Technical Report IRRP-97-1
February 1997

**US Army Corps
of Engineers**
Waterways Experiment
Station

Installation Restoration Research Program

Bench-Scale Remediation Composting: Process Principles and Protocol

by Kurt T. Preston, Steve Seiden, WES
Kyoung S. Ro, Louisiana State University

Prepared for Headquarters, U.S. Army Corps of Engineers

PRINTED ON RECYCLED PAPER

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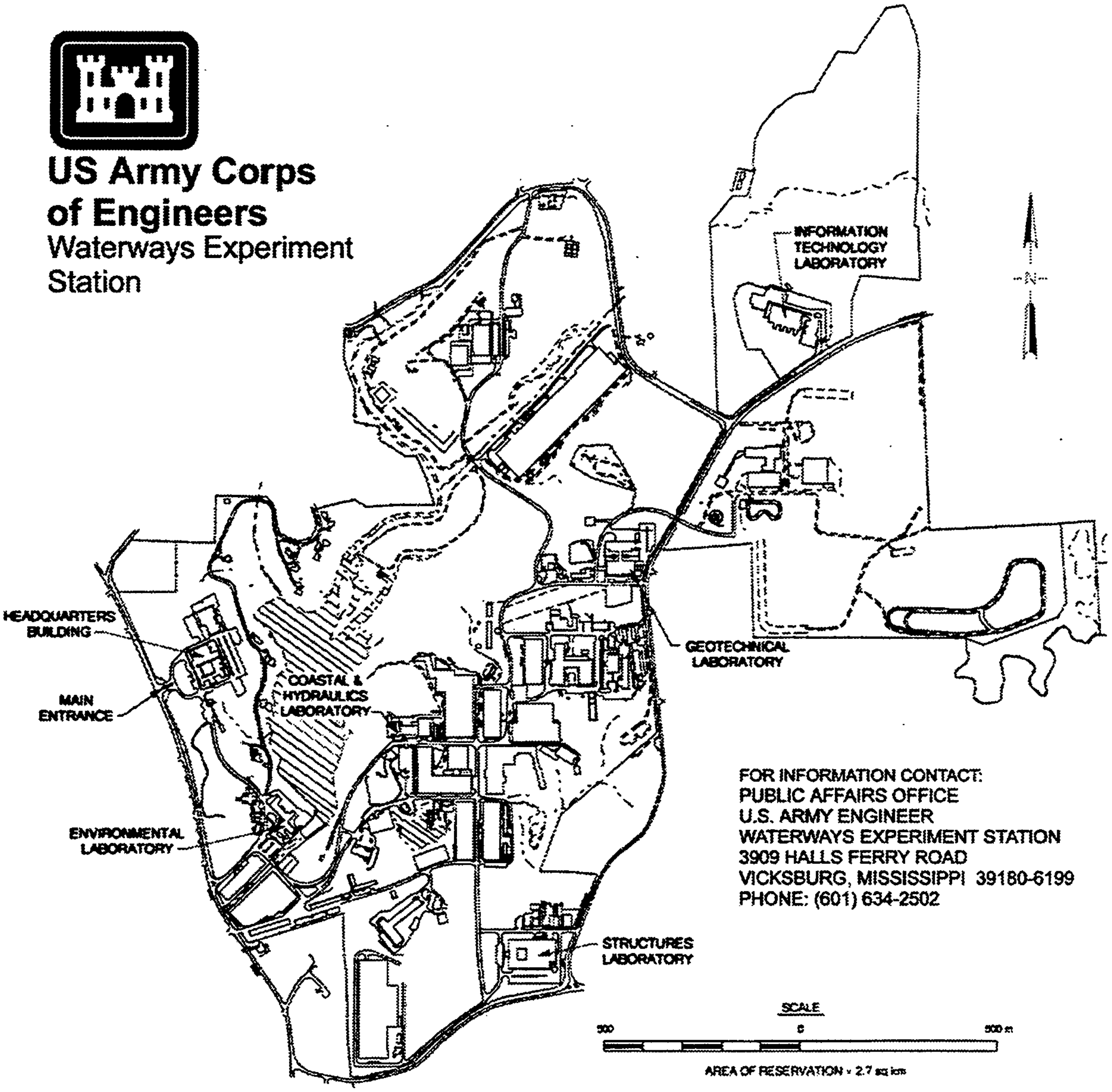
Final report

Approved for public release; distribution is unlimited

Prepared for U.S. Army Corps of Engineers
Washington, DC 20314-1000

US Army Corps of Engineers
Waterways Experiment Station



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Waterways Experiment Station Cataloging-in-Publication Data

Preston, Kurt T.
Bench-scale remediation composting : process principles and protocol / by Kurt T. Preston, Steve Seiden, Kyoung S. Ro ; prepared for U.S. Army Corps of Engineers.
100 p. : ill. ; 28 cm. — (Technical report ; IRRP-97-1)
Includes bibliographic references.
1. Compost — Design. 2. Soil remediation — Design. 3. Soil pollution — Environmental aspects. I. Seiden, Steve. II. Ro, Kyoung Sin, 1958- III. United States. Army. Corps of Engineers. IV. U.S. Army Engineer Waterways Experiment Station. V. Installation Restoration Research Program. VI. Series: Technical report (U.S. Army Engineer Waterways Experiment Station) ; IRRP-97-1.
TA7 W34 no.IRRP-97-1

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Preface

The work reported herein was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) as part of the Installation Restoration Research Program (IRRP) and the U.S. Army Environmental Quality Technology (EQT) Research Program.

Dr. Clem Meyer was the IRRP Coordinator at the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers (HQUSACE). Dr. Bob York of the U.S. Army Environmental Center and Mr. Jim Baliff of the Environmental Restoration Division, Directorate of Military Programs, HQUSACE, served as the IRRP Overview Committee. Dr. John Cullinane, WES, was the EQT Program Manager.

Dr. Kurt T. Preston of the Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES, prepared the report along with Dr. Kyoung S. Ro and Mr. Steve Seiden, under contract to ERB. At the time of publication, Dr. Ro was employed by the Civil Engineering Department, Louisiana State University, and Mr. Seiden remains under contract at ERB.

The work was conducted under the direct supervision of Mr. Danny Averett, Chief, ERB; and the general supervision of Mr. Norman Francingues, Chief, EED; and Dr. John W. Keeley, Director, EL.

At the time of publication, Dr. Robert W. Whalin was Director of WES. COL Bruce K. Howard, EN, was Commander.

This report should be cited as follows:

Preston, K. T., Ro, K. S., and Seiden, S. (1997). "Bench-scale remediation composting: Process principles and protocol," Technical Report IRRP-97-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

1 Introduction

Background

Past military and industrial activities have contaminated numerous U.S. Army installations with metals, solvents, and explosives. Federal law requires that the Department of the Army establish and implement an Installation Restoration Program (IRP) to clean up installations contaminated with hazardous material. Early assessments of the IRP revealed the immense scope of the needed restoration effort. Many of the contaminants found at these sites are unique to military-related activities. The installations require effective, efficient, and economic solutions to solve the problems created by the manufacturing, use, and disposal of hazardous and toxic materials, military unique and otherwise.

Composting is a complex biogeochemical process occurring at elevated temperatures. Haug (1993) defines composting as the biological decomposition and stabilization of organic substances under conditions that allow development of mesophilic temperatures (approximately 35 °C) and thermophilic temperatures (approximately 55 °C) as a result of biologically produced heat, with a final product sufficiently stable for storage and application to land without adverse environmental effects. Microorganisms such as bacteria and fungi break down solid organic substrates through extracellular hydrolysis and subsequent catabolic biodegradation, resulting in formation of heat, which raises the temperature of compost piles. Although composting has been used historically to improve soil fertility and stabilize municipal solid wastes (MSW), until recently few researchers have recognized its potential to become an economic and environment-friendly alternative remediation technology that may replace the current practice of incineration.

Several researchers investigated the fate of polycyclic aromatic hydrocarbons (PAHs) during composting. Suler (1979) reported that a synthetic oil was readily degraded in a composting system; however, crankcase oil waste was found not only difficult to degrade, but inhibitory to the degradation of organic substrates. Ryan, Kabrick, and Loehr (1988) discussed the successful pilot-scale composting system at Utah State University for treating diesel-fuel contaminated soils. Szabo et al. (1988) observed that more than 50 percent of PAHs disappeared after composting. Yusuf, Johnson, and Won (1991) investigated the mineralization of ring-labeled pyrene. They found that about 70 percent of original pyrene disappeared, but only about 20 percent was converted to CO_2. They assumed that the balance of the pyrene was biotransformed into intermediate metabolites. This research did not show any evidence for the assumption nor discuss the humification of the pyrene.

Composting was also used to treat soils and sediment contaminated with explosive compounds. Louisiana Army Ammunition Plant (LAAP) lagoon sediments contaminated with 2,4,6-trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrohydrazine (RDX), 1,3,5,7-hexahydro-1,3,5,7-tetranitrotriazine (HMX), and n-2,4,6-tetranitro-N-methylaniline (Tetryl) were composted with a mixture of horse manure, alfalfa, and horse feed in the form of ventilated static compost piles (U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) 1988; Garg, Grasso, and Hoag 1991). For the U.S. Army, the focus became the composting of soils contaminated with explosive compounds. This focus led to the performance of pilot operations in three locations around the country: LAAP, Badger Army Ammunition Plant, and Umatilla Army Depot Activity. Each of these investigations resulted in an apparent reduction of explosive contamination (USATHAMA 1988). The explosive compounds decreased with half-lives of 27.36 and 16.6 days for mesophilic and thermophilic conditions, respectively. Williams and Myler (1990) estimated the treatment cost of about $100 per ton of soil using composting, which was compared favorably with the incineration costs of about $250 per ton or higher.

Also, during the pilot work performed at Umatilla near Hermiston, WA, an investigation regarding microbial seeding of active compost already acclimated to the explosive compounds was conducted. The seeding did not improve the disappearance of explosive compounds from the contaminated soils (U.S. Army Environmental Center (USAEC) 1993).

The results of these pioneering pilot investigations suggest the potential of composting as an economical alternative technology to remediate soils contaminated with explosive compounds. Kaplan and Kaplan (1982a), however, warned that the biochemical fate of a hazardous compound must be known before composting could be considered as a viable treatment alternative. Using a laboratory composting system and ^{14}C-TNT, Kaplan and Kaplan (1982b) reported that no significant amount of CO_2 or volatile amines were produced from degradation of TNT, and a majority of radioactivity was recovered in the ether fraction. From further analysis, TNT, 2-amino-4,6-dinitrotoluene (2ADNT), 4-amino-2,6-dinitrotoluene (4ADNT), 2,2',6,6'-tetranitro-4,4'-azoxytoluene, and 2',4,6,6'-tetranitro-2,4'-azoxytoluene were recovered in solvent extracts after 91 days of composting at 55 °C. Approximately 22 percent of total radioactivity was recovered in the insoluble organic matter fractions, which were separated into humic acid, fulvic acid, and humin. Since these reduced TNT compounds were the major TNT biotransformation products through the reductive pathway hypothesized by Levinson, McCormick, and Feeherry (1976), Kaplan and Kaplan (1982b) postulated a similar biotransformation scheme for TNT in compost. The end products of the proposed biotransformation scheme are as toxic and mutagenic as TNT (Kaplan and Kaplan 1982c; Won, DiSalvo, and Ng 1976).

The hypothesis of reductive biotransformation pathway and the subsequent polymerization of amino-dinitrotoluenes was challenged by Doyle and Isbister (1982). Using laboratory- and pilot-scale compost reactors, they evaluated treatability of TNT and RDX. Although most of initial TNT concentration disappeared after 3 weeks of composting at 55 °C, less than 0.5 percent of ^{14}C-TNT was recovered as $^{14}CO_2$. In contrast, a significant portion of RDX was mineralized to $^{14}CO_2$ (55.8 percent). Interestingly, only small quantities of 2A- or 4A-DNTs, major mesophilic metabolites of the Kaplan and Kaplan's reductive composting biotransformation pathway, were found at the end of incubation. They postulated that another unique composting biotransformation pathway must be responsible for the incorporation of TNT into the solvent-insoluble fractions. Isbister et al. (1984) speculated on the possibility of Kaplan and Kaplan not achieving proper composting environment and/or the formation of the reductive by-products during drying or extraction procedures in order to explain the discrepancy.

Pennington et al. (1995) recently reported similar results to that of Kaplan and Kaplan from a composting study of contaminated soils from Umatilla Munitions Depot Activity, Umatilla, OR. Using radiolabeled TNT in a laboratory composting system, they completed the mass balance of the TNT in various compartments of the composting environment. The compartments were acetonitrile and ether extractable, humic and fulvic acids, humin, and cellulose fractions. More than half of the initial radioactivity was recovered in the cellulose and humic fractions after 20 days of composting at approximately 50 °C. The stability of TNT and other by-products in those organic fractions of the soil is not clearly understood at this time. The reductive TNT by-products (4A-DNT and 2A-DNT) clearly increased after 20 days of composting, which partially supported the Kaplan and Kaplan's hypothesis. Also, a significant portion of RDX was removed after 20 days of composting (about 68 percent), which compared well with 54- to 62-percent RDX reduction after 3 weeks of greenhouse composting reported by Doyle and Isbister (1982). However, only 20 percent of added ^{14}C-RDX was recovered in the laboratory compost systems after 3 weeks (Doyle and Isbister 1982).

The remediation composting technology is still in its embryonic stage. Although previous studies demonstrated that the parent explosive compounds and the bacterial mutagenicity and toxicity of the soils were substantially reduced from composting (Griest et al. 1993), the ultimate fate of the biotransformed explosives and the potential danger of slowly leaching the bound explosives and the by-products are not known at this time. The effects of many variables, such as physicochemical and biological characteristics of organic substrates and inert materials, other environmental conditions of the system on the fate of contaminants and the safety of the humified final products, and a better understanding of the ultimate fate of the compounds would aid acceptance of composting as a remediation method by scientific and regulatory communities and speed public support. At this point, the best evidence of the benefits associated with composting are clear indications of contaminant transformation and toxicity reduction.

A sound bench-scale remediation composting system that closely simulates the actual composting process is critically needed to conduct further comprehensive remediation composting study. The future remediation composting experiments must be pursued in controlled environments. Without the bench-scale remediation composting system, the high capital and operating costs of pilot- or field-scale composting severely limit the much needed composting research covering many experimental variables. The preliminary feasibility and optimization, the ultimate fate of the contaminants, and the health risk of composted products should be determined through the bench-scale tests. Then, pilot-scale studies can be initiated to cover the scale-up factors and the heterogeneity of field conditions, and, finally, successful field operations can be implemented.

The standard composting method of ASTM D5338 uses incubators in order to externally control the compost reactors at predefined temperatures (35 °C for 1 day, 55 °C for 28 days, and 35 °C for about 16 days). Most previous investigators have used similar apparatus for their laboratory-scale composting reactors. 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. 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 25 to 50 yd^3 in order to retain the heat (Hanif 1995).[1]

A few researchers used feed-back 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 Halbach 1994; Hogan, Miller, and Finstein 1989; Magalhaes et al. 1993). The small bench-scale remediation composting systems require much more precise design and operational parameters in order to be successful, compared with rather insensitive but more stable pilot-scale compost piles. Unfortunately, the design and operations of most compost systems have been based on empirical knowledge, and much of systematic engineering principles applied to other remediation technologies are absent. As a result, successful design and operation of one type of bench remediation system may not guarantee the success of other types of composting systems.

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[1] To convert cubic yards to cubic meters, multiply by 0.7645549.

Objectives

The objectives of this report are (a) to review principles of biochemical process kinetics, mass and heat transfer, and major process parameters of the remediation composting systems and (b) to provide a technical foundation for standard bench-scale remediation composting process protocol.

2 Process Kinetics, Mass and Heat Transfer of Composting

The important scientific and engineering considerations are process kinetics of biodegradable organic substrates, biotransformation of contaminants, oxygen and water vapor mass transport, and heat transfer within the compost matrix. Substrate utilization kinetic information determines how fast substrates are consumed by compost biomass. This activity in turn relates to substrate oxidation and heat generation. If the biogeochemical pathway of the contaminants in the compost produces environmentally safe by-products and end products, the contaminant degradation/transformation kinetic information provides the length of time required to achieve remediation goals.

Another important parameter is gas transfer. Oxygen acts as a terminal electron acceptor for microorganisms in the aerobic compost matrix. Water vapor absorbs heat from surroundings and evaporates into the unsaturated gas phase. Mass transport of water vapor at the water surface determines how fast water evaporates and, consequently, how fast it cools the compost. The amount of heat generated from degrading organic substrates must be enough to raise and maintain the compost temperature at thermophilic conditions, balancing the heat loss through conduction, convection, and evaporation.

Kinetics of Organic Substrate Utilization

A compost reactor is a three-phase heterogenous system. Organic substrates are in solid form, and the water is limited to bound water in the pore space between the solid particles. Gas fills the rest of the pore space. Most of the microorganisms attach to the substrate surface covered by water and solubilize the substrates before uptake to the cell membranes.

Haug (1993) hypothesized the following metabolic sequence of the events for organic substrates degradation.

a. The extracelluar hydrolytic enzymes released from microbial cells are transported to the substrate surface.

b. The solid substrate is hydrolyzed into low molecular weight fragments and into soluble fractions.

c. The solubilized substrate molecules are transported to the surface of cells and subsequently into the cells.

d. Oxygen is bulk transported from the pore air space through the liquid layers and into the cells.

e. Finally, the substrates and the oxygen are aerobically metabolized inside the cells.

The above microbial metabolic activities are illustrated in Figure 1.

Failure of the sequence may severely limit the overall kinetic process. For instance, if oxygen is unavailable, solubilization may be very slow and consequently control the overall kinetic process. In an anaerobic digester, solid substrates are solubilized by hydrolase released by anaerobic microorganisms. Therefore, the digested sludge will contain solid substrates that are resistant to hydrolysis. Assuming hydrolytic enzymatic reaction sequences similar to that of Michael Menten's saturation kinetic, the hydrolysis kinetic is expressed as (Haug 1993):

$$v = -ds/dt = (k_3 a_o e_o) / (K_a + e_o) \qquad (1)$$

where

v = rate of hydrolysis reaction

k_3 = rate coefficient

a_o = total number of reaction sites per unit volume of substrate

e_o = total concentration of hydrolytic enzymes

K_a = half-saturation concentration

t = time

s = substrate

Since the total enzyme concentration and the total number of reaction sites per unit volume of substrate can be related to a biomass concentration (X) and a specific surface area of substrate (a_v), Equation 1 becomes

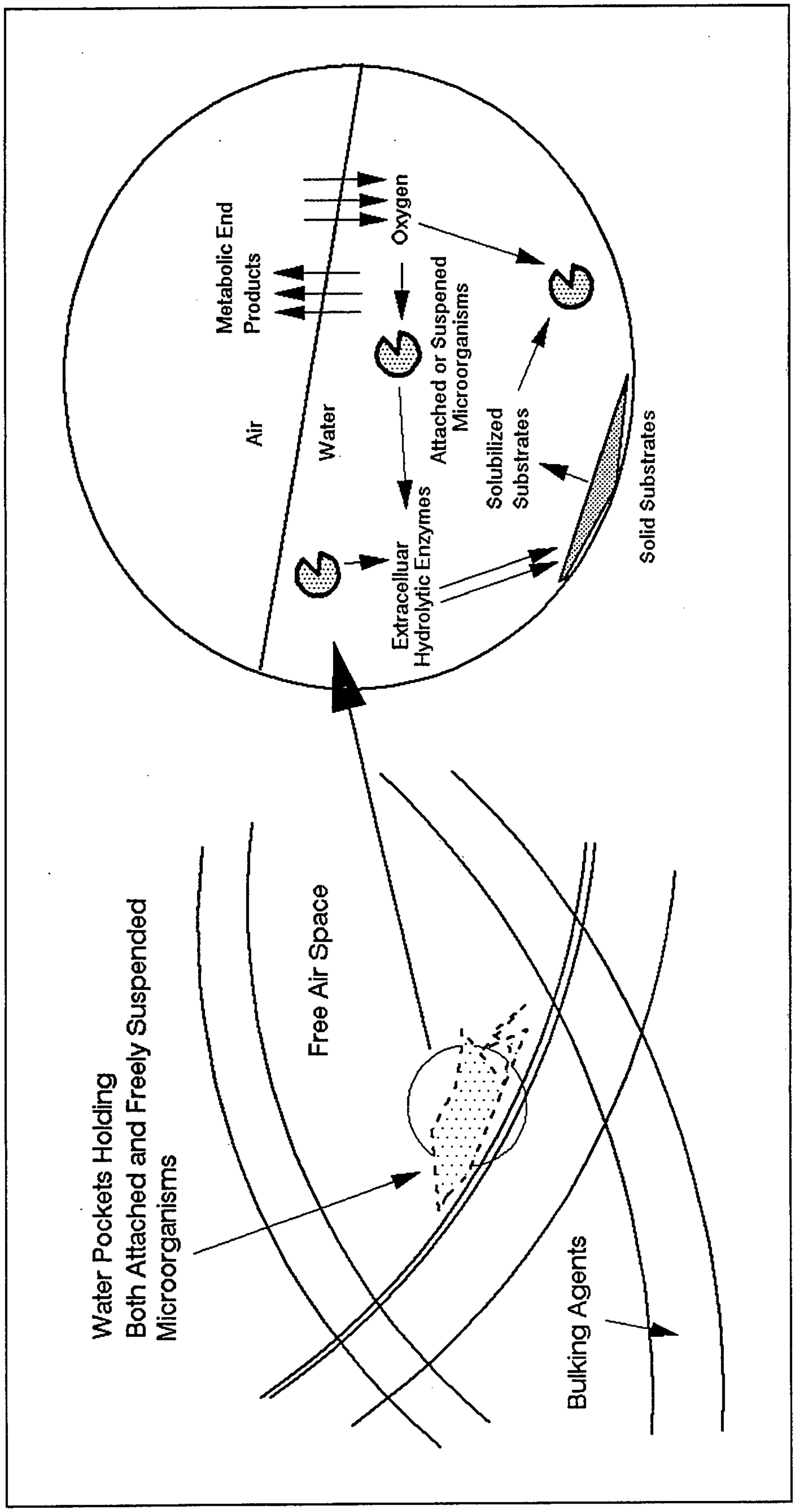

Figure 1. Hypothetical microbial metabolic processes in idealized compost matrix

$$v = -ds/dt = (ka_vX)/(K_x + X) \tag{2}$$

where

k = maximum rate of solid substrate hydrolysis

K_x = half-saturation concentration

X = biomass concentration

Once the solid substrate is solubilized, the Monod kinetic model can be used to describe the substrate depletion rate.

$$-dSs/dt = (km\,Ss\,X)/(Ks + Ss) \tag{3}$$

where

S_s = soluble substrate concentration

k_m = maximum soluble substrate utilization rate

K_s = half-saturation concentration for soluble substrate

The hydrolysis reaction rate changes from first order to zero order with respect to X as the biomass concentration increases as shown in Figure 2. In other words, the solubilization rate increases with the increase in biomass concentration up to a maximum value and stays the same regardless of the biomass concentration. However, the soluble substrate utilization rate increases linearly with the increase in biomass concentration.

