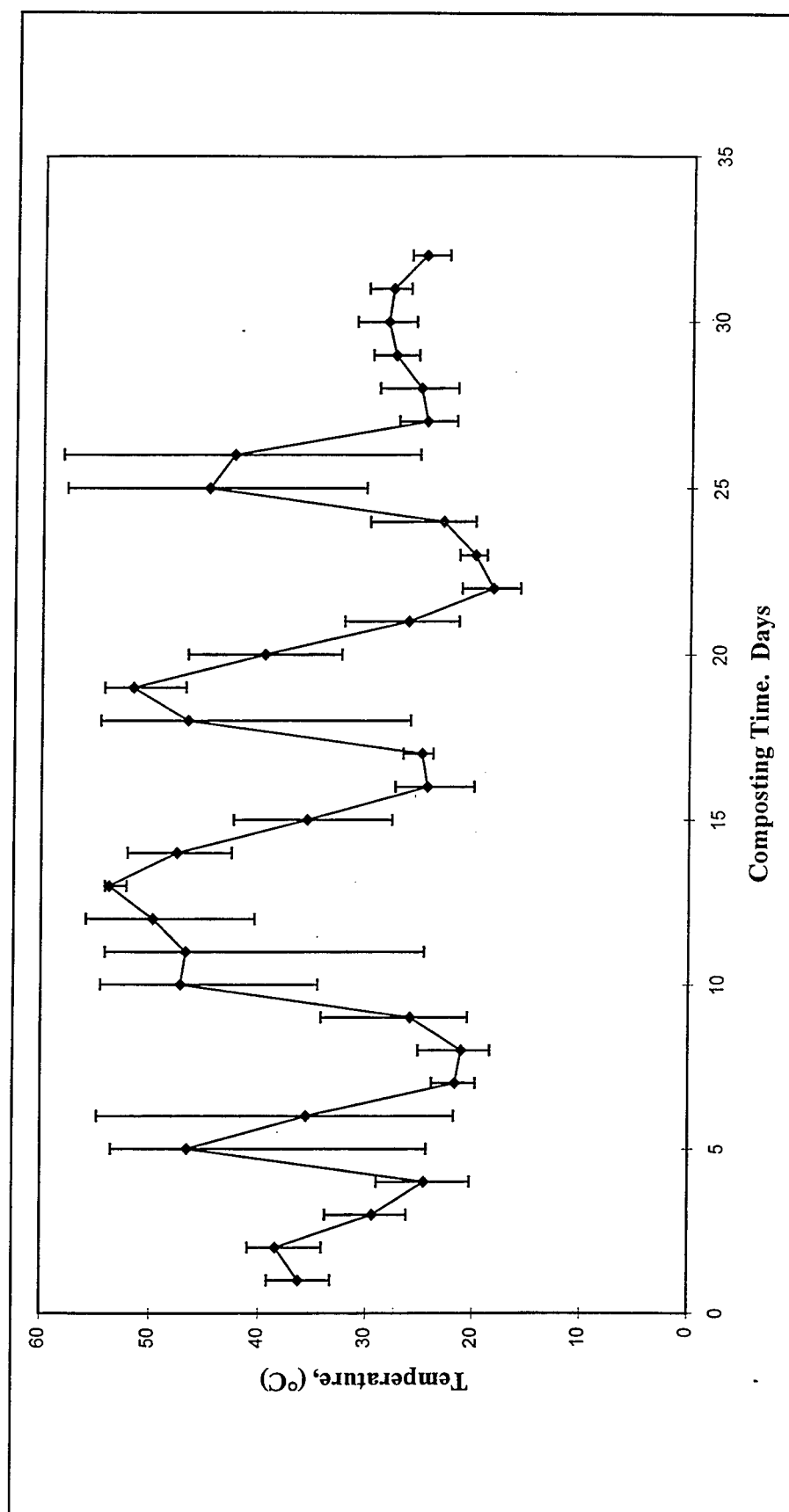


Figure 13. Mix 7B temperature profile

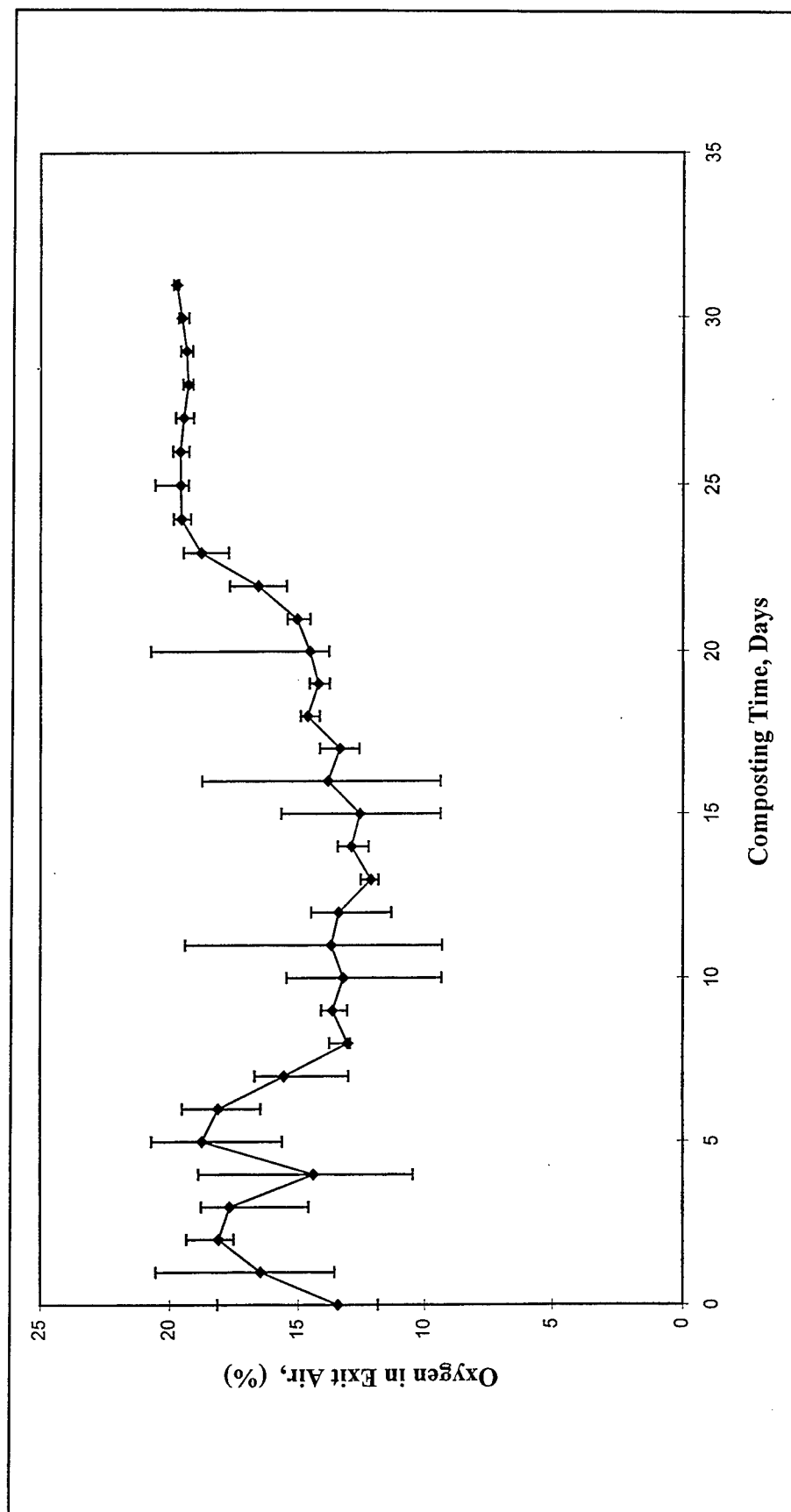


Figure 14. Mix 7A maximum and minimum oxygen in exit air profile

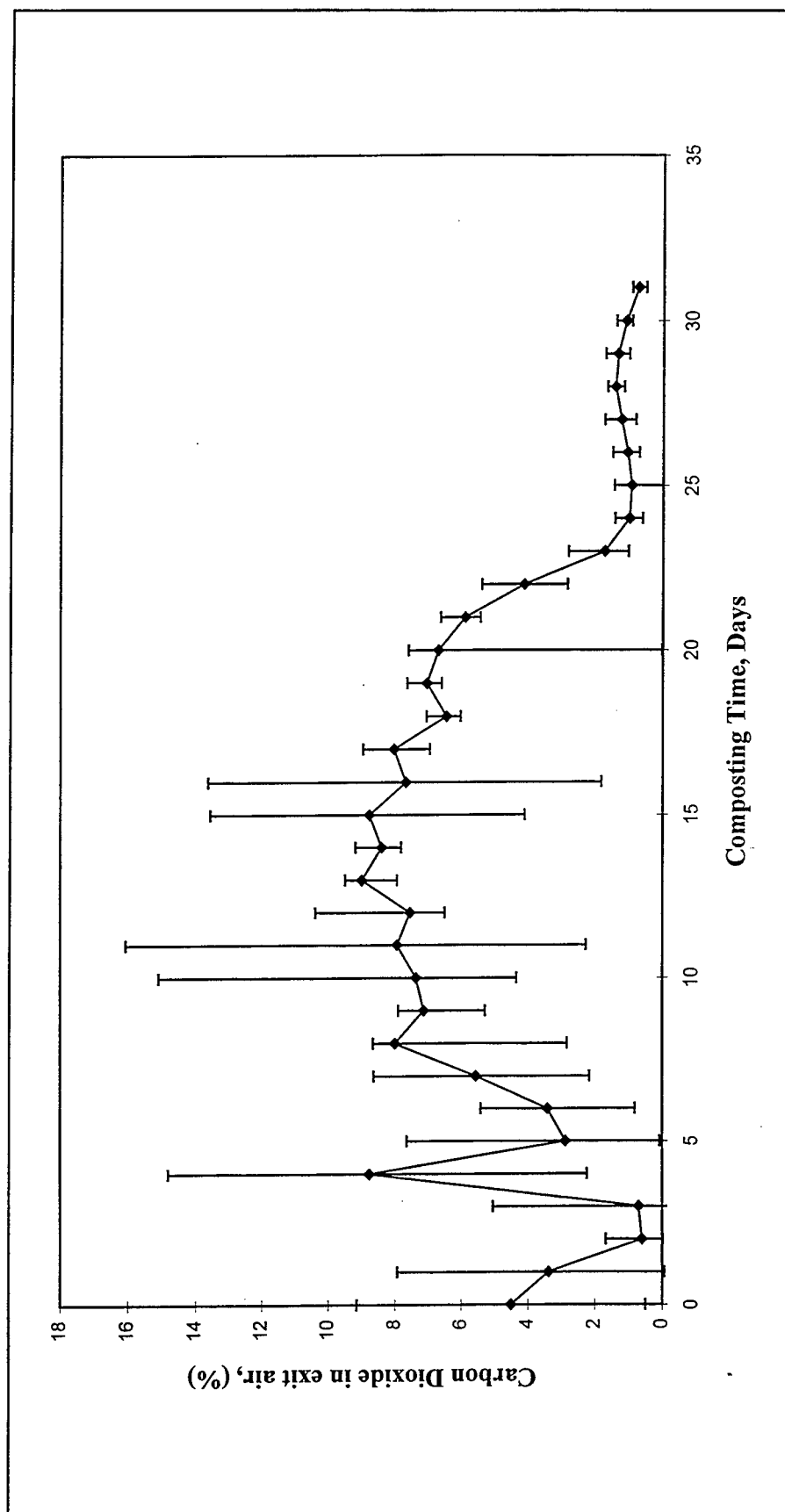


Figure 15. Mix 7A maximum and minimum carbon dioxide in exit air profile

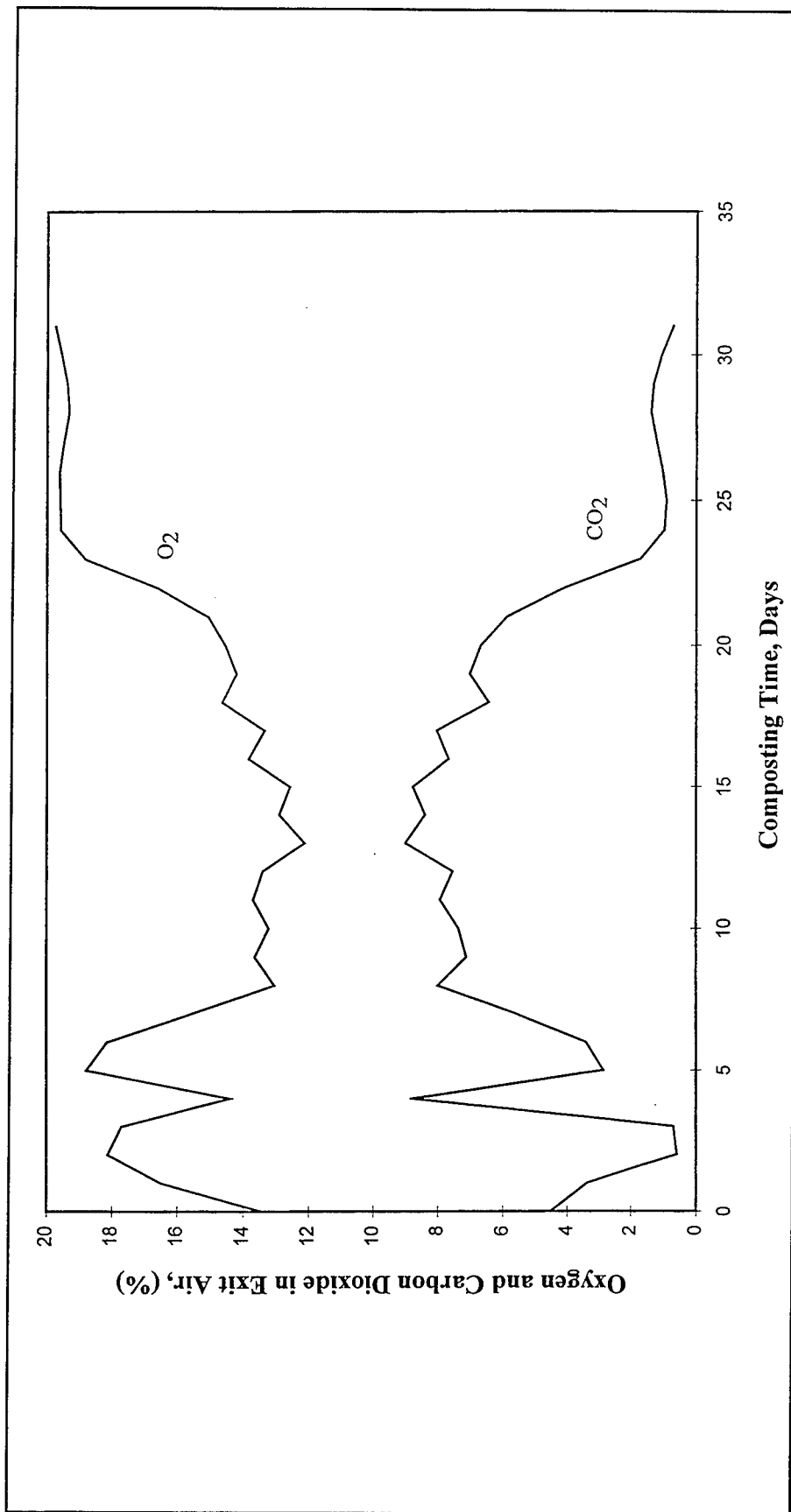


Figure 16. Mix 7A respiration rate during composting

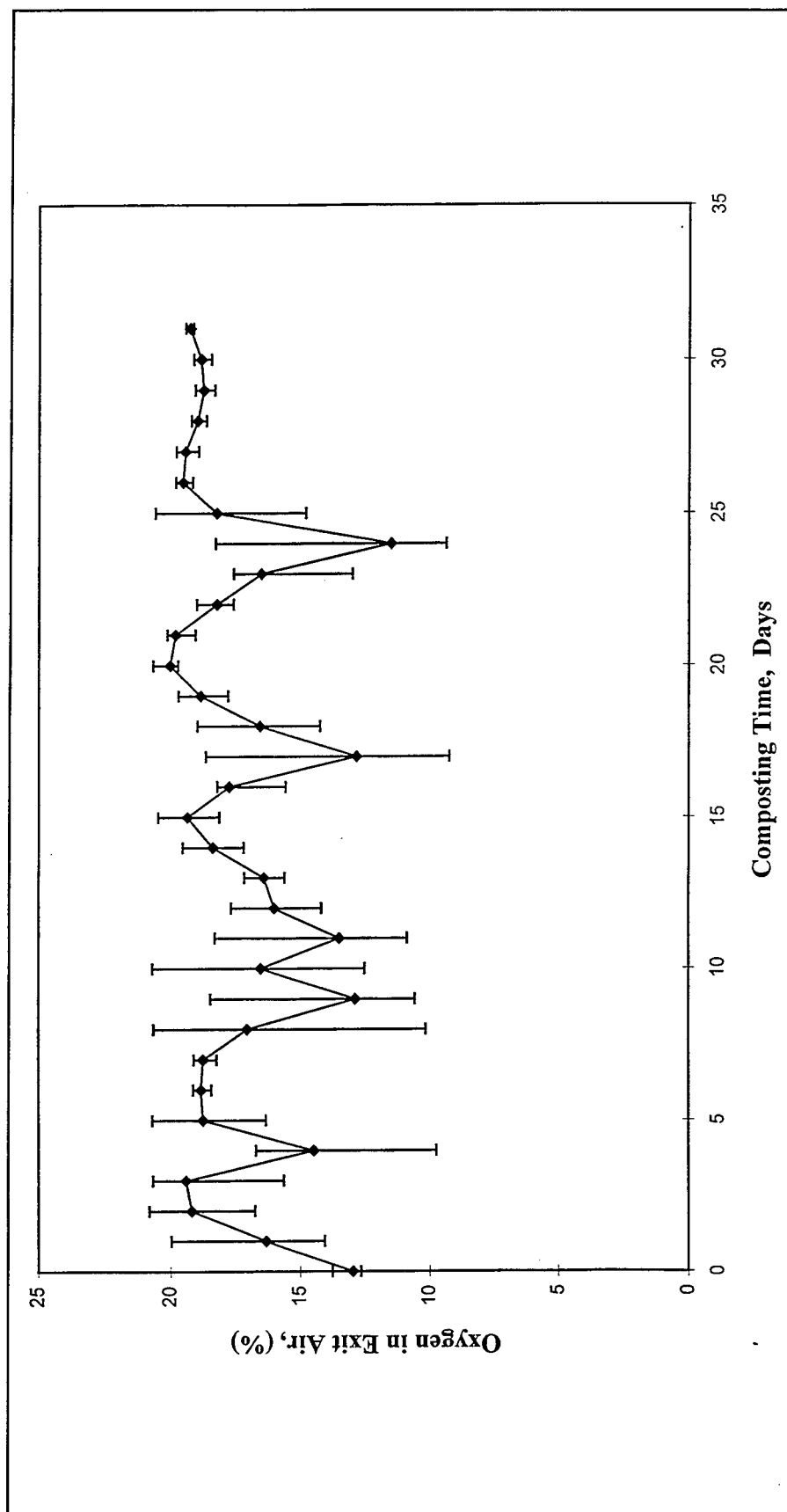


