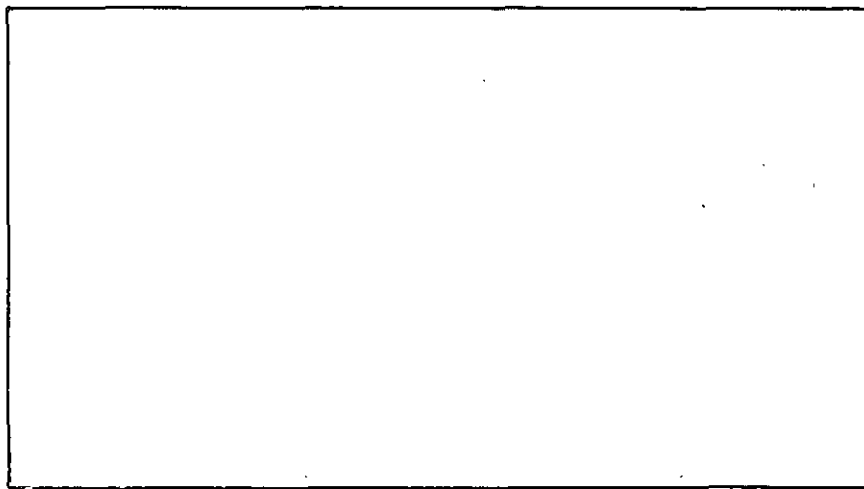


Environmental Engineering



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Technical Report

Trace Organics in Composted Sewage Sludge

Part 1. Literature Review

July, 1994

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R&D# 91-08

by

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ABSTRACT

The objective of this research was to produce a list of the trace organic compounds prevalent in sewage sludge compost and to attempt to determine the fate and removal mechanisms of trace organics during sludge composting. This was accomplished in three steps. First, a detailed literature review was completed examining information and collected data on the levels of trace organic compounds in municipal wastewater sludge and sludge compost. The fates of these compounds during composting was also investigated. The second step involved a survey of wastewater treatment plants currently practicing composting in western Massachusetts. From the list of treatment plants generated during the survey, three facilities were chosen for preliminary sampling. Finished compost from the three facilities (Holyoke, Springfield, and Williamstown) was collected and analyzed for trace organic contamination. The information gathered during the preliminary sampling permitted a rational choice of study site for the third part of this project. The third step involved collecting and analyzing raw and finished compost at the chosen plant (Holyoke). Five samples were collected over a nine-month period. The results of steps two and three are presented as a separate volume (Part 2) while the results of the literature review are presented in this technical report.

The information obtained during the literature review and the results from both the preliminary and final sampling all suggest that very few trace organic compounds are present in composted sewage sludge. In addition, research has shown that many of the trace organics belonging to the list of EPA priority pollutants are either biodegraded to some extent or volatilized during composting. Therefore, any trace organics which may be present in raw compost will probably be degraded and reduced to very low concentrations. The main conclusion reached from these findings and the results of this

project is that composted sewage sludge does not contain trace organic contamination which could otherwise limit its application to land or use as a beneficial sludge product.

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EPA List of Organic Priority Pollutants

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1.0 INTRODUCTION

1.1 Objectives

In response to the proposed 503 standards, this study, funded by the Massachusetts Division of Water Pollution Control (MDWPC), was undertaken to produce a list of the trace organics prevalent in sewage sludge and to attempt to determine the fate and removal mechanisms of trace organics during composting. This was accomplished in three steps. First, a detailed literature review was completed examining information and collected data on the levels of trace organic contaminants in municipal wastewater sludge and sludge compost. The specific topics addressed were:

- 1) What are the sources of trace organics in wastewater?
- 2) What is the fate of trace organics in wastewater treatment plants and how are they incorporated into the sludge?
- 3) Which trace organics are typically found in sewage sludge?
- 4) What is the fate of trace organics during composting?
- 5) Which trace organics (if any) are typically found in finished compost?

The results of this first step are reported in Part 1 of this technical report.

The second step was to survey wastewater treatment plants currently practicing composting in western Massachusetts. The objective was to gather any available data on trace organic contamination in sludge and compost. This information permitted a rational choice of study site for the third part of this project. Some preliminary sampling at the best perspective plants was necessary during this phase. The third step involved collecting and analyzing parent sludge and final compost at the chosen plant. Five samples were collected over a nine-month period. The results of steps two and three are reported in Part 2 of this technical report.

During the course of this project, the final Part 503 rule was published on February 9, 1993 in the Federal Register (58FR9248). After obtaining the results from the National Sewage Sludge Survey and conducting extensive scientific peer review, EPA realized that levels of trace organics in sewage sludge from wastewater treatment plants had significantly decreased since the 1978 Fate Study (upon which the proposed 503 pollutant limits were based) (16,20). Therefore, numerical limits for organic compounds were completely omitted from the final Part 503 rule. However, since organic pollutants may be included in the list of pollutants that EPA will identify for regulation in second stage (Round 2) rulemaking, this study focused on the organic compounds originally listed in the proposed 503 regulations under sections 503.13 (agricultural land) and 503.22 (distribution and marketing). These compounds, referred to in this report as the trace organic compounds of concern, are presented in Table 1-1.

Table 1-1 TRACE ORGANIC COMPOUNDS OF CONCERN

Aldrin/dieldrin (total)
Benzo (a) pyrene
Chlordane
DDT/DDE/DDD (total)
Dimethyl Nitrosamine
Heptachlor
Hexachlorobenzene
Hexachlorobutadiene
Lindane
Polychlorinated Biphenyls (PCBs)
Toxaphene
Trichloroethylene

The overall objective of this study was to provide some fundamental information on the fate of trace organics during sludge composting. The data should be valuable to

municipalities planning sludge composting facilities and to agencies responsible for monitoring and regulating treatment and disposal of sludge and compost.

1.2 Background

During the last twenty years, both the amount of sewage sludge produced and the number of regulations governing the disposal of sewage sludge have increased significantly. In response to the deteriorating quality of the nation's inland and coastal waters, Public Law 92-500 (referred to as the Clean Water Act) was passed in 1972. The Clean Water Act established secondary treatment as the minimum acceptable level of treatment prior to surface water discharge. The subsequent upgrading and expansion of wastewater treatment plants has greatly increased the volume of sludge generated in the Commonwealth of Massachusetts. Also during this period, environmental problems associated with sewage sludge disposal have prompted strict legislative actions.

Legislation controlling sludge disposal is contained in: the Clean Air Act of 1970 (sludge disposal by incineration), the Water Pollution Control Act of 1972 (fresh water dilution), the Marine Protection Research and Sanctuaries Act of 1976 (ocean dumping), and the Resource Recovery and Conservation Act of 1976 (landfilling). Under authority of Sections 405(d) and (e) of the Clean Water Act, the United States Environmental Protection Agency (EPA) has recently promulgated regulations to protect public health and the environment from any reasonably anticipated adverse effects of certain pollutants that may be present in sewage sludge. The regulations, 40 CFR Part 503, establish requirements for the final use of sewage sludge for three sludge disposal options, including: application to land for a beneficial purpose (including sewage sludge or sewage sludge products that are sold or given away for use in home gardens), disposal on land by placing it onto surface disposal sites (including sewage sludge-only landfills), and incineration.

Currently, some form of landfilling or land application is the most commonly used method for the disposal of sludge (83). Land application of sludge is used

extensively as a means of disposal, as a means of reclaiming marginal land for productive uses, and as a means of utilizing the nutrient content in sludge. However, landfilling and land application of sludge have become more strictly regulated. The number and capacity of landfills have been reduced and new landfill locations that meet environmental, social, and economic requirements are increasingly difficult to find. Incineration of sludge by large municipalities is also extensively used, but incineration operation and emission control are subject to greater regulatory restrictions. Thus, municipalities have been forced to find new practices for sludge treatment and resource recovery from sludge. The composting of sewage sludge is among the most promising of these practices (21).

Composting is a biochemical process in which organic materials are biologically degraded. It takes place under warm, moist, and aerobic conditions, and results in the production of organic or inorganic byproducts and energy in the form of heat (3,79,126). The composting process is facilitated by a high concentration of biodegradable organic material in the compost matrix and an active microbial population. Metabolic heat is trapped within the composting mass, leading to the phenomenon of self-heating that is characteristic of the composting process. This self-heating serves to increase the rate of microbial metabolism and also significantly reduces pathogens. Aeration of the compost pile, along with this heat, dry out the compost while conversion of organic matter to carbon dioxide reduces the mass of materials. Sewage sludge composting can provide: 1) organic matter stabilization, 2) pathogen destruction, and 3) mass, volume, and moisture content reduction (41,79). Properly composted sludge is aesthetically acceptable, essentially pathogen free, easy to handle, and valuable as a soil amendment (improves soil structure, increases water retention, and provides plants nutrients).

There are three broad categories of sludge composting: windrow, static pile, and in-vessel. In the first category, the mixture to be composted is formed into one or more long rows, or windrows. Periodically, the mixture is manually or mechanically turned to promote aeration and increase the contact between biomass and organic materials. The

static pile can either be uncontrolled or aerated. In the uncontrolled process, the mixture to be composted is formed into a pile and essentially left untouched. In the aerated static pile, a built-in aeration system provides oxygen and also removes excess heat from the matrix. The highest technological level of composting, in-vessel composting, involves placing the material to be composted inside a large containment vessel which is equipped with a temperature-controlled aeration system. Many in-vessel systems are also equipped with a mechanism to periodically mix or agitate the composting material. Most U.S. operations are of the static pile type. In all three categories, the process scheme is very similar. First, the sludge and bulking agent (ordinarily wood chips) are mixed. Next, the mixture is aerated by forced air or by turning. The mixture is then cured, dried (optional), and screened to recover the bulking agent. The bulking agent is recycled while the compost is stored for eventual marketing.

The practice of sewage sludge composting has grown considerably over the past decade. In 1983, there were 61 full-scale composting projects in the U.S., with 29 in development (45). In 1992, there were 159 facilities in operation and six in start-up. Additionally, there are 61 projects in advanced stages of development or construction, 13 pilot plants, and numerous other projects under consideration, for a grand total of 290 (27 in Massachusetts). As discussed earlier, the problems associated with landfill disposal of sludge, especially in the Northeast, are primarily responsible for this rapid increase.

One of the most significant obstacles to initiating sludge composting is final disposal of the compost. Concerns over the general disposal of sludge to land have been raised because some sludges may contain toxic inorganic and organic substances (100). These materials may have the potential to contaminate agricultural land and adversely affect the health of animals and humans who consume the crops (17).

The most widely developed market for compost is landscapers, followed by nurseries and public works applications. Other users include topsoil blenders, golf courses, mulch dealers, turfgrass applications, farmers, mine reclamation, tree farms and

schools (45). However, the spreading of compost on private property, farmlands, and public lands becomes more restrictive as contamination increases. Concentrations of heavy metals and polychlorinated biphenyls (PCBs) largely govern the classification of sludges in Massachusetts and thus determine sludge disposal options (Table 3-1). Disposal of compost is dictated by the same classification scheme. Most of the metals prevalent in compost belong to the group of contaminants listed in Table 3-1. However, many organic compounds of environmental and human health concern are not regulated. Compared to heavy metals, studies on the occurrence of trace organics in sewage sludge are quite scarce (36). Also, the studies conducted did not address the fate of trace organics during the composting process.

The 1982 EPA Fate Study (27) documented the presence of trace organic contaminants in sewage sludge. Fifty publicly owned treatment works were surveyed to study the occurrence and fate of the EPA-designated 129 priority pollutants. EPA found that most of the organic priority pollutants were detected in raw sludge at least once. However, many of these trace organics which were detected in sludge samples were not detected in influent samples. Most likely, the influent concentrations of the trace organics in the wastewater were too low to be measured but the trace organics were sequestered and concentrated in the sludge. Nineteen of the organic priority pollutants found in significant concentrations in the sludge were below detection limit concentrations in the wastewater influents.

In another study, EPA (36) investigated the occurrence of trace organics and inorganics in distribution and marketing (D & M) municipal sludge products. Most of the sludge samples obtained came from composted sludge products. Compared to the Fate Study, relatively few trace organics were identified in D & M sludges. In D & M products from 26 cities, only about 10 of the 121 targeted trace organics were detected. Of the volatile priority pollutants, only toluene and p-dichlorobenzene were found. Levels of extractables were also quite low. Chlordane, DDT metabolites, Bis-(2-

ethylhexyl) phthalate, and pyrene were found most frequently. EPA concluded that in general, the priority pollutant organics do not appear to be a cause for concern in these types of sludge products.

The fact that high levels of trace organic compounds were found in sewage sludges but were found in relatively low levels in D & M sludges suggests that composting reduces trace organic pollutant concentrations. Volatilization, biodegradation, and leaching might all contribute to contaminant reduction during composting. A detailed study of trace organic contaminant fate and degree of removal by the composting process has not been performed.

At the onset of this report, EPA was in the process of finalizing the Part 503 regulations. When the draft rules were initially proposed in 1989, they caused alarm in the sludge and composting industries because the proposed requirements were so strict (20). In particular, the proposed pollutant limits for a number of trace organic compounds were viewed very unfavorably. EPA claimed that these organic compounds were likely to be found in sewage sludge and, if disposed of improperly, could cause adverse human health or environmental effects. The proposed regulations were so strict that many municipalities feared that the rule would severely restrict a municipality's capacity to utilize sewage sludge or sewage sludge products such as compost (46).

In response to the proposed 503 standards, this study, funded by the Massachusetts Division of Water Pollution Control (MDWPC), was undertaken to produce a list of the trace organics prevalent in sewage sludge and to attempt to determine the fate and removal mechanisms of trace organics during composting. The primary objective was to provide some fundamental information on the fate of trace organics during sludge composting. The data should be valuable to municipalities planning sludge composting facilities and to agencies responsible for monitoring and regulating treatment and disposal of sludge and compost.

2.0 LITERATURE REVIEW

2.1 SOURCES OF TRACE ORGANICS IN WASTEWATER

Since the turn of the century, the number of organic chemicals that have been synthesized reportedly exceeds half a million, and approximately 10,000 new compounds are added each year (83). Because of their prevalence, many of these organic compounds are commonly found in the wastewaters from most municipalities and communities (6,94,118,119,120). Petrasek et al. (96) reported that most of the organic priority pollutants are present in municipal wastewaters at relatively low concentrations (less than 10 µg/L), although certain compounds have been detected at specific POTWs in much higher concentrations.

Industrial Sources

The principal source of trace organics found in the influents of most wastewater treatment plants is industrial discharge into the sewer system (26,27,33,121). In 1978 EPA (27) initiated a detailed program to study the occurrence and fate of the 129 priority pollutants in 40 POTWs (the 40-city study). Conclusions reached include:

1. In general, the higher the industrial contribution to a POTW, the higher the concentration of priority pollutants in the POTW influent. This trend is exhibited for all of the major priority pollutant fractions.
2. Priority toxic pollutants are principally byproducts of industrial processes. Conservative estimates indicated that a minimum of 54 percent of the volatile organics, 30 percent of the acid extractable organics, and 76 percent of the base/neutral extractable organics loadings are associated with industrial discharges.
3. The majority of priority toxic pollutants were detected Monday through Friday.
4. The contribution of priority toxic pollutants is associated largely with specific industrial categories.

5. Pollutants only infrequently measured in POTW influents may, in fact, be frequently present in the influent below their detection limits.

The number of industries that currently discharge wastes to domestic sewers has increased significantly during the past 20-30 years (83). In industries which do not practice internal recycling or reuse programs, it can be assumed that about 85 to 95 percent of the water used in the various operations and processes will become wastewater. In addition, rapid advances in industrial technology have brought about an ever-increasing introduction rate of organic chemicals from these industries (115).

Three of the major contributors of trace organics into domestic sewers include the organic chemicals, petrochemicals, and pesticides industries. The organic chemicals industry is exceedingly complex and is comprised of thousands of companies involved in the manufacture of a multitude of products from such organic chemical sources as petroleum, coal, and natural gas. Typical industry products include synthetic detergent bases, fuel additives, solvents, plastics, resins, and synthetic fiber bases. The wastewater produced during the manufacture of these products is often heavily contaminated with toxic substances. The petrochemicals industry also produces wastewaters rich in chemicals which can be extremely hazardous, and the manufacture of pesticides involves substantial production of toxic chemicals (28).