Instead of using above solubilization and substrate degradation kinetics, Haug (1993) used a simple empirical first order reaction rate with respect to biodegradable volatile solid in the compost probably due to the complexity of the equations, inability to obtain necessary kinetic parameters, and mathematical simplification of the first-order reaction rate.

$$d(\mathrm{BVS})/dt = -k_d(\mathrm{BVS}) \tag{4}$$

where

BVS = biodegradable volatile solid

k_d = rate constant

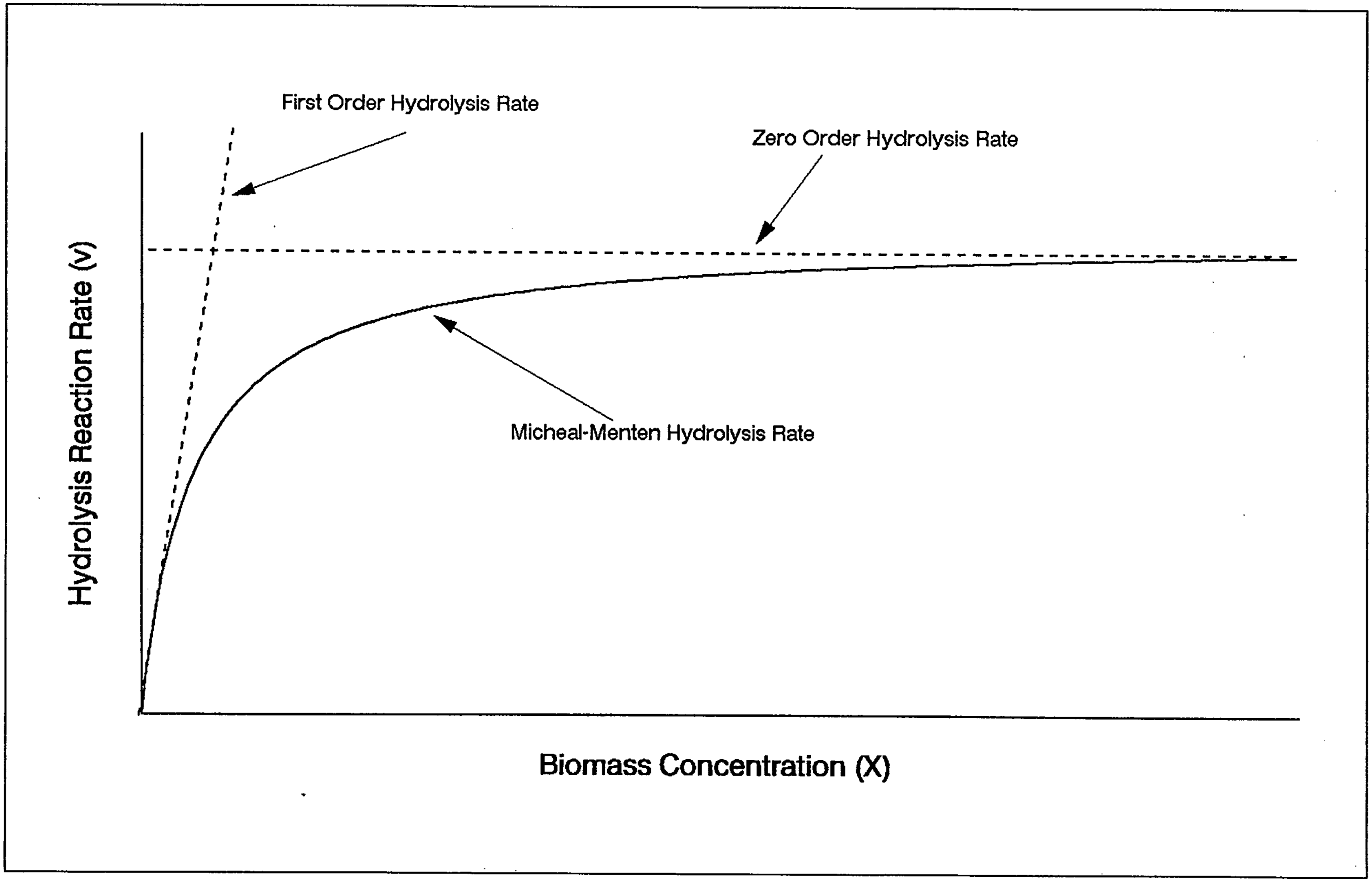

Figure 2. Enzymatic hydrolysis kinetic models

The values of k_d ranged from 0.0002 to 0.07 day^{-1} at 25 °C for various compost materials. Keener et al. (1993) used the same first-order reaction rate and also defined a dimensionless number, a compost mass ratio (M_R).

$$M_r = (m - m_e) / (m_o - m_e) = e^{-kt} \tag{5}$$

where

m = compost dry mass at any time

m_e = equilibrium, or noncompostable dry mass

m_o = initial compost dry mass

k = rate constant

Marugg et al. (1993) claimed that the mass ratio is a useful parameter even when Equation 5 is not valid due to change in k with respect to time, which is analogous to the moisture ratio in heat transfer analysis. BVS (Equation 4) and (m - m_e) (Equation 5) are analogous. As a result, k_d and k in Equations 4 and 5, respectively, are the same. Values of k for sludge and grass clippings were from 0.009 to 0.190 day^{-1} at 50 to 60 °C (Keener et al. 1993). The half-lives corresponding to k (Equation 5) are 77 days for 0.009 day^{-1} and 3.6 days for 0.19 day^{-1}. These values of k are considerably higher than that reported by Haug (1993) because Keener's values are for higher temperatures. Using the data from Schultze (1962) and assuming 50-percent biodegradability of volatile solids, Haug (1993) estimated the temperature dependency of k as:

$$k_d = 0.0126\,(1.066)^{T-20}\ (\text{mass BVS oxidized/mass BVS-}d) \tag{6}$$

In contrast to the above first-order empirical kinetic models, Hamelers (1993) developed a more mechanistic model, the composting particle kinetic model (CPK). In this model, the solid matrix contains micropores holding both fluid and air. The water contains dissolved organic and inorganic species, and biological activity takes place in the water phase or at the solid-water interfaces. The first-order solubilization of solid or polymeric substrates (hydrolysis) was used.

$$R_H = k_h S_p \tag{7}$$

where

R_H = hydrolysis rate

k_h = rate constant

S_p = solid or polymeric substrate concentration

When the biomass concentration is very small compared to K_x, Equation 7 becomes a special case of Equation 3. Using the double Monod model to account for both soluble substrates and oxygen concentrations, transport of the substrates, and oxygen via molecular diffusion, Hamelers derived a set of partial differential equations describing the concentrations of substrates and oxygen with respect to time and space. An implicit finite difference method was used to solve the equations. From the sensitivity analysis, three different degradation periods were identified. Initially, the biomass concentration limited the process. However, as biomass increased, biomass became less important. The second limitation to the process was a mass-transfer-limiting phenomenon. Diffusion of oxygen and substrates inside of the compost particles limited the overall process. Oxygen did not fully penetrate the particles, and both aerobic and anaerobic zones were formed within the particles. An important consequence of the presence of the anaerobic zone on the remediation composting is that both aerobic and anaerobic contaminant degradation pathways play roles in remediation. The hydrolysis rate limited the overall process at the end.

Hamelers argued that the empirical substrate-only models could not explain the initial surge and the gradual decline of oxygen uptake rate (OUR) typically observed in respirometric analysis. Also, the substrate-only model could not predict the effects of compost particle size, mixing, or turning on the composting process. Although the model can be useful for understanding the composting process, the complexity of the model requires estimation of many model parameters and numerical solutions of a system of nonlinear partial differential equations.

Kinetics of Explosive Compound Degradation/ Transformation

Explosive compounds are mineralized/biotransformed to varying extent. Previous studies indicated that while significant portions of RDX, HMX, tetryl, and nitro-cellulose were mineralized during composting (Doyle and Isbister 1982; Doyle et al. 1986), TNT was not mineralized, but biotransformed and incorporated into humic substance during composting (Pennington et al. 1990). An empirical first-order rate with respect to explosive compound concentration typically has been used to describe the disappearance of the contaminants regardless of their fates during composting (USAEC 1993; Doyle et al. 1986). The transformation rates of the contaminants were treated totally independent from the degradation of organic substrates, although the organic substrate composition and its degradation rate may affect the mineralization or transformation rate of the explosive compounds.

TNT and many hazardous contaminants are biodegraded/transformed by cometabolic process (Boopathy et al. 1994 a,b; Phelps et al. 1990; Strand, Bjelland, and Stensel 1990). Boopathy et al. (1994a) working with pure cultures isolated four *Pseudomonas* spp. from the soil contaminated with TNT. Among the isolates, less than 1 percent mineralized to CO_2, 6 to 13 percent converted TNT into cell mass (trichloroacetic acid precipitable material), and the remainder transformed to the reductive intermediates, amino-dinitrotoluenes. Growth substrate of succinate was necessary to promote growth of the isolates and the transformation of TNT, which suggest a cometabolic process. An initial TNT concentration of 100 ppm of TNT to aminodintrotoluenes required 4 to 8 days to completely biotransform. Furthermore, Boopathy et al. (1994b) tested seven different cosubstrates (succinate, citrate, malic acid, acetate, glucose, sucrose, and molasses). Microorganisms receiving 0.3-percent molasses transformed 100 ppm of TNT within 12 hr of incubation; whereas, the microorganisms receiving other carbon sources required more than 100 hr. Very little TNT (1 to 2 percent) was mineralized to CO_2, and major transformation intermediates were aminodinitrotoluenes. These knietics are not definitive, however, and more comprehensive kinetic expressions are needed to describe such cometabolic processes.

Most cometabolic kinetic studies focus on the transformation of nongrowth substrates by resting cells in the absence of growth substrates (Criddle, DeWitt, and McCarty 1990; Galli and McCarty 1989; Saez and Rittman 1991; Alexander, Schmidt, and Simpkins 1985). However, the rates and the extent of biotransformation of cometabolites are strongly affected by the presence of growth and energy substrates. Criddle (1993) developed a cometablic kinetic model for a system without competitive inhibition between the growth and nongrowth substrates. The growth substrate utilization rate was expressed using the Monod equation

$$-ds/dt = k_g [s_g / (K_{sg} + s_g)] X \tag{8}$$

where

s_g = growth substrate concentration

k_g = maximum specific growth substrate utilization rate

K_{sg} = half-saturation concentration of growth substrate

X = active biomass concentration

The biotransformation rate of the nongrowth substrates (cometabolites) was linked with the growth substrate utilization rate.

$$-dC/dt = [T_{g/c}(-ds_g/Xdt) + k_c]\,[(CX/(K_{sc} + C)] \qquad (9)$$

where

C = cometabolite concentration

k_c = maximum specific utilization rate of cometabolite

K_{sc} = half-saturation concentration of cometabolite

$T_{g/c}$ = growth substrate transformation capacity (= M_c / M_g)

M_c = mass of cometabolite

M_g = mass of growth substrate

Assuming that cometabolism imposes additional maintenance burden on the cell mass, the following equation for the specific biomass growth rate was hypothesized (Chang, Voice, and Criddle 1993).

$$mu_g = Y_m(-ds_g/dt) - b - 1/T_{g/c}(-dC/dt) \qquad (10)$$

where

Y_m = maximum biomass yield

mu_g = specific biomass growth rate

b = first-order endogenous decay coefficient

Equation 10 was successfully used by Chang, Voice, and Criddle (1993) to describe cometabolic degradation of p-xylene (cometabolite) in the presence of toluene (growth substrate) by a *Pseudomonas* isolate. The value of $T_{g/c}$ was 0.45 mg p-xylene/mg toluene. The growth substrate transformation capacity for trichloroethylene (TCE) by methanotrophic bacteria was reported in the range of 0.036 to 0.042 mg TCE/mg CH_4 (Phelps et al. 1990; Strand, Bjelland, and Stensel 1990).

In addition to the cometabolic process, the toxic or inhibitory effects of the explosive contaminants on the substrate degradation require consideration. Unless organic substrates are properly utilized for cell growth and provide the maintenance energy requirements, free from the negative toxic or inhibitory effects of contaminants, the amount of cell mass will not be sufficient for effective remediation. Furthermore, if the contaminants are toxic or significantly inhibitory, the compost temperature will not be raised to the optimal thermophilic conditions; consequently, valuable thermophilic microorganisms cannot be utilized for degradation of the contaminants.

Heat and Mass Transfer

Composting is by nature an exothermic reaction system. An understanding of the associated thermodynamics is required for process control. This is the approach that has been advanced by several researchers and engineers (Bach et al. 1987; Finstein 1980; Finstein et al. 1985, 1986; Haug 1993; Hogan, Miller, and Finstein 1989; Keener et al. 1993). The essence of their approach was to assume the composting system as a thermodynamically closed system. Then, the first law of the thermodynamics (i.e., conservation of energy) can be applied to the composting system to evaluate the relationship of various heat transfer terms, which can be used later to properly design and operate the process. The energy balance of an idealized compost reactor is shown in Figure 3.

The energy balance equation based on the first law for the ideal compost system assuming negligible radiative energy loss is

$$Q_c = Q_R + Q_a - Q_L - w \tag{11}$$

where

Q_c = accumulation rate of thermal energy of compost system

Q_R = energy release rate resulting from substrate degradation

Q_a = net heat transfer into/out of compost by air flow

Q_L = total heat loss rate from compost system through reactor wall

w = work done by compost system

Since the volume of the compost reactor does not change to an important extent and the reactor is static (not moving), the work done by the compost system will be negligible. The rate of thermal energy accumulated inside the compost system (Q_c) can be estimated using specific heat capacity at constant pressure (C_p).

$$Q_c = \rho_c V_c C_p \, dT/dt \tag{12}$$

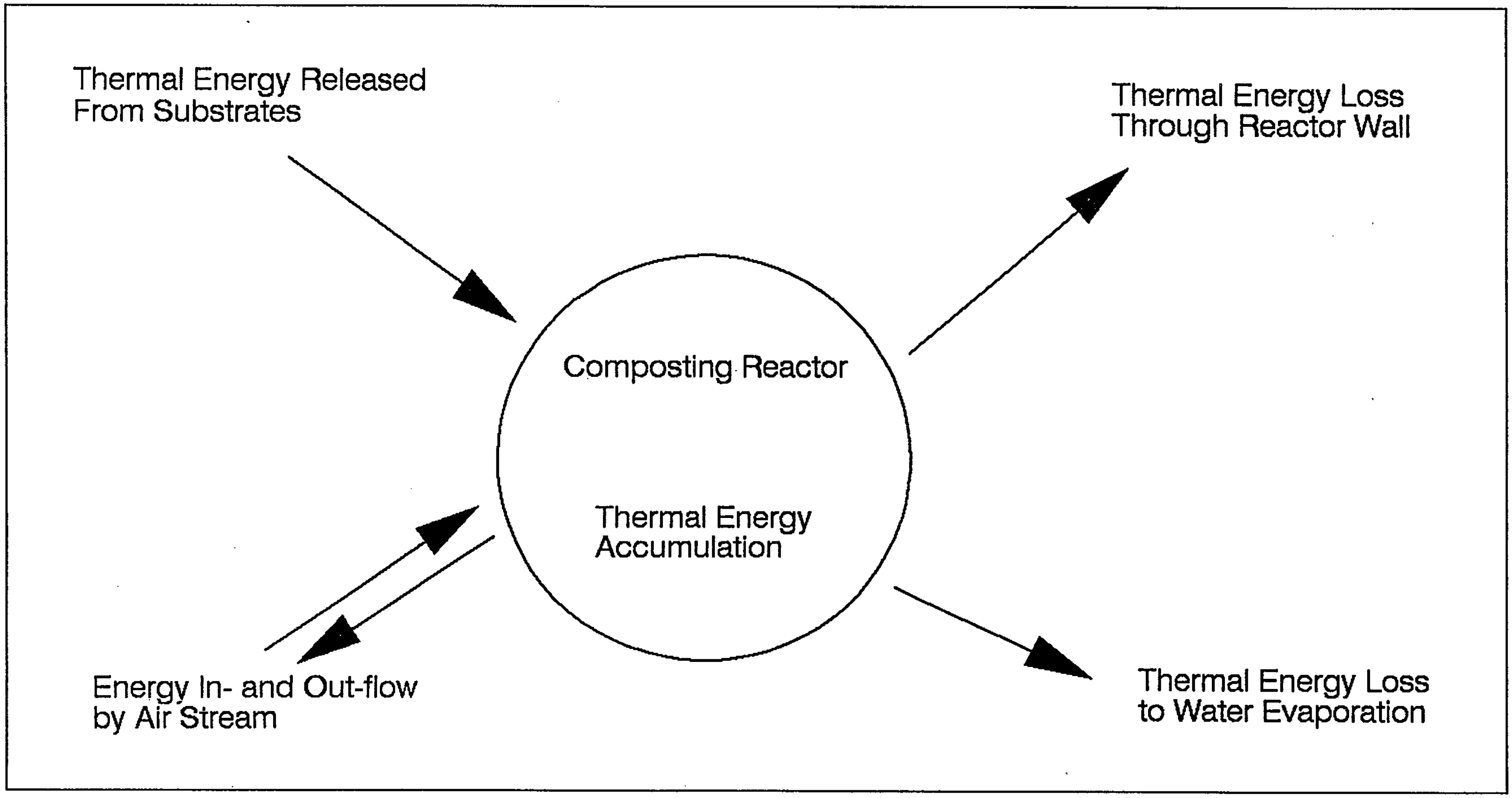

Figure 3. Energy balance of an idealized compost reactor

where

ρ_c = bulk compost wet density

V_c = volume of compost

C_p = heat capacity of compost matrix

T = temperature of compost

t = time

Mears et al. (1975) developed an empirical relationship for estimating the heat capacity and the thermal conductivity of compost material made of swine waste and straw. The specific capacity and the thermal conductivity were related with moisture content of the compost material.

$$C_p = 0.1551 + 0.00813\,M \tag{13}$$

$$K_{Tc} = 2.071 + 0.0341\,M \tag{14}$$

where

C_p = heat capacity, cal/g-C

M = moisture content, percent

K_{Tc} = thermal conductivity, cal/hr-cm-C

At 100-percent moisture content, both C_p and K_{TC} values approach the values for water according to Equations 13 and 14; therefore, Haug (1993) assumed that thermodynamic analysis of water and solid fractions of compost can be treated separately.

The rate of heat generated from degradation of organic substrates is

$$Q_R = -(d(\mathrm{BVS})/dt)\,H_R \tag{15}$$

where

$d(\mathrm{BVS})/dt$ = substrate degradation or destruction rate

H_R = heat of reaction

Available organic substrates including biomass are, over time, converted to CO_2 and H_2O. As a result, the heat of combustion of common organic substrates may be used to estimate the amount of heat released from degradation. Since metabolic microbial reactions occur in a hydrated environment whether conducted in the cellular cytoplasm or by extracellular enzymes, the end product H_2O is also in aqueous state. The values of heat of combustion must be such that the water produced is in aqueous state, rather than the gaseous state found in common heat of combustion tables. It requires more heat to condense the water, which is called the higher heat value (HHV) of combustion. The HHVs of combustion of common organic substrates are shown in Table 1.

Table 1
Heats of Combustion of Common Organic Substrates

Substrate	HHV, cal/g	Reference
Glucose	3,740	1
Wood (air dried)	3,060	1
Digested sludge (dry solids)	2,950	1
Municipal refuse (20-percent moisture)	2,720	1
Sludge (dry, ash-free)	5,560	1
Alfalfa seed straw	4,410	2
Wheat straw	4,185	2
Popular	4,632	2
Sudan grass	4,156	2
Sugarcane bagasse	4,142	2
Rice hulls	3,858	2

[1] Haug (1993).
[2] Ebeling and Jenkins (1985).

Determination of the heat of reaction for a compost mix includes estimation of the heat of combustion and biodegradability of each compost component. The heat of reaction for a compost mix is

$$H_R = \left[\sum B_i f_{vi} DS_i H_{ci} \right] / \left[\sum B_i f_{vi} DS_i \right] \tag{16}$$

where

B_i = biodegradability of component I

f_{vi} = mass fraction of volatile solid to dry solid of component I

DS_i = dry solid of component I

H_{ci} = heat of combustion for component I

For example, consider a compost mix (DS = 4,331 g and 43.7-percent moisture content) containing 5.6 ℓ of cow manure (bulk density = 747.0 g/ℓ), 5.6 ℓ of alfalfa (bulk density = 112.0 g/ℓ) and 2.8 ℓ of contaminated soil (bulk density = 1,028.2 g/ℓ). From initial laboratory analysis, the moisture contents and the volatile solid (VS) percents have been determined as shown in Table 2. Haug (1993) reported that 56.4 percent of cow manure VS and 77.2 percent of corn stalks VS were biodegradable. It is reasonable to assume that the biodegradabilities of the corn stalks and the alfalfa are the same, biodegradability of soil VS is zero since only a negligible amount of VS is present in the soil, and the heat of combustion of cow manure is equal to that of sludge in Table 1.

Table 2
Moisture Contents and VS Fractions of a Compost Mix

Component	Percent Moisture	Percent Volatile Solid
Cow Manure	70.5	59
Alfalfa	2.4	84.9
Soil	13.7	2

The heat of reaction for this compost mix is then calculated using Equation 16 and Table 2.

$$\begin{aligned} H_R &= [(5.6\,\ell)(747.0\,g/\ell)(100\% - 70.5\%)(59.0\%)(56.4\%)(5{,}560\,cal/g) \\ &+ (5.6\,\ell)(112.0\,g/\ell)(100\% - 2.4\%)(84.9\%)(77.2\%)(4{,}410\,cal/g) \\ &+ 0] / [(5.6\,\ell)(747.0\,g/\ell)(100\% - 70.5\%)(59.0\%)(56.4\%) \\ &+ (5.6\,\ell)(112.0\,g/\ell)(100\% - 2.4\%)(84.9\%)(77.2\%) = 4{,}992\,cal/g\text{-}BVS] \end{aligned} \tag{17}$$

where BVS is the biodegradable volatile solid.

The value of 4,992 cal/g-BVS appears to be somewhat higher. Considering the total dry mass of the compost mix, the heat value of the compost mix becomes (4,992)(812)/(4,331) = 936 cal/g-DS. Hogan, Miller, and Finstein (1989) reported 578 to 628 cal/g-DS for their compost mix containing rice hulls and rice flour.

The net heat transfer into or out of the compost system by the air flow is

$$Q_a = C_{pa}\,\rho_a\,G\,dT = h\,a(T - T_o) \tag{18}$$

where

a = volumetric surface area of compost matrix

C_{pa} = heat capacity of air

h = heat transfer coefficient inside compost matrix

ρ_a = density of air

G = volumetric air flow rate

T_o = exit air temperature

The compost reactor loses heat through the reactor wall and by evaporation of water from the compost matrix by air flow. The evaporative heat loss can be estimated using the latent heat of vaporization of water and the mass transfer rate of water vapor away from the evaporation site.

$$Q_v = H_v (dm_w/dt) \tag{19}$$

where

H_v = heat of vaporization

dm_w/dt = water evaporation rate

The water evaporation rate by the air flow is

$$dm_w/dt = -k_w a (H_i - H_o) \tag{20}$$

where

k_w = mass transfer constant of water vapor

H_i = humidity of air entering compost reactor

H_o = humidity of air exiting compost reactor

Assuming the compost reactor resembles a packed bed reactor filled with compost particles, the water vapor mass transfer coefficient may be estimated from a correlation for packed bed (Wakao and Kaguei 1982).

$$Sh = 2 + 1.1\, Sc^{1/3} Re^{0.6} \text{ for } 3 < Re < 3{,}000 \tag{21}$$

where

Sh = Sherwood number (= $k_m d_p/D$)

k_m = mass transfer coefficient

d_p = particle diameter

D = molecular diffusivity

Sc = Schmidt number (= $\mu/\rho D$)

rho = fluid density

Re = Reynolds number (= $d_p v^o \rho/\mu$)

v^o = superficial velocity

The overall heat transfer coefficient (U) conveniently characterizes the heat transfer through the reactor wall, insulating materials, and finally to the surrounding environment (Q_w).

$$Q_w = UA(T - T_{am}) \tag{22}$$

where

A = total surface area of compost reactor wall

T_{am} = ambient temperature

The overall heat transfer coefficient of the reactor wall surrounded by insulating materials or by water jackets is estimated using the electric resistance analogy.

$$U = 1/\sum (R_i) \tag{23}$$

where R_i is the thermal resistance of each heat transfer medium.

For conductive heat transfer, the resistance is

$$R_c = L/K_T \tag{24}$$

where

K_T = thermal conductivity

L = wall thickness

R_c = conductive thermal resistance

For convective heat transfer outside of the reactor wall, the resistance is

$$R_v = 1/h_v \tag{25}$$

where

h_v = heat transfer coefficient

R_v = convective thermal resistance

Oxygen mass transport through the compost matrix is also important. Haug (1993) used the two-film theory in order to estimate the oxygen transfer efficiency and the subsequent aeration time. Physical process description of the oxygen transport model was unclear and unconvincing. Another approach considers the compost reactor as a packed bed reactor filled with spherical compost particles. As a result, the mass transfer coefficient can be estimated from Equation 21. Knowing the oxygen mass transfer coefficient for the compost reactor, the oxygen mass transfer rate is then calculated as:

$$dm_{o2}/dt = k_m a(C_s - C) \tag{26}$$

where

m_{o2} = mass oxygen transferred

a = specific surface area

C_s = saturation dissolved oxygen (DO) concentration

C = DO of water film in compost matrix

3 Important Parameters for Bench-Scale Remediation Composting

Successful design and operation of bench-scale remediation composting requires careful consideration of numerous factors affecting the process. The factors can be divided into four classes: physical, chemical, biological, and thermodynamical factors. 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. A composting system with proper thermodynamical properties ensures the optimal thermophilic conditions.

Physical Factors

Porosity

Pore space is the open or void space between solid particles. The measure of pore space, generally on a percentage basis, is termed porosity. 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. Free air space is that portion of the pore space occupied by gas and not liquid. Free air space is critical for the movement of oxygen and other gases into and through the compost matrix by either diffusion, convection, or forced ventilation.

Figure 1 provides an illustration of the compost matrix in an idealized three-phase representation. The purpose of the idealized representation is to provide a concept of how a representative portion of the matrix might appear in nature. In this idealized representation, solid particles lie against one another in a random fashion.

Between the particles, a void space is formed. This region is the pore space. In the pore space, varying amounts of liquid and/or gas may be present. 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 limiting and 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 in the definition of the physical nature of the compost matrix.

Bulk property may be used to gain insight into the compost matrix porosity and the free air space. The porosity or the percent pore space (n) is defined by the ratio of void volume (V_p) to the total volume (V_t).

$$n = V_p/V_t \tag{27}$$

The porosity may also be defined as the total volume minus the solid volume (V_s) over the total volume.

$$n = (V_t - V_s)/V_t = 1 - V_s/V_t \tag{28}$$

The solid volume of the compost is calculated as:

$$V_s = DS/\rho_{ds} \tag{29}$$

where

DS = dry mass of compost

ρ_{ds} = true density of dry compost

Free airspace (FAS)

Free airspace (FAS) is the ratio of the empty pore space (V_a), or void volume not occupied by water, to the total volume.

$$\text{FAS} = V_a/V_t = (V_t - V_s - V_w)/V_t = 1 - [(V_s + V_w)/V_t] \tag{30}$$

where

V_w = volume of water

V_a = empty pore space

The volume of water is estimated from the mass of water evaporated during the dry solid measurement and the bulk wet density of compost (rho_c).

$$V_w = \rho_c V_t - DS \tag{31}$$

FAS may be managed by selection of the amendments and bulking agents. The definition of a bulking agent is a material added to a compost system to reduce bulk density and increase FAS. Bulking agent and amendment selection are perhaps two of the most critical design decisions. The selection of these will influence the nature of the compost, the efficiency of the operation, and the economics of the system. Research indicates that the optimal biological activity occurs with an FAS ranging from 0.20 to 0.35 (Haug 1993).

Moisture content

Water is the principal liquid of life on earth. It is the solvent in which all known biochemical relations occur, and 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 multifaced role. Water plays a key role in cooling of the compost systems. Also, moisture content influences the nutrient movement and the compost matrix structure.