Figure 17. Mix 7B maximum and minimum oxygen in exit air profile

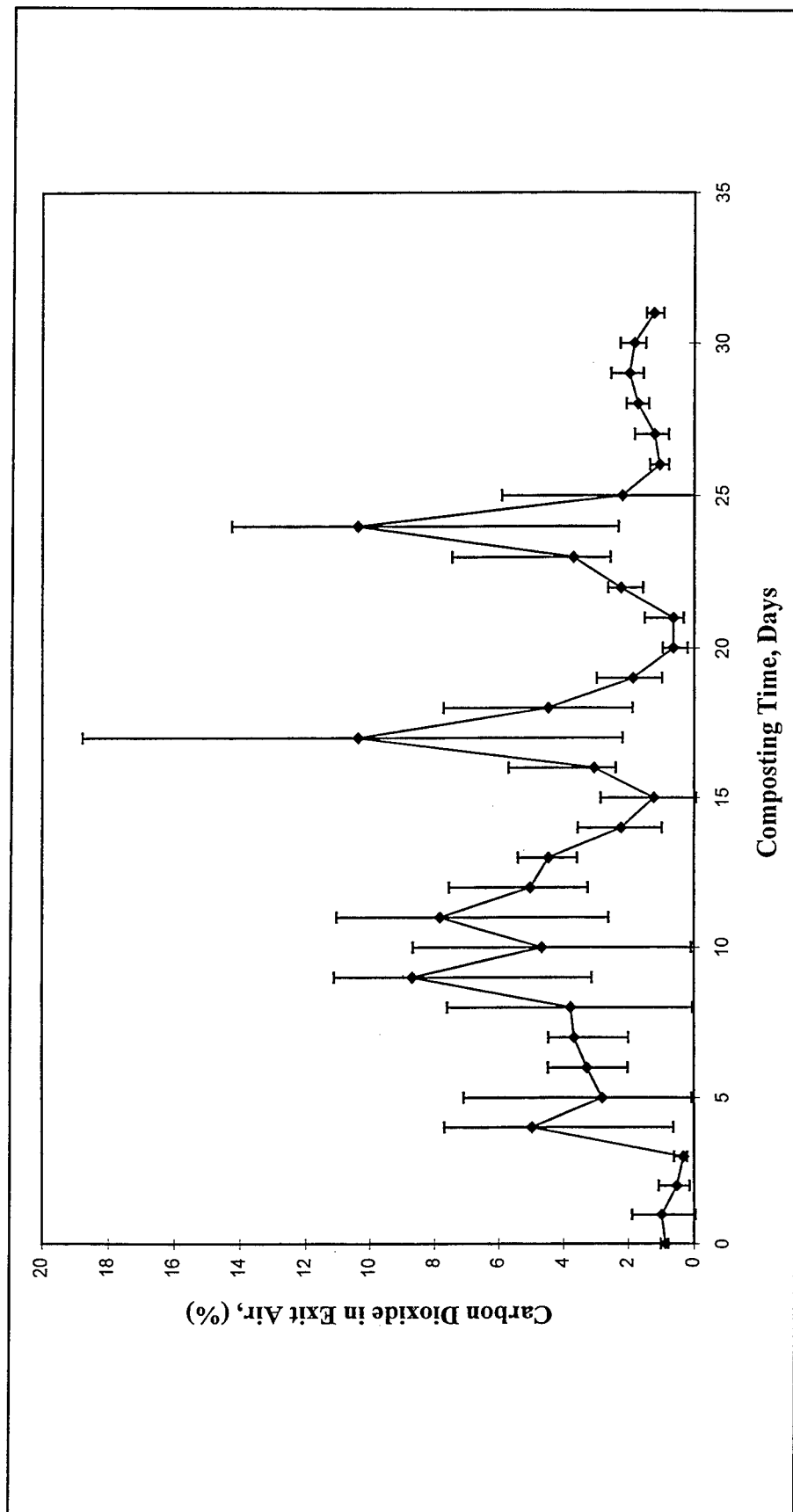


Figure 18. Mix 7B maximum and minimum carbon dioxide in exit air profile

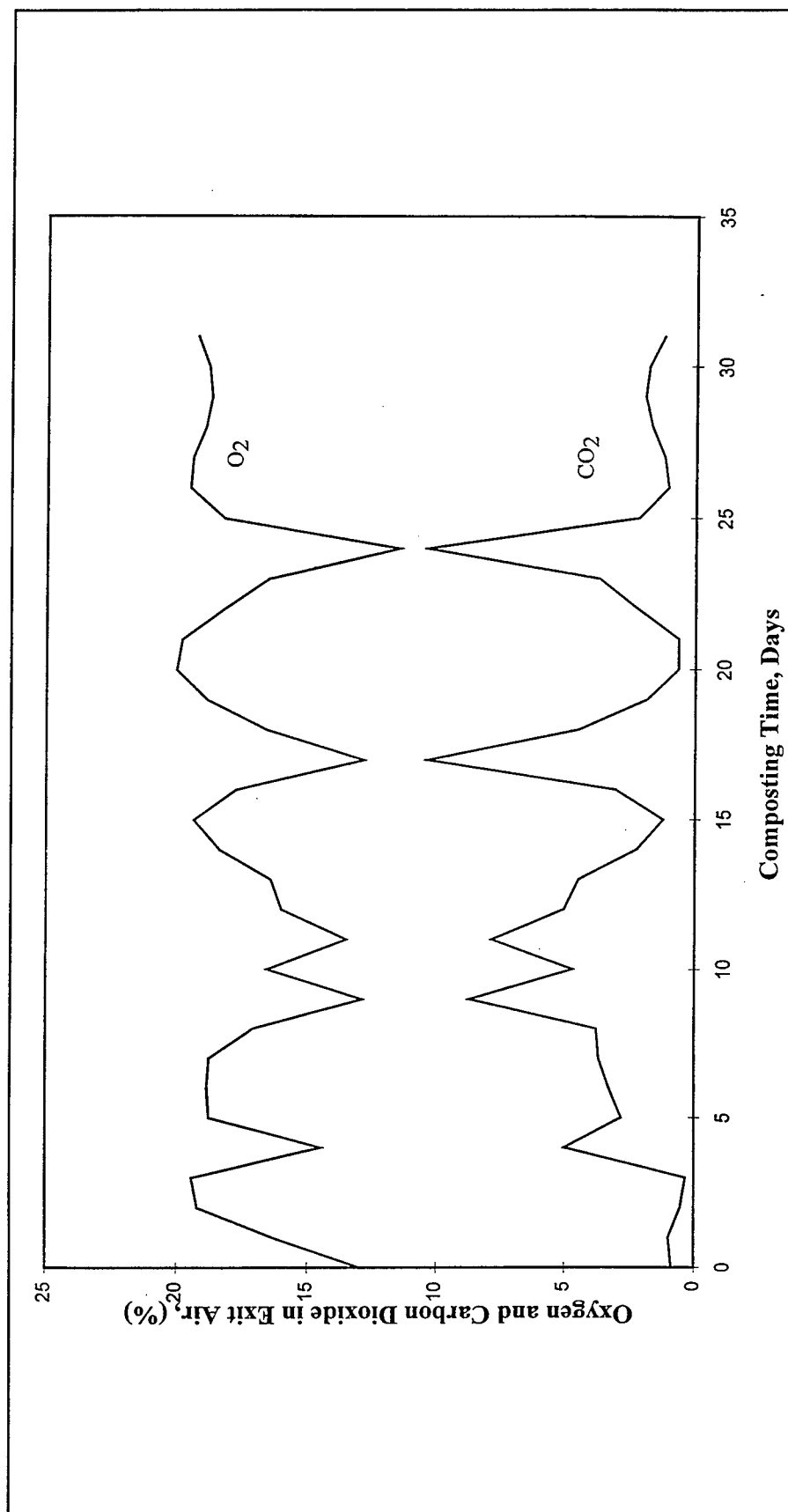


Figure 19. Mix 7B respiration rate during composting

Table 9
Pilot Scale - Result of Explosives Analysis and Standard Deviation (SD) for
Mix 7A and Mix 7B