Although industrial discharge into domestic sewers introduces a majority of the organic priority pollutants which enter POTWs, there are certain advantages in discharging these chemical and other industrial wastes to sewers for treatment at sewage disposal works. When treated in combination with sewage, the chemical and industrial wastes show an increased susceptibility to biological oxidation, and the domestic sewage stream can supply the necessary nutrients often lacking in industrial waters. Also, the dilution of the industrial wastes provided by the domestic sewage can reduce the potential inhibitory or toxic chemicals to a level harmless to the treatment microorganisms and

2.2 FATE OF TRACE ORGANICS IN WASTEWATER TREATMENT PLANTS

2.2.1 Introduction

Historically, wastewater treatment plants have been designed to remove biochemical oxygen demand (BOD), suspended solids, pathogenic organisms, and the nutrients nitrogen and phosphorous. Very little is known about the ability of wastewater treatment plants to remove organic priority pollutants from the wastewater stream (102,106). In a study of 40 publicly owned treatment works (POTWs), EPA (27) reported that the majority of most organic priority pollutants were removed by the secondary treatment process. Based on the 40 POTW data base, 50 percent of secondary treatment plants achieved a minimum of 82 percent reduction of total volatile priority pollutants and 65 percent reduction of the total base neutral priority pollutants. Melcer et al. (82) conducted intensive sampling at a full-scale municipal sewage treatment plant (STP) and concluded that STPs are capable of efficient trace contaminant removal. In a study of the fate of 22 toxic organics in wastewater treatment plants, Petrasek et al. (96) also found that a typical POTW significantly (up to 90 percent) reduced the concentrations of most of the compounds, although certain compounds were present in the effluent in relatively high concentrations. Michael et al. (84) discovered that POTWs substantially reduced the concentrations of volatile organics in wastewater. Thus, it is generally agreed upon that many trace organic compounds are removed in biological wastewater treatment plants. However, the fate of individual organic pollutants entering biological wastewater treatment processes is not well understood (6,35,93,95,96,102,119). The removal mechanisms for trace organics may include volatilization/air stripping, adsorption onto solids (biomass and primary solids), biodegradation, or a combination of these (6,35,56,64,76,119,124,125). If a trace organic compound is not removed by any of these mechanisms, the compound will pass through

the treatment plant and be a residual constituent in the treated effluent. Kincannon et al. (64) investigated the behavior of priority pollutants in wastewater treatment processes and noted that, in general, chemicals under the same classification had the same removal mechanisms. Determining the precise removal mechanisms for specific trace organics is very difficult because no one removal mechanism can be examined by itself without causing inaccuracies in experimental data obtained (35). These removal mechanisms are described below.

2.2.2 Volatilization/Air Stripping

Volatile organic compounds (VOCs) are organic compounds which have a boiling point less than or equal to 100° C and/or a vapor pressure greater than 1 mm Hg at 25° C (83) and therefore evaporate readily at normal temperatures and pressures. VOCs comprise 31 out of the 129 EPA-designated priority pollutants and are considered harmful to continually exposed human beings (90). VOCs entering wastewater treatment plants can be released to the atmosphere during collection and treatment, especially at the headworks and the activated sludge tank (83,90). Due to the difficulty in measuring VOC emissions, however, few data are available for VOC emissions during municipal wastewater treatment (90). The principal mechanisms responsible for the release of VOCs during collection and treatment of wastewater are volatilization and air stripping (83). Volatilization and air stripping are distinguished from each other by the manner of gas-liquid contact.

Volatilization

The release of VOCs from the surfaces of wastewater to the atmosphere is known as *volatilization*. Volatilization has been considered to be one of the main mechanisms for removal of VOCs from wastewater (90). VOCs are released because they partition between the gas and water phase until equilibrium concentrations are reached (38). The mass transfer of a compound between the two phases is a function of the compound

concentration in each phase relative to the equilibrium concentration. When the concentration in one of the phases is far from equilibrium, the transfer of the compound between phases is greatest. Since the concentration of VOCs in the atmosphere is extremely low, VOCs are usually transferred from the wastewater to the atmosphere (83).

Air Stripping

Air stripping of VOCs is the process of gas/liquid mass transfer in systems with dispersed gas or liquid phases (118). Air stripping can occur when air is temporarily entrapped in wastewater or is intentionally introduced into the wastewater as in aerated grit chambers and diffused-air activated sludge tanks (35,83,94). As the air bubble is formed, oxygen is transferred to the liquid and volatile compounds present in the liquid may be transferred to the air bubble and be released to the atmosphere (70). Stripping processes normally have a much greater interfacial area and may often be more turbulent than volatilization processes (118). The forces which control the mass transfer between phases are the same as in volatilization. Therefore, the maximum amount of stripping occurs when the air being introduced is contaminant-free.

It is widely reported that most of the organic compounds that may be air stripped have Henry's law constants (the ratio of equilibrium concentrations in the gas phase to the aqueous phase) greater than 10^{-3} atm-m³/mol (35,93,96,113). The principal locations where VOCs are emitted from wastewater collection and treatment facilities are preliminary treatment, equalization basins, secondary aeration/oxidation, primary treatment, and collection systems (2).

There are a number of factors which affect the propensity of a VOC to volatilize/air strip during wastewater treatment. They include:

1. Smith and other authors (107,108,109) have shown that the volatilization rate of chemicals can be controlled by mass transfer resistance in the liquid phase (for high volatility compounds), gas phase (for low volatility compounds), or a

combination of both (for transition volatility compounds), depending on the value of the Henry's law constant.

2. In typical activated sludge treatment, the fractional removal of organic contaminants by volatilization is likely to be greater with surface aeration than with bubble aeration (38,76).
3. The removal of organic contaminants by volatilization is greater in aeration tanks equipped with coarse bubble diffusers (low oxygen transfer efficiency) than those equipped with fine bubble diffusers (high oxygen transfer efficiency and lower airflows) (38,94).
4. Increased airflows have been shown to increase the degree of stripping. However, as the air flow increases, the extent of stripping increases but at a declining rate (70,94).
5. Hydraulic drops and areas of high velocity (which cause turbulence) will contribute to stripping (94).
6. The presence of contaminants such as suspended solids, surfactants, salts, oils, nonviable biomass, and other compounds can alter the stripping rate. With very few exceptions, contaminants cause a reduction in the stripping rate. Variations of ± 50 percent of the stripping rate may occur as a result of contaminants (12,70,118). The effect also seems to be the strongest for the higher volatility compounds (118).
7. Organic priority pollutants may adsorb to solid phase particles and thus not be available for stripping by the air stream (23).

A number of studies have been conducted to determine whether certain trace organic compounds volatilize during wastewater treatment. Namkung and Rittmann (90) investigated volatile organic compound emissions from two large POTWs in the Chicago area and found that 82 and 86 percent of the total input VOCs were removed at the

Calumet and West-southwest wastewater treatment plants respectively. The major volatile compounds entering the Calumet plant were toluene, benzene, ethylbenzene, and tetrachloroethylene and at the West-southwest plant were methylene chloride, toluene, and trichloroethylene. EPA (26) also reported that volatile organics were substantially reduced by the activated sludge process, most likely through air stripping or, to a lesser extent, biodegradation. In a study of the removal and fate of RCRA and CERCLA toxic organic pollutants in wastewater treatment, EPA (32) concluded that a significant amount of chlorinated aliphatic solvents may be volatilized from an activated sludge system. Petrasek et al. (96) studied the fate of toxic organic compounds in wastewater treatment plants and attributed the removals observed for toxaphene and heptachlor to stripping. They also noted that stripping was not a significant removal mechanism for lindane. Weber et al. (124) concur that volatilization is not considered a significant mechanism for the removal of lindane. Parker et al. (94) found that nonchlorinated compounds were degraded to the greatest extent and stripped the least. Conversely, the chlorinated compounds were degraded to a lesser extent and stripped to a greater extent. The percentage of trichloroethylene, a chlorinated compound, lost to stripping was 47.8 percent.

Another factor which affects the stripping of VOCs is biodegradation. Stover and Kincannon (112) reported that the removal of volatile, strippable organic compounds is enhanced by biological degradation, while volatile compounds that are only removed by stripping are limited by their physical characteristics and reactions. Lurker et al. (70) note that laboratory studies of air stripping of organic compounds from wastewater which do not incorporate the possible competitive effects of the acclimated biomass will overestimate the rate of stripping from the wastewater.

2.2.3 Biodegradation

The major goal of biological wastewater treatment (secondary treatment) is to remove the soluble organics that escape primary treatment and to provide further removal of suspended solids (98). In many locations, the removal of nutrients, specifically nitrogen and phosphorous, and trace organic compounds is also an important treatment objective (83). Biological treatment processes involve bringing a variety of microorganisms, principally bacteria, in contact with wastewater so that the organisms can consume the colloidal and dissolved carbonaceous organic matter as food and convert them into various gases and into cell tissue. Since cell tissue has a specific gravity slightly higher than that of water, the resulting cells can be removed from the treated liquid by gravity settling. All of the biological processes used for the treatment of wastewater are derived from processes occurring in nature. The biological degradation (biodegradation) of the waste is simply accelerated by controlling the environment of the microorganisms. Biological treatment processes attempt to achieve the proper environment required for optimum growth of the microorganisms involved. The basic ingredients needed for secondary treatment are the availability of (1) mixed populations of active microorganisms, (2) good contact between the microorganisms and waste material, (3) oxygen, (4) nutrients, and (5) maintenance of other favorable environmental conditions such as temperature, pH, sufficient contact time, etc. (98).

Suspended growth processes are the biological treatment processes in which the microorganisms responsible for the conversion of the organic matter and other constituents in the wastewater to gases and cell tissue are maintained in suspension within the liquid (83). Suspended growth systems are the most common of the secondary treatment processes in use today and will remain so as new facilities are built to comply with the Clean Water Act requirements. By far, the most commonly used suspended growth system for the secondary treatment of domestic wastewater is the activated sludge process and its numerous process modifications. In the activated sludge process, the

wastewater containing organic waste is introduced into a reactor where an aerobic bacterial culture is maintained in suspension. The microbial population is normally dominated by heterotrophic organisms that require biodegradable organic matter for energy and new cell synthesis. The complex series of biochemical reactions that actually occur can be simplified into three fundamental activities: oxidation, synthesis, and autoxidation. Oxidation involves the coupled release of energy through the conversion of organic matter to lower-energy products (carbon dioxide and water). Synthesis is the conversion of a portion of the organic matter, assisted by the energy released during oxidation, into new settleable biomass. Autoxidation is the conversion of some of the cell constituents to low-energy products, with the release of additional energy. The aerobic conditions maintained in the reactor are achieved by the use of diffused or mechanical aeration. These aerators also serve to maintain the bacterial culture in suspension and to mix the contents of the reactor. After a specified period of time, the mixture of old and new cells passes into a settling tank where the cells are separated from the treated wastewater by gravitational forces. A portion of the settled cells, known as return activated sludge, is recycled back to the reactor to maintain the desired concentration of organisms in the reactor. The remaining settled cells are wasted and are thus referred to as waste activated sludge.

Of all the removal mechanisms discussed, biodegradation represents the only destructive fate for organic compounds; sorption and stripping are non-destructive fates (105). Many organic compounds are rapidly oxidized by biological processes, and many more can be oxidized if the treatment plant biomass is able to acclimate to the specified problem compound and establish a stable population (12). However, even though biological treatment is effective for many organic compounds, for others it can result in chemical conversion, perhaps to even less acceptable products, or concentration within the sludge and have adverse effects on sludge handling and sludge disposal (95). Still other organic compounds are known to be completely resistant to biological oxidation,

but the number of these compounds is thought to be minimal (12). A number of chemical factors, both structural properties of the chemical and environmental factors, influence the persistence (resistance to biodegradation) of organic compounds (105). Structural properties include molecular size and weight, solubility, toxicity, and xenobiotic origin; environmental factors include dissolved oxygen concentration, temperature, pH, and the presence of nutrients and trace elements.

There are certain organic compounds that are not biodegraded very well in typical wastewater treatment plants because the treatment organisms cannot derive sufficient energy from their use as the sole carbon and energy source (91). For example, Hill and McCarty (59) concluded that none of the chlorinated hydrocarbon pesticides (the most persistent of the organic pesticides) are used by any organism as a carbon source for metabolism. However, these persistent compounds are sometimes metabolized by the microorganisms when other substrates are present to provide the organisms' energy needs. This mechanism, called secondary utilization, enables rapid biodegradation of individual trace-level compounds, even when they are present at very low concentrations, that could not otherwise provide enough energy to sustain the microbial culture (81,90,91). The primary substrate, which may be a single compound or the aggregate of many compounds, must be present at a concentration high enough to support long-term biological growth and maintenance, while individual trace organic compounds, none of which could support biological growth alone, are called secondary substrates. Although a secondary substrate can supply very small amounts of energy and carbon, it does not supply the energy requirements for cell growth and maintenance because of its low concentration (lower than the minimum concentration needed to sustain a steady-state biomass) or its short-term presence even at high concentrations. McCarty (77) stated that secondary utilization may be the main mechanism by which trace organic compounds are biodegraded. Also, Card and Corsi (14) noted that when VOCs biodegrade in secondary

wastewater treatment plants, secondary utilization is the likely biodegradation mechanism.

Numerous studies involving the biodegradation of individual compounds and groups of compounds in secondary wastewater treatment plants have been conducted. Parker et al. (94) recently investigated the fate of VOCs in treatment plants and found that more than 80 percent of the mass flow of non-chlorinated compounds and 46 percent of the mass flow of chlorinated compounds were biodegraded. Card and Corsi (14) reported that many VOCs, such as benzene, ethyl benzene, toluene, and xylenes, are degraded in biological treatment processes, but others such as chloroform, trichloroethylene, tetrachloroethene, and carbon tetrachloride are relatively non-biodegradable. Kobayashi and Rittmann (66) concur that trichloroethylene has a very low biodegradation rate. Since percent removals for trichloroethylene in wastewater treatment plants have been reported as high as 69 to 77 percent (82,90), volatilization is the most likely removal mechanism. Many studies (115,119,125) have found lindane to be totally resistant to biodegradation. However, other studies have found that biodegradation does occur (32,93). The key to the biodegradation of lindane seems to be the adaptation or acclimation of the microbial population. In both of the studies in which biodegradation occurred, the system was spiked continuously with lindane to produce an acclimated biomass. Nyholm et al. (93) found that a number of slowly degradable chemicals will be degraded only by adapted sludges, and that continuous loading may be required for successful degradation. Dieldrin, which is transformed from aldrin during secondary treatment (102), exhibits similar biodegradation behavior as lindane. Unacclimated systems show completely resistance to biodegradation (115), but acclimated systems have shown that biodegradation occurs (32). Other studies have shown that hexachlorobenzene is resistant to biodegradation (115) and that benzo(a)pyrene is substantially biodegraded (up to 41 percent) in wastewater treatment plants (22).

2.2.4 Adsorption

Adsorption is the process of collecting soluble substances that are in solution on a suitable interface (83,116). In this discussion, only the case of adsorption at the liquid-solid interface will be considered. The adsorption process involves three steps: macrotransport, microtransport, and sorption. Macrotransport (bulk transport) involves the movement of the organic contaminant with the water to the liquid-solid interface by advection. Microtransport involves the diffusion of the contaminant through the quiescent layer next to the particle. Sorption is the term used to describe the attachment of the contaminant to the surface of the particle and its subsequent movement within the particle structure. The *adsorbate* is the substance being removed from the liquid phase to the liquid-solid interface. The *adsorbent* is the solid phase onto which the accumulation occurs.

Although only a few studies of sorption onto wastewater solids have been reported (6,14,19,119,120), sorption has been deemed one of the fundamental processes controlling the removal of toxic organic compounds in wastewater treatment plants. Sorption can occur onto primary solids and/or biomass (biological solids) (6,19,56,90,119). Harrington et al. (56) state that sorption is the only removal mechanism assumed to remove significant amounts of organic chemicals in primary clarifiers. For organic compounds which are not biodegradable, Bell and Tsezos (6) concluded that physical adsorption seems to be the dominant removal mechanism in conventional biological wastewater treatment processes. Thus, adsorption can remove a number of trace organic compounds from the wastewater stream but also accumulates these pollutants in the sludge, which may create environmental hazards associated with ultimate sludge disposal (6,19,49,119).

Sorption onto suspended biomass in biological reactors is referred to as *biosorption*. Biosorption has been shown to be a physical-chemical phenomena similar to sorption (6). However, other parts of the cell (besides the cell walls) are responsible for a

substantial portion of the observed uptake (119). The biosorption process involves both sorption by cell walls and uptake by other cellular components of the microorganisms. Bell and Tsezos (6) reported that compared to activated carbon (with its much greater specific surface area), the adsorptive uptake of biomass was significantly less. However, they noted that the uptake per unit surface area is greater for biomass than for activated carbon. Studies show that the biosorption of toxic organic compounds is a rapid and completely reversible process (6,7,119). Factors contributing to desorption include changes in the liquid-phase concentration of the compound or temperature of the wastewater (14). Biosorption is also exhibited by both live and dead microbial cells (6,7,119). In the case of lindane, for example, Tsezos and Bell (119) found that the uptake by live biomass was less than the respective uptake by the same dead cells. Conversely, they also found that the uptake of PCB by live biomass was higher than the uptake by the same dead biomass. These findings demonstrate that biosorption by dead microorganisms is also an important removal mechanism of toxic organic compounds in wastewater treatment plants.