As a biochemical solvent, 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 concentration. 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 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. 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 minimum for most compost systems without argumentation by forced aeration.

The moisture content (M) is calculated as

$$M = m_w / m_c = \rho_w V_w / \rho_c V_c \tag{32}$$

where m_w is the water mass.

The optimal moisture content reported by previous researchers varied from 45 to 90 percent (Haug 1993; Golueke 1991; Gotaas 1956; Poincelot 1975). The reported optimal moisture content varied widely because of widely varying water absorption capacity of soil particles and composting materials used in research (Mathur 1991). Waksman (1938) reported that the maximum aerobic microbial activity occurred when the soil moisture content is two-thirds of its water-holding capacity at one-third bar suction. Generally, a moisture content of about 50 to 65 percent is used. Above this range, the pore space will be filled with water or, at the vary least, water tension in the pore space hinders the movements of gases between pores so that oxygen in the pore space becomes depleted. Below this range, free moisture is not available to the microbial communities. The remaining water 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 considered a nonliquid. 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.

Methods for moisture control in composting systems include amendment selection and direct addition of water. For instance, paper material may become soggy on wetting or decomposition. It will severely reduce porosity and the necessary oxygen transfer. In hazardous waste compost operations, amendments and bulking agents should be chosen to preclude the need for the removal of excess water.

Particle size

Various shredders and other mixing devices are used to break down and homogenize the compost materials into smaller and 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, porosity of the compost matrix will decrease with the decrease in particle size, and it will hinder the movement of oxygen and water in narrow interstitial spaces between the small particles packed together tightly. Generally, particle size between 1.3 to 5 cm is used for composting to yield sufficiently large surface area and, at the same time, to produce enough pore space for efficient oxygen and substrate transport (Forster and Wase 1987). The initial particle sizes appropriate for static piles and windrow systems are generally around 5 cm. Particle sizes as small as 1.3 cm have been used in forced aeration systems.

Contaminated soil loading

The economics of the remediation composting systems will be based on the amount of contaminated soil pushed through the system 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 for the possible inhibition by the contaminants on the compost 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 will slow microbial activities and result 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 desired reaction time due to lack of organic substrates.

In bench-scale remediation composting studies, experiments should test a range of contaminant concentrations and the soil loadings to provide some insight into the impact of contaminant concentration and the soil loading on the compost mixture under consideration. Prior respirometric tests may offer some preliminary information regarding the adequacy of the select remediation compost mix for possible inhibition by specific contaminant and its degradation rates.

Temperature

As the composting microorganisms degrade organic substrates, heat is generated 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, ambient temperature, and the heat values of substrates. Although higher temperature is beneficial in many ways, the microorganisms and enzymes are inactivated and the composting process will stop beyond 70 °C. Above 60 °C, most mesophile including fungi die or become inactive. After readily available substrates such as starches, sugars, lipids, and proteins have been consumed, the compost temperature will fall below 60 °C, and it will allow fungi and actinomycete to attack cellulose and lignin portions of the substrates. Recently, researchers agree that 55 to 60 °C is the optimal temperature range (Bollen 1985; Finstein and Miller 1985; Haug 1993).

Chemical Factors

Carbon-to-nitrogen ratio (C/N)

Compost microorganisms require adequate levels of carbon sources and nutrient sources including nitrogen, phosphorous, sulfur, and other trace minerals and growth factors. Among these, carbon and nitrogen 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 P on a dry weight basis (Alexander 1977). Assuming about one-half to two-thirds of carbon is converted to CO_2 and the rest to cell mass, the required C/N ratio would be between 23 and 35. The optimal ratios for different composting materials ranged from 20 to 35 (Haug 1993; Gotaas 1956).

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 will slow down the substrate stabilization rate. It may, however, be beneficial for remediation composting because dead microorganisms themselves are organic substrates and will 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 compost pH. For a compost mix with high C/N ratio, ammonia-releasing substrates such as blood, urine, or urea can be added. If phosphorous and other nutrients are low as in cases of using industrial solid wastes as substrates, these components need to be supplemented in order to avoid unnecessary rate limitations.

The C/N ratio of a remediation compost mix can be manipulated in order to promote degradation of explosive compounds that usually contain a significant amount of nitrogen. As Cook (1987) hypothesized, if the compost mix is deliberately made with a high C/N ratio, certain species of compost microorganisms may be forced to attack the explosive compounds in order to utilize nitrogen compounds. Similarly, if the C/N ratio of the compost mix is too low, i.e., more than enough nitrogen for microbial growth, microorganisms may not aggressively degrade or transform the explosive contaminants. Consequently, cometabolic degradation becomes the chief path for the degradation of the explosive compounds. As an example of this, aerobic biotransformation of atrazine has been shown to be inhibited by microorganisms in wetland sediment when an extra nitrogen source was supplied (Ro and Chung 1995). Atrazine and RDX are similar to the extent that both have a triazine ring in their chemical structure.

In order to determine the C/N ratio, the chemical composition of the substrates must be analyzed. The Total Kjeldahl nitrogen (TKN), in the Standard Methods of Water and Wastewater Quality Analysis (Greenburg 1992), can be used to estimate nitrogen concentrations. For carbon, a simple empirical correlation was suggested by Haug (1993):

$$\%\ carbon = (100 - \%\ ash)/1.8 \qquad (33)$$

Acidity (pH)

The pH of the compost matrix must be near neutral (i.e., near pH of 7) because most biological systems balance their cationic and anionic ions near neutrality. For all practical purposes, microbial growth is severely limited at pH values less than 3 or greater than 11. The optimum pH of composting was reported to be between 6.0 and 8.5 (Fitzpatrick 1993). At higher pH (strongly basic), ammonium ions (nitrogen source) will be lost as ammonia, and essential elements such as Ca and Mg may not be available to microorganisms due to precipitation as insoluble metal hydroxides or carbonates. At lower pH (strongly acidic), toxic metals like Al, Cu, Zn, etc., will be leached from minerals and substrates and may stop the composting process.

Overall, compost pH should be adjusted with cosubstrates or other pH-adjusting chemicals such as lime and baking soda. For instance, wood wastes and sludges from pulp and paper mills may have a pH of 5 to 6 and C/N 100 to 150. Addition of ammonia-releasing substrates such as urine or urea will neutralize the acidity and provide necessary nitrogen to microorganisms. Some depression of pH values (4.5 to 5.0) of compost materials stored in a closed container is not unusual due to anaerobic production of volatile fatty acids.

Biological Factors

Biodegradability and biodegradation rate

Substrate biodegradability determines the quantity of available heat and the stoichiometric oxygen demand. In literature, biodegradability of substrates varied 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, as cited by Haug (1993), reported that the lignin content was the single most important factor influencing the biodegradability and developed an empirical correlation for substrate biodegradability based on the lignin content.

$$B = 0.830 - (0.028)\,L \tag{34}$$

where

B = biodegradable fraction of volatile solids

L = lignin content, percent of VS

Without having to determine the lignin content of substrates, biodegradability can be easily estimated by directly measuring the volatile solid destruction during composting. For example, if the mass of fixed solid (i.e., nonvolatile fraction of solid substrates) is assumed to stay the same before and after the composting because its components are mostly inorganic, the biodegradability is then calculated as:

$$B = (f_{v1} - f_{v2}) / f_{v1} \tag{35}$$

where

f_{v1} = mass fraction of volatile solid to dry solid initially

f_{v2} = mass fraction of volatile solid to dry solid after composting

One complication with this approach to biodegradability estimation (Equation 35) is the assumption that all biodegradable volatile solids (BVS) have been destroyed after composting. This may be true for composting practices with long retention times and where the final mass of dry solid practically stays the same (i.e., m_e in Equation 5). For slowly composting materials (i.e., composting materials with low values of k in Equation 5), only about 50 percent of BVS will be destroyed even after 77 days of composting with k of 0.009 day^{-1} (Keener et al. 1993). However, a long retention time may not be needed nor desired for remediation of soils contaminated with explosive compounds. Most of the previous remediation composting studies indicated that less than 30 days were needed 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). Use of data from the composting practices with short retention times may lead to a serious error in estimating the substrate biodegradability (Equation 35). Respirometric analysis can be effectively used not only to estimate oxygen requirements but also the biodegradabilities and the biodegradation rates of substrates.

Respirometric analysis with less than a few hundred grams of compost substrates can provide valuable information. The accumulated oxygen uptake of the compost substrates with respect to incubation time provides direct information on the oxygen requirements of the substrates at various retention times. Biodegradability can be estimated by running the analysis until an accumulated oxygen uptake reaches a plateau (negligible oxygen uptake rate) and determining the volatile solid mass loss. Another way to estimate the biodegradability is by using the chemical oxygen demand (COD) test, since the solid substrate's COD is related to the total organic portion or volatile solid of the substrate. For example, Haug (1993) used 1.3 and 1.65 g O_2/g VS for the case study in his book. If the final value of an accumulated oxygen uptake in the plateau region is 0.8 g O_2/g VS and COD of the substrate is 1.6 g O_2/g VS, the biodegradability is 0.8/1.6 = 0.5, or 50 percent.

Furthermore, if the ratio of oxygen uptake of the compost to the corresponding volatile solid loss can be determined from the respirometric analysis, the biodegradation rate of the organic substrates can be also estimated using the familiar first-order biochemical oxygen demand (BOD) kinetics.

$$\text{BVS}_{destroyed} = \text{BOD}_u / Y_{o2/\text{BVS}} \; (1 - e^{-kt}) \qquad (36)$$

where

$\text{BVS}_{destroyed}$ = mass of BVS destroyed

BOD_u = ultimate BOD

$Y_{o2/\text{BVS}}$ = O_2 cosummed/BVS destroyed

Equation 36 assumes that the value of $Y_{o2/\text{BVS}}$ is rather constant throughout the incubation. The ultimate BOD is the total accumulated oxygen uptake in the final plateau region. Notice that $\text{BOD}_u / Y_{o2/\text{BVS}}$ is equal to the initial total biodegradable volatile solids of the compost mix (BVS). Once the rate coefficient and BVS are estimated from the respirometric experiment, the thermal energy generation rate can be calculated as a function of time (Equation 15). The composting temperature changes, and the rate coefficient may be estimated using Equation 6. For discrete time-series kinetic data, Equations 37 and 6 may be used to calculate the thermal energy generation rate with respect to time.

$$\begin{aligned} Q_{R,i} &= -(d(\text{BVS})/dt)_I \, H_R = r_i H_R = \\ & BV_{i-1}S \; (1 - \exp(-k_i \, \Delta t_i)) \; H_R \, / \, \Delta t_i \end{aligned} \qquad (37)$$

$$k_i = 0.0126 \; (1.066)^{T-20} \qquad (6)$$

where

$Q_{R,i}$ = energy generation rate at time I

r_i = BVS destruction rate at time I

BVS_i = BVS at time I

Δt_i = $t_i - t_{i-1}$

k = reaction rate constant at time I

T = compost temperature at time I

Stoichiometric oxygen requirements

Oxygen is essential for the metabolism of aerobic microorganisms, which are believed to be a major driving force for compost. The stoichiometric oxygen requirements can be determined if the organic matter chemical compositions and the extent of biodegradation during the process are known. Assuming all biodegradable organic carbon is converted to CO_2, the stoichiometric oxygen requirement can be estimated. For instance, degradation of proteinaceous material (100-percent biodegradable) may be represented by chemical expression:

$$C_{16}H_{24}O_5N_4 + 16.5\ O_2 \longrightarrow 16\ CO_2 + 6\ H_2O + 4\ NH_3 + \text{Heat} \qquad (38)$$

where the molecular weight of $C_{16}H_{24}O_5N_4$ and O_2 is 352 and 32, respectively.

The stoichiometric oxygen requirement of this proteinaceous substrate with 80-percent degradation during composting is (80 percent)(16.5)(32)/352 = 1.2 g O_2/g BVS. Since air contains 23.2-percent oxygen by mass, the air requirement for this substrate is 1.2/0.232 = 5.17 g air/g BVS. In this analysis, the oxygen demand for nitrification is not considered because ammonia is assumed to be volatilized at the thermophilic conditions. Haug (1993) reported the stoichiometric oxygen requirements of about 1.0 to 4.0 g O_2/g organics. For a mixed substrate system, fractional oxygen requirements for each substrate can be added to estimate the total oxygen requirements for the mix.

Aeration

Aeration in a composting system is important for two reasons: 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 existent within compost piles. Oxygen may also be supplied by forcing air through the compost matrix, or mechanically mixing the compost intermittently to enhance the oxygen transfer.

Aeration is also used to dry and subsequently cool the compost temperature through promoting evaporation of water. Approximately 10 to 30 times more aeration is required for drying of 20-percent solids than that for biological oxygen oxidation (Haug 1993).

In bench-scale remediation composting, retaining heat is perhaps more important than removing heat as in pilot- and field-scale composting due to high heat loss associated with a large specific surface area. Therefore, aeration in bench-scale remediation composting focuses on satisfying the oxygen requirements. Also, in order to minimize the heat loss by evaporation of water, the air is usually presaturated with water vapor, i.e., 100-percent humidity, before entering into the compost reactor (Hogan, Miller, and Finstein 1989; Cook, Bloom, and Halbach 1994; Magalhaes et al. 1993).

Thermodynamic Factors

The size, shape, and type of reactor and insulating materials eventually determine the heat loss characteristics through the reactor wall for the bench-scale remediation composting systems. The concept of overall heat transfer coefficient is very useful in order to properly design and size the bench-scale remediation composting system. First, the rate of energy generated by degrading substrates is estimated based on a desired composting temperature profile through various assumptions of biodegradabilities, the heat of reaction of the compost mix (Equation 37). Second, the evaporative and sensible heat losses and the utilization of heat used to heat the compost mix to a desired operating temperature are calculated (Equations 12, 18, 19, and 20). Third, the heat loss through the reactor wall is calculated using the energy balance at steady state (Equation 11). Finally, the required overall heat transfer coefficient (*U*) is calculated (Equation 22). The required *U* decreases as composting time increases because the system insulation efficiency must increase in order to maintain an optimum composting temperature as the amount of substrate and the rate of heat generation decrease during later stage of composting. The minimum *U* should be selected as a design value. Once the design *U* is determined for a particular compost mix, the reactor can be designed using various insulating materials and configurations in order to meet the design *U*.

In order to illustrate the design procedure, consider the following example. Using the heat of reaction of the example compost mix in Equation 17 (4,992 cal/g-BVS), Equation 6 for the rate coefficient, and the total biodegradable volatile solids of the compost mix (812 g), the heat generation rate at each time step ($Q_{R,i}$) can be estimated using Equations 37 and 6. In this example, the compost temperature is assumed to rise linearly from initial temperature of 25 °C to the optimum temperature of 55 °C within 3 days and maintain 55 °C for 30 days of composting. For this example, assume fully humidified air (2,880 ℓ/day) is introduced at 25 °C and leaves the system saturated and at a temperature practically the same as that of compost. Further assume that the moisture content of the compost remains at 43.7 percent during composting. Using 0.24 cal/g-°C and 1.2 g/ℓ as air heat capacity and density, respectively, the sensible heat loss rate by the air flow at time *I* can be calculated (Equation 18).

$$Q_{a,i} = (0.24)(1.2)(2{,}880)(T_i - 25) \tag{39}$$

Assuming volume, heat capacity, and density of the compost are 14 ℓ, 0.5 cal/g-°C, and 549 g/ℓ, respectively, the heat accumulation rate of the compost (Equation 12) at time ($Q_{c,i}$) is expressed as:

$$Q_{c,i} = (549)(14)(0.5)(T_i - T_{i-1})/(t_i - t_{i-1}) \tag{40}$$

Although the moisture content remains the same, water still evaporates from the compost pile. Knowing the amount of BVS degraded up to time I-1 and I, the evaporation rate of water is estimated as:

$$\begin{aligned} |dm_w/dt|_i &= (M_{w,i-1} - M_{w,i})/(\Delta t_i) \\ &= [f_{w,i-1}\ (DS_0 - \mathrm{BVS}_{\mathrm{d,i-1}})/(1 - f_{w,i-1}) \\ &\quad - f_{w,i}\ (DS_0 - \mathrm{BVS}_{\mathrm{d,i}})/(1 - f_{w,i})]/\Delta t_i \end{aligned} \tag{41}$$

where

$M_{w,i}$ and $M_{w,i\text{-}1}$ = mass of water at time i and i-1

$\Delta t_i = t_i - t_{i\text{-}1}$

$f_{w,i}$ and $f_{w,i\text{-}1}$ = mass fraction of water to dry solid at time i and i-1

DS_0 = initial dry solid

$\mathrm{BVS}_{d,i}$ and $\mathrm{BVS}_{d,i\text{-}1}$ = BVS degraded at time i and i-1

Once the evaporation rate of water is calculated, the evaporative heat loss rate is determined using the latent heat of evaporation. Using a value of 578.1 cal/g for the latent heat of evaporation, the evaporative heat loss rate is

$$Q_{V,I} = 578.1\ |dm_w/dt|_I \tag{42}$$

The total heat loss rate through the reactor wall by conduction and convection at time I ($Q_{w,i}$) is then estimated using Equation 11.

$$Q_{w,i} = Q_{c,i} - Q_{R,i} - Q_{a,i} - Q_{v,i} \tag{43}$$

For a cylindrical composting reactor with a diameter of 0.2 m and a length of 0.5 m, total surface area for heat conduction is 3,800 cm^2. The required overall heat transfer coefficient at time I (U_i) to maintain the desired temperature at that time is calculated (Equation 22).

$$U_i = Q_{w,i}/A\ (T_i - 25) \tag{44}$$

where A is the total surface area.

The results of this bench-scale composting design example are summarized in Table 3 and Figures 4 and 5. The heat generation rate reaches the maximum of 385,621 cal/day at Day 3 and gradually decreases to 21,769 cal/day at Day 30. The sensible heat loss by the air increases to 24,883 cal/day at

Table 3
Heat Transfer Rates, BVS, and *U* of Example Composting

t Days	BVS, g Destroyed	*Qr* Cal/Day	*T* C	*Qa* Cal/Day	*Qc* Cal/Day	*Qv* Cal/Day	*Qw* Cal/Day	*U* Cal/cm^2-hr-C
0	0	0	25	0	0	0	0	
1	26	131,052	35	8,294	38,430	11,780	72,547	0.080
2	46	228,901	45	16,589	38,430	20,575	153,307	0.084
3	77	385,621	55	24,883	38,430	34,663	287,646	0.105
4	65	325,258	55	24,883	0	29,237	271,138	0.099
5	59	295,775	55	24,883	0	26,587	244,305	0.089
6	53	266,136	55	24,883	0	23,922	217,330	0.079
7	48	239,813	55	24,883	0	21,556	193,374	0.071
8	43	216,052	55	24,883	0	19,420	171,748	0.063
9	39	194,649	55	24,883	0	17,497	152,270	0.056
10	35	175,367	55	24,883	0	15,763	134,720	0.049
11	32	157,994	55	24,883	0	14,202	118,909	0.043
12	29	142,343	55	24,883	0	12,795	104,665	0.038
13	26	128,242	55	24,883	0	11,527	91,831	0.034
14	23	115,538	55	24,883	0	10,385	80,269	0.029
15	21	104,092	55	24,883	0	9,357	69,852	0.026
16	19	93,780	55	24,883	0	8,430	60,468	0.022
17	17	84,490	55	24,883	0	7,595	52,012	0.019
18	15	76,120	55	24,883	0	6,842	44,395	0.016
19	14	68,580	55	24,883	0	6,164	37,532	0.014
20	12	61,786	55	24,883	0	5,554	31,349	0.011
21	11	55,665	55	24,883	0	5,004	25,778	0.009
22	10	50,151	55	24,883	0	4,508	20,760	0.008
23	9	45,183	55	24,883	0	4,061	16,238	0.006
24	8	40,707	55	24,883	0	3,659	12,164	0.004
25	7	36,674	55	24,883	0	3,297	8,494	0.003
26	7	33,041	55	24,883	0	2,970	5,188	0.002
27	6	29,768	55	24,883	0	2,676	2,209	0.001
28	5	26,819	55	24,883	0	2,411	-475	-0.000
29	5	24,162	55	24,883	0	2,172	-2,893	-0.001
30	4	21,769	55	24,883	0	1,957	-5,071	-0.002

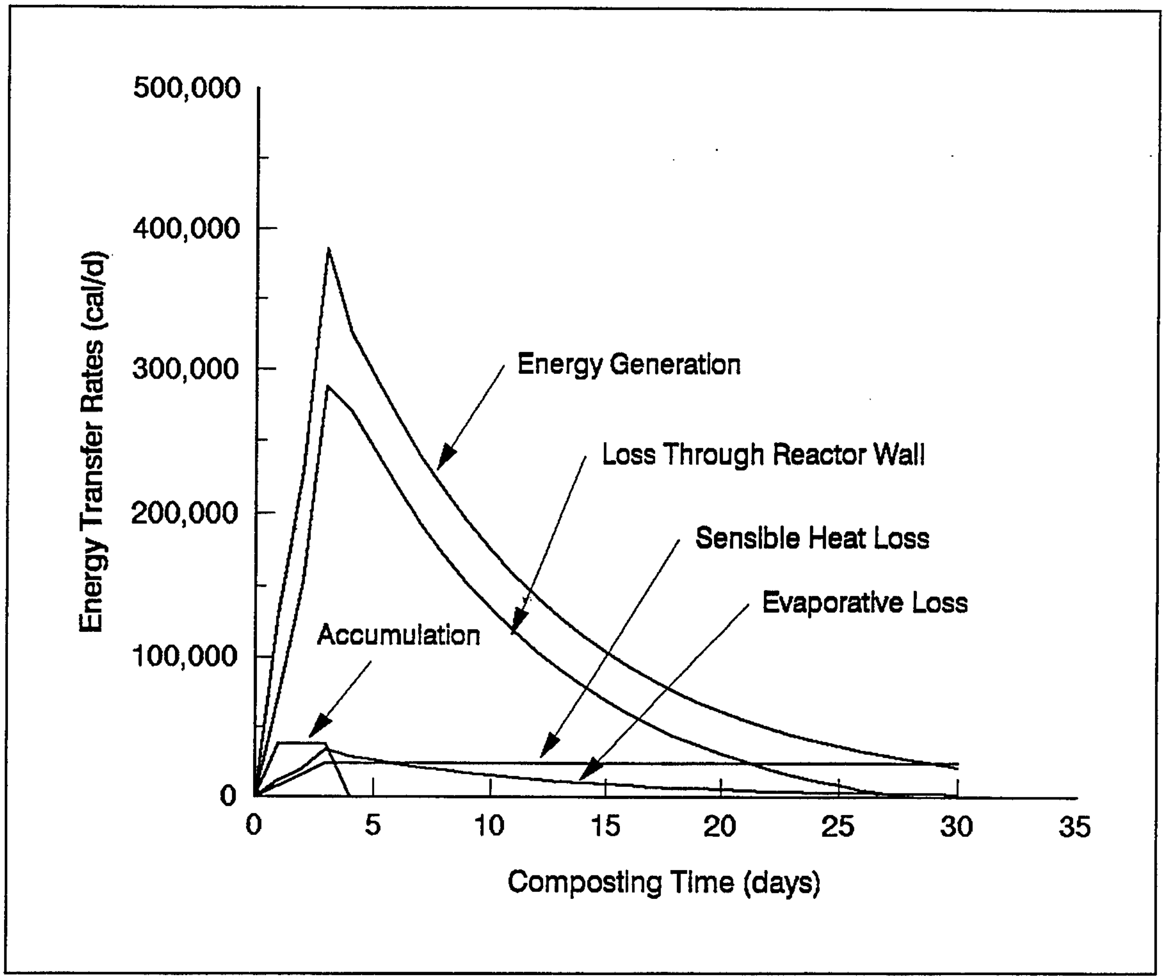

Figure 4. Various energy transfer rates during composting

Day 3 and stays the same because of the steady-state composting temperature of 55 °C. The heat accumulation rate is 38,430 cal/day for the first 3 days and becomes zero as the system reaches the steady-state temperature of 55 °C. It is constant for 3 days because the linear temperature is initially assumed to increase during this period. The heat loss rates through the reactor wall and evaporation both reach the maximum at Day 3 and gradually decrease as in the case of heat generation rate. Notice that after Day 28, the heat loss rate through the reactor wall is negative. In other words, heat must be added into the reactor in order to maintain the desired composting temperature of 55 °C. The required *U* increases to 0.105 cal/cm^2-hr-°C and also decreases as composting time increases.

Now, the above results are used to design a bench-scale composting reactor system. If one wants to design a similar system with an operational objective of achieving 55 °C in 2 days and maintaining the compost temperature at 55 °C for 5 days, the minimum *U* is 0.071 cal/cm^2-hr-°C for the first 7 days (Table 3). This will be our design *U*. This value is lower than the critical *U* of 0.18 cal/hr-cm^2-C reported by Seiden, Preston, and Chao (In preparation).