Mixture 7A Explosive Concentrations, mg/kg										
Day No.	TNT		RDX		HMX		4A-DNT		2A-DNT	
	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD
0	21,203	1,428	1,633	72	7,412	957	360	15	382	5
3	17,522	251	1,518	87	7,480	1,963	367	34	309	37
5	12,630	1,368	1,352	103	5,128	862	602	81	537	98
15	246	100	1,176	45	5,486	336	866	96	342	66
20	22	2	825	90	5,429	785	338	37	68	13
25	21	8	579	133	5,255	559	199	38	28	7
30	20	2	291	67	5,580	905	129	24	22	9
Soil	18,867	1,041	1,290	78	26,567	764	<10.0	---	<10.0	---
Mixture 7B Explosive Concentrations, mg/kg										
0	9,599	1,312	906	113	6,950	1,743	644	122	304	89
3	8,641	730	1,313	57	7,516	1,091	807	11	789	29
5	2,130	175	1,223	107	8,107	531	1,292	140	1,141	144
15	22	2	839	41	5,066	567	420	18	56	9
20	23	2	751	106	6,105	229	319	35	51	10
25	17	1	240	27	5,361	250	88	9	21	4
30	17	1	107	14	5,003	722	55	3	13	1
Soil	13,050	150	905	16	23,933	2,277	<10.0	---	<10.0	---

25 and 28 percent for Mixes 7A and 7B, respectively. RDX concentration was reduced by 82 and 88 percent for Mixes 7A and 7B, respectively. TNT concentration was reduced by 99.9 and 99.8 percent for Mixes 7A and 7B, respectively. The TNT biotransformation products (2A- and 4A-DNT) concentrations increased initially, but later decreased to less than 100 mg/kg, except for 4A-DNT in Mix 7A.