Sorption of toxic organic compounds onto primary solids and biomass has been correlated with the octanol/water partition coefficient (K_{OW}) (6,12,19,56,96). The octanol/water partition coefficient is a ratio of a compound concentration in the octanol phase to its concentration in the water (72). A high value indicates that a compound is susceptible to adsorption from water to an organic phase (90). For compounds with lower octanol/water partition coefficient values, sorption is not an important removal mechanism in biological treatment processes unless specific sorption reactions (ionic or polar compounds) or active uptake occur (11). Adsorptive uptake has also been reported to be roughly inversely correlated with adsorbate water solubility. However, the octanol/water partition coefficient is a better indicator of the relative extent of adsorption onto biomass than is water solubility (6). Dobbs et al. (19) agree that octanol/water partition coefficients are useful for estimating uptake of toxic organic compounds on

wastewater solids, but they contend that the modified Randic indexes offer a more fundamental method for assessing sorption of toxic organic compounds based on structural features of the molecule.

A number of studies have been conducted to determine whether certain toxic organics sorb onto wastewater solids during treatment. In an investigation of the fate of priority toxic pollutants in POTWs, EPA (26) concluded that biosorption was the primary removal mechanism for acid and base/neutral compounds. Hannah *et al.* (52,53) report that semi-volatiles seem to associate with the solids in process sludges, but that volatile organics do not have a high affinity for wastewater solids and therefore do not concentrate in sludges. Other authors agree that adsorption is a negligible sink for VOCs (64,90). Card and Corsi (14) agree that many VOCs do not adsorb easily to solid particles and biomass, but they also claim that most VOCs do partition to solid particles in wastewater although to only a very small extent. In a review of available literature on removal of pesticides from wastewater, Convery (18) reported that DDT, dieldrin, and lindane tend to concentrate in primary sludge, while PCBs and chlordane concentrate in either the primary or secondary sludge. Hill and McCarty (59) report similar findings. Petrasek *et al.* (96) also noted that PCBs and the pesticides heptachlor, lindane, and toxaphene partitioned approximately equally between the primary sludge and the return activated sludge (32 percent found in the primary sludge and 33 percent found in the return activated sludge). Trichloroethylene and toluene have been shown not to sorb strongly onto biomass (11,94). Other studies have shown moderate-to-significant adsorption of lindane onto biomass (6,93,125).

Adsorption/biosorption differs from biodegradation and volatilization/air stripping in that organic substances are collected onto solid particles instead of being destroyed or emitted into the atmosphere. Therefore, sorption is the process by which trace organics are removed from the wastewater stream and incorporated into the sludge. Thus, any trace organics present in the parent sludge of composting processes are a direct result of

adsorption. An important point to note is that although the concentrations of pollutants may be low in the influents and effluents of a biological wastewater treatment plant, the concentrations of these pollutants in the microbial sludge can be magnified significantly by the biosorptive phenomena, so that sludge disposal may present a significant environmental hazard (6,27,120).

2.3 TRACE ORGANICS PREVALENT IN MUNICIPAL WASTEWATER SLUDGE

2.3.1 Introduction

Wastewater treatment residuals are the result of several unit processes that take place during the treatment of wastewater and include screenings, grit, scum, and sludge. The sludge resulting from wastewater treatment operations and processes is usually in the form of a liquid or semisolid liquid that contains from 0.25 to 12 percent solids by weight, depending on the operations and processes used (83). The principal sources of sludge in conventional secondary wastewater treatment include primary and secondary sedimentation, in which primary solids and suspended solids (biomass produced by the biological conversion of BOD), respectively, are removed by gravity settling. Of the constituents removed by treatment, sludge is by far the largest in volume, and its processing and disposal is possibly the most complex problem facing the engineer in the field of wastewater treatment. In 1988, EPA (29) reported that an estimated 7 to 9 million dry tons of sludge were produced annually, and this amount was expected to increase significantly in the future as more wastewater treatment plants achieve secondary and tertiary treatment.

Sludge generated in municipal sewage treatment plants is principally organic matter that contains various levels of plant nutrients, although measurable quantities of metals, minerals, and other compounds are present (92,127). In addition, numerous

microorganisms are found in sludge. These microorganisms can be classified into two general classes - beneficial and pathogenic. The beneficial organisms are essential in the decomposition of the sludge when applied to land or composted. Pathogens are found in sludges as a result of discharge of human waste into the sewer system and their subsequent removal during wastewater treatment. Since municipal wastewaters contain industrial and commercial wastes (as explained earlier), the potential exists for toxic materials to also be found in sludge.

A multitude of organic compounds can be found in sewage sludge (127). However, from an environmental and human health point of view, the organic compounds of greatest concern are the ones belonging to the group of 129 EPA-designated priority pollutants (see Appendix). Many of these compounds are considered highly toxic by EPA. However, relatively few studies have reported the analyses of priority pollutant organics in sewage sludge. This is due to the extensive and complicated sampling, extraction, and analytical methods that must be employed to determine the concentrations of these trace organics in sludge (128). Significant problems which exist in the analysis and interpretation of these data include (128):

- 1) Sludges are heterogeneous and obtaining a representative sample can be difficult.
- 2) Day-to-day variations in composition occur.
- 3) Analytical protocols vary widely in extractions, separations, and cleanup procedures which in turn affect the number and types of compounds recovered.
- 4) For some groups, recoveries from a complex matrix like sludge can be poor.
- 5) Data are reported in various units ($\mu\text{g/l}$, mg/kg , etc., some on a wet weight basis, and others on dry weight).
- 6) Limits of detection in some cases are poor or are not reported.
- 7) Confirmation of each organic, if any were done, is not reported.

Because of these problems and a very limited database, definitive statements regarding the prevalence of organic compounds in sewage sludge cannot be made. The studies which have been conducted do, however, illustrate certain similarities between sludges. The most notable finding is that, in general, the concentrations of organic compounds found in sewage sludge samples have been very low (trace amounts).

2.3.2 The EPA Fate Study

The first major investigation into the presence and quantification of priority pollutants in sewage sludge was the EPA Fate Study (27), also known as the "40-City Study." The study was conducted to determine the fate and occurrence of the 129 priority pollutants in 40 POTWs (plus 10 supplemental POTWs), all of which provide secondary treatment. The geographically distributed plants provided a cross section of the types of facilities and wastewater and sludge characteristics found in a broad spectrum of communities. Four of the plants were located in Region I (the specific locations of each plant were not given). While several of the plants selected had flows less than 10 million gallons per day (MGD), most of the plants served larger cities. The median flow was 30.4 MGD, the flow equivalent to that from a population of about 300,000 people (71). Industrial contributions ranged from 5 to 50 percent of the flow, and the median level was 19 percent.

At most of these plants, a minimum of 6 days of 24-hour sampling of influent, effluent, and sludge streams was conducted in order to comprehensively analyze the frequency and concentration of pollutants. Sludge was sampled at one or more locations within each treatment plant. Sludge types were designated as primary sludge, secondary sludge, heat treated sludge and decant, combined sludge, digested sludge (aerobic and anaerobic) and others. Each sample was analyzed for conventional, selected non-conventional, and priority pollutants. Two objectives of the study were (1) to determine the quantity of priority pollutants in POTW sludge streams, and (2) to quantify pollutants

found in sludges but not detected in POTW influents. A key finding of the Fate Study was that some pollutants found in POTW influents at low frequencies of occurrence were regularly measured at higher frequencies in the corresponding sludge streams. Another key finding was that 78 priority pollutants were detected at least once in raw sludge samples (43 pollutants were detected in more than 10 percent of the samples).

Upon publication of the Fate Study, it became the prime source of information on the occurrence of toxic pollutants in municipal wastewater sludge. Soon afterwards, however, questions were raised as to whether the results of the EPA study were representative of sludges nationwide; in other words, would the same pollutants appear in other municipal sludges and at relatively the same frequencies and concentrations? To answer this important question, EPA and Camp, Dresser and McKee initiated a comparative analysis of the Fate Study with other available municipal sludge data bases (43). The sources of data used in this comparative analysis included three surveys of sludge quality conducted in Michigan; a "New York City Permit Application" detailing sludge quality at 12 New York City POTWs; an Indiana sludge survey for 58 POTWs; a Missouri survey of 74 POTWs; and sludge quality surveys for four POTWs in Albuquerque, New Mexico, three POTWs in Galveston, Texas, and two plants in Phoenix, Arizona.

Approximately 40 percent of the pollutant concentrations in the combined studies fell within a range of one-half to two times the EPA values. Approximately 60 percent fell within a range of one-fifth to five times the EPA value, and nearly 80 percent are within the same order of magnitude. The concentrations for organics and pesticides showed greater variability than the concentrations for metals. However, since the concentrations of organics and pesticides may be expected to vary from day to day at a POTW, and since many are often present at concentrations near their detection limits, it was decided that the organics and pesticides in the combined studies would be considered equal to the corresponding EPA value if the two fell within one order of magnitude of one

another. With the application of this criterion, it was concluded that the EPA Fate Study is generally representative of POTW sludges. It was also concluded that the data from the other studies could supplement the EPA study, especially for pesticides and PCBs. A complete listing of the frequencies of detection and concentrations of the trace organics of concern in the EPA and the combined studies is shown in Tables 2-3-1 and 2-3-2.

Table 2-3-1 FREQUENCY OF DETECTION OF SELECTED TRACE ORGANICS IN SLUDGE: EPA SURVEY AND COMBINED STUDIES (REF. 43)

POLLUTANT	EPA POTW SURVEY			COMBINED STUDIES		
	POTWs analyzed	Number detected	Percent detected	POTWs analyzed	Number detected	Percent detected
Aldrin	44	0	0	19	4	21
Benzo(a)pyrene	44	5	11	18	10	56
Chlordane	44	0	0	44	32	73
4,4'-DDD	44	0	0	44	5	11
4,4'-DDE	44	1	2	34	7	21
4,4'-DDT	44	0	0	32	16	50
Dieldrin	44	1	2	19	16	84
Dimethyl nitrosamine	44	1	2	15	0	0
Heptachlor	44	1	2	17	2	12
Hexachlorobenzene	44	7	16	279	103	37
Hexachlorobutadiene	44	2	5	232	103	44
Lindane	44	3	7	19	2	11
PCBs	44	0	0	343	121	35
Toxaphene	44	0	0	17	2	12
Trichloroethylene	44	37	84	24	5	21

As a group, the pesticides and PCBs were detected less frequently and at lower concentrations than any of the other compounds. Chlordane was the most frequently detected at 36 percent of the POTWs, with PCBs next at 31 percent. The mean concentration of PCBs was relatively high because of the influence of one data set with a

median value of 80.3 mg/kg dry weight. Bis (2-ethylhexyl) phthalate was the most prevalent base/neutral compound and was also found at a concentration higher than any of the other base/neutral compounds. Trichloroethylene, benzo(a)pyrene, hexachlorobenzene, hexachlorobutadiene, and dimethyl nitrosamine (n-Nitrosodimethylamine) were also detected.

Table 2-3-2 ACTUAL AND NORMALIZED CONCENTRATIONS FOR EPA STUDY AND COMBINED STUDY (REF. 43)

POLLUTANT	EPA Mean Concentration (mg/kg dry wt.)	Weighted Mean Concentration (mg/kg dry wt.)	Normalized Ratio*
Aldrin	ND	0.15	NA
Benzo(a)pyrene	256.6	1.34	0.005
Chlordane	ND	3.01	NA
4,4'-DDD	ND	0.21	NA
4,4'-DDE	0.06	0.25	4.167
4,4'-DDT	ND	0.28	NA
Dieldrin	0.02	0.08	4.000
Dimethyl nitrosamine	0.04	NA	NA
Heptachlor	0.02	0.10	5.000
Hexachlorobenzene	1.25	468.0	374.400
Hexachlorobutadiene	4.5	0.22	0.049
Lindane	0.02	0.04	2.000
PCBs	ND	29.06	NA
Toxaphene	ND	7.88	NA
Trichloroethylene	9.10	NA	NA

ND = Not Detected

NA = Not Available

Note: Weighted means include Michigan, New York City, Indiana, Galveston, Albuquerque, and Phoenix surveys only.

*Normalized Ratio = Weighted Mean Conc. divided by EPA Mean Conc.

2.3.3 The National Sewage Sludge Survey

In February, 1989, EPA proposed regulations establishing requirements for the final use and disposal of sewage sludge (proposed 40 CFR Part 503) as required by section 405(d) of the Clean Water Act of 1977 (CWA). The regulations were to identify uses for sewage sludge, including disposal, and factors to be taken into account in determining the measures and practices applicable to each use or disposal. In addition, the regulations were to specify concentrations of pollutants which would interfere with sewage sludge use or disposal. The Water Quality Act of 1987 (WQA) amended section 405(d) to add the requirement that EPA establish sludge use and disposal standards that include management practices and numerical limitations for the toxic pollutants in sewage sludge identified by EPA that may adversely affect public health or the environment. These standards were to be adequate to protect public health and the environment from any reasonably anticipated adverse effects of the pollutants.

Section 405(d) required EPA to rely on available information in developing the proposed 40 CFR Part 503. At the time, the primary source of information on the occurrence and concentrations of pollutants in sewage sludge was the EPA Fate Study. The Fate Study by far provided the most comprehensive and best documented nationwide database on the concentrations of pollutants in sewage sludge and was thus considered an appropriate basis for developing the proposed regulations. However, EPA recognized several deficiencies in using the study. The major drawback was that data on final processed sludge was generally not available. The Fate Study was not designed to measure pollutant concentrations in sludge leaving the plant, but to determine what happened to the priority pollutants in POTWs. The study approach required that some sludge samples be taken at points within the POTW prior to final sludge processing in order to account for organic pollutants that may be transformed into more elementary compounds or gases by final sludge processes such as anaerobic digestion. The second deficiency of the data collected was that it was no longer current. Sewage sludge quality

might have changed since 1978 due to the initiation of many pretreatment programs, development of new facilities discharging wastewater into the POTW, and changes in wastewater processes. Thus, concentrations from the Fate Study might no longer have reflected the quality of sewage sludge. Other factors included the advancements in the analyses of pollutants in the presence of sewage sludge that had taken place since 1978 and that the procedure used to select the POTWs in the Fate Study did not follow the statistical methods required to support unbiased national estimates of pollutant concentrations in POTW sludge. Even though there were other sources of data on sewage sludge quality, these studies also suffered from similar deficiencies rendering them unsuitable for regulatory purposes.

Although EPA believed that the Fate Study data were appropriate on which to base the proposed 503 regulations, EPA realized that the data needed to be replaced (or at a minimum supplemented) to support the final regulations. Therefore, EPA (34,40), undertook the National Sewage Sludge Survey (NSSS) to obtain a current and reliable database for developing the final Part 503 rule. The database would also be used in developing a list of pollutants from which EPA would select additional pollutants for further analyses and potential regulation under section 405(d) of the CWA.

Data collection for the NSSS began in August, 1988 and was completed in September, 1989. Participants in the NSSS were selected from 11,407 POTWs which used at least secondary treatment in the United States, Puerto Rico, and the District of Columbia. EPA collected samples at 180 POTWs and analyzed the sludge samples for more than 400 pollutants, including every organic, pesticide, dibenzofuran, dioxin, and PCB for which EPA had gas chromatography-mass spectrometry (GC/MS) standards. The remaining pollutants analyzed for were metals and inorganics. Each of the POTWs was assigned to one of four flow group categories. The four survey flow groups are: (1) more than 100 MGD, (2) greater than 10 MGD but less than or equal to 100 MGD, (3) greater than 1 MGD but less than or equal to 10 MGD, and (4) less than or equal to 1

MGD. The weights (fractions of the total number of POTWs) for the groups one through four are shown in Table 2-3-3.