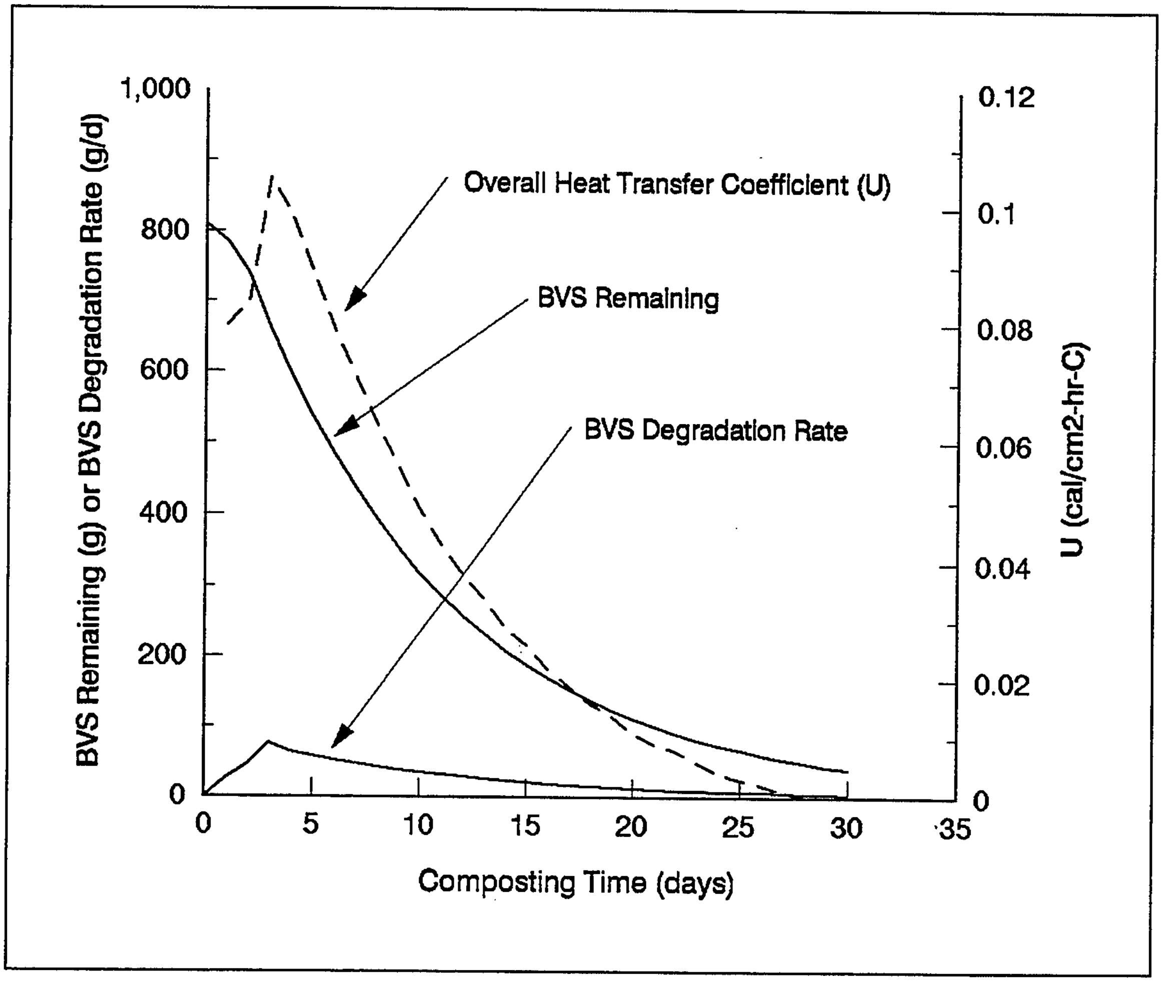

Figure 5. BVS degradation rate, *U*, and BVS remaining during composting

Seiden et al. developed a model for composting glucose and reported that the *U* value of the bench-scale composting reactor should be higher than a critical *U* value of 0.18 cal/hr-cm^2-°C in order to achieve thermophilic conditions within 5 days of composting. In contrast, Hogan, Miller, and Finstein (1989) indicated that a bench system would have to be covered with polyurethane foam (insulating material with K = 0.344 cal/cm-hr-°C) to a thickness of 3 m in order to maintain compost temperature 14 °C higher than room temperature. Neglecting other heat transfer resistance (i.e., conductive transfer through the reactor wall and convective transfer just outside of foam), the overall heat transfer coefficient can be estimated as $U = (0.344/300) = 0.00115$ cal/cm^2-hr-°C. With this system, compost described should be able to maintain 55 °C for 27 days according to Table 3.

The assumption is made that one has a reactor made of 0.32-cm-thick stainless steel (K_{ss} = 118.7 cal/cm^2-hr-°C) and decides to use glass wool (K_{gw} = 0.344 cal/cm-hr-°C) to insulate the system. The determination has to be made of how thick the glass wool must be in order to provide the desired *U* of 0.071 cal/cm^2-hr-°C. Figure 6 shows heat transfer scheme for this

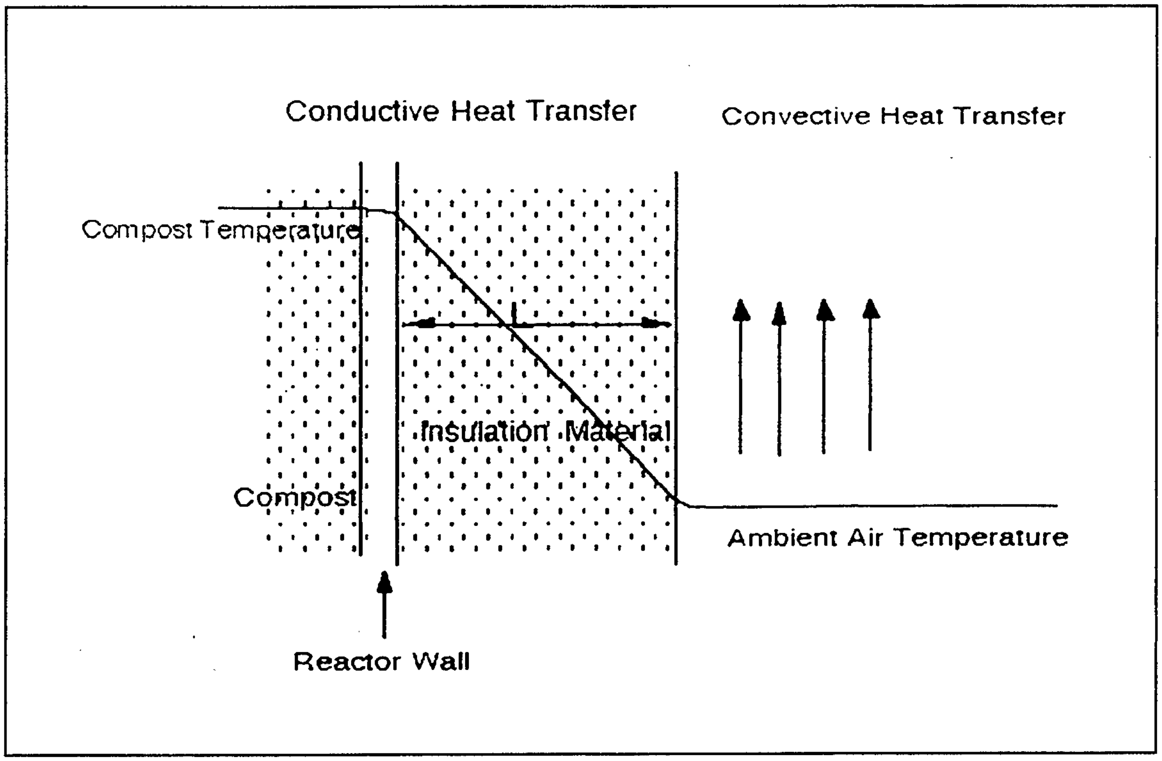

Figure 6. Heat transfer through reactor wall

example. Equations 23, 24, and 25 can be used to estimate the thickness of the glass wool. A value of 0.37 cal/cm^2-hr-°C is used for the convective heat transfer coefficient of the insulating material (Lienhard 1981).

$$\begin{aligned} 1/U &= (L/K_{SS})_{wall} + (L/K_{foam})_{wall} + (1/h_v)_{ins} \\ 1/U &= 1/0.071 = 0.32/118.7 + L/0.344 + 1/0.37 \end{aligned} \tag{45}$$

where L is the thickness of insulating material.

Solving Equation 45 for L, the design thickness of glass wool is 3.91 cm. The reason for this huge discrepancy in thicknesses of the insulating materials with similar thermal conductivities is not clear although a series of assumptions have been made to arrive at this point and different compost mixes have been used for this example.

Summary of Remediation Composting Parameters

All key parameters are briefly summarized in Table 4.

Table 4
Key Parameters for Remediation Composting Systems

Parameters	Class	Importance
Porosity	Physical	-Conduit for nutrients and air movement -Reservoir for moisture
Free airspace	Physical	-Oxygen and water vapor mass transfer -Heat transfer within compost matrix
Moisture content	Physical	-Provide water to compost microorganisms -Cools the overheated compost by evaporation
Paricle size	Physical	-Microbial reaction rates (surface area) -Pressure drop -Heat and mass transfer
Contaminated soil	Physical	-Affects the heat capacity of compost -Determines the amount of contaminants
Temperature	Physical	-Affects various microbial reaction rates -Determines the degree of pathogenic microorganism kill efficiency -Selects certain groups of microorganisms -Important parameter to ensure proper composting operation
Carbon to Nitrogen Ratio (C/N)	Chemical	-Provide adequate carbon and nitrogen to microorganisms -Provide energy and carbon for cell mass synthesis and maintenance
pH	Chemical	-May inhibit microbial processes if too acidic or basic -Affects the humification process
Contaminants	Chemical	-May inhibit the composting process -Compost microorganisms may not have adequate enzyme systems to break down the contaminants -Biodegradation versus biotransformation and incorporation into humic matter in soil
Biodegradability and biodegradation rate	Biological	-Biodegradability of each compost component varies -Affects the total amount of heat generated -Affects the process kinetics
Overall heat transfer coefficent	Thermodynamic	-Affects steady-state reactor temperature -Important design variable of the compost reactor

4 Standard Remediation Composting Protocol

The standard remediation composting protocol provides information required to systematically implement remediation composting at the pilot and operational levels. The objective of the standard composting protocol is to assist the compost system designer in designing the most economical, robust, and efficient compost system possible. The composting protocol has four steps: (a) initial site characterization, (b) respirometric experimentation, (c) bench-scale composting experimentation, and (d) toxicological experimentation (optional).

Initial Site Characterization

Initial site characterization consists of the initial site visit, soil characterization, and identification of the contaminant concentration. The initial site characterization is very important because it provides the foundation upon which the resulting investigation and implementation rests.

The initial site visit should begin with an orientation on the climate, physical geology, and agricultural practices in the region surrounding the site. Some preparation can be performed prior to the site visit, a general outline of site characteristics can be obtained from the U.S. Geological Survey (USGS) and U.S. Department of Agriculture, Soil Conservation Survey (USDA-SCS). The USDA-SCS soil survey documentation is of particular importance because not only soil types but also predominant agricultural practices in the region are provided. Agricultural practices may have a direct bearing on what amendments are available at the site and at what cost.

The investigator should visit the site and be prepared to review any documentation available on the extent of the soil contamination. The investigator should begin with site surveys and site remediation histories. The installation environmental coordinator will be the investigator's main point of contact and will generally be helpful in ensuring that all documentation is available. It is important, however, to meet as many people as possible who have historical knowledge concerning past practices at the installation.

Sufficient sample should be collected and sent to the laboratory for testing. A 55-gal drum holds approximately 0.2 m^3 and is generally sufficient. The soil should be relatively dry and friable. Upon receipt of the soil, it should be passed through a sieve to separate out explosive chunks, stones, plant roots, and other debris. The soil should be further screened to 2 cm. Larger material is discarded by appropriate means. The soil is then homogenized by passage through a riffle splitter no less than three times to produce a consistent sample for future study. The soil should be characterized regarding the following:

a. Contaminant concentration.

b. Soil type.

c. pH and buffer capacity.

d. Total organic carbon.

e. Particle-size distribution (hygrometric).

f. Moisture content.

g. Bulk density.

h. Nutrient levels (nitrogen and phosphorous, if needed).

i. Cation exchange capacity.

Finally, the soil should be stored in air-tight containers at 4 °C until needed for testing.

Respirometric Analysis

Respirometric analysis is an important step in designing subsequent bench-scale remediation composting experiment. A respirometer is a device that measures oxygen usage or carbon dioxide evolution from microbial metabolic activities in a small, closed reactor. By monitoring the total accumulated oxygen uptake and its rate, biochemical oxygen demand and the substrate degradation kinetics can be estimated (Chapter 3).

This information is used to calculate the thermal energy generation rate due to substrate degradation and to design bench-scale composting reactor insulating configuration. In addition to the kinetic information of substrate degradation, monitoring the fates of the target explosive compounds and their transformation products provides valuable information regarding feasibility of the design compost mix and the retention time for subsequent bench-scale composting experiment in order to meet the treatment goal. Contaminant transformation information should be taken, if possible, to gain insight into the possible success of the process. However, there should be no expectation that the observed transformation rates will correspond to later observations. Other valuable information derived from the respirometric test includes confirmation of the range of contaminant concentrations likely to be observed in the bench experimentation, comparison of many treatment approaches, and immediate respiration data.

The disadvantage of the respirometric analysis is that while temperature is adjustable, the incubation must be done at a constant temperature. As a result, mesophilic and thermophilic microbial communities are not able to develop in the same manner as in the bench-scale remediation compost system and in the actual compost piles. However, respirometric tests are still useful as a screening tool to determine which of the multiple composting parameters are significantly influential to a specific soil and contaminants.

Respirometric test cells should consist of the following combination in order to produce maximum information. Generally, run times are on the order of from 10 to 30 days. Given the small volume of most commercial respirometers, sampling techniques are limited to initial evaluation and sacrificial evaluation at the end of the experiment.

a. Blank cell - There is no "good" method of inhibiting microbial growth in compost mixtures. Both autoclaving and mercury poisoning have complications in regard to altering the form of the contaminant, safety, and expense. Blank cells should be prepared, however, either by autoclaving or poisoning the test compost mixture that contains both organic substrates, bulking agent, and the contaminated soils. This cell will be used to compare treatments with and without inhibition.

b. Test cells - Test cells should be made of the same amount of organic substrates and bulking agents, but with varying amounts of contaminated soils. The data from these cells will provide preliminary information regarding the maximum soil loadings and possible inhibitory levels of the contaminants.

Bench-Scale Remediation Composting Experimentation

Upon completion of the respirometric testing, bench-scale remediation composting experimentation is necessary in order to further optimize composting and to confirm that the treatment goals can be met with the appropriate process parameters obtained from the respirometric experimentation.

Bench-Scale Compost Reactor Configuration

The bench-scale reactor should simulate, as close as possible, field- or pilot-scale conditions. To accomplish this, it is imperative that the temperature elevation in the test cell occur due to the conservation of metabolically generated heat and the temperature be managed by manipulation of reactor ventilation. This is imperative because in almost all implementation and pilot scenarios, internal self-heating is used to ensure matrix heating through the mesophilic and thermophilic ranges; pile ventilation either by force aeration and/or frequent turning will be the method of heat management.

Several researchers achieved the optimal thermophilic conditions in their bench-scale composting system by using a compost reactor temperature feedback control system for conservation of the metabolically generated heat by raising reactor wall temperature to minimize the conductive heat loss through the wall (Cook, Bloom, and Halbach 1994; Hogan, Miller, and Finstein 1989; Magelhaes et al. 1993; USAEC 1994). At the U.S. Army Engineer Waterways Experiment Station (WES), two different types of bench-scale composting systems were developed in order to investigate the fate of explosive compounds during composting and the effects of various process variables on the remediation efficiency. Detailed description of these efforts are provided in Appendixes A, B, and C. Table 5 summarizes brief descriptions of these bench-scale composting systems. These systems use the temperature feedback control system, which constantly monitors the compost temperature and adjusts the reactor wall temperature a few degrees below the compost temperature either by heating water surrounding the reactor wall or by heating tapes. In this way, the heat flux through the reactor wall is minimized; at the same time, external heat does not flow into the reactor and influence the microbial activities. A few of these investigators also used prehumidified air in order to prevent the evaporative heat loss from the reactor.

One can design the bench-scale compost reactor without using the sophisticated temperature feedback control system. As discussed in Chapters 2 and 3, investigators should determine appropriate compost ingredients first and calculate the quantity of heat that could be generated by degradation of substrates at various time intervals using the degradation kinetics and the heat of reactions. The evaporative heat loss can be estimated for two extreme cases: (a) dry air inlet and fully humidified air outlet and (b) fully humidified air inlet and outlet. For the first case, the evaporative heat loss is calculated by using Equation 17. For the second case, the evaporative heat loss may be negligible. Knowing all other heat generation and loss terms for a desired operating condition (i.e., temperature, retention time, etc.) except for the heat loss through the reactor wall term, a design overall heat transfer coefficient is calculated using the first law of thermodynamics. One can achieve desired reactor insulating characteristics in order to meet the design overall heat transfer coefficient by manipulating insulation materials, quantity, or ambient temperature.

Table 5
Bench-Scale Composting Systems

Reactor Size, ℓ	Heat Conduction Control Scheme	Aeration Scheme	Temperature Control Scheme	Reference
14	Insulation and Air	Humidified Air at 18 °C	Feedback Control to Electric Chamber	Hogan, Miller, and Finstein 1989
10	Insulation and Heating Tape	Humidified Air at 30 °C	Feedback Control to Heating Tape	Magelhaes et al. 1993
20	Water Bath	Ambient Air	Feedback Control to Water Bath	Cook, Bloom, and Halbach 1994
1 to 3	Water Bath	Ambient Air	Feedback Control to Water Bath	USAEC 1994
14	Water Batch and Insulation	Humidified Air at Near Compost Temperature	Feedback Control to Water Batch	Appendix A, B, and C of this report

Loading Procedures

The first step in bench reactor loading is mixing of the compost. Ideally, a single batch of compost material should be mixed for all of the bench reactors. The dry compost materials should be mixed before the contaminated soil is added. Water should then be added to the optimum moisture content. Additional soil and moisture can then be added to the mixture to produce the higher soil-loaded reactors. Mixing separate batches of materials for each bench reactor or pair of reactors requires great care to ensure that the same proportions of all materials are added to each batch. Consistent moisture levels for each batch is critical for the replication of the experiment.

The dry components of the compost mixture should be completely mixed in a low-shear mixer or by hand. Care should be taken not to ignite the explosive-contaminated soil. Complete mixing of the contaminated soil with the other materials is necessary. However, overmixing must be avoided, as it may cause loss of structure and porosity. This should be accomplished with the driest materials added first to a rotary or drum mixer so that a consistent material is produced. A small cement mixer has been used successfully.
A rotary or tumbling mixer may also be appropriate. High sheer mixers such as those with blades or paddles (like dough mixers) are usually detrimental to the structure of the compost materials. For small samples, the twin-shell, dry soil blender (Paterson-Kelley Co., East Stroudsburg, PA) has proved to be useful.

Next, water is added to bring the compost mixture up to a final moisture content. Establishing the optimum moisture content is often best accomplished by visual inspection of the compost as it is being mixed. The compost material should be moist, but must remain friable and crumbly. Clumping must be avoided. The optimum moisture content is usually the maximum amount of moisture that can be added without loss of structure in the compost mass.

Finally, representative samples are collected from the overall compost mass for comparison. Subsamples should be taken to provide information on bulk density, moisture and nitrogen contents, organic carbon, and contaminants. Compost should be extracted for analysis of contaminants and breakdown products immediately or kept frozen until the extraction procedure is performed.

The compost mixture is then added to the reactors as soon as possible after mixing to guard against drying and/or premature microbial activity. The placement of the compost mixture in the bench reactor is a critical step as it is a common source of variability. The compost material should be uniformly packed throughout the vessel and a good seal made with the sides of the vessel to prevent short-circuiting of the air between the compost material and the side of the vessel. At the same time, the material should not be compacted excessively, as this will lessen its free air space and impede the flow of air, perhaps allowing anaerobic pockets to develop.

Operational Procedures

Overall system operation should be confirmed to the extent possible prior to the reactor loading. Sampling ports should be provided in the side of the reactor to allow the removal of sample during operation. Sampling scheme will vary given the particular objective of the experiment; however, care should be taken that the volume removed from the reactor during operation be limited to that absolutely necessary for process monitoring. Removal of greater than approximately 5 percent of the total reactor volume during the life of the experiment should be considered excessive.

Operational parameters such as reactor temperature, prehumidifier temperature, gas flow rate, input air pressure, and oxygen or carbon dioxide concentration in the exit air should be continually monitored, if possible. At a minimum, the reactor temperature and the oxygen content in the exit air should be continually monitored.

Analytic procedures for samples taken from the reactors will vary with the objective of the experiment. In taking reactor samples, an effort should be made to take representative samples from various parts of the reactor. Some specific analyses for consideration include compost pH, moisture content, ash and volatile solids, bulk density, concentrating contaminants and the breakdown products concentrations, and microbial population.

Upon completion of the experiment, all the internal parts of the reactors should be cleaned with a nonphosphorus mild detergent, triple rinsed. Next, the internal parts of the reactor should be rinsed and dried thoroughly. This cleaning should then be followed by a cleaning with an organic solvent such as isopropyl alcohol.

Data Analysis

Data analysis and interpretation should include an estimation of kinetic parameters of destruction/transformation of the contaminants. Since the first-order disappearance rate with respect to the contaminant concentration is most widely used, the rest of the section will discuss how to obtain the kinetic coefficients (k_c) and the half-life ($t_{1/2}$). Without considering the reactor temperature variation during composting, an apparent first-order rate coefficient is calculated as:

$$k_a = - In\ (C_t/C_o)/t \tag{46}$$

where

k_a = apparent first-order rate coefficient

C_t = contaminant concentration at time t

C_o = initial contaminant concentration

t = composting time

For a set of kinetic data, a linear regression should be used to best estimate the apparent rate coefficient with the least residual. Once the rate coefficient is calculated, the time required to dissipate half of initial contaminant concentration, half-life ($t_{1/2}$), is calculated as:

$$t_{1/2} = - In\ (1/2)/k = 0.693/k \tag{47}$$

Notice that if the apparent rate coefficient is used in Equation 47, the half-life is also apparent, i.e., this value is limited to the same reactor temperature conditions throughout the incubation. It is usually desirable to estimate kinetic parameters as a function of temperature. The temperature dependency of kinetic parameters is usually modeled using the Arrhenius relationship.

$$k_T = k_{20}\, \theta^{T-20} \tag{48}$$

where

k_{20} = rate coefficient at 20 °C

k_T = rate coefficient at T °C

θ = temperature-activity constant.

The rate coefficient at 20 °C and the value of theta for a set of kinetic data can be estimated from the following equation.

$$k_{Ti} = -\,In\,(C_{i+1}/C_i)/(t_{i+1} - t_i) = k_{20}\,\theta^{Ti-20} \tag{49}$$

where

k_{Ti} = rate constant at $T = T_i$ and $t = t_i$

C_i = contaminant concentration at $t = t_i$

C_{i+1} = contaminant concentration at $t = t_{i+1}$

T_i = reactor temperature at $t = t_i$

With the kinetic data, two kinetic parameters (k_{20} and *theta* in Equation 49) are estimated using a nonlinear multiparameter evaluation scheme. Another way is to assume a value of the *theta* and estimate k_{20}. The values of *theta* are usually very close to unity; for instance, the range of *theta* for trickling filter processes is between 1.02 and 1.08 (Metcalf and Eddy, Inc. 1991). Equation 6 suggests a value of 1.066 for the temperature-activity constant for composting systems.

Toxicological Examination (optional)

Composting is an innovative technology whose focus is the reduction of the apparent toxicity of hazardous contaminants in the soil matrix. Although toxicity evaluations for the composting soils contaminated with explosive compounds are available in the literature (Griest 1993), some evaluation of the reduction of toxicity associated with a particular composting site will be very helpful given a particular regulatory situation. As such, toxicity evaluation during bench studies may become a vehicle to ensure, at the earliest point of consideration, that the technology will accomplish the intended goal, i.e., reduction of the risk associated with the contaminants in the environment. For this reason, genotoxicity and acute toxicity testing should be considered for performance on the unaltered soil and on the soil/compost mixture at the end of bench studies. Testing might include, but is not limited to, genotoxicity testing to include Mutatox assay testing, Ames testing, or TA-100 (base-pair mutations), and chronic toxicity testing to include worm casting and/or seed germination studies.

5 Summary

In this report, principles of biochemical process kinetics, and mass and heat transfer during composting were highlighted. In regard to organic substrate utilization, the kinetics of organic substrate utilization and the kinetics of explosive compound degradation/transformation were discussed. Substrate utilization kinetics were used to link rate constants for degradation with biodegradable volatile solids. Explosive degradation kinetics were discused in some detail; however, whether the energetics degradation is the result of metobolism or cometabolism remains to be elucidated and linked to overall substrate utilization.

Four classes of process parameters, physical, chemical, biological, and thermodynamical, were addressed in detail. Physical parameters include porosity, free air space, moisture content, particle size, and temperature. Equations for determining each parameter and the appropriate limitations for each were provided. Examined next were chemical parameters such as the effects of contaminant loading, the optimum carbon to nitrogen ratio, and the acidity (pH) with the suggested optimal values presented. Biodegradability, biodegredation rate, stoichiometric oxygen requirements, and aeration come examined under the heading of biological factors, each discussed in detail. Finally, the overall heat transfer coefficient and related concepts were examined under the heading of thermodynamics factors. Possible development of an overall critical heat tranfer coefficient is discussed as its implications on bench- and pilot-system sizing.

Various methods were suggested to estimate many process parameters, and the impact of these parameters on the efficiency of remediation composting was discussed. Furthermore, a practical example was provided to design an insulation system for a bench-scale composting reactor based on physicochemical and biological properties of compost mix, process kinetics, desired operating conditions, and heat transfer phenomena.

Finally, a standard remediation composting protocol was established to help others to conduct a bench-scale composting study. The protocol discussed initial site characterization, respirometric experimentation, bench-scale composting experimentation, and toxicological experimentation. Various parameters to be measured during site characterization and preliminary respirometric analysis were discussed as were various bench-scale composting system configurations currently used by researchers. Loading and operational procedures and data analysis were described. Finally, toxicological tests of the composted soil that will help to gain more support from regulatory agencies and the public were suggested.