The concentration of the majority of the explosives was significantly reduced after 15 days of composting. The explosive removal efficiency from the 14-L bench-scale system (WACS II) and the 40-L pilot-scale system (Oxymax) was similar (Figure 20) except for HMX. The results of the explosives concentration in the soil and standard deviation are also presented in Table 9. As in the WACS II system, the concentrations of explosives in the Rockeye soil compared with the day 0 concentrations were different. An explanation would be the heterogeneity of the soil matrix and possible TNT crystals in part of the soil matrix. Overall, the explosives half-lives, substrate degradation rate, and SBR were comparable except for HMX (Table 10). The half-life of TNT was approximately 4 days for each

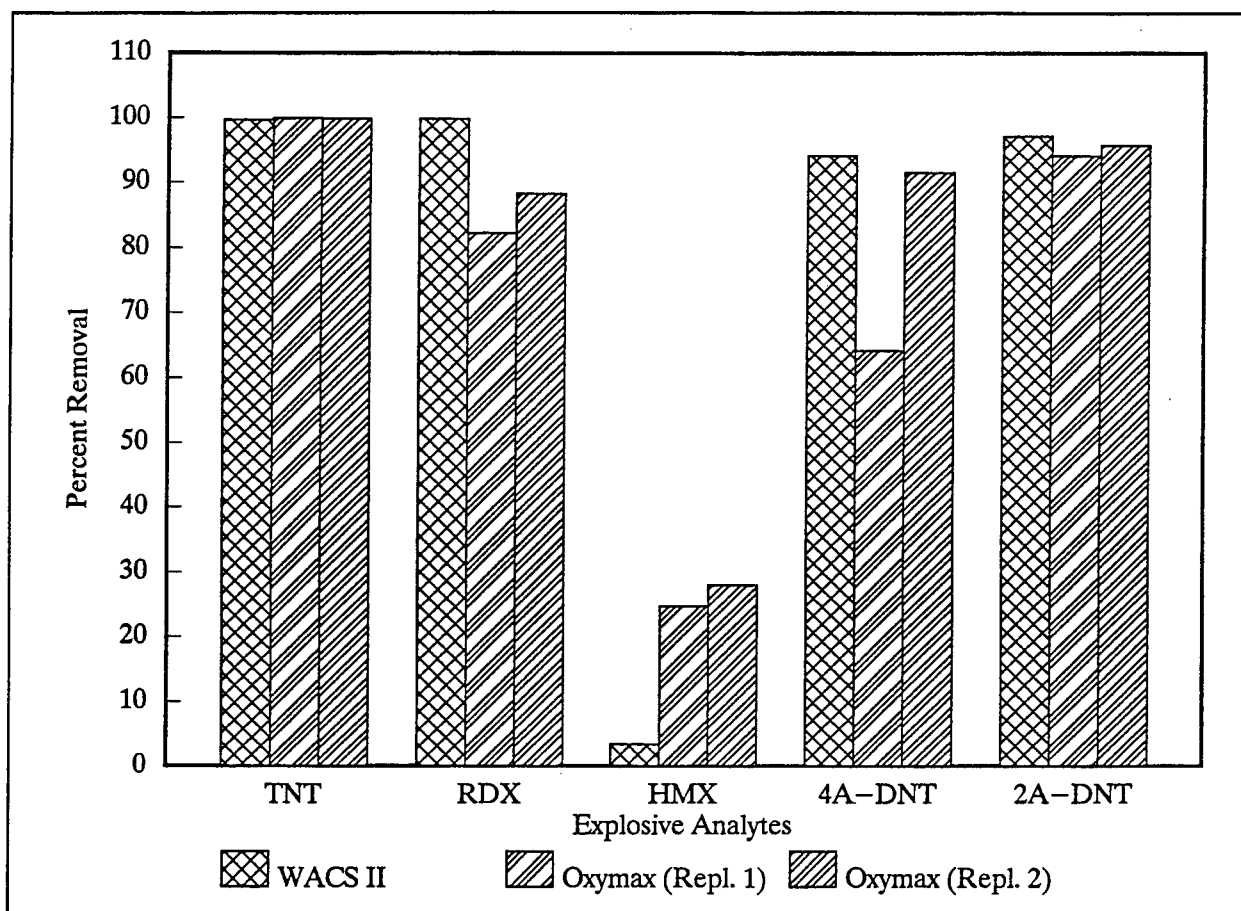


Figure 20. Percent removal of explosive analytes for each compost system

Table 10

Compost Mixture 7 - Explosives Result Comparison of the WACS II and Oxymax Compost Systems

Compost Systems	Explosive and Transformation Analytes														
	TNT			RDX			HMX			4A-DNT			2A-DNT		
	$t_{1/2}$ days	k_d d ⁻¹	SBR d ⁻¹	$t_{1/2}$ days	k_d d ⁻¹	SBR d ⁻¹	$t_{1/2}$ days	k_d d ⁻¹	SBR d ⁻¹	$t_{1/2}$ days	k_d d ⁻¹	SBR d ⁻¹	$t_{1/2}$ days	k_d d ⁻¹	SBR d ⁻¹
WACS II	3.64	0.190	0.033	3.29	0.211	0.033	619.39	0.001	0.001	7.35	0.094	0.031	5.90	0.118	0.032
Oxymax (Mix 7A)	3.98	0.174	0.033	12.03	0.058	0.027	73.23	0.010	0.008	7.45	0.093	0.021	7.28	0.095	0.031
Oxymax (Mix 7B)	3.28	0.211	0.033	9.73	0.071	0.029	63.25	0.011	0.009	8.45	0.082	0.031	6.60	0.105	0.032

compost system. The half-life of HMX was as low as 63 days for the Oxymax (Repl. 2) system and as high as 619 days for the WACS II system.