Table 2-3-3 WEIGHT GROUPS FOR GROUPS 1 THROUGH 4

GROUP	FLOW RATE	WEIGHT
1	> 100 MGD	0.002
2	10 < Flow <= 100 MGD	0.029
3	1 < Flow <= 10 MGD	0.170
4	Flow <= 1 MGD	0.799

The results of the NSSS provided EPA with a current database and information essential to establishing numerical pollutant limits in the final Part 503 rule that would encourage the beneficial reuse of sewage sludge and provide a greater degree of public health than the original proposal. The pollutant concentration estimates from the NSSS for the trace organic compounds of concern are shown in Table 2-3-4 (34,40). They are estimates for the distribution among POTWs of pollutant concentrations (dry weight basis) in sewage sludge that is ready for disposal and that is generated by secondary-or-better treatment of wastewater.

Table 2-3-4 POLLUTANT CONCENTRATION ESTIMATES FROM THE NATIONAL SEWAGE SLUDGE SURVEY (REF. 40)

Pollutant	Flow group	Number of samples	Percent Detect	Mean Conc. (µg/kg)
Aldrin	> 100 MGD	26	4	3.57
	10<Flow<=100	61	5	7.36
	1<Flow<=10	69	4	2.60
	Flow<=1 MGD	42	2	1.50
	National	198	3	1.86
Benzo(a)pyrene	> 100 MGD	26	0	-
	10<Flow<=100	61	5	-
	1<Flow<=10	70	3	217.48
	Flow<=1 MGD	43	2	230.51
	National	200	3	-
Chordane	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	69	1	22.02
	Flow<=1 MGD	42	0	-
	National	198	0	-
Dieldrin	> 100 MGD	26	4	2.24
	10<Flow<=100	61	0	-
	1<Flow<=10	69	3	2.70
	Flow<=1 MGD	42	5	3.17
	National	198	4	-
Heptachlor	> 100 MGD	26	0	-
	10<Flow<=100	61	2	2.81
	1<Flow<=10	69	0	-
	Flow<=1 MGD	42	0	-
	National	198	0	-
Hexachlorobenzene	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	70	0	-
	Flow<=1 MGD	43	0	-
	National	200	0	-
Hexachlorobutadiene	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	70	0	-
	Flow<=1 MGD	43	0	-
	National	200	0	-
Lindane	> 100 MGD	26	0	-
	10<Flow<=100	61	2	3.88
	1<Flow<=10	69	1	5.70

	Flow<=1 MGD	42	0	-
	National	198	0	-
Dimethyl Nitrosamine	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	70	0	-
	Flow<=1 MGD	43	0	-
	National	200	0	-
PCB-1016	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	69	0	-
	Flow<=1 MGD	42	0	-
	National	198	0	-
PCB-1221	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	69	0	-
	Flow<=1 MGD	42	0	-
	National	198	0	-
PCB-1232	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	69	0	-
	Flow<=1 MGD	42	0	-
	National	198	0	-
PCB-1242	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-
	1<Flow<=10	69	0	-
	Flow<=1 MGD	42	0	-
	National	198	0	-
PCB-1248*	> 100 MGD	26	12	106.23
	10<Flow<=100	61	10	223.39
	1<Flow<=10	69	12	153.20
	Flow<=1 MGD	42	10	64.66
	National	198	10	84.34
PCB-1254*	> 100 MGD	26	8	2,463.55
	10<Flow<=100	61	2	44.25
	1<Flow<=10	69	4	132.67
	Flow<=1 MGD	42	10	148,576.26
	National	198	8	118,762.55
PCB-1260*	> 100 MGD	26	15	182.89
	10<Flow<=100	61	8	72.47
	1<Flow<=10	69	9	112.43
	Flow<=1 MGD	42	10	178.59
	National	198	9	164.33
Toxaphene	> 100 MGD	26	0	-
	10<Flow<=100	61	0	-

	1<Flow<=10	69	0	-
	Flow<=1 MGD	42	0	-
	National	198	0	-
Trichloroethylene	> 100 MGD	26	4	8.18
	10<Flow<=100	61	5	59.42
	1<Flow<=10	70	4	-
	Flow<=1 MGD	43	0	-
	National	200	1	-
4,4'-DDD	> 100 MGD	26	4	61.75
	10<Flow<=100	61	0	-
	1<Flow<=10	69	0	-
	Flow<=1 MGD	42	0	-
	National	198	0	-
4,4'-DDE	> 100 MGD	26	4	55.63
	10<Flow<=100	61	2	51.50
	1<Flow<=10	69	3	65.03
	Flow<=1 MGD	42	0	-
	National	198	1	-
4,4'-DDT	> 100 MGD	26	12	22.49
	10<Flow<=100	61	3	22.82
	1<Flow<=10	69	1	25.43
	Flow<=1 MGD	42	2	30.22
	National	198	2	29.18

All concentrations reported as $\mu\text{g}/\text{kg}$.

"-" = Nonestimatable.

National estimates determined as weighted sums of flow group estimates.

"*" = PCB concentrations, although not detected frequently, indicate a violation of the Lognormal Distribution assumption used to generate estimates. Therefore, estimates are not considered realistic

2.3.4 Conclusions

Although only a few other studies report the concentrations of the trace organic compounds of concern in municipal sewage sludge, the concentrations reported in these studies (17,128) are similar to the values listed in the EPA studies. The concentrations of individual trace organics measured in the EPA and other studies exhibit wide variability between sludges from different municipalities but are consistently very low.

It should also be pointed out that Tables 2-3-2 and 2-3-3 do not necessarily imply that an "average" sludge would contain all of the pollutants listed at the concentrations listed. In fact, it is highly unlikely that any sewage sludge would contain even most of the trace organic compounds of concern. For example, in the NSSS, the national mean concentration of aldrin is listed as 1.86 µg/kg. However, aldrin was only detected in 8 out of 198 POTWs and at concentrations of roughly 19, 20, 21, 26, 30, 30, 39, and 46 µg/kg. The national mean concentrations were calculated using the assumption of a lognormal distribution but do not necessarily indicate the amount of a particular trace organic present in a national "average" sludge.

2.4 COMPOSTING

2.4.1 Introduction

Composting is a solid-phase biochemical process in which organic material undergoes accelerated biological degradation under controlled conditions (39,67,83). Although composting as a *phenomenon* occurs widely in nature, as evidenced by the annual conversion of fallen forest tree leaves to humus, composting as a *process* implies that human beings somehow force or manage the phenomenon. Composting reduces the volume and mass of organic solid waste by converting the organic materials to more stable, humus-like forms and to inorganic byproducts (principally carbon dioxide and water), giving off heat as a metabolic byproduct (48). It has been reported that all organic compounds are potentially biodegradable (39). However, the rate and extent of biodegradation varies with the chemical nature of the compounds and the conditions under which the compound is degraded. Although composting can occur under anaerobic or aerobic conditions, aerobic composting is more efficient and is used for essentially all sewage sludge composting applications (39,83). Aerobic composting accelerates microbial decomposition and results in the higher rise in temperature necessary for

pathogen destruction. Aerobic composting also minimizes the potential for objectionable odors. The moisture content should range from 40 to 60 percent on a wet weight basis. At moisture contents below 40 percent, microbial enzymes are deactivated and the process slows down, whereas above 60 percent the free pore space is reduced and improper aeration occurs (75). The biologically degraded humus-like organic material resulting from the composting process (mostly stable biological cell material) can be handled, stored, and/or applied to land without adversely affecting the environment (10).

In 1932 the first full-scale composting plant began operation in the Netherlands (75), but it wasn't until the mid-1970s that composting began receiving attention as a cost effective (low capital investment and low energy requirements) and environmentally sound alternative for the stabilization and ultimate disposal of municipal sewage sludge (41,68,83). Increased confidence in the composting process was brought about by an increase in scientifically based knowledge of the process (68). In the period from 1983 to 1992 alone, the number of full-scale operating facilities in the United States increased from 61 to 159 (45). As stated previously, the problems associated with landfill disposal of sludge, especially in the Northeast, is primarily responsible for this rapid increase.

In a comparison of compost sludge to the more conventional sludges produced in the anaerobic and aerobic stabilization (digestion) processes, Higgins *et al.* (58) assessed the relative effectiveness of these processes in degrading and stabilizing raw wastewater sludge. They discovered that the compost stabilization process exhibited the greatest overall reduction in the volatile solids, chemical oxygen demand (COD), and total organic carbon (TOC), which are all indicators of the effectiveness of biological treatment. A comparison of the COD/TOC ratios of the various sludges indicated that the composting process produced the most highly oxidized sludge. It will also have the least aesthetic environmental impact of all the sludges studied. From the standpoint of stability, the residue produced in the composting process was clearly the most desirable.

This study clearly revealed that composting provides a significant advantage over the other processes studied if land-based disposal techniques are practiced.

2.4.2 Composting Methods

In most composting methods, the process scheme is very similar (see ref (24)). First, the dewatered sludge and bulking agent are mixed. The bulking agent, usually wood chips, is used to provide structural support and to increase the porosity of the mixture for effective aeration. Next, the compost pile is aerated either by forced air or mechanical turning. Aeration is required not only to supply oxygen, but to control the composting temperature and remove excess moisture (the removal of heat by aeration is the only practical means of controlling the composting process). After the composting period, the mixture is cured, dried (optional), and screened to recover the bulking agent. The bulking agent is recycled and the compost is stored for eventual marketing.

The three major types of composting methods used are the aerated static pile, in-vessel (enclosed mechanical) system, and windrow. In a 1992 survey of municipal sewage sludge composting projects (including operational facilities and facilities in the development stage), 35.5 percent were aerated static pile, 28.8 percent were in-vessel, and 23.2 percent were windrow (45). These three major methods account for 87.5 percent of all full-scale composting facilities.

Aerated Static Pile

The aerated static pile system consists of a grid of aeration or exhaust piping over which a mixture of dewatered sludge and wood chips is placed (see ref (8)). The perforated aeration pipes are connected to a pump which can draw or blow air through the piles. The pile is actively composted for 21 to 28 days and is then usually cured for another 30 days or longer. Typical pile heights are approximately 7 to 8 feet. A layer of screened, finished compost is often placed on top of the pile to provide insulation.

Disposable corrugated plastic drainage pipe is commonly used to provide aeration, and each individual pile should have its own individual blower for more effective aeration control. Many new facilities cover or enclose all or significant portions of the system to improve process and odor control.

Windrow

The mixing and screening operations in the windrow system are similar to those for aerated static pile operation (8). The sludge/bulking agent mixture is placed in elongated piles, or windrows, and aerated by periodically mechanically turning the piles (typically two to three times per week) with a machine such as a front-end loader or specially designed equipment. Windrows are constructed from 3 to 6 feet (1 to 2 meters) high and 6 to 14 feet (2 to 4.3 meters) wide at the base (83). Turning of the windrows is often accompanied by the release of objectionable odors. The composting period is roughly 21 to 28 days, followed by a curing stage of 30 days. As in the aerated static pile operations, some windrow operations are covered or enclosed.

In-vessel Systems

In-vessel composting systems, the highest technological level of composting, involves placing material to be composted inside large containment vessels equipped with temperature-controlled aeration systems. In-vessel systems are designed to minimize odors and process time by controlling environmental conditions such as air flow and temperature. Many in-vessel systems are also equipped with a mechanism to periodically mix or agitate the composting material. The use of in-vessel systems has increased rapidly in recent years because of advantages such as process and odor control, faster throughput, lower labor costs, and smaller area requirements (83).

In-vessel composting systems can be divided into two major categories: plug flow and dynamic (agitated bed). In plug-flow systems, the relationship between

particles in the composting mass stays the same throughout the process, and the system operates on a first-in, first-out principle. In a dynamic system, the composting material is mechanically mixed during the process. Examples of each category are shown in reference (83).

Hart (57) claims that all three composting methods are equally capable of degrading hazardous wastes but also acknowledges that the in-vessel method has notable advantages over the other two methods. They are: (1) frequent mixing more fully distributes any hazardous material throughout the compost mass, thus providing maximum opportunity for degradation of the unwanted material and its dilution (if it were toxic at the initial mixing concentration), (2) more control over the environment is provided, thus hastening the biodegradation process and thereby shortening the biological half-life of hazardous wastes to their minimum, and (3) off-gas and vapors are easier to manage than from the other two methods. These findings should also apply to the trace organic compounds of concern.

2.4.3 Process Microbiology

The three main classes of microorganisms primarily involved in the composting process are bacteria, actinomycetes, and fungi (10,13,71,79,87). They are widespread in soil, natural waters, and wastes (61). As stated previously, these microorganisms oxidize organic materials to carbon dioxide and water and generate metabolic heat. Microorganisms also incorporate some of the organic matter into new cellular material in order to grow and divide (1,79). Even though microbial populations differ with the type of material being composted and even with the locale of a compost operation, the rate of composting sewage sludge is mainly controlled by the degradability of solid substrates and not by the kinds of microorganisms inhabiting the compost (10,88). Although the interrelationship of these microbial populations is not fully understood, bacterial activity appears to be responsible for the decomposition of proteins, lipids, and fats at

thermophilic temperatures, as well as for much of the metabolic heat energy produced (83). Pseudomonads, the most active bacteria in land treatment, are also among the predominant microorganisms in composting (though the rate and extent of activity in composting significantly surpasses landfarming because of greater control of environmental conditions of importance in composting) (104). Fungi and actinomycetes are also present at varying levels during the mesophilic and thermophilic phases of composting (discussed below) and appear to be responsible for the destruction of complex organics and the cellulose supplied in the form of amendments or bulking agents. However, they do not appear in visibly appreciable numbers until the process has been well advanced. It is the growth and biodegradative ability of the actinomycetes that give finished compost its earthy smell and humus-like character, and can be readily detected visually and olfactorily. When they do become apparent, they appear as a blue-gray to light green powdery to somewhat filamentous layer in the outer 4 to 6 inches of the pile (actinomycetes are not visible in mechanized in-vessel composting, though, because of the mixing action that takes place).

The composting process can be divided into three major microbiologically important phases, which are dictated by temperature (42). These phases may have considerable overlap based on temperature gradients and differential temperature effects on microorganisms. The phases are: (1) the mesophilic phase, (2) the thermophilic phase, and (3) the cooling phase. The terms *mesophilic* and *thermophilic* refer to the types of microorganisms that are primarily responsible for the biodegradation that is occurring in these phases. Bacteria are classified as psychrophilic, mesophilic, and thermophilic according to the temperature range in which they function best. Typical temperature ranges for these three categories of bacteria are presented in Table 2-4-1 (83).

Table 2-4-1 TYPICAL TEMPERATURE RANGES
FOR VARIOUS BACTERIA

TYPE	RANGE, °C	OPTIMUM, °C
Psychrophilic	-10 - 30	12 - 18
Mesophilic	20 - 50	25 - 40
Thermophilic	35 - 75	55 - 65

Temperatures below the optimum usually have a more significant effect on growth rate than temperatures above the optimum. Growth rates double with approximately every 10° C increase in temperature until the optimum temperature is reached.

The composting process is initiated by the microbiological decomposition of organic material at the mesophilic temperature range (42,57,86). Prior to active composting, however, there is an initial brief lag period during which the indigenous microorganisms develop, adapt, and multiply (acclimate) to the level required for rapid proliferation and intense activity (10). As the mesophilic organisms begin to degrade the organic materials, metabolic heat is generated. Since the material being composted is a poor thermal conductor, the heat generated is conserved within the system and causes the temperature of the compost pile to increase (60). During this first phase, the temperature in the composting mass increases from ambient to approximately 40° C (104° F). At this point, the temperature in the pile becomes prohibitive to mesophiles but suitable for thermophiles. The shift into the thermophilic phase is gradual as the mesophiles become thermally inactivated and are replaced by thermophiles as the predominant microorganisms present. Many of the mesophilic microorganisms enter a vegetative state and survive the higher temperatures by forming colonies in the compost material but contribute almost nothing to the degradation of the organic material. It is during this elevated-temperature phase of composting that the maximum biological degradation and stabilization of organic material occur. The rates of degradation and biomass formation are much higher during this second phase than in the first phase. The bacteria attack the

food using different metabolic enzyme systems and pathways; what one microorganism cannot do, or can only do partially, sets the stage for another microorganism to take over (57). The third phase of composting, the cooling phase, is brought about because the amount of readily available carbon (food supply) becomes a rate-limiting factor. Microbial activity, and thus metabolic heat output, decline during this period. The thermophilic bacteria sporulate or die and mesophilic microorganisms once again predominate. However, the mesophilic recolonization is attributed to fungal invasion because their spores can withstand temperature extremes along with lower moisture content levels and because of their ability to utilize lignin and waxy fractions (42). These fungi may be effective in metabolizing hazardous waste materials that bacteria were unable to (39). During this cooling phase, further evaporative release of water from the composted material will occur, as well as stabilization of pH and completion of humic acid formation.