6 Recommendations for Future Study

For future study in composting explosive-contaminated soils, the following recommendations are presented.

More comprehensive study in the fate and the biogeochemical pathways of many target contaminants is critically needed in order to gain the acceptance of this technology by regulatory agencies. The study should include the effects of many process variables on the target contaminants degradation or transformation and humification of the original contaminants and the transformation products. For example, effects of pH, aeration, C/N ratio, and types and concentration of growth substrate on contaminants degradation/ transformation and on the humification are not clearly understood at this time. Furthermore, a long-term leaching potential of humified contaminants and the transformation products needs to be assessed if these compounds are toxic.

Oxygen transport mechanisms and its profiles within the compost matrix are not clear and need to be thoroughly investigated. Microelectodes may be used for in situ measurement of the oxygen level within the compost matrix. Manipulation of aerobic, anoxic, and anaerobic zones within the compost matrix may have a profound effect on target contaminants degradation. This study introduced a theoretical framework for systematically designing an adequate insulation system for the bench system based on energy balance, process kinetics, and the overall heat transfer coefficient. This procedure needs to be verified with a series of careful experiments. Most of all, clear engineering design criteria for bench-scale composting systems based on the theoretical framework must now be fully developed in order to assist users to properly design self-heating composting systems. These design criteria will assist the scientific communities for further research in fate and leaching studies, U.S. Army and other military installations for preliminary feasibility and optimization studies, and regulatory agencies for establishing proper guidelines for this technology.

References

Alexander, M. (1977). *Introduction to soil microbiology.* John Wiley, New York.

Alexander, M., Schmidt, S. K., Simpkins, S. (1985). "Models for the kinetics of biodegradation of organic compounds not supporting growth," *Applied Environmental Microbiology* 50, 323.

Bach, P. D., Nakasaki, N., Shoda, M., and Kobota, H. (1987). "Thermal balance in composting operations," *Journal of Fermentation Technology* 65(2), 199.

Bollen, G. J. (1985). *Composting of agricultural and other wastes.* J. K. R. Gasser, ed., Elsevier Applied Science, London.

Boopathy, R., Kulpa, C. F., Manning, J., and Montemagno, C. D. (1994b). "Biotransformation of 2,4,6-trinitrotoluene (TNT) by cometabolism with various co-substrates: A laboratory-scale study," *Biores. Technology* 47, 205.

Boopathy, R., Wilson, M., Montemagno, C. D., Manning, J. F., and Kulpa, L. F. (1994a). "Biological transformation of 2,4,6-trinitrotoluene (TNT) by soil bacteria isolated from TNT-contaminated soil," *Biores. Technology* 47, 19.

Chang, M. K., Voice, T. C., and Criddle, C. S. (1993). "Kinetics of competitive inhibition and cometabolism in the biodegradation of benzene, toluene, and p-xylene by two pseudomonas isolates," *Biotechnology and Bioengineering* 41, 1057.

Cook, A. M. (1987). "Biodegradation of s-triazine xenobiotics," *FEMS Microbiology Review* 46, 93.

Cook, B. D., Bloom, P. R., and Halbach, T. R. (1994). "A method for determining the ultimate fate of synthetic chemicals during composting," *Compost science and utilization, winter*, 42.

Criddle, C. S. (1993). "The kinetics of cometabolism," *Biotechnology and Bioengineering* 41, 1048.

Criddle, C. S., DeWitt, J. T., and McCarty, P. L. (1990). "Reductive dehalogenation of carbon tetrachloride by escherichia coli k-12," *Applied Environmental Microbiology* 56, 3240.

Doyle, R. C., and Isbister, J. D. (1982). "Treatment of TNT and RDX contaminated soils by composting." *Proceeding of National Conference on Management of Uncontrolled Hazardous Waste Sites*. November 29 - December 1, Washington, DC, 209.

Doyle, R. C., Isbister, J. D., Anspach, G. L., and Kitchens, J. F. (1986). "Composting of explosive/organics contaminated soils," *U.S. Army Report* AMXTH-TE-CR-86077. Aberdeen Proving Ground, MD.

Ebeling, J. M., and Jenkins, B. M. (1985). "Physical and chemical properties of biomass fuels," *Transportation ASAE* 28(3), 899.

Finstein, M. S. (1980). "Composting microbial ecosystem," *Compost Science and Land Utilization* 21(4), 25.

Finstein, M. S., Miller, F. C., MacGregor, S. T., Psarianos, K. M. (1985). *The rutgers strategy for composting: Process design and control*. EPA/600/2-85/059, U.S. Environmental Protection Agency, Cincinnati, OH.

Finstein, M. S., and Miller, M. C. (1985). *Composting of agricultural and other wastes*. J. K. R. Gasser, ed., Elsevier Applied Science, London.

Finstein, M. S., Miller, F. C., and Strom, P. F. (1986). "Monitoring and evaluating compost process performance," *Journal of the Water Pollution Control Federation* 58, 272.

Fitzpatrick, G. E. (1993). "A program for determining cocompost blending ratios," *Compost science and utilization,* Summer, 30.

Forster, C. F., and Wase, D. A. J. (1987). *Environmental biotechnology*. John Wiley and Sons, New York.

Galli, R., and McCarty, P. L. (1989). "Kinetics of biotransformation of 1,1,1-trichloroethan by *clostridium sp.* strain TCA IIB," *Applied Envrionmental Microbiology* 55, 845.

Garg, R., Grasso, D., and Hoag, G. (1991). "Treatment of explosives contaminated lagoon sludge," *Hazardous Waste and Hazardous Materials* 8(4), 319.

Golueke, C. G. (1991). "Principles of composting." *The biocycle guide to the art and science of composting*. J. Waste Recycling, The JG Press, Inc.

Gotaas, H. B. (1956). "Composting sanitary disposal and reclamation of organic wastes," World Health Organization, Monograph series, No. 31, Geneva.

Greenburg, A. E., Clesceri, L. S., and Eaton, A. D., Joint Editorial Board. (1992). *Standard methods for the examination of water and wastewater.* American Public Health Association, Washington, DC.

Griest, W. H., et al. (1993). "Chemical and toxicological testing of composted explosives—contaminated soil," *Environmental Toxicology and Chemistry* 12, 1105.

Hanif, M. (1995). "Focus on composting," *Hazardous Technical Information Services* May/June, 7.

Haug, R. T. (1993). *The practical handbook of composting engineering.* Lewis Publishers, Ann Arbor, MI.

Hogan, J. A., Miller, F. C., and Finstein, M. S. (1989). "Physical modeling of the composting ecosystem," *Applied and Environmental Microbiology* 55(5), 1082.

__________. (1989). "Physical modeling of the composting ecosystem," *Applied and Environmental Microbiology* 55(5), 1082.

Isbister, J. D., Aspach, G. L., Kitchens, J. F., and Doyle, R. L. (1984). "Composting for decontamination of soils containing explosives," *Microbiologies* 7, 47, Cited in Williams et al. (1992). "Composting of explosives and propellant contaminated soils under thermophilic and mesophilic conditions," *Journal Industrial Microbiology* 9, 137.

Kaplan, D. L., and Kaplan, A. M. (1982a). "Composting industrial wastes—biochemical consideration," *BioCycle* May/June, 42.

__________. (1982b). "Thermophilic biotransformations of 2,4,6-trinitrotoluene under simulated composting conditions," *Applied and Environmental Microbiology* 44(3), 757.

__________. (1982c). "Mutagenicity of 2,4,6-trinitrotoluene-surfactant complexes," *Bulletin of Environmental Contamination Toxicology* 28, 33.

Kayhanian, M., and Tchobanoglous, G. (1992). "Computation of C/N ratios for various organic fractions," *BioCycle* May, 33.

Keener, H. M., Marugg, C., Hansen, R. C., and Hoitink, H. A. J. (1993). "Optimizing the efficiency of the composting process." *Science and engineering of compost design, environmental, microbiological and utilization aspects.* H. A. J. Hoitink and H. M. Keener, ed., Renaissance Publications, Worthington, OH, 59.

Klein, S. A. (1972). "Anaerobic digestion of solid waste," *Compost Science* Jan/Feb, Cited in Haug (1993).

Levinson, H. S., McCormick, N. G., and Feeherry, F. E. (1976). "Microbial transformation of 2,4,6-trinitrotoluene and other nitroaromatic compounds," *Applied and environmental microbiology* 31(6), 949.

Lienhard, J. H. (1981). *A heat transfer textbook.* Prentice-Hall, Inc., New Jersey.

Magalhaes, A. M. T., Shea, P. J., Jawson, M. D., Wicklund, E. A., Nelson, D. W. (1993). "Practical simulation of composting in the laboratory," *Waste Management and Research* 11, 143.

Marugg, C., Grebus, M., Hansen, R. C., Keener, H. M., Hoitink, H. A. J. (1993). "A kinetic model of the yard waste composting process," *Compost Science and Utilization,* Premier Issue, 38.

Mathur, S. P. (1991). "Composting processes." *Bioconversion of waste materials to industrial products.* A. M. Martin, ed., Elsevier Science Publishers LTD., New York.

Mears, D. R., Singley, M. E., and Gholam, A., and Rupp, F., III. (1975). "Thermal and physical properties of compost." *Energy, agriculture, and waste management.* W. L. Jewell, ed., Ann Arbor Science Publisher, Inc., Ann Arbor, MI.

Metcalf and Eddy, Inc. (1991). *Wastewater engineering: Treatment, disposal, reuse.* McGraw-Hill, Inc., New York.

Osmon, J. L., Klausmeir, R. E. (1972). "The microbial degradation of explosives," *Developments in Industrial Microbiology* 14, 247-252.

Pennington, J. C., et al. (1995). "Fate of 2,4,6-trinitrotoluene in a simulated compost system," *Chemosphere* 30(3), 429.

Phelphs, T. J., Niedzielski, J. J., Shram, R. M., Herbes, S. E., and White, D. C. (1990). "Degradation of trichloroethylene in continuous recycle expanded-bed bioreactors," *Applied Environmental Microbiology* 56, 1702.

Pointcelot, S. P. (1975). "Biochemistry and methodology of composting," Connecticut Agric. Expt. Sta. Bulletin 754.

Ro, K. S., and Chung, K. H. (1995). "Wetland sediment biotransformation of atrazine under different nutrient conditions - II: Aerobic," *Journal of Environmetal Science and Health* A30, 121.

Ryan, J. R., Kabrick, R., and Loehr, R. (1988). "Biological treatment of hazardous wastes," *Civil Engineering* 58(2), 65.

Saez, P. B., and Rittmann, B. E. (1991). "Biodegradation kinetics of 4-chlorophenol and inhibitory co-metabolites," *Research Journal of the Water Pollution Control Federation* 63, 838.

Schulze, K. L. (1962). "Continuous thermophilic composting," *Compost Science* 22.

Seiden, S., Preston, K. T., and Chao, A. "Mathematical model for determining the overall heat transfer coefficient of a bench-scale composter," Report in preparation, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Strand, S. E., Bjelland, M. D., and Stensel, H. D. (1990). "Kinetics of chlorinated hydrocarbon degradation by suspended cultures of methane-oxidizing bacteria," *Research Journal of the Water Pollution Control Federation* 62, 124.

Suler, D. (1979). "Composting hazardous industrial wastes," *Compost Science/Land Utilization* July/August, 25.

Szabo, Z., Horvath, A., Schiefner, K., Vaughn, B., Dora, G., and Szabo, K. (1988). "Treatment of hazardous wastes by composting." *Hazardous waste: Detection, control, treatment*. R. Abbou, ed., Elsevier Science Publishers B.V., Amsterdam, Netherlands, 1663.

U.S. Army Environmental Center. (1993). "Windrow composting demonstration for explosives-contaminated soils at the Umatilla Depot Activity Hermistron, Oregon," Contract No. DACA31-91-D-0079, Report No. CETHA-TS-CR-93043.

__________. (1994). "Amendment selection and process monitoring for contaminated soil composting," Contract No. DACA 31-91-R-0009, Report No. ENAEC-TS-CR-93109.

U.S. Army Toxic and Hazardous Materials Agency. (1988). "Field demonstration composting of explosive contaminated sediments at Louisiana Army Ammunition Plant (LAAP) Final Report," Contract No. DAAK-11-85-D-007, Report No. AMXTH-IR-TE-88242, Aberdeen Proving Grounds, MD.

__________. (1989). "Field demonstration - composting of propellants contaminated sediments at the Badger Army Ammunition Plant (BAAP) Draft Final Report," Contract No. DAAK-11-85-D-007, Report No. CETHA-TE-CR-89061, Aberdeen Proving Grounds, MD.

__________. (1991). "Final Report - optimization of composting for explosive contaminated soils," Contract No. DAA-15-88-D-0010, Report No. CETHA-TS-CR-91053, Aberdeen Proving Grounds, MD.

U.S. Environmental Protection Agency. (1992). "Nitroaromatics and nitramines by high performance liquid chromatography," SW846 Method 8330, Office of Solid Waste and Emergency Response, Washington, DC.

Wakao, N., and Kaguei, S. (1982). *Heat and mass transfer in packed beds*. Gordon Breach Science Publishers, New York.

Waksman, S. A. (1938). *Humus*. Williams and Wilkins Co., Baltimore, MD, Cited by Mathur (1991).

Williams, R. T., and Myler, C. A. (1990). "Bioremediation using composting," *BioCycle* November.

Williams, R. T., Ziegenfuss, P. S., Sisk, W. E. (1992). "Composting of explosives and propellant contaminated soils under thermophilic and mesophilic conditions," *Journal of Industrial Microbiology* 9, 137.

Won, W. D., DiSalvo, L. H., and Ng, J. (1976). "Toxicity and mutagenicity of 2,4,6-trinitrotoluene and its microbial metabolites," *Applied and Environmental Microbiology* 31, 576.

Yusuf, M., Johnson, J. H., and Won, L. (1991). "Detoxification of contaminated sludge via in-vessel composting." *The Proceedings of the 23rd Mid-Atlantic Industrial Waste Conference.* 2417.

Appendix A
U.S. Army Engineer Waterways Experiment Station Experience

Introduction

Fate of explosive compounds during composting and the effects of various process variables were investigated at the U.S. Army Engineer Waterways Experiment Station (WES) using bench-scale remediation composting systems. The investigation was divided into two phases of experiments using two different composting reactor systems: Waterways Experiment Station Adiabatic System I and II (WACS-I and WACS-II). The WACS-I was stainless steel reactors with water jackets, and the WACS-II was insulated, polyvinyl chloride reactors.

The goals of the WES investigations were (a) to study the fate of explosive contaminants under different process conditions using the WACS-I (Phase-I) and (b) to study the effects of aeration, temperature feedback control, and contaminated soils on the bench-scale composting reactor system using the WACS-II (Phase-II).

Materials and Methods

Composting reactor systems

Both systems (WACS-I, -II) had a working volume of about 14 ℓ and used water as a heat transfer medium to heat or cool the outside of the reactors in order to minimize the conductive heat loss by providing very small temperature gradients between the compost matrix and the outside of the reactor. Thermistors continuously monitored the inside temperature of compost matrix, thermal control units heated or cooled water to the temperature a few degrees below that of the compost matrix, and centrifugal pumps circulated the water either inside of the water jacket for WACS-I or into the heat exchangers to heat the insulating chambers for WACS-II. A schematic diagram of the first

WACS system is shown in Figure A1. A complete description of the two systems developed at WES, WACSI and WACS II, are in Appendixes B and C.

In addition to the sophisticated temperature feedback systems, WACS-I had CO_2 and VOCs traps using KOH and tenax filters. These traps were used during the experiments using radiolabeled TNT compounds in order to complete the mass balance of added radioactivity.

WACS-I was programmed to blow dry air into the composting reactor only when the compost temperature was higher than 55 °C. The prime objective of aeration was to cool the overheated compost. In contrast, air was introduced for a minute for every 10-min interval in WACS-II. The air for WACS-II was presaturated with water in order to minimize water evaporation and subsequent cooling of compost. The air was preheated to near the compost temperature by bubbling through a heat exchanger filled with water at or near the compost temperature.

Compost Compositions

The compost consisted of six ingredients: alfalfa, apples, cow manure, potatoes, sawdust, and contaminated soil. This compost composition was chosen in order to simulate the static compost pile (SP-8) of the Umatilla Army Depot Activity (UMDA) pilot study (USATHAMA 1991).[1] The contaminated soil was obtained from UMDA. Physical characteristics and the contaminant concentrations of the soil are shown in Table A1. The soil occupied 10 percent of the compost volume or 1.5 ℓ within the reactor. Sawdust and alfalfa (each about 3 ℓ or 22 percent by volume) were used as bulking agents. Apples (0.8 ℓ or 6 percent by volume) and potatoes (2.3 ℓ or 17 percent by volume) were used as additional carbon sources for compost biomass. The cow manure (4.5 ℓ or 33 percent by volume) provided active biomass population.

Reactor Loading and Sampling

The 5-gal Kelly-Patterson twin shell mixer was used to homogenize the compost mix. The sawdust, alfalfa, and soil were mixed first for no less than 1 hr; the apples and the potatoes were then added, and the compost was mixed again for a minimum of 1 hr. Finally, the bovine manure was mixed for a minimum of 2 hr. The compost was then loaded into the reactor (s).

Compost was removed from the sampling ports during operation. To gain access to the compost, one of the threaded plugs was unscrewed from the

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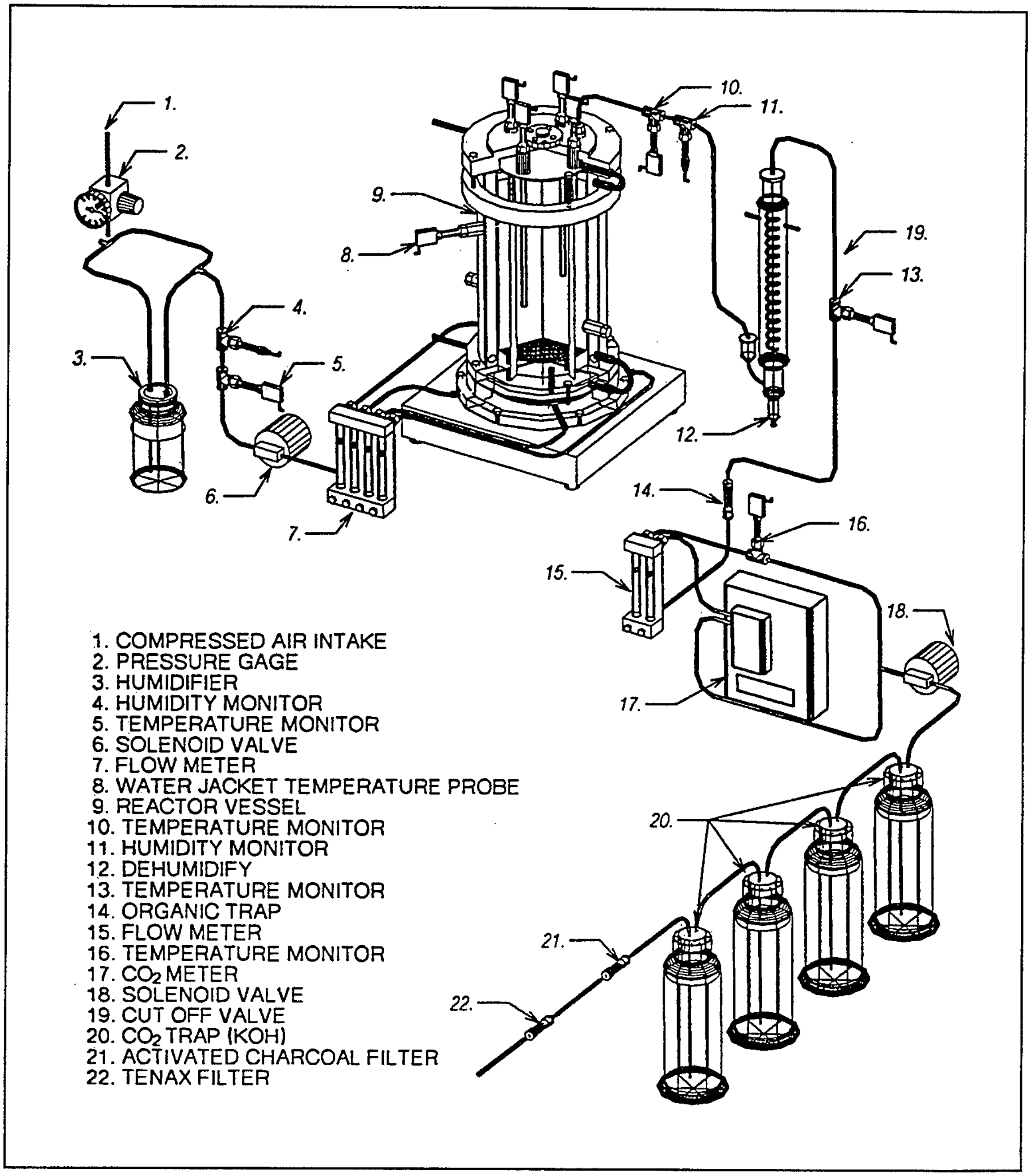
[1] References cited in this appendix are located at the end of the main text.



1. COMPRESSED AIR INTAKE
2. PRESSURE GAGE
3. HUMIDIFIER
4. HUMIDITY MONITOR
5. TEMPERATURE MONITOR
6. SOLENOID VALVE
7. FLOW METER
8. WATER JACKET TEMPERATURE PROBE
9. REACTOR VESSEL
10. TEMPERATURE MONITOR
11. HUMIDITY MONITOR
12. DEHUMIDIFY
13. TEMPERATURE MONITOR
14. ORGANIC TRAP
15. FLOW METER
16. TEMPERATURE MONITOR
17. CO_2 METER
18. SOLENOID VALVE
19. CUT OFF VALVE
20. CO_2 TRAP (KOH)
21. ACTIVATED CHARCOAL FILTER
22. TENAX FILTER

Figure A1. Schematic diagram of the WACS

Table A1
Physical Characteristics and the Contaminant Concentrations of the Soil

Physical Properties	
Color pH	10YR 2/2, Very Dark Brown 7.59

Average Densities of Fractions (oven-dried at 60 °C)	
Sample Description	**Average Density, g/cc**
Bulk < 2.00 mm, dry-sieved	2.6364
Bulk < 0.85 mm, dry-sieved	2.9446
Bulk < 0.85 mm, wet-sieved	2.5193

Sample Fractions

Dry-Sieve Analysis (2,000.00 as-is, 1972.80 g dry wt.)				
Sieve Fraction	**Raw Wt., g**	**Solids per 1 Gram Sample**	**Oven-Dried Wt. (Moisture Test)**	**Percent Dry Fraction**
>200 mm	272.22	0.988845	269.18	13.65
0.063 - 2.00 mm	1,687.28	0.987096	1,665.51	24.42
<0.063 mm	33.94	0.957500	32.50	1.65
Loss	6.56		5.61	0.28

Wet - Sieve Analysis (2,000.00 g as-is, 1972.80 g dry wt.) 9.75 ℓ Rinse Water				
>2.00 mm	262.52	0.946449	248.46	12.59
0.063 - 2.00 mm	1,900.45	0.754162	1,433.25	72.65
0.0027 - 0.063 mm	29.95 g/ℓ	20.57 g/ℓ	200.56	10.17
<0.0027 mm	2.57 g/ℓ	0	0	0
Loss			90.53	4.59

Moisture Tests (oven-dried at 60 °C)				
Sample	**Initial Wt., g**	**Dry Wt., g**	**Percent Moisture**	**Percent Solids**
Bulk <2.00 mm dry-sieved	14.00	13.81	1.36	98.64
Bulk <0.85 mm dry-sieved	2.00	1.97	1.33	98.67
Bulk <0.85 mm wet-sieved	2.69	0.14	94.92	5.08

Hydrometer Procedure			
Time	**Temp, F**	**Hydrometer Reading**	**Reading Correction**
0 hr	80.6		
40 sec	80.6	0	2.52
2 hr	77.0	-3	-1.20
24 hr	73.4	-3	-1.92

Percent (Silt + Clay)	Percent Sand	Percent Silt	Percent Clay (Coll + Noncoll)	Colloidal Clay	Noncolloidal Clay
5.04	94.96	5.04	-2.4	-3.84	0

sampling port. A mechanical fingers were inserted into the center of the reactor through the ports to remove the 40 to 50 g of compost.

Analytical Protocols

The Environmental Chemistry Branch, Environmental Laboratory, WES, received much of the compost samples for analysis. Explosive compounds TNT, RDX, HMX, and some of known transformation products, such as 4A-DNT, 2A-DNT, 2,4-DNT, and 2,6-DNT, were extracted from the samples with acetonitrile and subsequently analyzed with high performance liquid chromatography (HPLC) according to EPA SW-846 Method 8330 (USEPA 1992).

Radiolabeled Examination

Umatilla soil (2,470 g oven-dried weight or 2,470 g ODW) was amended with 19.82 mg [U-ring-^{14}C] TNT (New England Nuclear Research Product, 26.3 mCi/mmol with 99-percent purity). Analysis was performed as described by Pennington et al. (1995). The resulting radioactivity was 2.05×10^6 DPM/gODW. The final compost contained 3.96 g ^{14}C-TNT/g ODW and 1.01×10^6 DPM/g ODW. Compost samples taken at the initiation of the study (T_0) and after 20 days (T_{20}) of the phase-I composting were subjected to organic matter fractionation (Pennington et al. 1995). The compost was extracted wet, but was allowed to dry slightly between additions of different solvents. Carbon dioxide traps were assayed on days when WACS-I were aerated, i.e., Days 7, 9, and 12-20. Radiolabeled CO_2 was determined by counting 0.5 ml of KOH with 2.5 ml water and 15 ml of Ultima Gold liquid scintillation cocktail (Packard Instruments, Meridan, CT).