Researchers previously reported that the majority of the disappeared TNT was incorporated into humic material (Pennington et al. 1995). Hence, the toxicological tests were conducted to evaluate how safe and environment-friendly the finished compost was with explosive compounds binding into the humic material.

Mutatox™

Mutatox™ results are presented in Table 11. Each number represents the average degree of light output from four replicate samples. In some instances, the dilutions were acutely toxic to the bacteria. The values indicate the range of mutagenicity of the extract dilution series as determined by the modified two-fold rule. A higher number indicates a higher degree of mutagenicity. Table 11 shows that the Rockeye soil was acutely toxic at 1:1 to 1:64 dilutions and the three lower dilutions (1:80, 1:128, and 1:160) were mildly mutagenic. The Mix 7A initial and Mix 7B initial samples caused bacterial mortality, but to a lesser degree than the Rockeye soil, probably due to the dilution of the Rockeye soil with the compost amendments. The degree of mutagenicity in the Rockeye soil and in the two initial mixes are relatively comparable.

Table 11					
Pilot Scale - Mutatox™ Results					
Dilution	Rockeye Soil	Mixture 7A		Mixture 7B	
		Initial	Final	Initial	Final
1:1	Toxic	Toxic	972	Toxic	2,176
1:2	Toxic	Toxic	5,077	Toxic	2,961
1:4	Toxic	Toxic	2,578	Toxic	1,282
1:8	Toxic	183	3,644	Toxic	199
1:16	Toxic	124	489	Toxic	51
1:32	Toxic	56	55	Toxic	13
1:40	Toxic	38	13	147	7
1:64	Toxic	37	8	25	7
1:80	54	--	7	36	7
1:128	19	--	6	6	4
1:160	12	--	--	--	--
Note: Value indicates range of mutagenicity.					

Composting apparently reduced the bacterial acute toxicity of the extracts as shown by the lack of toxicity in the two final mixes. However, the degree of mutagenicity increased dramatically. This can probably be attributed to TNT degradation products formed during composting.

Earthworm acute toxicity

Table 12 contains earthworm acute toxicity results. Each number represents the mean percent mortality of three replicate samples. The Rockeye soil was extremely toxic, with 100 percent mortality at all dilutions. The Mix 7A initial and Mix 7B initial samples yielded LC_{50} of 4.4 percent as determined by linear interpolation (Stephen 1977). Therefore, a mixture of 4.4 percent of either Mix 7A initial or Mix 7B initial in noncontaminated soil would be expected to kill 50 percent of the earthworms exposed to the mixture. The decrease in toxicity can again be contributed to the dilutional effect of adding the composting amendments to the Rockeye soil.

Table 12
Pilot Scale - Percent Mortality from the Earthworm
Acute Toxicity Results

Dilution	Rockeye Soil	Mixture 7A		Mixture 7B	
		Initial	Final	Initial	Final
1:1	100	100	100	100	50
1:2	100	100	100	100	0
1:4	100	100	0	100	0
1:8	100	100	0	100	0
1:16	100	100	0	100	0
1:32	100	0	0	0	0

Mix 7A final and Mix 7B final samples yielded LC_{50} of 35.3 percent and 100 percent, respectively. Apparently, composting reduced the acute toxicity of the Rockeye soil to the earthworms (the higher the LC_{50} value, the less toxic).

6 Conclusions and Recommendations

Conclusions

Mixture or various combination of amendments and bulking agents were evaluated for composting using the respirometer as a screening tool. The bench-scale composting with the compost mixture selected from the respirometry was used to test the effectiveness of explosives compounds removal in actual composting environments. The efficacy of the selected compost mixture was evaluated in reducing the toxicity of explosives-contaminated soils by the Mutatox™ assay and earth-worm acute toxicity.

Based on the results of the respirometric, bench-scale/pilot-scale compost, metal leachability, and toxicity experiments, the following is concluded:

- a. Of eight compost mixes used in the respirometric study, Mix 4 (40 percent pig manure, 40 percent recycled paper, and 20 percent soil) and Mix 7 (40 percent cow manure, 40 percent alfalfa, and 20 percent soil) were ranked the highest.
- b. Although most effective in removing explosives from the respirometric study at 40 °C, SBR and the substrate rate coefficient of Mix 4 were the lowest among the eight mixtures. This low substrate degradation rate may lead to insufficient self-heat-generation capability and anaerobic conditions if used in actual field compost piles. Since unsanitized and odor producing compost may be the outcome of the Mix 4, Mix 7 was selected for subsequent bench-scale compost study.
- c. The bench-scale composting study had an overall average rate of aeration of 0.43 m³ air/kg VS-d. The moisture content decreased slightly but maintained at an optimal range of 44.9 to 48.2 percent. The substrate degradation rate slowed down considerably during the later stage of composting, resulting in the temperature drop, and almost no volatile solid destruction was observed after 15 days of composting.