Since carbon dioxide is given off as organic materials are biodegraded, the rate of carbon dioxide evolution has been considered a useful measure of composting activity (89,111). Racke and Frink (99) observed an explosive production of carbon dioxide accompanying the initial rise in temperature to the thermophilic region. Conversely, as rates significantly reduce, compost may be approaching maturity (unless other environmental factors are limiting). Oxygen consumption and heat energy given off should also indicate compost maturity because of direct relation to microbial respiration (41,111).

Following the active stage of composting, compost is usually stored for a period of 30 days up to one year. This storage time is called the curing stage. The curing pile is usually kept at a reasonable moisture content (30 to 40 percent) and sometimes a bit of secondary heating may occur. Any further breakdown of organic material which takes place is usually accredited to fungi and actinomycetes (57,110). These microorganisms are very destructive of organics and may well produce a more effective environment for

the biodegradation of many toxic organic substances. Actinomycetes develop far more slowly than most bacteria or fungi and are rather ineffective competitors when nutrient levels are high. Moreover, as they are generally more tolerant to high temperature, they become more active in a later period near 60° C, when the level of nutrients become lower (86).

The useful microorganisms indigenous to the waste organic material to be composted are usually not the only microorganisms present. Pathogenic (disease carrying) microorganisms enter the wastewater from infected individuals and often concentrate in the sludge due to their density or through adsorption to larger molecules (24,29,99). The pathogens of concern in sewage sludge are members of four basic groups; these are the bacteria, fungi, parasites, and viruses. Pathogens present in sludge products create the potential for transmission of disease if the sludge products are utilized in agricultural uses, especially if the sludge products are used on food chain crops or public access areas. Since compost is often used on home lawns and vegetable gardens, concerns have been raised over the ability of the composting process to effectively eliminate pathogenic microorganisms. However, it is widely reported that the metabolic heat produced in the composting process destroys most plant and animal pathogens and the eggs of human intestinal parasites (10,71,89,114). Usually, all of the pathogens are killed during the thermophilic period (8 to 14 days). To assure adequate pathogen reduction, EPA requires that the composting temperatures must be allowed to reach 55° C for 3 days for in-vessel and aerated static pile composting and 55° C for 15 days for windrow composting (123). Also, certain actinomycetes produce antibiotics which support pathogen kill (80).

2.4.4 Composting Parameters

There are various chemical and physical factors which have effects on the microbial communities active during the composting of sewage sludge. These factors can

be classified under the headings "nutritional" and "non-nutritional" (environmental). The major nutritional factors are the concentration and availability of carbon, nitrogen, phosphorous, and potassium; environmental factors include temperature, aeration, moisture content, and pH. These factors usually have upper and lower limits and must be properly maintained in order to sustain desired growth and functioning of the microorganisms involved in the composting process.

Nutritional Factors

Carbon: Carbon is used by microorganisms as a source of energy through metabolic oxidation and as the most essential component in the synthesis of new cells (48). It is the oxidation of carbon to carbon dioxide that accounts for the greatest reduction of mass and generation of heat that are characteristic of composting. An important point to note that is usually overlooked regarding the carbon in the substrate is the ability of the desired microorganisms to utilize it. In other words, the carbon must be "available" to the bacteria in appropriate substrate molecules. What is meant by the carbon being "available" is that the bacteria possess the enzymatic systems capable of breaking up target molecules and thereby rendering the carbon accessible to microbial utilization. If the carbon in a substrate cannot be utilized by the various microorganisms, then the substrate will not be able to be composted. The enzymatic systems may originate either in the active microorganisms or may be supplied by other microorganisms. This requirement also holds true for other essential nutrients.

In general, the more complex the compound, the more extensive and comprehensive is the enzyme system required (10). Substances made up of complex molecules such as cellulose (e.g., paper) and lignin (e.g., wood) are broken down more slowly than are others (sugars, proteins, most fats). A practical example of the ability of wood to resist degradation is the use, repeated recovery, and reuse of woody residue

(sawdust, woodchips, etc.) as a bulking agent in compost. Thus, microbial ability to break down the compounds in a waste is ultimately the decisive factor in determining whether or not the waste can be utilized as a carbon source or the rate at which the waste can be broken down.

Nitrogen, Phosphorous, and Potassium: All microorganisms must have access to a supply of the elements of which their cellular matter is composed to be able to reproduce and for biodegradation to occur (10). Other elements are required which enter into the metabolic activities of the microorganisms by serving as an energy source or as an enzyme constituent. The respective amounts required from the elemental makeup of the substrate molecules determine their nutritional utility to the microorganisms. The more abundant the elements of nutritional significance in a substrate to microbes, the greater will be the number of microorganisms supported by it, and hence the more extensively and rapidly it will be composted.

Nearly every element is utilized by microorganisms to some extent, and the relative amount of each element required varies. Those elements needed in large quantities are referred to as *macronutrients*; those needed in trace amounts are known as *micronutrients*. Besides carbon, the principal macronutrients are nitrogen, phosphorous, and potassium. Since nitrogen is a major constituent of protoplasm, it ranks with carbon in importance. Microbial growth cannot occur unless nitrogen is present. The respective amounts of nutrients required vary at a somewhat constant ratio to each other. In other words, a balance is struck. This balance is especially important with regard to the macronutrients. In general, micronutrients are present in most wastes in an abundance.

C/N Ratio: The C/N ratio is the ratio of available carbon to available nitrogen in the material to be composted (sludge/bulking agent mix). For example, a material having 30 times as much carbon as nitrogen is said to have a C/N ratio of 30/1, or simply a C/N of

30. The C/N ratio is undoubtedly the most important balance in composting. Optimum C/N ratios for the composting of sewage sludge have been reported to be in the range of 20 to 35 (10,24,42,48,111). The underlying biological basis of the optimum C/N ratio is unclear. To some degree, C/N ratios can be controlled through the addition of raw materials. Nitrogen sources, such as grass clippings, can be added to reduce a high C/N ratio. Conversely, carbon sources can be added to elevate extremely low C/N ratios.

If the C/N ratio is too low (lower than 18 or 19/1), the microbial degradation leads to excess ammonia formation, which increases the pH and thereby enhances ammonia volatilization to the atmosphere. This happens because at low C/N ratios, the energy source (carbon) is less than that required for converting available nitrogen into protoplasm. In such an event, the microorganisms make full use of available carbon and eliminate the excess nitrogen as ammonia. If ammonia is produced in sufficient amounts, it may also be toxic to the microbial community. If the C/N ratio exceeds 35, then the excess of carbon over nitrogen is too great (nitrogen becomes limited) and microbial activity slows down. In addition to limiting the growth and amount of biomass, nitrogen limitation may lead to extensive organic acid formation from carbonaceous waste, which would tend to lower the pH and retard the microbial activity. The operational effects caused by high C/N ratios include longer time requirements to complete the process and drops in metabolic heat production.

Environmental Factors

Temperature: Of all the chemical and physical parameters that affect the rate of composting, temperature has repeatedly been found to be the dominant factor (42,79,80). Small variations in temperature have been shown to affect microbial activity and biomass in composting sewage sludge much more dramatically than small changes in moisture, pH, organics, or C/N ratios (80). Ultimately, the composting process is determined by

the temperature profile. Changes in temperature are commonly used as a measure of the microbial activity underlying the composting process. Thus, the temperature profile of composting can be used to determine the stability of organic material (42).

Recent studies have reported that the temperature of the composting process should not exceed 55 to 60° C (10,42,80,111). Results of these studies have shown that the greatest microbial activity occurred between 35 and 50° C and decreased dramatically when temperatures exceeded 55 to 60° C. Although composting temperatures must be allowed to increase to levels which assure adequate pathogen destruction (generally 55° C for 3 days), temperatures higher than this result in thermal inactivation of the microorganisms responsible for carrying out the composting process (spore-forming organisms enter the spore or resistant stage and activity diminishes practically to zero). Thus, precise temperature control is necessary to provide pathogen reduction while maintaining a healthy community of microorganisms.

The distribution of active microorganisms is dictated by the temperature in composting. As discussed previously, as the temperature in the pile enters the mesophilic and thermophilic ranges, their respective microorganisms predominate. However, it should be noted that there is no single, precise temperature which is optimum for either the mesophilic or thermophilic groups of microorganisms present (10). For example, the optimum temperature for the bacterium *Pseudomonas dilphinii*, a mesophile, is 25° C; whereas for *Clostridium acetobutylicum*, another mesophile, it is 37° C. It should also be noted that unless a closely controlled in-vessel system is used, at no time is the temperature uniform throughout the pile (except at the start and end of the process when all material is at ambient temperature). Therefore, the composting process represents the integrated activity of a number of different microorganisms, and the optimum temperature of the process as a whole is a compromise between the optimums of the various microorganisms involved in the process.

Aeration: Since composting of sewage sludge is more efficient under aerobic conditions, it is necessary to provide a supply of oxygen to the process. The oxygen needed is supplied by aeration of the pile. Aeration can be accomplished in a number of ways. In aerated static pile and in-vessel systems, aeration is provided by either blowing or drawing air through the compost. In the windrow method, the compost is aerated by turning of the piles, which exposes the compost to the oxygen in the atmosphere. The bulking agent is added because dewatered sludge (approximately 78 percent water) will not compost aerobically alone because sufficient air cannot penetrate the biomass, either by diffusion or forced aeration. The precise amount of air to be introduced into the composting material is extremely difficult to determine. The theoretical amount required depends upon the amount of carbon to be oxidized and is not amenable to straightforward analysis. Because of the dynamics of the composting process, the oxygen consumption rates change during the process and therefore rate estimates may be valid only for limited periods (42). However, it has been reported that an atmosphere containing 5 to 15 percent oxygen is required throughout the pile to ensure aerobic conditions (24). The oxygen uptake rate can also be used as a measure of biological activity (10,111).

Aeration also controls the temperature of the compost pile and removes moisture, carbon dioxide, and other gases. To keep the temperature in the pile below a certain level, aeration can be used to remove the metabolic heat generated during the composting process. However, the amount of aeration can become excessive when it exceeds the rate at which heat is generated and thus cools the pile. It can also become excessive when it accelerates evaporation to a point at which the moisture content of the mass becomes so low that microbial activity is inhibited and the composting process slows or stops completely. Either one of these situations can impart the false impression that the composting mass has reached true stability. Thus, it is vital to carefully monitor aeration when it is used as a temperature control mechanism.

Although modern composting systems are designed for aerobic processes, anaerobic zones inevitably exist, regardless of the aeration system used (42). Even though oxygen may be present in the discharge air stream, localized anaerobic zones may be present because of inadequate mixing or tumbling in a digester unit which prevent bacteria from having access to oxygen (10). An indication of anaerobic zones can be the emanation of objectionable odors. These odors can be minimized by an increase in the aeration rate or more frequent turning of a windrow.

Moisture Content: The moisture content of a composting material is a function of the individual moisture contents of the sludge and bulking agent and the relative proportions of these materials in the mix. One of the purposes of the bulking agent is to reduce the moisture content of the sludge, which typically contains 70 to 87 percent water (13 to 30 percent solids) (24). For example, in composting sewage sludge with woodchips, two volumes of woodchips are mixed with one volume of sludge (about 1:1 on a weight basis) to lower the moisture content to about 60 percent (39).

Moisture content and aeration are interrelated because of the fact that the major oxygen supply for the microbial population in the composting mass is the air in the interstices (pores) in the mass. The more that these voids are filled with water, the less they will be filled with air. Loss of pore space can be compensated by increasing the rate of aeration so that the microorganisms have access to sufficient oxygen. This will also accelerate the rate of water evaporation and thereby increase free air space.

The theoretical optimum moisture content is the maximum moisture content at which aerobic conditions can still be maintained. In practice, the moisture content should not be allowed to drop below 40 percent (42). Below this level, bacterial metabolic activity is severely inhibited because there is not enough water to meet the physiological needs of the microorganisms. The moisture content should also not exceed 60 to 65

percent (24,42). Above this level, free air space is reduced and the compost pile tends to become anaerobic. This can lead to emission of objectionable odors.

During the composting process, the metabolic heat generated and aeration of the pile tend to reduce the moisture content of the composting material. If the material becomes too dry, water can be added to raise the moisture content. In mechanical in-vessel systems, water can be added at any time. In windrow composting, it is better to add water during the turning of the piles since windrows tend to shed water when it is sprinkled on them. Climate and precipitation are also factors that can affect the moisture levels in aerated static pile and windrow systems.

pH: The optimum pH value for composting sewage sludge is in the range from 5.5 to 8.0 (10,42). Although bacteria favor a near-neutral pH (6.0 to 7.5), fungi tolerate a wider pH range (5.5 to 8.0). The pH of the composting material is a function of both the sludge pH and the pH of the bulking material. Sewage sludge generally has a pH in the range of 5.5 to 6.5 (79). The pH of the bulking agent depends on the material used and can have a significant impact on the pH of the mixture. For example, sawdust can be acidic (24). The effects of extreme pH on the composting process are directly related to the effect of pH on microbial activity or, more specifically, on microbial enzymes (42).

In practice, little can or should be done to adjust the pH of the mixture (10). In general, the pH drops at the beginning of the composting process. This occurs because of the activity of the acid-forming bacteria which break down complex carbonaceous materials to organic acid intermediates. A part of the acid formation may take place in localized anaerobic zones, while another part may be due to the conditions of abundance of carbonaceous substrate and the resulting accumulation of intermediates. Regardless of the causes, the pH may drop to as low as 4.5 to 5.0. Although microbial activity is inhibited to a degree, the effect is only temporary. As these organic acids are synthesized, microorganisms capable of utilizing the acids as a substrate develop. The

net effect is that after a few days, the pH of the compost pile begins to rise. The pH rises until it reaches 8.0 to 9.0, at which point the compost mass becomes alkaline. Thus, finished compost will have a pH in the range of 8.0 to 9.0 regardless of the initial pH of the mixture (24,79).

2.4.5 Operational Concerns

There are certain operational concerns that must be taken into account in the operation and maintenance of a composting facility. The three major concerns are leachate, odor, and worker health (111). A brief discussion of each follows.

Leachate

Leachate is the liquid that drains from the composting piles (24). The sources of moisture in compost piles are precipitation and condensation (the formation of liquid in the piles from the moisture in the air). The amount of condensate generated from composting depends on the moisture content of the materials and on ambient conditions. Although most of the precipitation that falls on a compost pile is adsorbed or evaporated, EPA (24) estimates that 10 to 30 gallons of condensate are generated per dry ton per year. The amount of leachate generated is similar.

Leachate is a concern at those composting facilities (usually outdoor facilities) in which water may become contaminated through contact with the compost pile before draining into the ground or surface waters and entering into groundwater systems. The biochemical and chemical oxygen demand of leachate from sludge compost can be very high. The level of potential contamination by trace metals and toxic organics depends on the chemical composition of the wastes being composted. If a supplemental nitrogen source is added to compost feedstock, leachate from the piles can be relatively high in nitrates and can potentially contaminate groundwater drinking supplies.

In static pile and windrow systems, leachate and condensate can be controlled by installing collection devices underneath the piles. These collection devices are connected

to a system consisting of condensate traps, leachate pumps, and a collection pond (24). Aerated static piles are much less sensitive to moisture since only the surface, which is a layer of finished compost, is directly exposed to precipitation.

Odor

Odor control is the single most important factor that determines whether a composting facility will be permitted to operate (24). It is also the biggest problem facing composting facilities currently in operation (10). Odors are generally generated by the sewage sludge rather than the compost mix. Odors tend to be generated in facilities where sludge piles are left exposed to the atmosphere before mixing and also from localized anaerobic zones in compost piles. Odors tend to fluctuate, rising at the start of the composting process and dropping quickly (111). Most odor problems are attributed to the more highly volatile compounds in the wastes. The main gaseous components identified from a sewage sludge composting operation were hydrogen sulfide, methyl mercaptan, sulfur dioxide, dimethyl sulfide, and dimethyl disulfide (111).

The best form of odor control is to minimize odor generation by maintaining the correct oxygen supply (aeration) and temperatures during composting and by keeping the compost site clean and orderly (24). Another process control which can reduce odors is the proper and timely mixing of the sludge and bulking agent. Dewatered sludge deliveries should be scheduled so that mixing and other operations can be performed without sludge accumulation for long periods. Ensuring a moisture content of less than 60 percent by mixing proper amounts of sludge and bulking agent is crucial for effective aeration, which tends to reduce odors. Also, a uniformly mixed and porous material can reduce odors because clumps of unmixed sludge can lead to anaerobic, and thus odorous, conditions. In addition to odor prevention, methods for controlling odors that are produced include biological filters, enclosure of composting facilities, stack/fan dispersion, chemical scrubbers, and masking agents (45).