Results and Discussion

Phase-I study

A total of five composting experiments were performed using WACS-I reactors. Among these composting runs, only the first run achieved the thermophilic temperature (55 °C or higher), and the rest of the runs failed to achieve temperature higher than 40 °C due to failure of the thermal control unit (TCU). The second run was abruptly stopped when the TCU was found to be malfuntional. However, subsequent composting Runs 3, 4, and 5 were continued for 20 days each despite the TCU failure, and the profiles of explosive contaminants in the compost were analyzed under mesophilic composting conditions. Since aeration was programmed to start only when the compost temperature was higher than 55 °C, most composting runs were carried out under anaerobic conditions except for Run 5 and a part of Run 4. Compost Run 4, the ^{14}C-TNT run, aerated on Days 7, 9, and 12-20 despite the compost temperature being lower than 55 °C in order to trap CO_2 to complete mass balance for subsequent radioactive analysis. Data from both phase-I and -II study are summarized in Appendix C.

WACS-I Run 1

Figure A3 shows temperature, moisture content, and pH profiles of WACS-I composting Run 1. Compost temperature rose to about 55 °C within 5 days due to active mesophilic microbial activity and gradually decreased to about 46 °C after 20 days of composting. This trend is similar to the temperature within a static compost pile (SP-8) of the UMDA study (USATHAMA 1991). Percent moisture was maintained between 46 and 55 percent throughout the composting. Since the WACS-I system was programmed to aerate only when the compost temperature was higher than 55 °C, and since the system achieved a temperature greater than 55 °C for only 1 day (Day 6), the compost probably became anaerobic especially after the 5 days of active mesophilic activity. Due to the volatile fatty acids accumulation from anaerobic decomposition processes, the compost pH was acidic (around pH 4.5) as shown in Figure A2.

TNT concentration of the Umatilla soil was 40,000 mg/kg and was reduced to 17,800 mg/kg after mixing with other compost constituents. Concentrations of TNT transformation products such as 2A-DNT, 4A-DNT, 2,4-DNT and 2,6-DNT of the soil were negligible. However, when the composting system started, a significant amount of TNT was already decreased from 17,800 to 12,700 mg/kg,and the concentrations of 2A-DNT and 4A-DNT were increased from less than 25 to 74.7 and 192 mg/kg, respectively. Transformation of TNT had already taken place while preparing for the composting experiment, which consisted of 3 days of mixing the compost material, measuring and adjusting optimum moisture content, and loading the reactor.

TNT continuously decreased to about 8,000 mg/kg after 20 days of composting as shown in Figure A3. Assuming a first-order decay reaction, the half-life and the apparent first-order rate coefficient were estimated from regression analysis of linearized TNT concentrations (Equations 46 and 47 of main text). The half-life and the rate coefficient were 23.1 days and 0.03 day^{-1}, respectively ($R^2 = 0.8$). This half-life was comparable with that of Doyle and Isbister (1982), about 3 weeks, and was slower than $t_{1/2} =$ 12 days obtained from the Louisiana Army Ammunition Plant (LAAP) thermophilic static pile study (Williams et al. 1992). 4A-DNT increased to 472 mg/kg after 5 days and decreased slightly to 350 mg/kg after 20 days. The 2A-DNT profile was similar to 4A-DNT except that the 2A-DNT concentration rapidly reached 437 mg/kg after 10 days and rather gradually increased to 540 mg/kg after 20 days. The total amount of disappeared TNT (4,538 mg/kg) was much greater than the total production of the metabolites (2A-DNT and 4A-DNT) of 890 mg/kg. Most previous TNT degradation studies suggested that negligible amounts of CO_2 and volatile amines were produced from degradation of TNT during composting (Kaplan and Kaplan 1982a,b; Doyle and Isbister 1982; Pennington et al. 1995). Neither

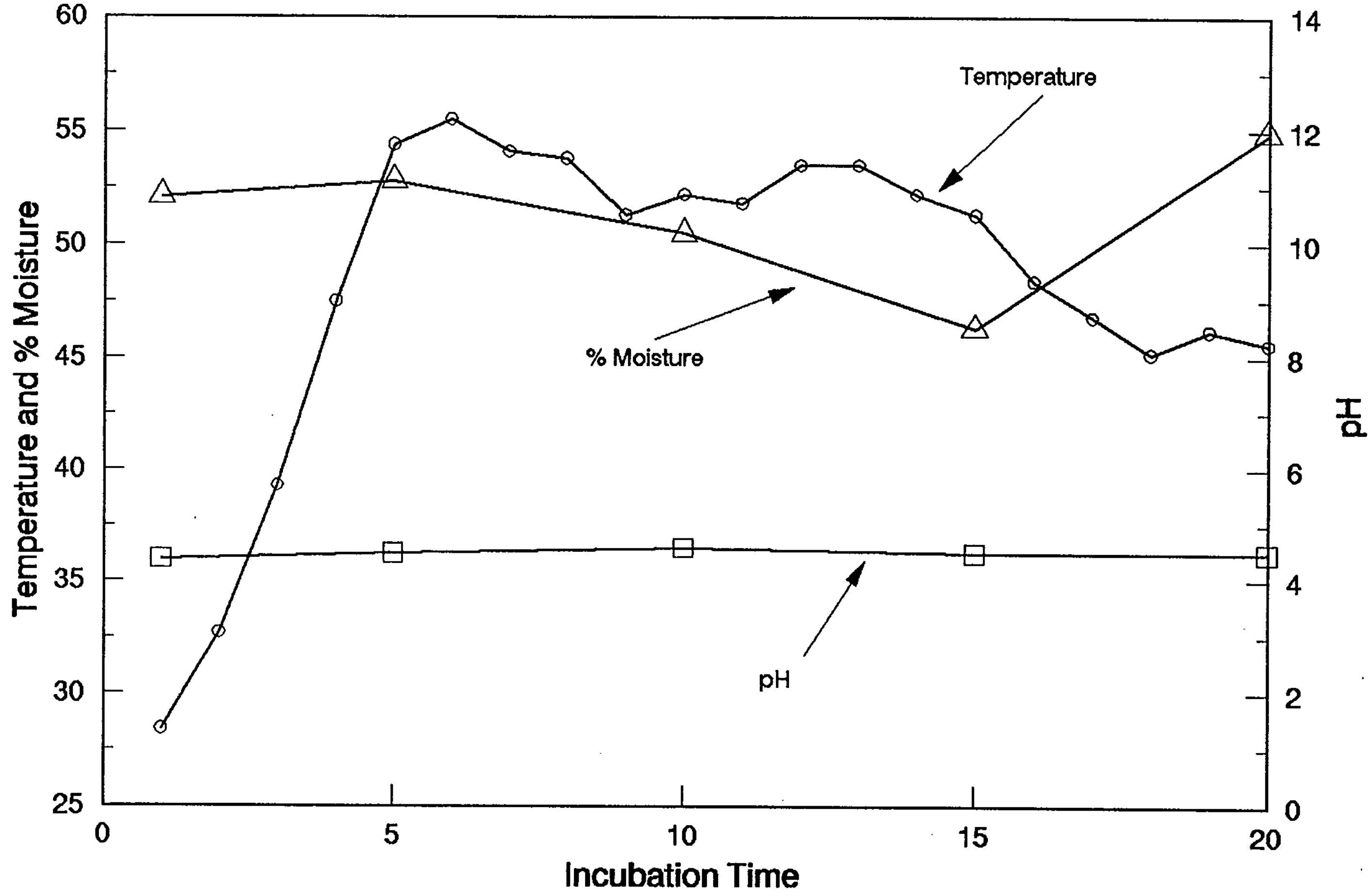


Figure A2. Temperature, pH, and percent moisture of Run 1

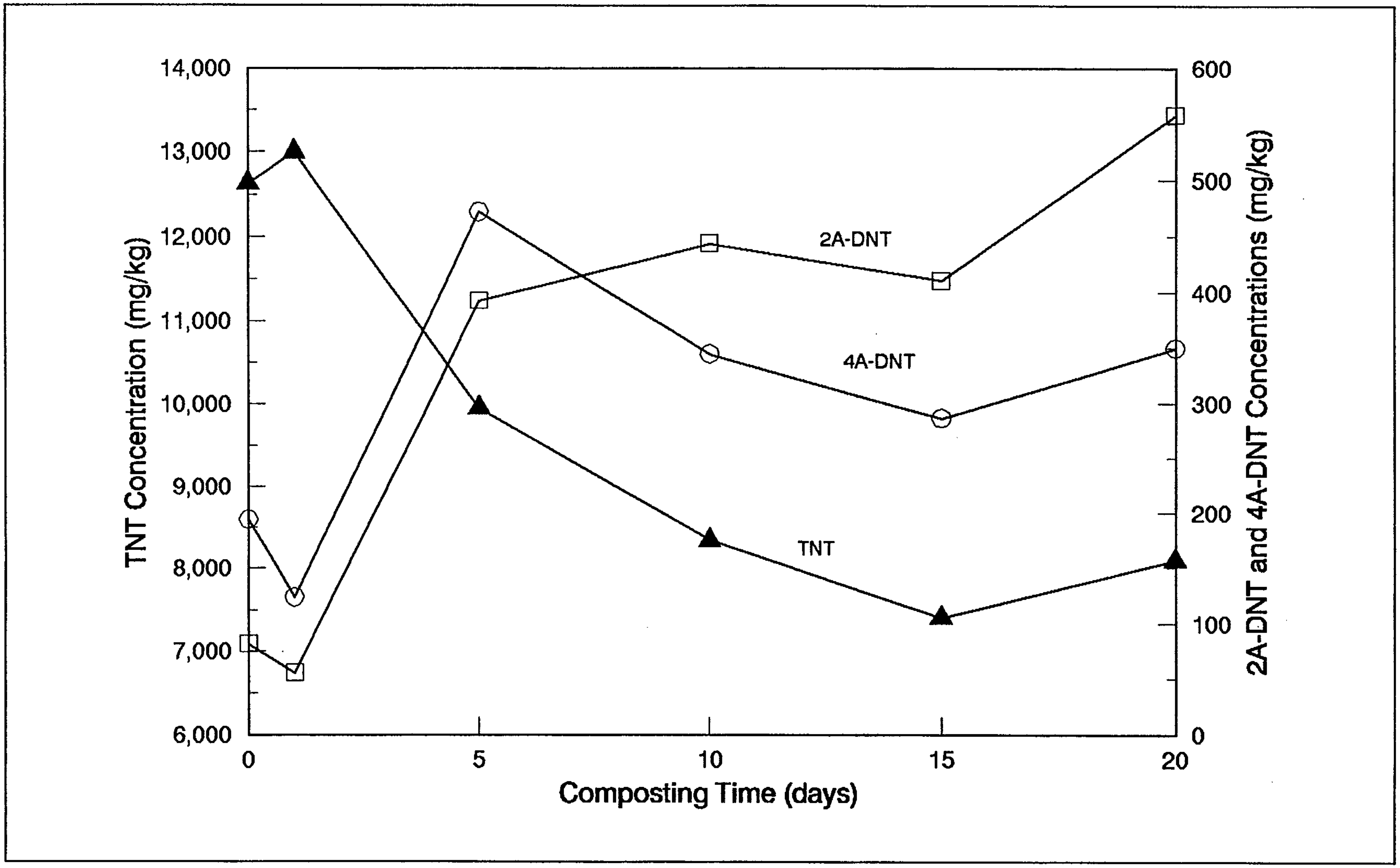


Figure A3. TNT, 2A-DNT, and 4A-DNT profiles during composting Run 1

2,4-dinitrotoluene (2,4-DNT) nor 2,6-dinitrotoluene (2,6-DNT) were present before and after the composting. This could be explained by both mesophilic and thermophilic TNT transformation pathways hypothesized by Levinson, McCormick, and Feeherry (1976) and Kaplan and Kaplan (1982b). In the pathways, all nitrogroups were reduced to amino groups first before the deamination process took place. As a result, 2,4-DNT and 2,6 DNT were not produced. The balance of the disappeared TNT was assumed to be incorporated into organic matter of the compost.

Other explosives (RDX, HMX, and TNB) were not transformed by the composting process as shown in Figure A4. In fact, this trend was true for both composting runs (Runs 1 and 3) that monitored these compounds. In contrast, Doyle and Isbister (1982) reported that about 20 percent of RDX was mineralized after 3 weeks of composting, and Pennington et al. (1995) reported that about 65.6 percent disappeared after 20 days of composting. This finding was quite interesting because the experimental conditions (compost components and soils) of this study were almost identical to those of Pennington et al. (1995). The difference between these two separate experiments were as follows: Pennington et al. (1995) fixed the compost temperature around 55 °C using a water bath and provided continuous aeration of 10 ml/min; the initial RDX concentration was much lower (about 1,260 mg/ℓ) than that of this study (3,911 mg/kg). Reaching a compost temperature of 50 °C or higher soon after the start of incubation by Pennington et al. (1995) may have suppressed the growth of mesophiles and promoted the growth of thermophiles that possibly have a better enzymatic system for degrading RDX. Since the compost of this study also reached above 50 °C after 5 days (Figure A3), one should observe a substantial depletion of RDX, although not as much as in Pennington's if the abundance of thermophiles was the factor. The reactor of this study was not aerated most of the composting period and became anaerobic as evidenced by low pH (Figure A3). However, anaerobic conditions should have also promoted RDX transformation. Why RDX did not degrade in this instance remains of interest.

Levinson, McCormick, and Feeherry (1976) reported that RDX was only biodegradable under anaerobic conditions as also mentioned by Kaplan and Kaplan (1982a). This result directly contradicted their findings. Finally, this study's system had higher RDX concentration, which might be inhibitory. However, Doyle and Isbister (1982) had even higher initial RDX concentration (greater than 9,000 mg/kg) in their greenhouse compost systems, which was later decreased to 3,284 and 5,093 mg/kg after 3 weeks of composting. At this time, it is not clear what has caused the big difference in RDX disappearance.

WACS-I Run 3

Figure A5 shows the profiles of TNT, 2A-DNT, and 4A-DNT during 20 days of composting, composting Run 3. The trend was similar to that of Run 3 although the compost temperature never reached thermophilic range.

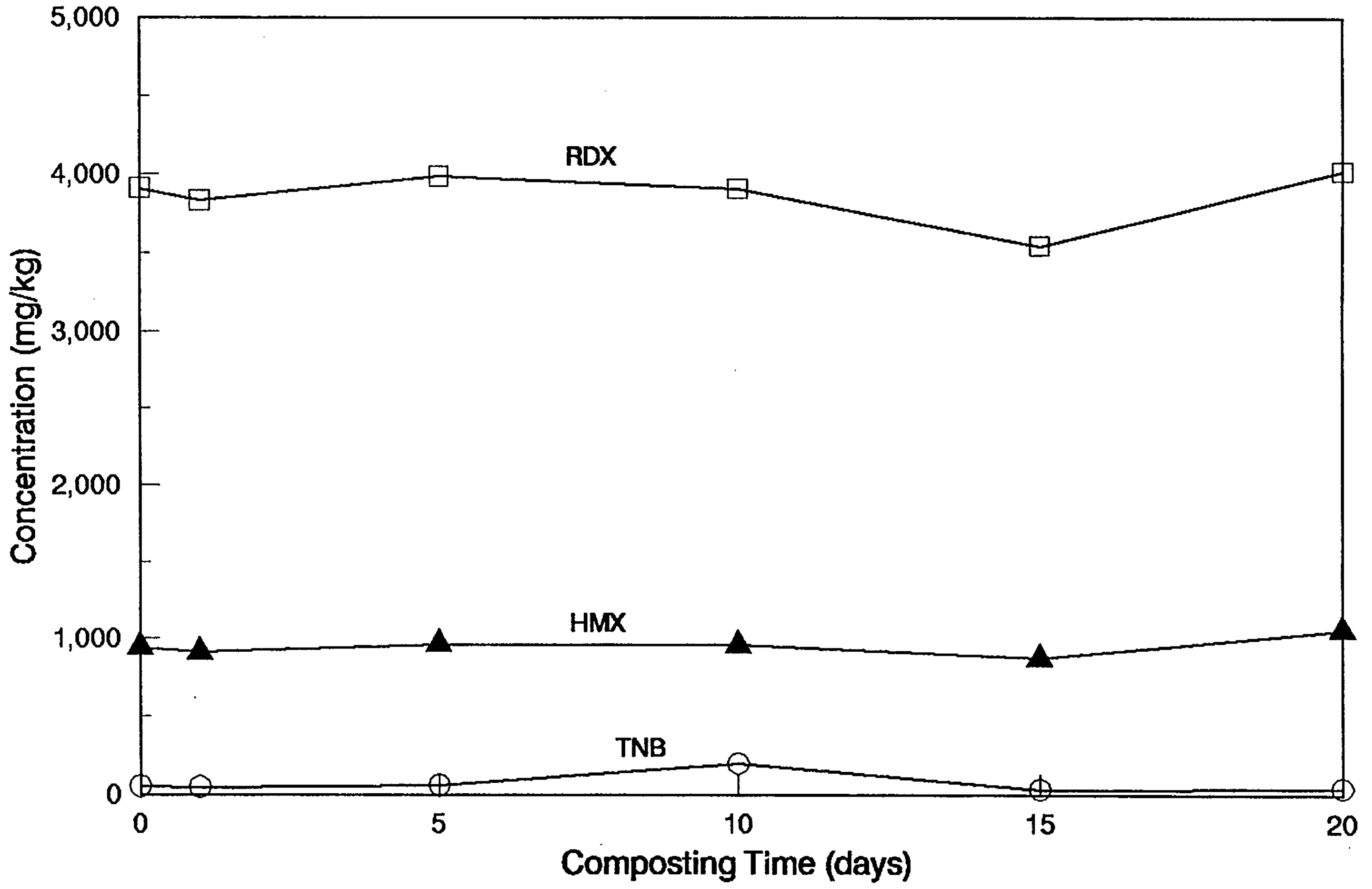


Figure A4. HMX, RDX, and TNB profiles during composting Run 1

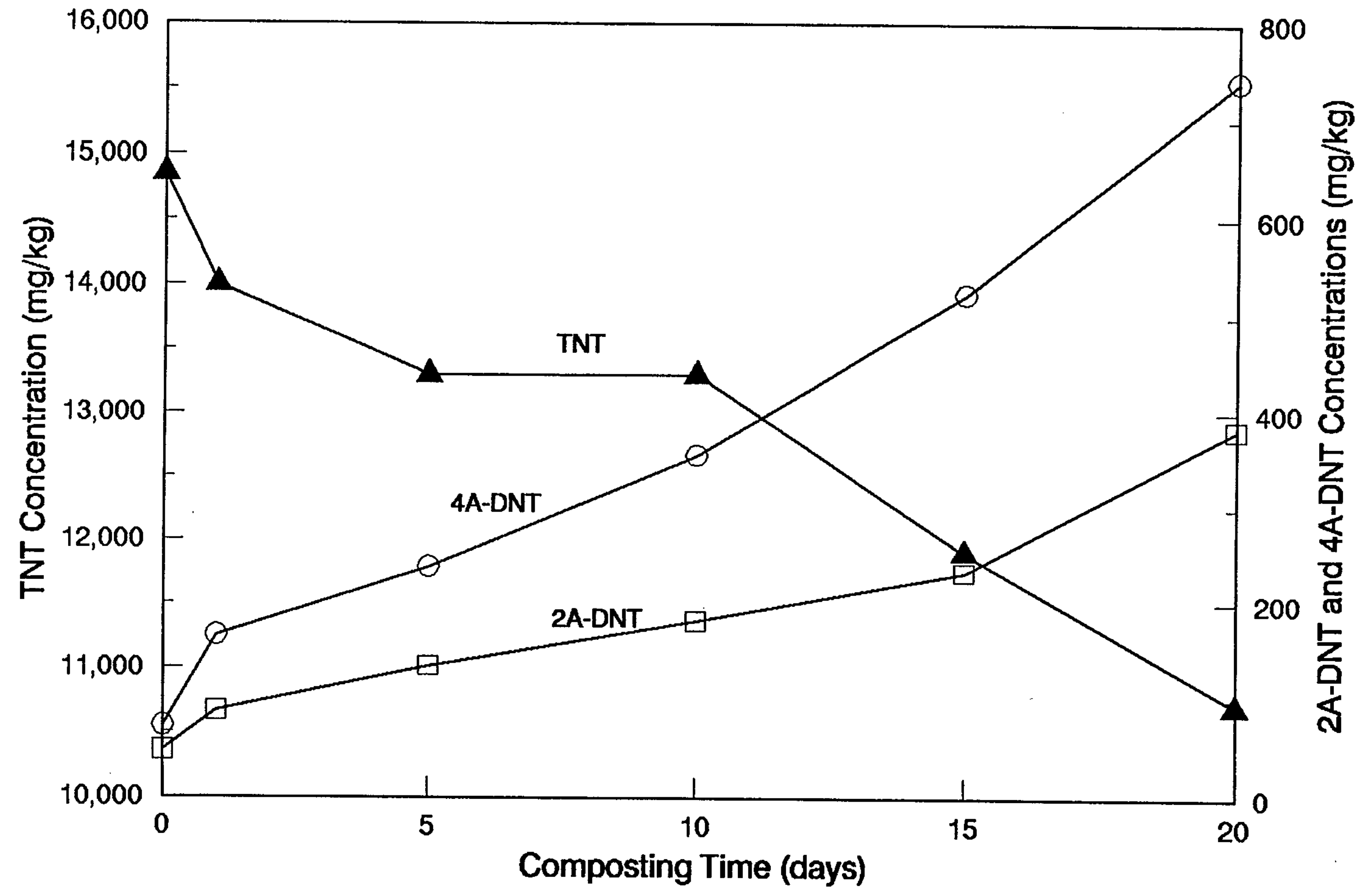


Figure A5. TNT, 2A-DNT, and 4A-DNT profiles during composting Run 3

TNT decreased from 14,850 to 10,700 mg/kg after 20 days. The corresponding half-life and the rate coefficient were 46.2 days and 0.015 day^{-1}, respectively (R^2 = 0.92). Although this half-life was slower than that for LAAP mesophilic static pile system ($t_{1/2}$ = 22 days) by Williams et al. (1992), the trend of slower mesophilic transformation rate compared with that of thermophilic system ($t_{1/2}$ = 12 days) was quite similar. In both studies, the half-lives were increased approximately twice from mesophilic to thermophilic systems. Figure A5 also clearly indicated that the transformation rate of 4A-DNT was faster than that of 2A-DNT. This finding agreed with the statement by Kaplan and Kaplan (1982b), the preferential reduction in the para position of TNT to the ortho position.

WACS-I Run 4

In this run, ^{14}C-TNT was spiked into the soil in order to study the fate of TNT and its transformation products during composting. Figure A6 shows the percent recovery of added radioactivity in each fraction of compost samples taken at t_0 and t_{20} days. In both samples, the percent recovery in the CO_2 and VOCs traps were negligible, and the ether extracts contained the most radioactive TNT (28.2 percent for t_0 and 32.2 percent for t_{20} days). Although the percent recovery of 32.2 percent at t = 20 days was quite lower than that of 67.4 percent at t = 24 days reported by Kaplan and Kaplan (1982b), it was much higher than that of 9.84 percent at t = 20 days reported by Pennington et al. (1995). The humin fraction of the compost samples contained the next majority of the added radioactivity at both t = 0 and t = 20 days. This value was similar to 21.94 percent at t = 20 days of Pennington et al. (1995), but was much greater than 1.3 percent at t = 24 days of Kaplan and Kaplan (1982b). However, one should expect differences since run composition and conditions varied between Kaplan and Kaplan (1982b), Pennington et al. (1995), and this study.

The percent recoveries of the added radioactivity in humic acids, fulvic acids, and cellulosic fractions increased over 20 days of composting. Interestingly, ^{14}C-TNT redistributed itself into various organic fractions right after loading the reactor. If experimental errors during the preparation of samples and the actual instrumental analysis were assumed to be negligible (statistical treatment of data not available), this fast redistribution of added TNT suggested the importance of the sorption process of TNT.

Figure A7 shows the concentration profiles of TNT, 4A-DNT, and 2A-DNT during 27 days of composting. The wide variation of TNT concentration was probably due to incomplete mixing of the compost material resulting in heterogeneous matrix. The preferential reduction of para positioned nitrogroups to ortho position resulted in higher concentrations of 4A-DNT than 2A-DNT.