- d. TKN values continuously decreased over the entire composting period. Several reasons for this observation may be volatilization loss of ammonia-N during the initial composting phase and nitrification during the final phase of composting. The decrease in TKN during the later stage of composting resulted in an increase in C/N ratio from 30.7 on day 15 to 34.7 on day 35.
- e. EC values followed the C/N ratio trend during composting. The volatile organic acid destruction in the beginning and the generation of nitrate at the later state may be the reasons for the decrease and increase in values.
- f. Majority of the explosive and transformation product concentrations using the WACS II system were reduced within the first 15 days of composting. The explosive concentration results were similar to those of the 10-day respirometric study except for the HMX concentration. Compost Mix 7 apparently did not reduce the HMX concentration compared with the 40 percent reduction from the 10 days of respirometric study.
- g. From the Oxymax system, HMX concentration was reduced 25 and 28 percent for Mixes 7A and 7B, respectively. RDX concentration was reduced 82 and 88 percent for Mixes 7A and 7B, respectively. TNT concentration was reduced 99.9 and 99.8 percent for Mixes 7A and 7B, respectively. The transformation products, 2A- and 4A-DNT, concentrations increased initially, but later decreased to less than 100 mg/kg, except for 4A-DNT in Mix 7A.
- h. The Oxymax and the WACS II systems' overall degradation and explosives removal data were similar, except for HMX.
- i. From the TCLP results, Pb and Cd are not expected to be leachable.
- j. The similar removal patterns of most explosives compounds from both respirometry and composting support the use of simple and short respirometric tests to screen for the best compost mixtures. However, the exceptions, like HMX, still necessitate the use of bench-scale composting in order to verify or reinstate the removal capacity of the chosen mixes under actual composting environments before implementing pilot-/field-scale composting systems.
- k. The toxicity study showed that the Rockeye soil was extremely toxic, with 100 percent mortality, even after dilutions.
- l. The composting process apparently reduced the acute toxicity of the Rockeye soil; however, the finished compost product was still acutely toxic and cannot be considered ecologically safe. The increased mutagenic potency of the compost extracts points to the production of reactive degradation products during the composting process.

Recommendations

Based on the results of this study, it is recommended that a compost mixture of cow manure and alfalfa be utilized in the pilot-scale study at NSWC sites. Turkey manure, POTW, and sawdust (Mix 7A and 5) may also be proven to be beneficial in a pilot-scale study. Additional toxicity studies should be conducted to relate the remediation composting engineering design and operation to the quality of compost in terms of target chemical removal and toxicity reduction.

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13. ABSTRACT (Maximum 200 words) Bench-scale compost and toxicology studies were conducted at the Waterways Experiment Station to evaluate the treatment of explosives-contaminated soil at Crane, Indiana. The goal of the study was to evaluate and to select the best combination of amendments, contaminated soils, and bulking agents to be utilized in the compost technology for remediation explosives-contaminated soils. The utilization of the technology for remediating explosives-contaminated soils is economically advantageous if inexpensive amendments were available in adequate quantities. The respirometric test was utilized to provide a general indication of biological activity within eight compost mixtures. The respirometry was used as a tool for the specific screening of compost mixtures. The bench-scale compost reactor test was to extend the respirometric study by evaluating the applicability of the screened compost mixtures. Another goal of the bench-scale test was to determine the leachability of lead, cadmium, and mercury. The toxicity test was used to evaluate the toxicity of the composted soils. A survey of locally available sources of amendments and bulking agents was conducted. Several combinations of these amendments and bulking agents were evaluated via computer program to determine the best (Continued)					
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combination. This program calculated the carbon/nitrogen ratio of a mixture by using input values of each amendment and bulking agents such as percent carbon, nitrogen, organic matter, and moisture. Eight compost mixtures were evaluated to determine if biological activity and if the reduction in explosive concentration would occur using the respirometer. The oxygen sensing respirometer was used as an isothermic compost reactor to determine optimal substrate utilization of each mixture. Each mixture was evaluated for explosive degradation. Using the substrate rate and explosive degradation rate, an overall ranking of explosives half-life was determined for each mixture. The results showed two mixes had the best overall ranking (cow manure and alfalfa (Mix 7) and swine manure and recycled paper (Mix 4)). Although most effective in removing explosives from the respirometric test, substrate rate and substrate rate coefficient of Mix 4 were the lowest of the eight mixtures. This low substrate degradation rate along with its slurry form may lead to insufficient self-heating capability and anaerobic conditions. The slurry form of Mix 4 appeared not to possess the structural integrity of normal compost. This was not observed during the respirometer test. Therefore, Mix 7 was the only mix that advanced to the bench-scale composting test.

The bench-scale composting study validated the explosives removal capacity of the Mix 7. The WACS II (14-L reactor) and Oxymax (40-L pilot-scale) systems performed well in simulating the actual field-scale compost piles by providing adequate insulation so that the amount of energy generated was able to raise its temperature above thermophilic range. The Oxymax system provided enough composted material to perform metal leachability, toxicological, and mutagenic experiments. Both systems reached thermophilic temperature (50 °C). The compost mixtures returned to ambient temperature after 10 days of composting. The compost tests were conducted for 30 days. The majority of the explosives and transformation products were removed within the first 15 days of composting. These results paralleled that of the 10-day respirometric study except for HMX. The HMX concentration was not reduced, contrasting 40 percent reduction during the respirometric study. The TCLP test was conducted on the final compost mix. The results show that lead and cadmium were not expected to be leachable. The TNT concentrations were reduced to below detection limits.

The toxicity test was conducted on the composted material of Mix 7 and the Rockeye soil. Two assays were used to evaluate the efficacy of composting in reducing the toxicity of the explosives-contaminated soils: the Mutatox™ assay and the earthworm acute toxicity test. The Mutatox™ assay is a proprietary assay that determines the mutagenic potential of sample extracts. The earthworm acute toxicity test estimates the acute toxicity of the composted material to the earthworms in a 14-day static test. It also assesses the toxicity of only the bioavailable contaminants. The combination of the Mutatox™ and earthworm acute assays provides a picture of the acute and mutagenic toxicity of the soil in addition to the bioavailability of the soil contaminants.