Worker Health

Sewage sludge compost has been found to contain enteric viruses, infectious and/or endotoxin producing bacteria, allergenic fungi, and parasitic protozoa (111). Human contact with unfinished compost creates the potential for transmission of disease. Also, endotoxins produced by bacteria can be present in dust and can cause tissue damage if inhaled in large amounts. Symptoms include fever, diarrhea, fatigue, headaches, nausea, irritation, nasal irritation, chest tightness, cough, and phlegm production. Workers may also be exposed to volatile organic compounds that vaporize during composting.

The control of environmental conditions can be used to minimize the hazard to workers. Aeration is used to control the temperature and moisture content of the composting mass. Temperature is the most significant factor in pathogen destruction, and low moisture in the pile creates more dust. Adequate ventilation can control dust from the shredding, grinding, and separation of materials operations. Dust generated by vehicles can be controlled by sweeping and watering roads.

2.4.6 Compost Utilization

Compost is a valuable material with no shortage of potential for application. Composting should be viewed as a generator of a valuable resource, not a form of waste disposal. A major advantage of land application of sewage sludge composts is that it avoids the accumulation of raw sewage sludge in the environment (44). Sewage sludge compost contains greater than 50 percent organic matter and almost all the nutrients needed by plants, therefore representing beneficial application in agriculture and horticulture. Compost application (under controlled conditions) can enrich and replenish soil with valuable organic matter (the single most important measure of a soil's fertility), trace minerals, and slowly-released nutrients and can also renovate the physical and

microbiological characteristics for long-term growth requirements (71). The organic nitrogen in compost is much less likely to cause groundwater pollution than chemical N-fertilizers. As a soil amendment, compost can be used as a mulch, bedding material, or to enhance the physical properties of the soil. In general, the amendment of a soil with compost will increase the soil water holding capacity, cation exchange capacity (CEC), soil porosity and aeration, and pH (111). Under certain conditions, compost can even suppress diseases and reduce the need for pesticides and herbicides.

However, the application of sewage sludge compost to land is not without drawbacks. The addition of compost to soil is not always beneficial to crops, since application of immature compost sometimes causes severe damage to plant growth due to nitrogen starvation and the production of toxic metabolites (44). Another problem involves heavy metals and persistent organics. There is concern that indiscriminate disposal of sewage sludges on agricultural lands may lead to decreased crop yields and/or may endanger the human food chain through excessive accumulation of some of these metals and persistent organics in edible portions of the crops.

In a study which evaluated the effect of fall and spring applications of sewage sludge compost on crop growth and soil properties under field conditions, Bevacqua and Mellano (9) determined that the cumulative effect of multiple applications had the positive effects of lowering the soil pH from 7.7 to 7.4, increasing organic matter from 0.77 to 1.50 percent, and increasing the levels of primary plant nutrients (nitrogen, phosphorous, and potassium). It also had the negative effect of increasing soluble salts from 1.52 to 2.44 dS/m. Although the concentrations of the heavy metals increased in the soil, these increased amounts were still far below the levels that could cause plant toxicity. They also concluded that at applications of less than 80 MT/ha, the compost serves as an organic fertilizer; at rates above that figure, it has additional value as a soil conditioner. In another study, Baxter *et al.* (4) analyzed soil at a sewage sludge disposal site for heavy metals and persistent organics. They found that the application of sludge to

land did not measurably increase the levels of persistent organics over the levels normally found in these soils.

In a 1990 survey of the 35 sludge composting facilities operating in New England, seven primary compost uses were identified (10). They were loam production, agriculture, land reclamation, use by public agencies, contractors, home owners, and private brokers. Of the 35 facilities, 18 had developed more than one end use for the product.

Public Agencies: Nineteen facilities reported providing compost for public agencies to use. Typical recurring uses included the maintenance of parks, recreational areas, cemeteries, road embankments, and building grounds. Workers apply compost as mulch around trees and shrubs or as a top dressing on lawn areas. Bristol, Connecticut uses all of its compost as daily cover on their landfill.

Large, one-time uses of compost have included the construction of baseball fields, cemeteries, and the installation of roadside curbing. By far, the largest bulk use of compost by the public sector has been in the operation and closure of landfills. One town uses compost as a grading material prior to capping, and seven use compost for development of vegetative support layers on their capped landfills.

Contractors: General and landscape contractors also represented a major market for compost in New England. Nine facilities reported sale or giveaway of compost to contractors. In Kennebunkport, Maine, facility operators call contractors each spring to take the compost stockpiled throughout the winter. In the spring of 1989, the facility distributed 800 to 900 cubic yards of compost in less than three hours. Operators reported lines of waiting trucks.

Loam Production: Five facilities reported the use of their compost in the production of loam. Where markets have developed, loam represents a significant segment. Contractors bought nearly 75 percent of the compost produced by the Scarborough, Maine facility for \$3 per cubic yard. The contractors mix the material with

sandy soil at volumetric compost to soil ratios ranging from 1:2 to 1:5. Loam sells for \$10 to \$14 per cubic yard along the Maine sea coast.

Homeowners: This sector also represented a significant market at several facilities. The Bangor, Bar Harbor and Old Orchard/Saco facilities in Maine dispense the bulk of the compost to homeowners. Recipients typically pick up compost at the plant in containers ranging from five gallon buckets to pickup trucks. A disadvantage of this method of distribution is the amount of time the operating staff spends helping homeowners load containers. Educating individual users on the proper use of the product also takes time.

Agriculture: As of 1990, The agricultural market in New England was underdeveloped. Only two facilities (Rockport/Gloucester, Massachusetts and Scarborough, Maine) reported using compost as a top dressing in hay fields.

Private Brokers: Private brokers understand the benefits of using compost and are often associated with large volume soil users. As a result, they can develop markets for compost, ranging from nurseries to the establishment of golf courses. Municipalities benefit by having their product professionally marketed, provided they maintain the quality of their compost. Two of the facilities in the survey had entered contracts with private brokers and a third had an agreement pending successful classification of their compost by the Massachusetts Department of Environmental Protection (DEP).

Land Reclamation: Two facilities reported the use of their compost to reclaim exhausted gravel pits and a third reported using compost in reclaiming a sandpit.

2.5 FATE AND REMOVAL OF TRACE ORGANICS DURING COMPOSTING

2.5.1 Introduction

The organic contaminants which represent the greatest concern with respect to sewage sludge compost utilization are the highly chlorinated compounds (listed in Table 1-2) which resist degradation (4). These toxic organics persist in the environment and tend to accumulate in the body fat of animals occupying higher trophic levels (13). Although a great deal of research has been conducted regarding the mechanics of composting (i.e. composting methods and operations, process microbiology, compost maturity, etc.), little research has focused on the fate of these organic contaminants in compost (39,67,99). The notion that all toxic organic compounds are readily broken down during the composting process has not been thoroughly evaluated (67).

There are a number of possible routes of removal of trace organic compounds during composting, including mineralization (i.e. complete biodegradation), biotransformation (e.g. dehalogenation), assimilation as nutrients into microbial biomass, polymerization, volatilization, leaching, and sorption (42). However, most of the literature concerning the degradation of trace organic compounds in composting deals with biodegradation and biotransformation. Other authors have also investigated the volatilization of trace organic compounds in composting. A discussion of these fate and removal mechanisms and examples of experimental results follows.

2.5.2 Biodegradation/Biotransformation

The available information on the biodegradation of trace organic compounds during composting is very limited. What is known about biodegradation in general is that there are naturally occurring microorganisms capable of degrading many organic contaminants such as pesticides and PCBs (42,75). The degradation occurs because the

microorganisms gain energy needed for growth, repair, reproduction and other biological functions needed for survival (117). Simple organic molecules are readily metabolized and biodegraded through enzyme-catalyzed reactions. Oxidation reactions take place where electrons are transferred along an electron chain with compounds accepting and passing on electrons to a terminal electron acceptor. Mineralization is almost always the result of microbial activity (5). Cometabolism, a slower process in which another compound is used as the basic carbon and energy source and trace organic compounds are incidentally degraded, is also an important biodegradation process. There are also some synthetic organic compounds which are not transformed or are transformed slowly. These compounds are referred to as persistent or recalcitrant.

Although bacteria need a continuous carbon source for growth and cell maintenance, if too much substrate is added the bacteria will initially be unable to metabolize it. Microorganisms need a period of acclimation where they are synthesizing enzymes, growing, and perhaps even undergoing genetic changes. If any intermediates formed are toxic, then the bacteria may be killed or the formation of the next strain that metabolizes it may be stopped so that it accumulates and destroys the system. Bacteria often work with a succession of strains so that complete mineralization needs more than one microorganism which does not alone have the required genetic capability. Mixed cultures can degrade better both qualitatively and quantitatively than single cultures.

The important point is that if microorganisms found in nature can break down certain hazardous organic compounds in the laboratory or in soil, then they should be able to accomplish the breakdown in a compost environment (1). Successes attained in the composting of certain hazardous wastes give validity to this conclusion (30,31,103).

Another important point is that composting is a biological process and thus has all the advantages and limitations of a biological process. A major advantage is that the composting process, due to its solid phase nature, is receptive to both hydrophilic and hydrophobic wastes. Chief among the limitations is the fact that the potential capacity

and performance of all compost systems are determined by those of their microbiological components (48). Another limitation is that engineered biological systems have certain retention times which limit the amount of time that the organic compounds are in contact with the microorganisms. If retention time were not a consideration, then all but the most refractory of organic wastes (hazardous and non-hazardous) would be suitable for composting (104). However, for some organic compounds the process is so slow that it entails infeasibly long retention times.

Although little is known about why man-made or even some naturally occurring organics are not biodegraded during composting, several explanations have been postulated. One reason may be that the microorganisms which are naturally present cannot produce the enzymes necessary to bring about transformation of the original compound to a point which the resultant intermediates can enter into common metabolic pathways and be completely mineralized (66). Enzymes and their functions are discussed below.

Enzymes

Metabolic processes in all life forms are governed by the actions of organic catalysts called enzymes (75). Enzymes have a high molecular weight, are primarily protein, and are manufactured by living cells. As biological catalysts, enzymes have the capability of increasing the speed of chemical reactions and can be recovered at the completion of the reaction. Enzymes are specific for each type of reaction. Also, enzymes are sensitive to heat, extreme pH fluctuations, ultraviolet light, and excessive mechanical agitation.

An enzyme is comprised of a three dimensional polypeptide chain of protein. Each protein has a specific amino acid arrangement. Certain amino acids are known as the "active site" of the enzyme molecule, and this "active site" is called the apoenzyme. The apoenzyme is responsible for the specificity of enzyme activity. Another part of the enzyme, the coenzyme, determines what chemical reaction will occur. Coenzymes are

like apoenzymes in that they have a definite structure, but differ in that apoenzymes are highly specific in their reactions. Coenzymes can work with different apoenzymes to produce the same chemical reaction on different chemical compounds.

Because organic nutrients and other substances are often presented to microorganisms as large, insoluble macromolecular complexes, these complexes must first be degraded to smaller compounds which may then be internalized and used as a source of nutrients and for the synthesis of new cellular material (13). This initial degradation is accomplished as a result of the secretion of stable, extracellular enzymes synthesized by the microorganisms. Since many organic contaminants are physically adsorbed in the composting material, they are less available for uptake and metabolism by microorganisms. The action of these extracellular enzymes may provide a mechanism by which some trace organic compounds are made more accessible for biodegradation.

In some cases, microorganisms may have the enzymatic capability to degrade the organic compound, but the compound may not be present in sufficient concentrations to induce the enzymes required for degradation (13,66). When the concentration of a trace organic compound is reduced to only a few parts per million, the biological half-life of the compound lengthens and may even become infinite (57). In other words, no further biodegradation occurs. It is believed that this phenomenon occurs because the residual amount of the specific trace organic simply does not contain enough energy to sustain the attacking microbiota. This suggests that for certain trace organic compounds, complete biodegradation cannot be accomplished unless the compound can be used as a secondary substrate.

Furthermore, many hazardous compounds are highly toxic to microorganisms. Toxicity has been regarded as the most important limitation of wastes to be composted (75). However, organic compounds that are toxic at higher concentrations may be biodegraded when dilute (57). For example, a 10 percent formalin solution is used to preserve specimens, but formalin at 0.1 percent is biodegradable.

The trace organic compounds in the composting material may not be readily available for microbial attack for a variety of reasons (42). Active degradation of a trace organic molecule is an intracellular event, and thus the entry into the cell is a necessary prerequisite for biodegradation. The uptake and transport of nonpolar substances such as aromatic pesticide molecules across cell membranes are believed to be largely due to differences in partitioning coefficients and dynamic equilibrium conditions. Therefore, these conditions will be different for each organic compound. Adsorption of trace organics to composting material may also render these compounds unavailable for microbial degradation or at least slow the rate of degradation. A related phenomenon is the physical entrapment of trace organics in sites which are effectively protected from microbial invasion and colonization and thereby provide microsite protection.

As mentioned earlier, not all breakdown in the composting process is biological. Chemical and physical factors established by the process can exert an important influence on the breakdown of certain organic compounds (103,104). Examples of these chemical and physical factors include ultra-violet (UV) light, temperature, and pH. These factors can induce abiotic removal mechanisms such as adsorption, thermal conversion, radiation, and volatilization (42). The temperatures and pH levels reached during composting are those at which pesticides, for example, decompose most rapidly. Since many trace organic are vulnerable to these factors, isolating and determining the role of microorganisms in the breakdown of these compounds is very difficult. Also, a decrease in the concentration of a toxic organic compound does not necessarily mean that the environmental hazard is reduced; instead, the compound may be converted to other forms which may not be detectable by the standard analytical procedures employed (42). There is also evidence that organic compounds that are not completely mineralized may be biologically transformed to organic products which chemically react with and actually become part of the compost residue (126).

Biodegradability Studies

Tabak *et al.* (115) collected information from studies undertaken to determine the biodegradability of the 114 organic priority pollutants. The biodegradability data collected were based on studies in which the priority pollutants were subjected to a specific set of controlled experimental conditions and culture-enrichment techniques within the framework of a static culture flask biodegradability screening test. Their goal was to ascertain the extent of microbial degradation and to determine the acclimation periods for the various compounds. The following is a brief discussion of the results for certain classes of compounds.

Organochlorine pesticides. The priority pollutants consisting of aldrin, dieldrin, chlordane, DDT, DDE, DDD, heptachlor, and lindane were shown to be recalcitrant to bio-oxidative activity of wastewater microbiota at 5 and 10 mg/L for the four successive 7-day incubation periods of the static-flask-culture method. Data based on the chromatographic analysis of methylene chloride extracts indicate 0 percent losses of these pesticides. The chromatographic results indicate no reduction of the chromatographic peaks characterizing each parent pesticide and concomitant absence of new peaks with different retention times suggesting possible transformation metabolites, thus providing evidence of persistence of the parent substrate.

The absence of any biodegradative activity in the static culture flask studies is corroborated by the results from literature-reported studies with regard to dieldrin, chlordane, DDE, and DDD. Possible transformation activities by *microorganisms* in the static-culture-flask studies, such as aldrin to dieldrin, cometabolic transformation DDT to DDE, heptachlor to heptachlor epoxide, and lindane to metabolites, were not established by the analytical procedures used. The results for the chlorinated pesticides are consistent with published work on this class of compounds, which show resistance to biodegradation.

Polychlorinated biphenyls. The individual PCBs vary widely in their susceptibility to biodegradation. The mono-, di-, and trichlorinated species may be significantly biodegraded or biotransformed, as well as volatilized. PCBs with five or more chlorine atoms per molecule have a tendency to adsorb to suspended materials and sediments, bioaccumulate because of very low solubility, photodissociate, and are quite resistant to biodegradation. The priority pollutant PCBs are Aroclors or technical mixtures of individual PCBs made by the partial chlorination of biphenyl in the presence of a suitable catalyst. The PCBs 1016, 1221, 1232, 1242, 1254, and 1260 are Aroclors which differ from one another in the average chlorine content on a weight basis and in types of the individual PCBs composing the mixture.

Biodegradability data for the priority pollutant PCB Aroclors have demonstrated that PCB Aroclor 1221 (with an average chlorine content of 21 percent and limited to mono- and di-chloro isomers) and PCB Aroclor 1232 (with an average chlorine content of 32 percent and limited to mono-, di-, tri-, and tetra-chloro isomers) were the only PCB Aroclors exhibiting significant biodegradation with rapid acclimation. PCB Aroclor 1016 (a new mixture limited to mono-, di-, tri-, and tetra-chloro isomers) and PCB Aroclor 1242 (with an average chlorine content of 42 percent and limited to di-, tri-, and tetra-chloro isomers) showed little bio-oxidation at 5 mg/L, and no oxidative activity at 10 mg/L. PCB Aroclor 1248 (with an average chlorine content of 48 percent and limited to tri-, tetra-, and penta-chloro isomers), PCB Aroclor 1260 (with an average chlorine content of 60 percent and limited to penta-, hexa-, and hepta-chloro isomers) demonstrated recalcitrance to microbial metabolism at 5 and 10 mg/L. The biodegradability of PCBs is a function of the number of C-H bonds available for hydroxylation. The fewer the chlorine atoms, the more common the adjacent unchlorinated carbons, and the higher the rate of biodegradation.