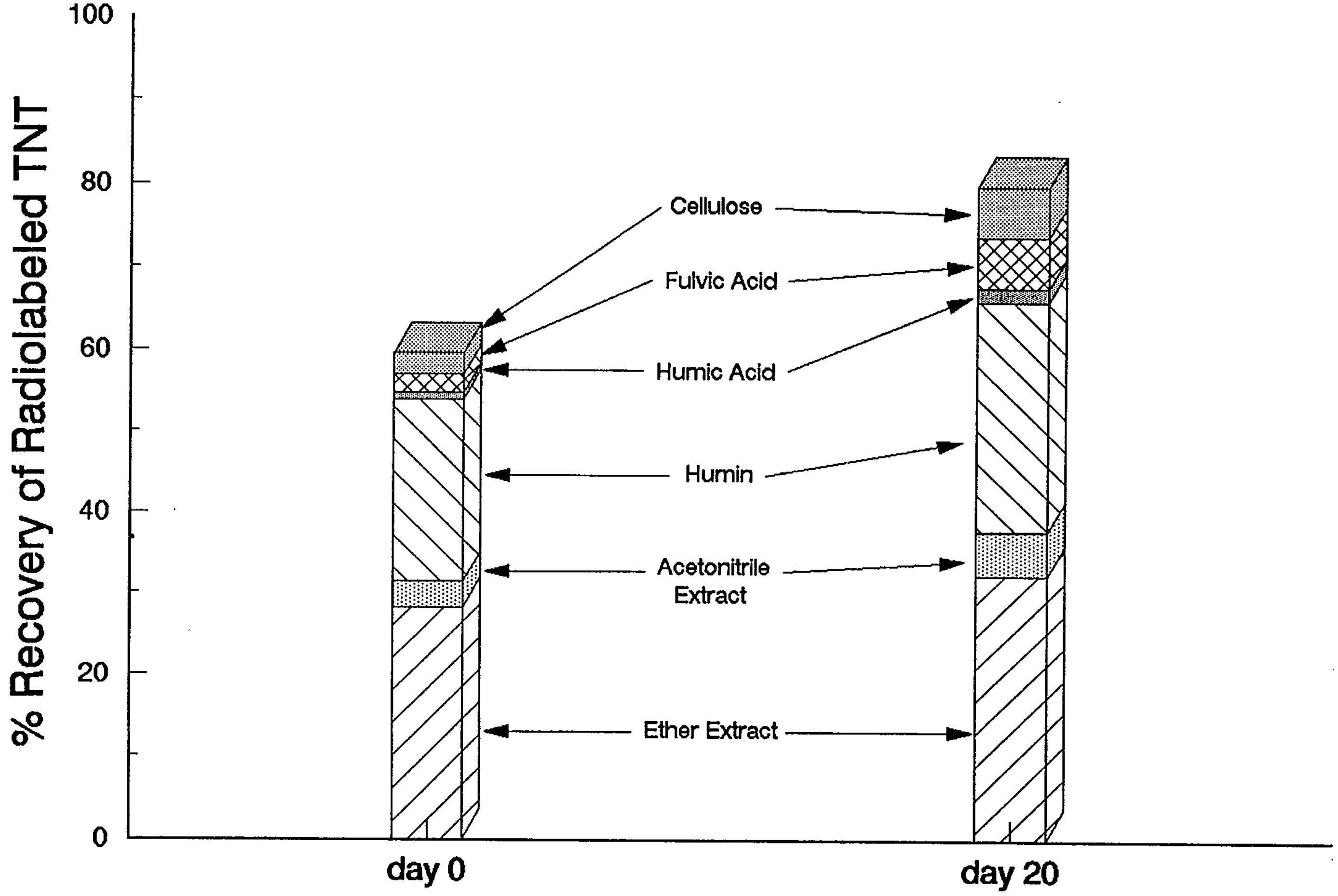


Figure A6. Distribution of TNT into various fractions of compost

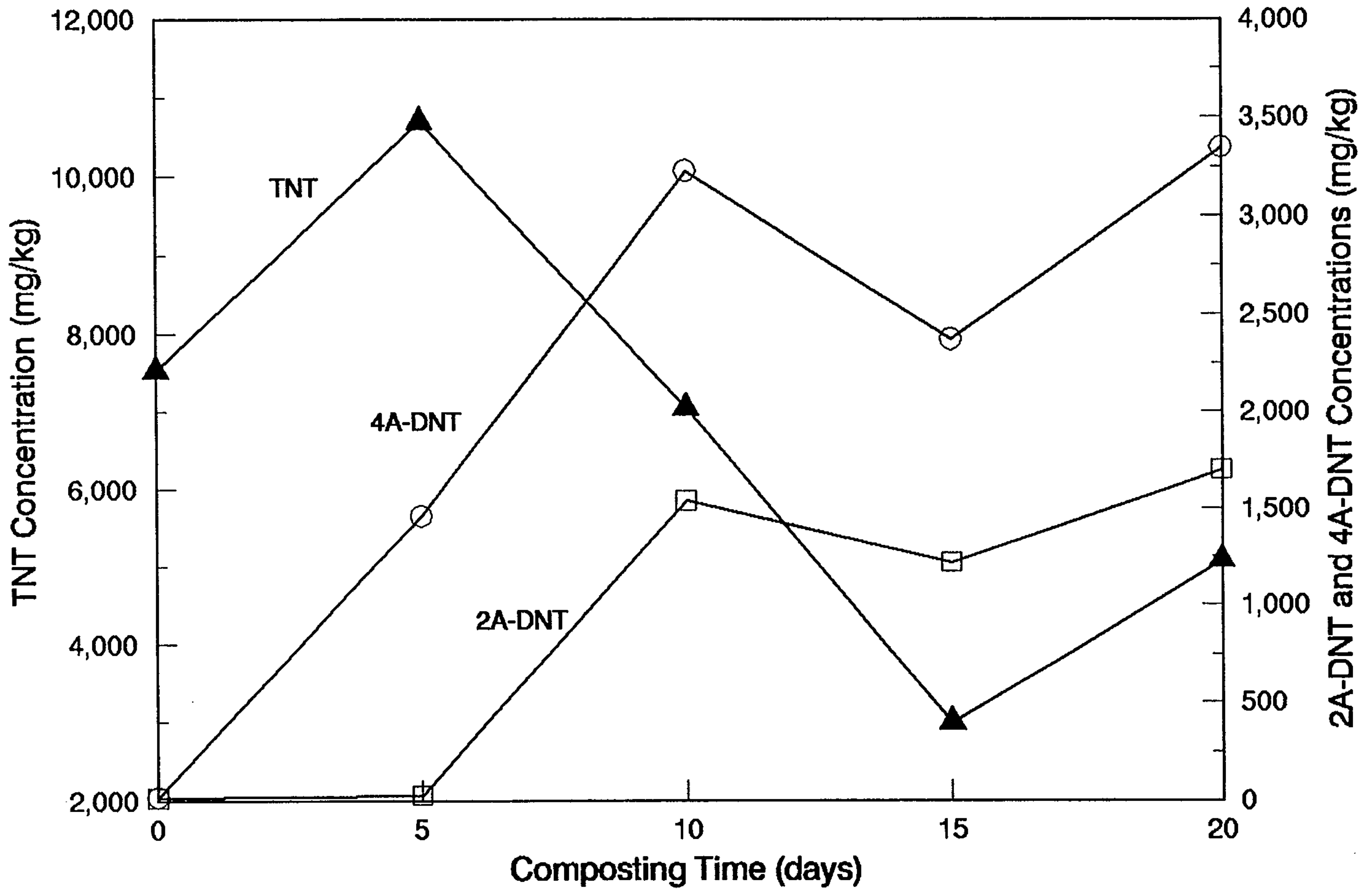


Figure A7. TNT, 2A-DNT, and 4A-DNT profiles during composting Run 4

WACS-I Run 5

In this last experiment of the phase-I study, air was continuously introduced at 2,000 ml/min. This resulted in much faster dissipation of TNT than any other runs in this phase-I study. The TNT level dropped to 216 mg/kg after only 10 days of composting from an initial concentration of 17,650 mg/kg. However, the Day 20 sample showed an unusually high concentration of TNT (7,320 mg/kg). Once again, incomplete mixing and subsequent heterogeneous compost material was blamed for this high variation of data. These data with a wide variation as observed in Runs 4 and 5 suggested the importance of thorough mixing and careful sampling. Investigators must exercise extra caution in preparing representative samples and interpreting compost sample data. The preferential reduction to 4A-DNT was also evident in Figure A8.

In order to see the effects of compost temperature and aeration, the TNT profiles of all phase-I experiments (Runs 1, 3, 4, 5) were plotted together as shown in Figure A9. Comparing Run 1 and Run 3 (both were anaerobic), the mesophilic condition in Run 3 slowed down the TNT dissipation rate. Although Run 4 was also mesophilic, air was introduced (Days 7, 9, and 12-20) in order to trap $^{14}C-CO_2$. A drop in TNT concentration was observed after aeration was introduced. The mesophilic Run 5, in which continuous aeration was introduced, also showed a big drop in TNT concentration although the unusually high TNT concentration at Day 20 sample imposed uncertainty in the validity of this trend as representative of whole compost.

Phase II Study

In this phase, a total of 10 composting experiments (Runs 6 to 15) were performed for 4 to 7 days using two WACS-II reactors. The effects of two important operational factors, i.e., aeration and temperature feedback control, on the system temperature were examined. Compost Runs 6 to 13 used uncontaminated soils, whereas, Runs 14 and 15 used the Umatilla soil heavily contaminated with explosive compounds. In the last two runs (Runs 14 and 15), the importance of pH adjustment of the compost was tested. All data are summarized in Appendix C.

WACS-II operation without aeration and without temperature feedback control (clean soil)

Without aeration, the compost became anaerobic and as shown in Figure A10. The acidity was probably as a result of volatile fatty acids accumulation. Since the anaerobic metabolic process is not an efficient energy production process, the heat generated from the metabolic process will not be enough to raise the compost temperature to thermophilic range. Figure A10 shows the profiles of pH, compost temperature, and the percent moisture. While preparing the compost mix, mesophilic activity started and raised the

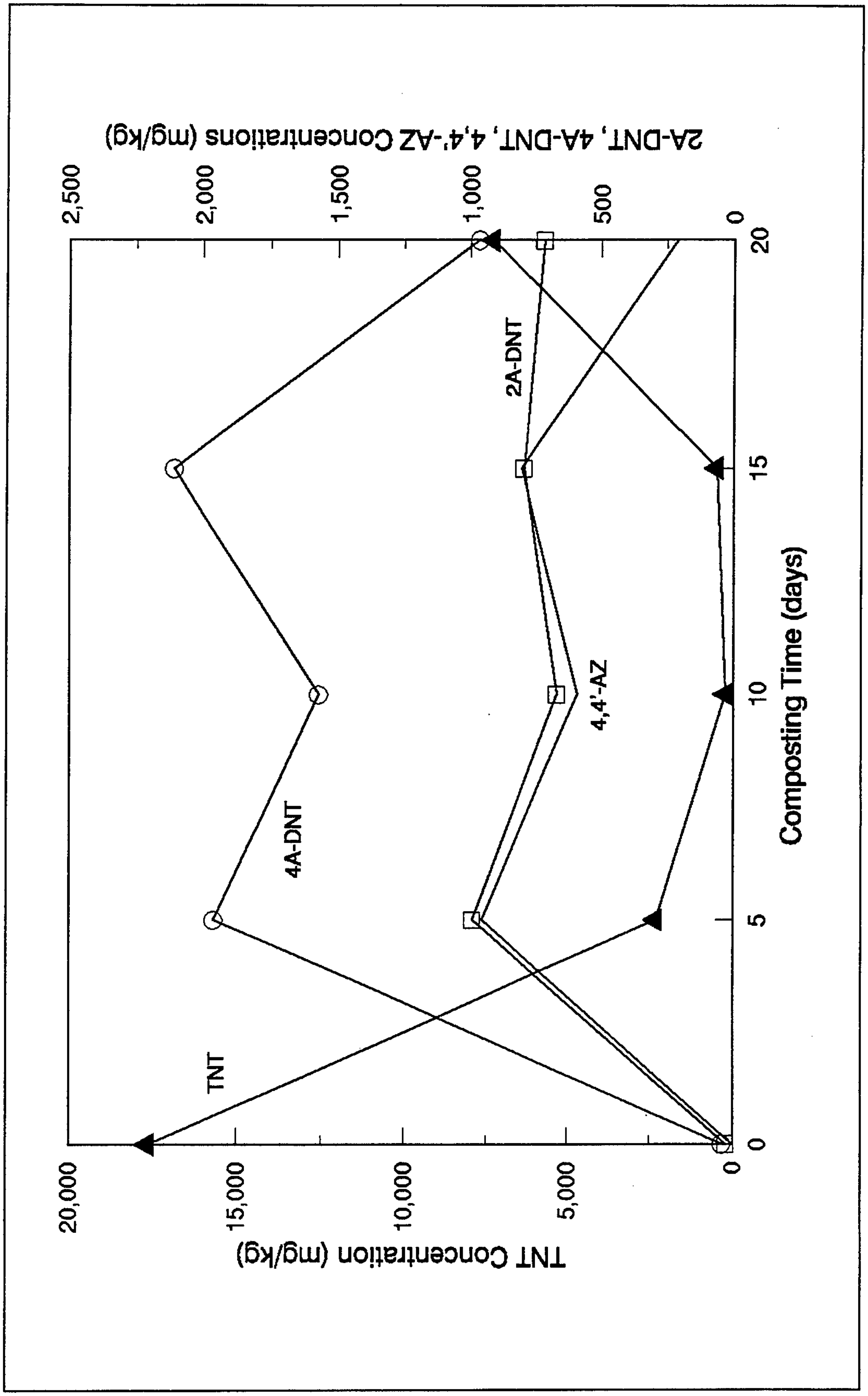


Figure A8. TNT, 2A-DNT, and 4A-DNT, and 4,4'-AZ profiles during Run 5

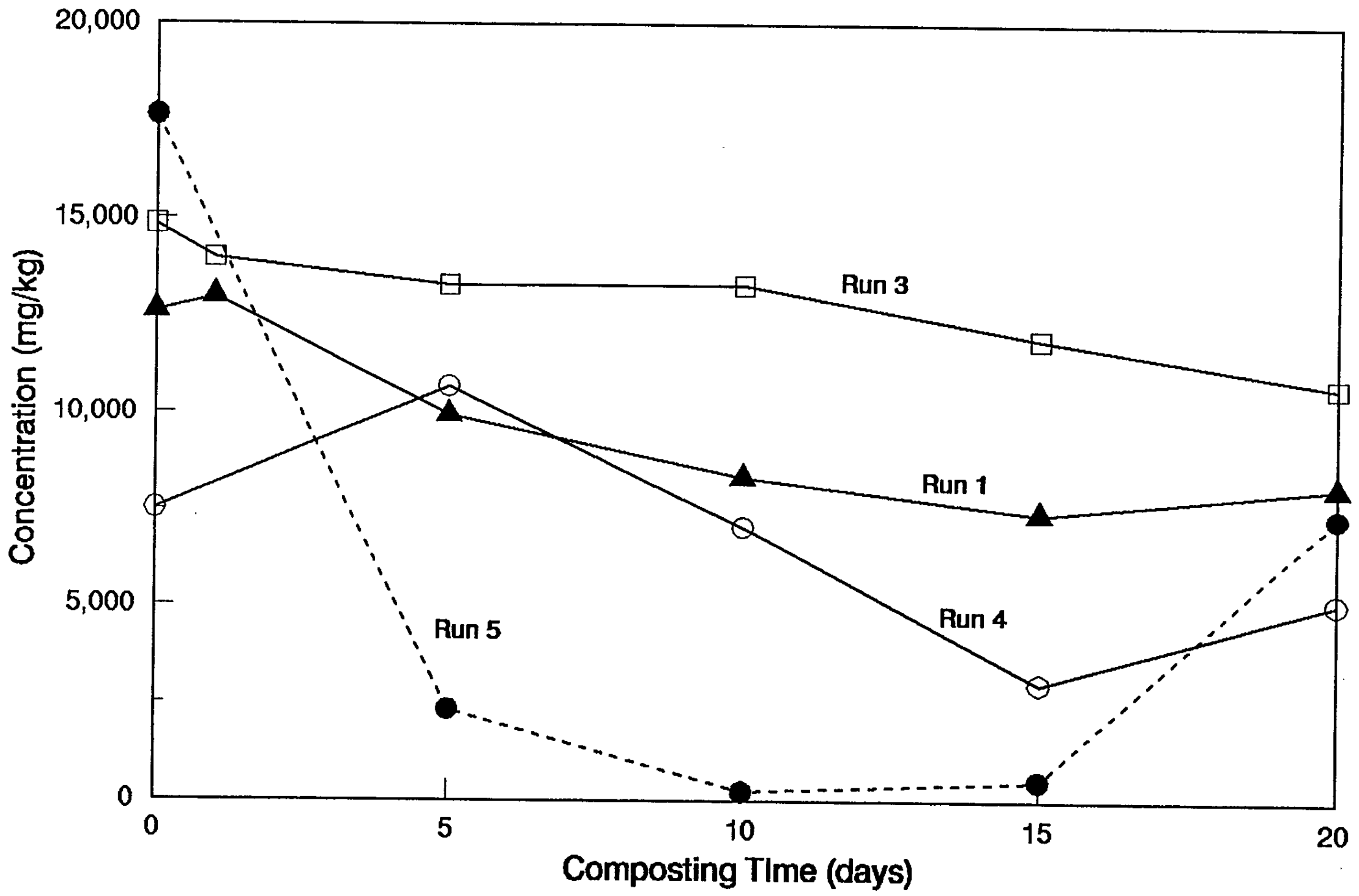


Figure A9. TNT profiles during composting Runs 1, 3, 4, and 5

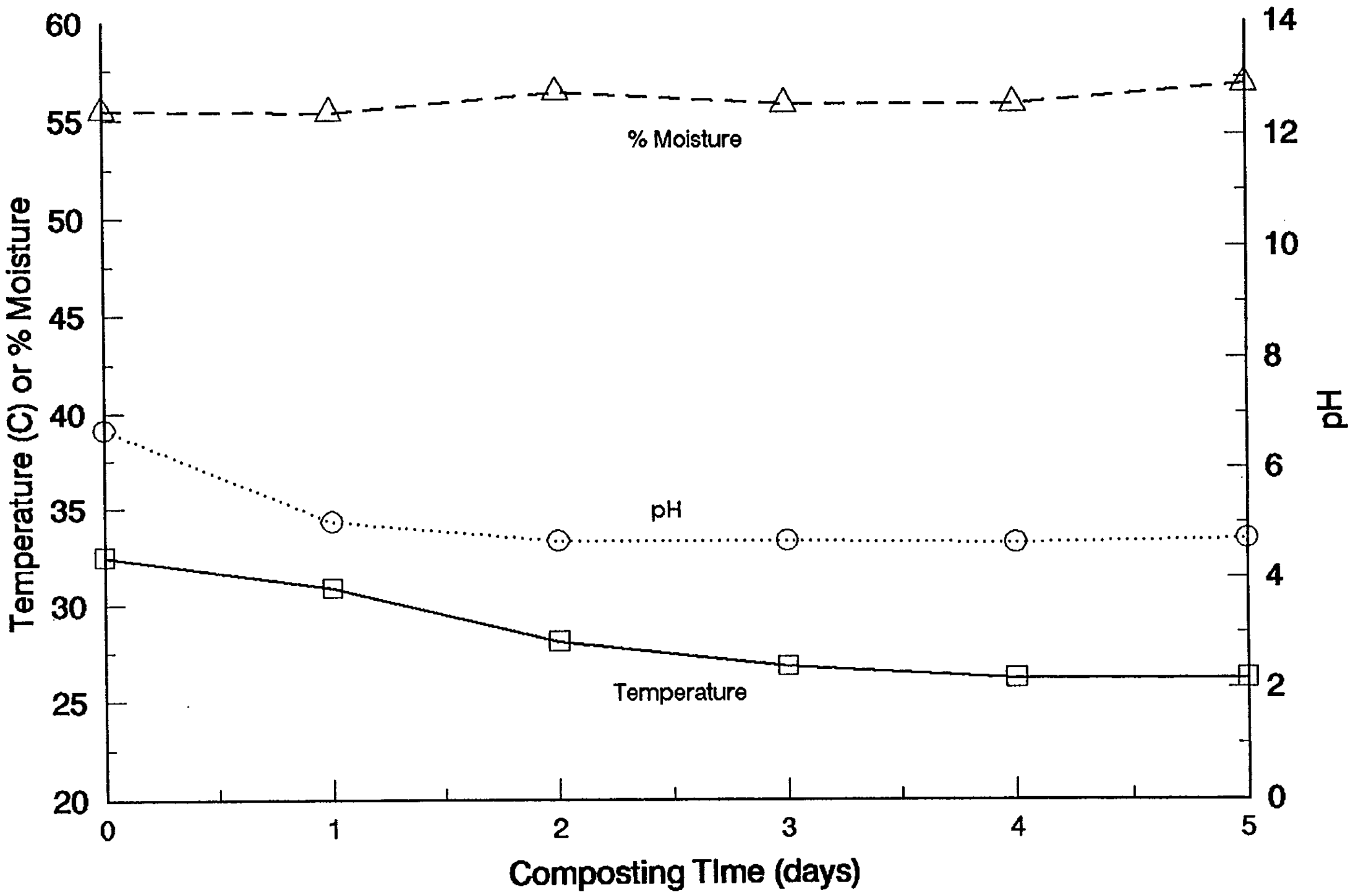


Figure A10. pH, temperature, and percent moisture profiles of WACS-II operation without aeration and without temperature feed back control compost temperature to 33 °C when the experiment began. After loading the reactor, the compost became anaerobic and the pH dropped to about 4.7; the compost temperature slowly decreased to room temperature. Without aeration, the percent moisture was rather constant at 56 percent.

WACS-II operation with aeration and with temperature feedback control (clean soil)

The compost temperature of the WACS-II system with both aeration and active temperature feedback control reached the thermophilic range within 5 days as shown in Figure A11. The pH was maintained around neutral range since aerobic conditions prevailed the reactor. The percent moisture dropped from 53 to 43 percent after 5 days of composting. This was rather surprising because air was presaturated with water in order to minimize evaporation. Other runs with aeration did not show any percent moisture reduction (Appendix C).

WACS-II operation with aeration and with temperature feedback control (contaminated umatilla soil)

The last two runs (14 and 15) used the same compost mix except for the soil. This time, soil was heavily contaminated with explosive compounds (Umatilla soil). The WACS-II reactors were operated with both aeration and temperature feedback control on. In Run 15, a pH adjusting chemical ($NaHCO_3$) was added after observing acidic pH with the Umatilla soil in Run 14 (Figure A12). Even with aeration, pH of Run 14 decreased from 6.7 to 5.0 after 5 days. However, Day 7 sample of Run 14 showed pH of 8.8. The cause of this sudden jump in pH was not clear. The compost temperature of Run 14 did not reach higher than 37 °C even with the temperature feedback control. Considering other runs with uncontaminated soils, which achieved the thermophilic temperature with the temperature feedback control, minor interference of explosive compounds on the compost metabolic activity was suspected initially. In fact, Osmon and Klausmeier (1972) showed that TNT slightly decreased the 4-day biochemical oxygen demand (BOD_4) of raw sludge. However, the compost temperature reached 53 °C with the same Umatilla soil in Run 15 with the addition of $NaHCO_3$. The pH of Run 15 was maintained between 7.2 and 8.9. Also observing the compost temperature at Day 7, which was raised from 30.4 °C at Day 6 to 36.7 °C at Day 7 and the increase in pH from 5.0 at Day 5 to 8.8 at Day 7, in Run 14 indicated that the acidic pH appeared to be the important factor that caused the lower compost temperature in Run 14. The cause of acidic pH from the Umatilla soil was not clear.

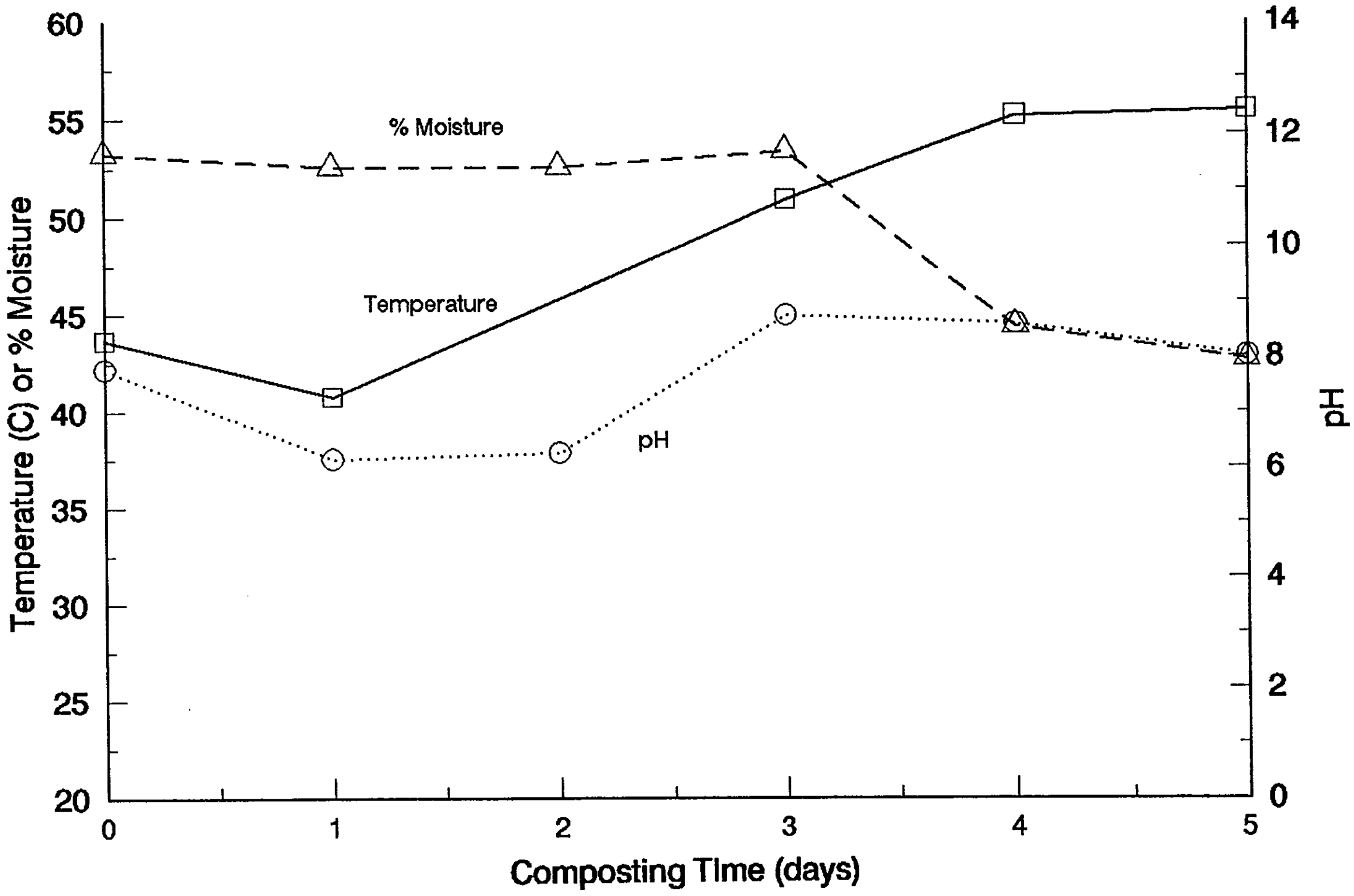


Figure A11. pH, temperature, and percent moisture profiles of Run 13 (both aeration and temperature control on)

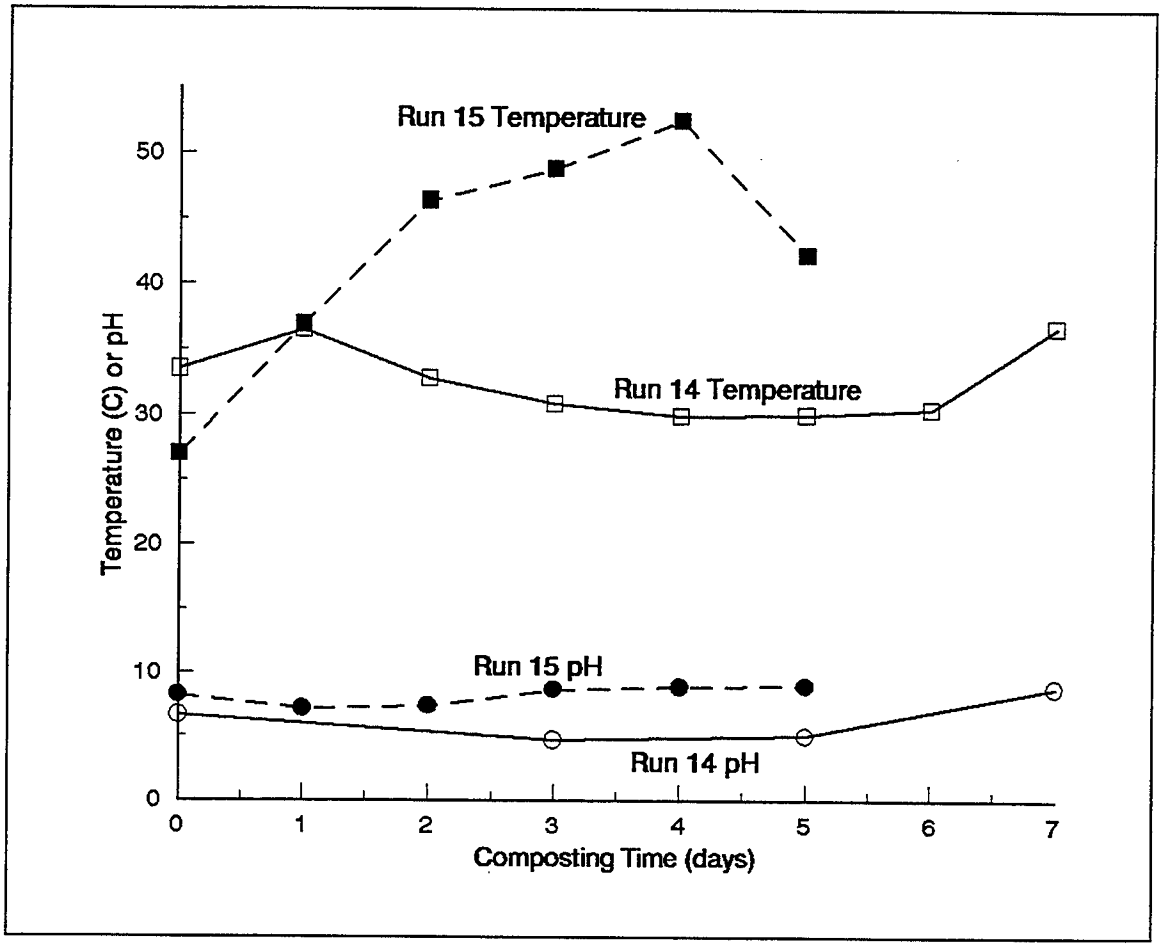


Figure A12. Temperature and pH of composting Runs 14 and 15 (soils contaminated with explosive compounds)

Conclusions

Phase I study

Findings from the phase-I study were as follows: A substantial amount of TNT disappeared and two TNT transformation products (2A-DNT and 4A-DNT) were produced during 20 days of composting both at thermophilic and mesophilic conditions. The 4A-DNT level was consistently higher than the 2A-DNT level indicating faster transformation of TNT to 4A-TNT in the biochemical pathway suggested by Kaplan and Kaplan (1982). The TNT transformation rate was higher in the thermophilic conditions than in the mesophilic conditions. Effects of aeration on the TNT transformation may be more significant than that of composting temperature. A large fraction (20 and 36 percent) of the radiolabeled TNT was found in the humin fraction both at the start and the finish of the composting. Incorporation of ^{14}C-TNT into humic and fulvic acids and cellulosic fractions increased at 20 days of composting. The explosives RDX, TNB, and HMX were not significantly degraded over the 20 days of composting.

Phase II study

Without aeration control, compost became acidic probably because of accumulation of volatile fatty acids under anaerobic conditions. Without temperature feedback controls, the compost temperature did not reach to thermophilic range with this reactor system. The Umatilla soil became acidic unless $NaHCO_3$ was added in the beginning. As a result, the compost did not reach to thermophilic range without addition of $NaHCO_3$, although both aeration and temperature controls were activated.

Appendix B
U.S. Army Engineer Waterways Experiment Station Adiabatic Compost Systems (WACS) Description

WACS I: System Description

The WACS I consisted of a water-jacketed, stainless steel reactor constructed for the purpose of studying the dynamics of composting explosive-contaminated soils. The reactor cylinder was 27.9 cm in diameter and 43.2 cm in depth with temperature probe and sampling ports. A 2.54-cm-high aluminum diffuser base plate was placed in the bottom of the reactor to allow for air flow. A center baffle was placed inside the reactor to prevent air short circuiting. Besides the reactor, the system included the inlet air system, the offgas system, the reactor control unit, the thermal control unit, and the data acquisition program (Figure B1).

The air inlet system was designed to provide humidified air to the system. Before arrival at the diffuser base, incoming air was split into two streams. One air stream was then saturated with water vapor and both streams remixed before entry to the reactor base. The actual incoming relative humidity was monitored using an RH-PLUS 2250 single channel analyzer. The output of this analyzer was passed to the computer.

The offgas monitoring system integrated several analog detectors to track important parameters. The most important detectors in this system were the carbon dioxide and oxygen analyzers. Both sensors were real-time monitors indicating current operating conditions of the system. The gas-trapping system measured the quantity of carbon dioxide that this system produced. Offgases were passed through a condenser prior to carbon dioxide and oxygen analysis. The system also had the capability to measure gas mass flow rate. During labeled studies, CO_2 traps were used followed by two tenex traps in series for capturing VOCs.

Figure B1. Photo of WACS I

Temperature was monitored using tip-sensitive resistance temperature probes (RTDs). RTDs were also used to measure offgas temperatures. These data were sent to the reactor controller that housed all the digital readouts, the water-jacket controller, the relative humidity analyzer, and 24-V DC power supply. All the temperature probes transmitted a milliamp signal to the controller. This information was interpreted and relayed to solenoid valves for control of the reactor's water-jacket temperature. There were eight temperature probe inputs per system. Four of them displayed the core compost temperatures, one displayed the water-jacket temperature, and the three others displayed offgas temperatures. Voltage readings for the four compost core temperatures together with the average temperatures were displayed on the visual readout.

The water-jacket controller was a proportional-integral and derivative (PID) controller. The controller accepted two data signals, the water-jacket temperature and the compost average core temperature. The WACS1 used a remote sensing scheme to minimize heat loss across the interior wall of the reactor. The controller transmitted an output signal to a voltage to pressure (I/P) transducer. The transducer opened or closed two pneumatic valves that supplied either cold or hot water. The water flowed through a mixing tank and then into the reactor water jacket.

WACS II: System Description

A second reactor was designed and installed to overcome two shortcomings identified in the first design, excessive weight and high thermal transmissivity. The second reactor, WACS II, consisted of a single-walled cylindrical reactor mounted on a stage within an insulated chamber (Figure B2). The cylindrical reactor was constructed of polyvinyl chloride (PVC) mounted between a top plate and bottom plate. The cylinder was 20.3 cm in diameter, 45.7 cm long,

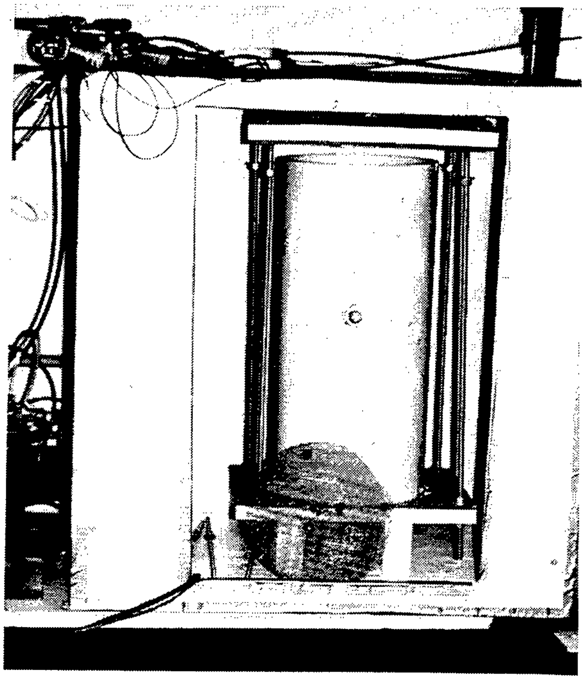


Figure B2. Photo of WACS II

and had a working volume of approximately 14 ℓ. The top plate and bottom plates were a cork/wood composite with a 1.27-cm layer of hardwood board overlain with a 0.635-cm layer of cork. Once loaded, four threaded rods were tightened until the cylinder seated against the cork layers of both the top and bottom plate. Silicon caulking was then applied to the seams between the cylinder and the respective top and bottom plates.

The top plate of the reactor had three 1/8-in.-diam ports. RTDs were friction fitted into the ports and into the compost. One probe was positioned within the core of the compost cylinder, another was positioned along the inside wall of the reactor, and a third was positioned at the exterior of the reactor between the first and second layer of exterior insulation. Temperature probes were tip sensitive. Additionally, a 0.635-cm threaded exhaust port was located on the top plate for offgases.

The base plate was constructed in the same manner as the top plate with the exception that only one through-plate entry was made. This port provided for an air inlet port. Air was passed into the reactor through this port at 2.44 kg/m^2 and a flow rate of 300 ml/min. The base plate was mounted on a 4-in. stage to allow a complete flow of air around the test cell within the insulated chamber.

On the exterior of the cell, a 2.54-cm-diam sampling port provided access to the material in the interior. A fine wire mesh screen secured 2.54 cm above the base plate in the interior of the test cell acted as a false bottom to keep compost from clogging the air inlet hole. The screen also acted as a diffuser to distribute air evenly over the bottom of the test material.

One insulated container with two chambers (Figure B2) was constructed to allow simultaneous operation of two test cells. The insulated container measured 137 cm long, 63.5 wide, and 63.5 cm high. Each of the two chambers were identically arranged with a 12- by 20-cm heat exchanger and a 12-V fan.

The heat exchanger was connected to a thermal control unit. The thermal control unit provided water as a heat exchange fluid to heat exchanger from a thermally stabilized mixing tank.

Water returning from the heat exchanger in the interior of the chamber passed through a second heat exchanger in the inlet air-sparging vessel. The chamber was designed to ensure that inlet air would enter the sparging column, become completely saturated, and leave the sparging vessel at a temperature near or below the compost in the cylinder. As a result, the heat capacity of the humidified air entering the reactor was allowed to be dynamic. The temperature of the water in the sparging vessel was monitored with an RTD probe. A solenoid valve allowed air to enter the test cell 1 min in 10 when the interior temperature was below 55 °C. Above 55 °C, the system was aerated continuously.

The thermal control unit was operated by a PID software controller. The controller was tuned using a closed-loop tuning procedure and transmitted an output signal to a voltage to pressure (I/P) transducer. The converted pressure opened and closed two pneumatic valves. One valved supplied cold water and the other supplied hot water to a mixing tank. The mixing tank had two outlets, one to the overflow and the second to the recirculation system. Duplicate systems were provided for each test chamber. Water, acting as a heat transfer media, was pumped from the mixing tank, through the first heat exchanger in the test chamber, through the heat exchanger in the inlet air system, and back into the mixing chamber.

The I/P transducer received a 4-20 mV signal. This input was converted into proportional 3 to 15 psia pressure that in turn opened or closed the hot and cold valves to the mixing tank. The cold water valve opened between 3 and 9 psia, and the hot water valve opened at between 9 and 15 psia. At 9 psia, both valves were closed. Valve positions were visible to the operator from the front of the thermal control unit.

Data acquisition from the test cell and the inlet air system was performed using a data acquisition package tailored to this application. Labview, an object-oriented programming language developed by National Instruments (NI), was the system selected for this purpose. Rather than using conventional syntax (Basic, C. Fortran), Labview used icons or pictures to represent action and lines of code. Labview created a virtual instrument, which represented a sensor being monitored and displayed the data (Figure B3).

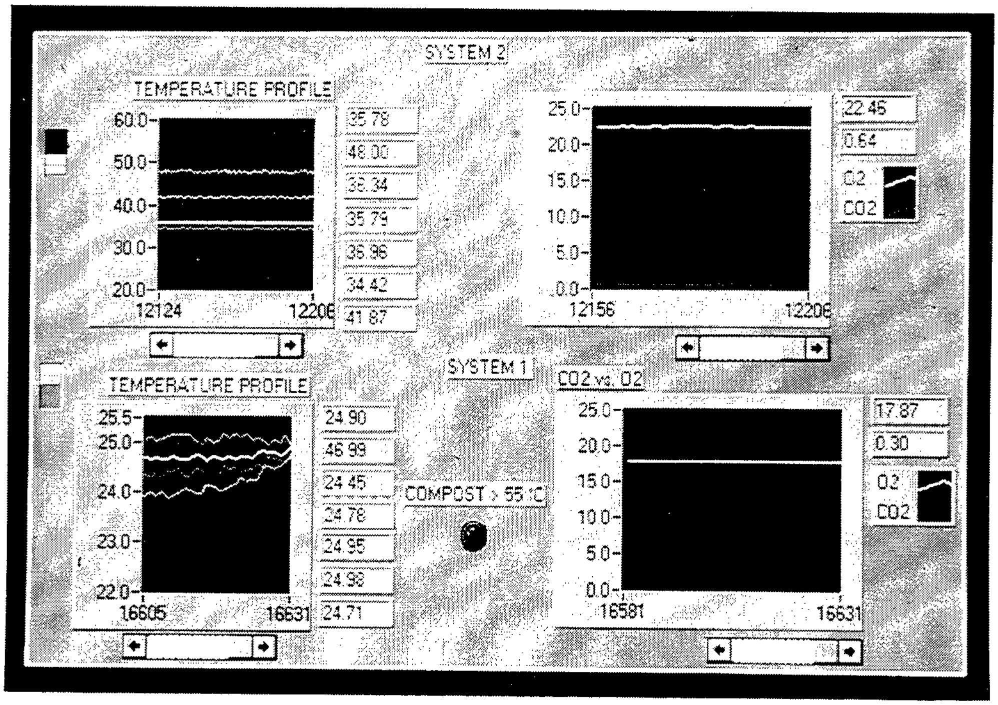


Figure B3. Example of virtual instrument display

Appendix C
Data Summary

Phase-I, Run 1 (T1R1, 8/21/93 - 8/24/93 - 9/13/93)

Fate of TNT (extractable with ether and acetonitrile)

days		TNT (mg/kg)		avg	std
soil	37800	40000	43000	*40267*	*2131*
		17800			
0	12200	12700	13000	*12633*	*330*
1	12600	13000	13400	*13000*	*327*
5	9700	9950	10200	*9950*	*204*
10	8030	8340	8650	*8340*	*253*
15	7320	7400	7480	*7400*	*65*
20	7850	8095	8340	*8095*	*200*

days		2A-DNT (mg/kg)		avg	std
soil		< 25.0			
0	62.1	74.7	81.7	*73*	*8*
1	52	53.8	55.5	*54*	*1*
5	385	389	393	*389*	*3*
10	429	436.5	444	*437*	*6*
15	393	402	411	*402*	*7*
20	521	540	558	*540*	*15*

days		4A-DNT (mg/kg)		avg	std
soil		< 26.0			
0	167	192	226	*195*	*24*
1	123	124	125	*124*	*1*
5	466	472	478	*472*	*5*
10	340	345	349	*345*	*4*
15	280	287	294	*287*	*6*
20	336	350	363	*350*	*11*

Negligible concentrations of 2,4-DNT (<25 mg/kg) and 2,6 DNT (<26 mg/kg)

Other Explosive Compounds

days	HMX (mg/kg)			avg	std
soil	2350	2457	2600	*2469*	*102*
Mix	1046	1093	1157	*1099*	*46*
0	933	941	957	*944*	*10*
1	885	913	941	*913*	*23*
5	948	964	980	*964*	*13*
10	957	960	964	*960*	*3*
15	873	874	874	*874*	*0*
20	1040	1055	1070	*1055*	*12*

days	RDX (mg/kg)			avg	std
soil	9450	9840	10400	*9897*	*390*
Mix	4205	4379	4628	*4404*	*174*
0	3900	3913	3920	*3911*	*8*
1	3730	3835	3940	*3835*	*86*
5	3930	3985	4040	*3985*	*45*
10	3900	3910	3920	*3910*	*8*
15	3490	3545	3600	*3545*	*45*
20	3890	4020	4150	*4020*	*106*

days	TNB (mg/kg)			avg	std
soil	104	112	117	*111*	*5*
	46	50	52	*49*	*2*
0	46.9	50	51.2	*49*	*2*
1	45.8	47.5	49.1	*47*	*1*
5	55.8	55.9	56	*56*	*0*
10	37.2	193.6	350	*194*	*128*
15	28.8	30.1	31.3	*30*	*1*
20	35.6	36.6	37.6	*37*	*1*

Negligible concentrations of DNB (<25 mg/kg) and Tetryl (<65 mg/kg)

Temperature, % moisture, and pH Profiles

days	Core	Jacket	%M	pH
1	28.4	28.9	52.1	4.4
2	32.7	32.7		
3	39.3	39.3		
4	47.5	47.5		
5	54.4	54.4	52.8	4.5
6	55.5	55.5		
7	54.1	53		
8	53.8	53.8		
9	51.3	51.3		
10	52.2	52.3	50.5	4.6
11	51.8	51.8		
12	53.5	53.5		
13	53.5	53.5		
14	52.2	52.2		
15	51.3	51.3	46.3	4.5
16	48.4	48.4		
17	46.8	46.8		
18	45.2	45.9		
19	46.2	46.2		
20	45.6	46	54.9	4.5

Aeration: 2000 mL/min
at 24 C and 45% RH
when T > 55 C

Phase-I, Run 2 (T1R2A, 8/21/93 - 9/2/93)

The reactor failed to achieve thermophilic temperatures.
Experiment abruptly terminated after 10 days.

Phase-I, Run 3 (T1R2B, 9/7/93 - 9/27/93)

Fate of TNT (extractable with ether and acetonitrile)

days	pH	TNT (mg/kg)			avg	std
0	4.9	14700	14850	15000	*14850*	*122*
1	4.5	13800	14000	14200	*14000*	*163*
5	4.7	13200	13300	13400	*13300*	*82*
10	4.6	13200	13300	13400	*13300*	*82*
15	4.8	11900	11900	11900	*11900*	*0*
20	4.6	10600	10700	10800	*10700*	*82*

days	pH	2A-DNT (mg/kg)			avg	std
0	4.9	48	48.1	48.1	*48*	*0*
1	4.5	85.1	87.8	90.4	*88*	*2*
5	4.7	126	134.5	143	*135*	*7*
10	4.6	177	181.5	186	*182*	*4*
15	4.8	222	233	244	*233*	*9*
20	4.6	377	383	388	*383*	*4*

days	pH	4A-DNT (mg/kg)			avg	std
0	4.9	71	72.9	74.7	*73*	*2*
1	4.5	166	166.5	167	*167*	*0*
5	4.7	227	239	251	*239*	*10*
10	4.6	342	356	370	*356*	*11*
15	4.8	492	524	556	*524*	*26*
20	4.6	732	741	750	*741*	*7*

Negligible concentrations of 2,4 and 2,6 DNT.
HMX: 997 (day 0) to 1170 (day 20) mg/kg
RDX: 4185 (day 0) to 4610 (day 20)mg/kg
TNB: 42.7 (day 0) to 37.5 (day 20) mg/kg

%M: 47.7% to 49.4%

Phase-I, Run 4 (T2R1, 10/28/93 - 11/25/93)

Variation of data not available.

days	TNT	2ADNT	4ADNT	44AZ
0	7531	12.2	16.7	
5	10700	25	1460	
10	7050	1540	3230	53.2
15	2990	1220	2370	49.2
20	5080	1700	3350	72.3
27	5940	1460	2800	64.3

days	pH	TKN	COD	TVS %
0	5.5	6040	316000	42
5				
10				
15				
20	4.28	8690	604000	46
27				

days	ether	acetonitrile	Humin	Humic	Fulvic	Cellulos	Total %
0	28.2	3.15	22.6	0.83	2.21	2.57	59.56
20	32.2	5.48	28.1	1.77	3.4	6.1	77.05

Phase-I, Run 5 (T2R2, 10/28/93 - 11/25/93)

Variation of data not available.

days	TNT	2ADNT	4ADNT	44AZ
0	17650	25	40	1.88
5	2320	990	1960	952
10	216	667	1570	590
15	492	793	2110	801
20	7320	716	966	210

days	pH	TKN	COD	TVS %
0	5.21	6640	452000	46
5				
10				
15				
20	4.96	10200	279000	50

Continuous aeration

Phase II – WACS–II (6/10/94 – 8/14/94)

A = Aeration On
T = Feedback Temperature Control On
O = No Aeration or No Feedback Temperature Control

Temperature

days	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15
	O/O	O/T	A/O	O/O	A/T	A/O	O/T	A/T	A/T	A/T
0	31	31.4	31.7	32.5	44.9	31.1	33.8	43.7	33.5	27
1	28.2	30.2	31.7	30.9	53	31.3	33.3	40.8	36.5	36.9
2	25.7	32.3	30.4	28.1	55.1	31.2	32.8		32.8	46.4
3	24.7	31.1	43.2	26.8	54.8	30.7	32	50.9	30.8	48.8
4	24.7	29.6	44	26.2	53.1	30.3	30.9	55.2	29.9	52.5
5		28.8	33.1	26.2			29.9	55.5	30	42.2
6									30.4	
7									36.7	

Moisture

days	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15
	O/O	O/T	A/O	O/O	A/T	A/O	O/T	A/T	A/T	A/T
0	52.5	53.8	56.8	55.5	55	57.6	54.8	53.3	54.4	52.7
1		57	57.8	55.4	54.8	55.5	55.3	52.6		
2		55.9	57.1	56.4	52.2	56.8	54.7	52.6		
3		54.4	56.6	55.8	56.3	56.6	49.7	53.4	56.6	
4	50.2	56.6	57.1	55.8	52.4	57.9	55.4	44.4		
5		55.8	57.3	56.8			57	42.7	56.1	
6										
7										

pH

days	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15
	O/O	O/T	A/O	O/O	A/T	A/O	O/T	A/T	A/T	A/T
0	6.47	6.58	6.84	6.7	6.9	6.75	6.24	7.77	6.66	8.22
1	5.67	4.4	4.77	5.02	6.68	6.5	5.43	6.15		7.19
2	5.43	6.19	4.99	4.66	8.49	6.3	3.92	6.26		7.36
3		6.26	7.44	4.66	8.44	5.96	4.97	8.74	4.69	8.64
4	5.6	5.95	6.23	4.63	7.86	6.21	4.94	8.59		8.85
5		7.1	5.97	4.7			4.94	8.01	4.99	8.9
6										
7									8.75	

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY ***(Leave blank)***

2. REPORT DATE
February 1997

3. REPORT TYPE AND DATES COVERED
Final report

4. TITLE AND SUBTITLE
Bench-Scale Remediation Composting: Process Principles and Protocol

5. FUNDING NUMBERS

6. AUTHOR(S)
Kurt T. Preston, Steve Seiden, Kyoung S. Ro

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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Baton Rouge, LA 70803

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report IRRP-97-1

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Corps of Engineers
Washington, DC 20314-1000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

The purpose of this report is to apply the principles of biochemical process kinetics, mass and heat transfer, and major process parameters in the design and application of bench-scale compost systems. The premise is that understanding the fundamentals of the system in the engineering sense will assist to provide a technical foundation for standard bench-scale composting protocols. Process kinetics as they relate to organic substrate use, overall, and the kinetics of explosive compound degradation/transformation are discussed. Also discussed are the physical, chemical, biological, and thermodynamic factors central to the application of bench-scale compost systems. Finally, the outline of a standard remediation composting protocol built on a foundation of fundamentals is provided. The approach described in this report is providing a basis for two currently ongoing bench-composting investigations.

14. SUBJECT TERMS

Army	Kinetics	TNT
Composting	Remediation	
Explosive contamination	Soil contamination	

15. NUMBER OF PAGES
100

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102