Monocyclic Aromatics. Based on the biodegradability data accumulated for the priority pollutant benzenes, toluenes, and their chlorinated and nitrated derivatives,

certain conclusions can be drawn about their relative susceptibility to microbial bio-oxidation and their persistence and stability in aqueous environments. The analytical data, based on GC and TOC determinations, have demonstrated significant biodegradation of some of the benzene and toluene compounds, with varying degrees of acclimation depending on the test compound and the dose concentration of substrate in the culture media. Hexachlorobenzene was shown to be relatively resistant to degradation by the microorganisms under the conditions of the static-flask methodology. Hexachlorobenzene did not demonstrate significant bio-oxidation and the necessary acclimation for bio-oxidation activity within the 28-day incubation period under the conditions of the static-flask-culture method. Significant biodegradation with rapid acclimation was observed for benzene, toluene, and nitrobenzene. Toluene and nitrobenzene were shown to be completely biodegradable after the first week of incubation at 5 and 10 mg/L levels. According to reported studies, the more highly halogenated the benzene molecule becomes, the more resistant it is to microbial degradation.

Polycyclic Aromatic Hydrocarbons. The polycyclic aromatic hydrocarbons (PAHs) demonstrated varied rates of biodegradation with different acclimation periods, depending on the test compound and the dose of substrate in culture media. Fluoranthrene, pyrene and chrysene demonstrated significant degradation at 5 mg/L substrate levels, but low oxidative activity at 10 mg/L.

The PAHs in general have been reported to be potentially biodegradable compounds, particularly by soil microorganisms and in soil systems which provide better conditions for biodegradation than aquatic systems. The biodegradability data have shown that the tricyclic aromatic hydrocarbons are more susceptible to biodegradative action than the tetracyclic and higher polycyclic hydrocarbons.

Chlorobutadienes. The compound hexachloro-1,3-butadiene demonstrated a 100 percent loss of substrate at 5 and 10 mg/L at the end of the original culture incubation

period and this bio-oxidative activity continued over the next three 7-day incubation periods. The volatility control systems showed almost no loss from volatilization of hexachloro-1,3-butadiene at both the refrigeration and 25°C holding temperatures.

Phthalate esters. Phthalate esters are reported to be metabolized in the aquatic environment by a variety of microorganisms and degraded by mixed microbial systems at rates which vary widely, depending on environmental conditions. These compounds undergo primary and ultimate biodegradation in naturally occurring microbial populations by mechanisms of enzymic hydrolysis. The rate of degradation depends on the temperature, pH, the presence of oxygen, and phthalate structure.

Bis-(2-ethylhexyl) phthalate was significantly bio-oxidized, but with a gradual adaptation process needed over a 3-week period to achieve 95 and 94 percent loss in 5 and 10 mg/L substrate containing cultures respectively at the end of the third subculture incubation. Bis-(2-ethylhexyl) phthalate was shown to be one of the most persistent of the phthalates studied under the conditions of the static-flask screening test.

Nitrogenous organic compounds. The carcinogenic nitrosamine, dimethyl nitrosamine, which was not included in the biodegradability studies, is reported to exhibit resistance to microbial degradation in soil and in wastewater.

Chloroethylenes. The chloroethylene aliphatics, trichloroethylene and tetrachloroethylene, were shown to be significantly degradable with gradual adaptation observed. The relatively significant volatilization in the non-biological volatility control series did not preclude the biodegradative activity of microbiota in culture media from the relatively high total percentage of loss of substrate throughout the study. In another study, McClellan *et al.* (78) found that aerobic bacteria can substantially degrade trichloroethylene. However, the results suggested that the degradation only occurs within a narrow range of conditions.

2.5.3 Volatilization

Chemicals that transfer readily from solid or liquid phases to the vapor phase are termed volatile. Volatile organic compounds (VOCs) may be synthetic or of natural origin. Volatilization is an environmental factor that is frequently overlooked as a route of removal of VOCs from compost piles. However, bench-scale studies have shown that volatilization represents a major route of substrate removal for many synthetic VOCs, including certain pesticides (42,65). At commercial composting facilities, substantial stripping may even occur on the tipping floor before composting actually begins (65). Volatility generally increases as the temperature rises, so the heating that accompanies the composting process can be expected to contribute to VOC loss. In addition, mechanical aeration (i.e. turning of windrows) is practiced at many facilities. Computer simulations suggest that elevated temperatures and mechanical aeration rates typically encountered in composting should lead to rapid stripping of VOCs (65).

A number of factors affect the volatilization of VOCs during composting. Guenzi and Beard (50) reported that the seven principal factors controlling the volatilization of pesticides from soil are (1) chemical and physical properties of the pesticide, (2) adsorptive characteristics of the soil, (3) pesticide concentration, (4) soil-water content, (5) air-flow rate, (6) temperature, and (7) diffusion. Since the properties and solid matrix of soil are similar to that of compost, it is likely that these factors also control volatilization from the composting process. A brief discussion of these factors follows.

1. Chemical and physical properties of the pesticide

Henry's Law constants, vapor pressure, solubility in water, type of basic nucleus (i.e., phenyl, alkyl, pyridine, etc.) and number, kind, and position of functional groups all provide important clues regarding a particular compound's volatility in soil. Henry's Law constants (K_H) for the trace organic compounds of concern are given in Table 2-5-1. Compounds with K_H values greater than 10^{-3} m³-ATM/mol are considered volatile, while compounds with K_H values less than 10^{-7} are considered non-volatile. Those compounds

with K_H values inbetween 10^{-3} and 10^{-7} are referred to as semi-volatile. However, caution must be exercised in predicting volatilization from soil based only on the K_H values.

2. Adsorptive characteristics of the soil

Adsorption of a pesticide by the inorganic and organic fractions of a soil may be the result of one or more of the following forces: (i) chemical adsorption (Coulombic forces), (ii) physical adsorption (van der Waals forces), and (iii) hydrogen bonding. The chlorinated hydrocarbons are probably held to the soil primarily by the organic fraction. The degree to which the compounds are adsorbed to soil particles will affect the tendency of the compound to volatilize.

3. Pesticide concentration

The concentration of a pesticide in the vapor in soil is related to its concentration in that soil. Vapor phase concentrations increase with increases in pesticide concentration until a level is reached where the soil air becomes saturated. At this level, the soil vapor concentration is equal to the vapor density of the pure pesticide without

Table 2-5-1

HENRY'S LAW CONSTANTS FOR THE TRACE ORGANIC COMPOUNDS OF CONCERN

Compound	Henry's Law constant (m ³ -ATM / mol) {25°C}
Aldrin	4.96 x 10 ⁻⁴
Benzo (a) Pyrene	1.26 x 10 ⁻²
Chlordane	4.8 x 10 ⁻⁵
DDD	2.16 x 10 ⁻⁵
DDE	2.34 x 10 ⁻⁵
DDT*	5.2 ± 3.8 x 10 ⁻⁵
Dieldrin	5.8 x 10 ⁻⁵
Dimethyl Nitrosamine	NA
Heptachlor	1.48 x 10 ⁻³
Hexachlorobenzene	1.70 x 10 ⁻³
Hexachlorobutadiene	1.03 x 10 ⁻²
Lindane*	3.2 ± 0.2 x 10 ⁻⁶
PCB-1016	1.8 x 10 ⁻⁴
PCB-1221	3.24 x 10 ⁻⁴
PCB-1232	8.64 x 10 ⁻⁴
PCB-1242	5.7 x 10 ⁻⁴
PCB-1248	3.5 x 10 ⁻³
PCB-1254	8.37 x 10 ⁻³
PCB-1260	7.1 x 10 ⁻³
Toxaphene	4.89 x 10 ⁻³
Trichloroethylene	1.17 x 10 ⁻²

* - values from Mackay and Shiu, J. Phys. Chem. Ref. Data, Vol. 10, No. 4, 1981 (Ref. 73)
(all other values from Treatability Manual, Vol. 1,2. EPA-600/2-82-001a) (Ref. 37)

soil. In other words, pesticide concentration influences vapor concentration (to a threshold value), which in turn regulates vapor loss.

4. Soil-water content

The role of water in the volatilization of pesticides from soil is probably one of the most important factors, and to some extent, the most controversial. Although researchers disagree on the exact role water plays, there is no question that the presence of water in a soil enhances the volatilization of pesticides. Since material being

composted is very moist, pesticide volatilization from the composting process should also be enhanced.

5. Air-flow rate

The rate of air flow can influence pesticide volatilization directly and indirectly. If the relative humidity of the air is not 100 percent, then increases in air flow will accelerate the drying of the soil. This indirect effect alters the soil-water content which, as mentioned earlier, has a profound effect on volatilization. The direct effect of increased air movement involves a more rapid removal of pesticide vapors from the soil surface, and results in an increased movement of pesticide vapors to the soil surface. In composting, the air flow not only contacts the surface of the material (as wind does to soil) but also contacts the entire mass. Thus, air-flow rate has an even greater effect on composting material than it has on soil.

6. Temperature

The overall effect of increasing the temperature in a soil-pesticide system is to increase the amount of pesticide volatilized. Temperature influences a number of soil and pesticide properties, and these intricate interactions are not completely understood. However, one of the main factors is the effect of temperature on vapor density of the pesticide. Temperature affects the volatilization of a given pesticide from soils by a direct influence on the vapor density of the pesticide and by temperature influences on the physical and chemical properties of the soil. The net effect is more pesticide volatilization from soil with increases in temperature.

7. Diffusion

Once the pesticide is removed from the soil surface, the surface loss of the remaining pesticide by volatilization will become a diffusion-controlled process. A compound can diffuse in both the vapor and non-vapor phases; the ratio of these two is dependent on soil-water content. Diffusion is also influenced by bulk density, temperature, pesticide concentration, and relative humidity. In composting, diffusion will

probably play a greater role in operations in which forced (or drawn) aeration is not utilized. In forced aeration operations, advective forces should minimize the effects of diffusion.

Volatilization of trace organic contaminants is usually not desirable for two important reasons. First, volatilization is not a destructive removal mechanism; it simply changes the phase of the contaminant from liquid or solid phase to vapor phase. Although the contaminant may be removed from the composting material, the environmental hazard associated with the contaminant has not been eliminated because aerial release of VOCs can contribute to air pollution. In addition, the volatilization of toxic organic compounds can pose a threat to workers in confined spaces that are not well ventilated. In situations where air emissions of VOCs pose a safety concern, an important factor is the manner in which aeration systems are operated (drawn or forced aeration). Although there is evidence that forced aeration provides more uniform air flow through the solid matrix than drawn aeration does, forced aeration blows air out of the compost pile from all points and control of air emissions is difficult unless the whole system is inside an enclosed structure (126). The use of drawn aeration provides for collection of all exhaust gases at a central point, the blower. Exhaust gases may be conveniently passed through an activated carbon scrubber or possibly a pile of uncontaminated compost to remove volatile organics (i.e. a biofilter).

In many instances it is extremely difficult to single out the role of volatilization as a removal mechanism of the test compound because of the lack of carefully controlled experimental conditions (42). Vapor capture in compost free air space and exit gas, as well as subsequent analytical determination of its concentration and composition, must be improved for compost systems. Two methods were previously evaluated for this purpose (110), neither of which was deemed satisfactory. The first method, which involved a series of two condensers, was suspected of yielding a low recovery because of insufficiently low temperature and adsorption of volatiles in the Tygon tubing. The

second system, involving activated carbon adsorption and the use of Teflon tubing, was superior to the condenser method, but problems were encountered with the loss of volatile compounds from activated carbon. Thus, the analytical methods for capturing and detecting VOCs must be improved (42).

2.5.4 Experimental Research and Results

An extensive literature search was conducted to collect information and collected data on the levels and fates of trace organic compounds in sewage sludge compost. The individual research studies will first be discussed, followed by a summary of the results for individual trace organic compounds of concern.

One of the first comprehensive research studies on how effective composting might be for biodegrading trace organic compounds and to determine the degree of breakdown of compounds while in contact with high-rate composting was supported by the National Science Foundation and was conducted by the Snell Environmental Group (110). In this study, an artificial compost mixture consisting of shredded newspaper (as both a bulking agent and for some carbohydrate content), horse manure and sewage sludge (the basic food and the source of the compost microorganisms), sawdust, peat moss, soil, powdered milk, and fertilizer was prepared. Toxic organic chemicals were mixed with this actively composting mixture. This was accomplished by inserting fifty-nine aliquots (test cells) into a large box of compost. Each cell consisted of the artificial compost mixture spiked with a different toxic organic compound to obtain a concentration of approximately 500 mg/kg. It was claimed that the conditions inside and outside the test cells were identical except for the target compounds of interest. Samples were analyzed after 7 days of composting and again after 30 days.

Of the 59 toxic organic chemicals studied in this project, susceptibilities to biodegradation by composting were found to range from 100 percent to nearly 0 percent. Composting biodegraded 32 of the 59 organic chemicals studied moderately well or

better. Table 2-5-2 summarizes the susceptibility to biodegradation during high-rate composting for the trace organic compounds of concern. Volatile hydrocarbons are

Table 2-5-2 SUSCEPTIBILITY TO BIODEGRADATION IN A HIGH-RATE COMPOSTING ENVIRONMENT

	Percent Biodegradation after 7 days	Percent Biodegradation after 30 days
<u>Very High (96-100%)</u>		
Hexachlorobutadiene	100	100
<u>High (76-95%)</u>		
PCB 1221	77	75
<u>Moderately High (51-75%)</u>		
PCB 1016	21	72
PCB 1254	95	60
Hexachlorobenzene	31	62
Lindane	66	73
<u>Moderate (31-50%)</u>		
PCB 1242	29	39
Chlordane	0	44
<u>Moderately Low (16-30%)</u>		
Benzo (a) Pyrene	27	0
<u>Low (0-15%)</u>		
PCB 1260	2	7
DDT	0	7
Dieldrin	0	11
Toxaphene	0	4

Table 2-5-3

Chemicals degraded more rapidly during first 7 days

- PCB 1221
- PCB 1260
- PCB 1242
- PCB 1254
- Benzo (a) Pyrene
- Trichloroethylene
- Lindane
- Hexachlorobutadiene
- Hexachlorobenzene

Table 2-5-4

Chemicals degraded better during the last 23 days

- PCB 1016
- Dieldrin
- DDT
- Toxaphene

omitted from this table because the amount of these chemicals vaporized and swept out of the reaction cell unchanged could not be measured. By finding how much the chemicals degraded after 7 days and then again after 30 days, rough rates of biodegradation were determined. Table 2-5-3 lists the chemicals which biodegraded most rapidly during the first 7 days of composting, and Table 2-5-4 lists those chemicals which biodegraded better during the last 23 days of composting.

During the study, it was found that benzo (a) pyrene degraded more in 7 days (27 percent) than in 30 days (0 percent) of composting. This inconsistency could not be explained. Of the pesticides, lindane showed moderate biodegradability (73 percent), but dieldrin, DDT, and toxaphene showed low susceptibility for biodegradation (all below 11 percent). Chlordane had moderate tendency to biodegradation with 44 percent breakdown. It should also be noted that dieldrin, DDT, chlordane and toxaphene underwent all their degradation during the last 23 days of composting.

PCBs 1221, 1016, and 1254 showed moderately high to high susceptibility to biodegradation under composting conditions. The inconsistency in PCB 1254 degrading 95 percent in 7 days and only 60 percent in 30 days was attributed to an uneven distribution of the chemical in the two different test cells. The one with the chemical

limited to only a few highly concentrated areas might be expected to degrade less. This is because if the chemical is limited to only a small area in the compost, the *microorganisms* will have less exposure to it. In addition, the higher concentration might have a toxic effect on the organisms. PCB 1260 was very resistant to biodegradation with a breakdown of only 7 percent in 30 days.

Conclusions reached by the Snell Group include: (1) all of the chemical families showed moderate to moderately high susceptibility for biodegradation by composting, (2) all of the chemical families had most of their biodegradation occur in the first 7 days, and (3) the more rapid or high-rate the composting, the more biodegradation of organic contaminants is enhanced. Based on these findings, the Snell Group recommends composting for treating sewage sludge, claiming that trace organic compounds will most likely be degraded.

The Snell Group conceded that due to their small budget, they were unable to eliminate all other avenues by which the chemicals could disappear. Consequently, they cannot unequivocally say that composting biodegraded the chemicals that disappeared. However, they maintain that the odds are highly in favor of biodegradation for the chemicals that were reduced. Other authors (42) have questioned the claim that the conditions inside and outside the test cells were identical, asserting that the plastic screening of the test cells probably had an effect on physical parameters such as aeration and moisture content.

In a study to evaluate composting as a means of decontaminating soil containing PCBs, Isbister *et al.* (63) found that PCB concentrations were significantly reduced by aerobic and anaerobic composting. Aerobic composting resulted in the greatest decrease in PCB concentration, with an average reduction of 62 percent. Composts were sacrificed after two and four weeks of incubation. Aerobic composts yielded 41.6 to 48.1 percent decreases after two weeks of composting and 55.7 to 67.6 percent decreases after four weeks. PCB reductions were significantly less in anaerobic composts, with 18.4 to

28.0 percent reduction after two weeks and 27.9 to 46.9 percent after four weeks of composting.

The experiments were carried out with a soil that was intentionally spiked to yield 2000 mg/kg of Aroclor 1242, which is a mixture of chlorinated biphenyls composed of approximately 1 percent monochlorobiphenyl, 16 percent dichlorobiphenyl, 49 percent trichlorobiphenyl, 25 percent tetrachlorobiphenyl, 8 percent pentachlorobiphenyl, and 1 percent hexachlorobiphenyl. Analysis of experimental and control chromatograms indicated that a significant decrease in trichlorobiphenyl and one of the tetrachlorobiphenyls had occurred during the first two weeks of aerobic composting. No decrease in the higher chlorinated biphenyls was observed. However, after four weeks of aerobic composting, significant decreases in all of the chlorinated biphenyls occurred, with less than 25 percent of the trichlorinated biphenyls remaining.

The authors concluded that the mechanism of PCB degradation in compost appears to be rapid dechlorination of biphenyls containing three chlorines or less, since no buildup of the mono- or dichlorinated compounds was observed. Dechlorination of the tetra- and pentachlorinated molecules is slower but does occur at a useful rate. The authors also claim that degradation rates observed in larger systems may be twice as rapid as those observed in the laboratory-scale studies.

In a composting physical model demonstration, Hogan *et al.* (61) performed a mass balance of hydrocarbons and PCBs. They found that the amount of Aroclor 1232 decreased in the composting material and increased in the exhaust traps. Over the 35-day period, 81.4 percent disappeared (83.0 percent disappeared from the pile but 1.6 percent was recovered in the exhaust traps). Aroclor 1232 is a mixture of the following congeners (percent by weight): non-chlorinated biphenyls, 0.1; monochlorobiphenyls, 31; dichlorobiphenyls, 24; trichlorobiphenyls, 28; tetrachlorobiphenyls, 12; pentachlorobiphenyls, 4; heptachlorobiphenyls, 0.1. Thus, mono-, di-, and trichlorobiphenyls comprise 83 percent of the mixture. These are known to be degraded

microbially, though not necessarily completely mineralized to carbon dioxide, water, and chlorine. Microbial degradation of tetra- and hexachlorobiphenyl PCBs is problematic. Based on the mass balance data at termination of the experiment, 17 percent of the Aroclor 1232 remained in the composted material. This corresponds closely to the 16 percent of the Aroclor comprised of the tetra-, penta-, and hepta chlorobiphenyl congeners. The researchers concluded that the bulk of Aroclor 1232 was probably degraded microbially. The emitted (1.6 percent) PCBs were presumably the lighter congeners which otherwise might have been degraded.

In August of 1992, the Illinois Office of Recycling and Waste Reduction (ORWR) completed a preliminary study (62) that analyzed the contaminant levels in compost produced from landscape waste (i.e. grass clippings, leaves, and brush). The study sampled raw and mature compost from eleven facilities in the state. Six of the sites were in the Chicago metropolitan area, and five were in the predominantly rural downstate area. Compost samples, 88 in all, were analyzed for metals, pesticides, and PCBs. Two key findings of the study were: 1) levels of pesticides were, overall, consistently higher in the Chicago metropolitan area samples (attributed to a heavier use of pesticides by homeowners and landscapers), and 2) only four pesticides (DDE, methoxychlor, 2,4,5-T and trifluralin) were detected in finished compost. The remaining seventeen organochlorine, carbamate, and organophosphate pesticides that were detected in the raw compost appear to have degraded or leached during the composting process. It is possible that the increase in DDE concentration could be attributed to the degradation (biological conversion) of DDD. PCBs were tested for but were not detected in any samples. Trace organic compounds of concern that were detected in the raw compost were chlordane, DDD, DDE, dieldrin, heptachlor, and lindane. The percentage of these compounds that degraded during composting were: chlordane-24 percent; DDD-21 percent; DDE- -56 percent (gain); dieldrin-16 percent; heptachlor-100 percent; and lindane-37 percent.

Müller and Korte (85) investigated the microbial degradation of benzo (a) pyrene and dieldrin (a biological conversion product of aldrin) in waste composting. The measured reductions were 7 percent for benzo (a) pyrene and 12 percent for dieldrin.

Another study (74) confirmed the conclusions of Müller and Korte that polycyclic aromatic hydrocarbons (PAHs) undergo little microbial degradation in fresh composts. However, these authors argued that degradation studies performed only with fresh compost materials do not represent the situation of degradation in practice. The authors claimed that extremely different environmental conditions (temperature and substrate) for growth of microorganisms in fresh and ripe composts cause quite different compositions of microbial populations and so different capacities for degradation are feasible. The results of their analysis and experiments with PAHs suggest that during a complete compost process, considerable amounts of these xenobiotic compounds will be degraded.

Conclusions reached by Hagenmaier *et al.* (51) agree with these findings. The concentrations of PAHs were found to increase during the composting process, most likely due to the fact that losses of organic material takes place by the action of aerobic bacteria. However, an inverse effect was observed in composting plants with composting periods of more than half a year. This suggests that under prolonged aerobic composting conditions, *microbial degradation of PAHs can occur.*

In an evaluation of treating hazardous wastes by composting, Szabò *et al.* (114) concluded that the organic extract, mineral oil, and total PAH content of an oil-containing sludge decreased to almost half of the original value.

Although Hogan *et al.* (61) reported more than 87 percent disappearance of three PAHs (phenanthrene, fluoranthrene, and pyrene) during 35 days of laboratory sewage sludge composting at 50°C, the object of the study was the *destruction of hazardous wastes*, not the fate of environmental contaminants. Therefore, an unusually high aeration rate, a high initial PAH concentration, and a microbial compost inoculum that had been acclimated to these PAHs for up to seven months were used. Although these

percent reductions cannot be considered representative of typical sewage sludge composting, they do exhibit the potential biodegradability of these compounds.

Racke and Frink (99) found that between 89 and 93 percent of the initially applied phenanthrene persisted unchanged during sewage sludge composting. The authors found their results rather surprising because phenanthrene is considered the most biodegradable PAH.

Other reports in the literature on the fate of trace organics in composting were also found. Rose and Mercer (101) investigated the composting of insecticides in agricultural wastes. The degradation of DDT amounted to 65 percent of its original concentration at the end of 50 days (2.2 to 0.8 ppm). The DDT breakdown products DDD and DDE were not detected in the composted material. They also found that the concentrations of the pesticides diazinon and parathion were rapidly decreased by continuous thermophilic composting. Petruska *et al.* (97) examined pesticide disposal by composting. The production of carbon dioxide (used as a measure of microbial activity) from compost containing chlordane was very low. Approximately one-half of the activity was recovered in solvent extracts of the polyurethane foam used, indicating a high level of chlordane volatility. The authors concluded that chlordane metabolism was negligible in the compost. The major loss was reportedly due to volatilization (approximately 50 percent) of the parent material. In a study (54) which investigated the turnover of toxic organic compounds in waste composts, it was discovered that PCBs were present in all of the sludge samples and in all of the compost samples. Although concentrations were not provided, complete biodegradation is obviously ruled out.

The disposal of hazardous organic wastes by composting has been mentioned numerous times in the literature. Savage *et al.* (103) state that there are two convincing reasons which favor composting as an option for treating biodegradable hazardous wastes. The first is the impressive array of organic chemical compounds, some of which are hazardous, that has been demonstrated in laboratory studies to be susceptible to

breakdown by microbes isolated from enrichment cultures. The second is an abundance of experience that has demonstrated the breakdown of many organic compounds when incorporated into the soil. Alpert and Epstein (1) report that composting is suitable for industrial waste when low-level biodegradable toxic organics are present in the wastes. Hart (57) states that pesticides may be reasonable candidates for compost biodegradation. However, the concentration must be above the refractory limit (the minimum concentration at which biodegradation will still occur). Thus, Hart claims that composting will not be suitable for cleaning up soils and groundwater contaminated in the parts per million range, but may be effective for cleaning up spill areas.

Table 2-5-5 is a summary of the results found in the literature for the trace organic compounds of concern. The percent reductions reported for the trace organics during composting are shown.

Table 2-5-5

TRACE ORGANICS' REDUCTIONS DURING COMPOSTING

Compound	Percent reduction reported	References
Aldrin	NA	-
Benzo (a) Pyrene	7-27	85,110
Chlordane	24-50	62,97,110
DDD	21	62
DDE	-56*	62
DDT*	7-65	39,110
Dieldrin	11-16	62,85,110
Dimethyl Nitrosamine	NA	-
Heptachlor	100	62
Hexachlorobenzene	62	110
Hexachlorobutadiene	100	110
Lindane*	37-73	62,110
PCBs (total)	62	63
PCB-1016	72	110
PCB-1221	77	110
PCB-1232	81	61
PCB-1242	39	110
PCB-1248	NA	-
PCB-1254	95	110
PCB-1260	7	110
Toxaphene	4	110
Trichloroethylene	99	110

*- Negative sign represents a gain in the concentration of the compound. The DDE concentration most likely increased because it is a conversion product of DDT.

3.0 REGULATIONS

3.1 Federal Regulations

Legislation controlling sludge disposal is contained in: the Clean Air Act of 1970 (sludge disposal by incineration), the Water Pollution Control Act of 1972 (fresh water dilution), the Marine Protection Research and Sanctuaries Act of 1976 (ocean dumping), and the Resource Recovery and Conservation Act of 1976 (landfilling). Under authority of Sections 405(d) and (e) of the Clean Water Act, the United States Environmental Protection Agency (EPA) has recently promulgated regulations to protect public health and the environment from any reasonably anticipated adverse effects of certain pollutants that may be present in sewage sludge. The regulations, 40 CFR Part 503, establish requirements for the final use of sewage sludge for three sludge disposal options, including: application to land for a beneficial purpose (including sewage sludge or sewage sludge products that are sold or given away for use in home gardens), disposal on land by placing it onto surface disposal sites (including sewage sludge-only landfills), and incineration. The following is a brief discussion of the history of the Part 503 regulations (adapted from Water Environment Federation, Ref. 122).

In the spring of 1984, EPA enlisted the assistance of federal, state, academic, and private sector experts to determine which pollutants likely to be found in sewage sludge should be examined closely as possible candidates for numerical limit regulation. These experts screened a list of approximately 200 pollutants in sewage sludge that, if disposed of improperly, could cause adverse human health or environmental effects. The experts were requested to revise the list, adding or deleting pollutants as they deemed necessary. The test for inclusion or exclusion was the potential risk to human health and the environment when sewage sludge containing a particular pollutant was applied to the land, placed in a landfill, or incinerated. EPA also requested that the experts identify the most likely route which a pollutant could travel to reach target organisms, whether

human, plant, or wild or domestic animals. The experts attending the meetings recommended that EPA gather additional information on approximately 50 pollutants.

During 1984 and 1985, EPA collected data and information from published scientific reports on the toxicity, persistence, means of transport, and environmental fate of these 50 pollutants. EPA also developed preliminary information on their relative frequency of concentration in sewage sludge by analyzing the sewage sludge of 43 to 45 POTWs (depending on the pollutant) in 40 cities (27). The sewage sludge data from the "40-city study" (EPA Fate Study) consists of concentrations of 40 pollutants (12 metals, 6 base neutral organic compounds, 6 VOCs, 9 pesticides, and 7 PCBs) in sewage sludge analyzed from the target POTWs.

Using this preliminary information on the relative frequency and concentration of pollutants in sewage sludge, their toxicity and persistence, the pathways by which the pollutants travel through the environment to a receptor organism (plant, animal, or human), the mechanisms that transport or bind the pollutants in the pathway, and the effects of the pollutants on the target organism, EPA made an assessment of the likelihood that each pollutant would adversely affect human health or the environment. For this analysis, EPA relied on simple screening models and calculations to predict the concentration of a pollutant that would occur in surface or ground water, soil, air, or food. EPA then compared the predicted concentration with an Agency human health criterion, such as a drinking water standard promulgated under the Safe Drinking Water Act, to determine whether the pollutant could be expected to have an adverse effect on human health. For purposes of this initial screening, EPA assumed conditions that would maximize the pollutant exposure of an individual, animal, or a plant, as well as the worst possible pollutant-related effects.

Based on the factors previously listed (concentration, toxicity, persistence, and others), EPA scored each pollutant and ranked them for more rigorous analysis. EPA excluded two categories of pollutants for further evaluation. First, EPA excluded

pollutants which, when compared to a simple index, presented no risk to human health or the environment at the highest concentration found in the "40-city study" or in other available data bases. Second, EPA deferred consideration of pollutants for which EPA lacked human health criteria or sufficient data.

On February 6, 1989 EPA proposed the Part 503 Standards for the Use and Disposal of Sewage Sludge (54 Federal Register 5746, 5791-5855). The proposed standards included numerical pollutant limits, management practices, and other requirements that defined a level of control which owners or operators of treatment works and users or disposers of sewage sludge must attain over the use or disposal of sewage sludge in order to protect human health and the environment. EPA proposed pollutant limits, management practices, and other requirements that were specific to the method of use or disposal employed by the treatment works use.

EPA proposed requirements that owners or operators of treatment works and users or disposers of sewage sludge would have to meet whenever they ultimately used or disposed of the sludge. The use or disposal methods included in the proposal were: (1) application to agricultural or non-agricultural land, (2) distribution and marketing (now referred to as sale or give-away of sludge), (3) disposal in monofills, (4) disposal on surface disposal sites, and (5) incineration.

In the preamble to the Part 503 rule, EPA solicited public comment on a wide range of issues contained in the proposed rule. Also, EPA committed to seek and support scientific peer review of the technical bases of the rulemaking package during the public comment period on the proposed rule. The Agency worked with two peer review groups during the public comment period to review in detail the scientific and technical bases of the proposed rule. These two peer review groups were the Land Practices Peer Review Committee and the EPA Science Advisory Board (SAB). In addition to these two peer review groups, EPA received in excess of 5,500 pages of comments from 656 commenters during the 183-day public comment period on the proposed rule.

The public and scientific peer review groups provided a comprehensive range of opinions, comments, and recommendations. Many of the comments were critical of the Agency's risk assessment methodology, the risk levels used by the Agency, the selection of data and parameters used in the exposure assessment analyses, and the impacts the proposed rule would have on beneficial reuse of sewage sludge.

In addition, three data-gathering efforts were undertaken by EPA to obtain information for the final part 503 regulation. They include the National Sewage Sludge Survey (previously discussed in this report), a sewage sludge incinerator study, and a domestic septage sample collection and analytical study. A major finding of the National Sewage Sludge Survey was that levels of heavy metals and organics in sludge had vastly improved in typical wastewater treatment plants since the "40-city study" was conducted in 1978. EPA found that many pollutants were at such low concentrations that they were not detectable, even using advanced analytical methods. Because of the large number of nondetectable readings for organics, extrapolation to higher concentration values for those pollutant would create a high degree of uncertainty in the pollutant concentrations.

On November 9, 1990 the Agency released a notice which made public the findings from these studies and announced the changes they were considering making to the proposed 503 regulation as a result of these studies. Furthermore, the notice requested comments on a number of changes to the use and disposal standards that were being considered for the Part 503 proposal in light of the comments submitted earlier, peer review of the Agency's effort, and new information developed since the 503 regulations were proposed. The 60-day public comment period ended on January 8, 1991. During that time, EPA received more than 1,000 pages of comments from 153 commenters. Many of the comments made by the commenters supported the changes identified in the notice as revisions that the Agency was considering for the final Part 503 rule.

EPA published its Part 503 regulations on February 19, 1993 in the Federal Register (58FR9248). After further analysis of information provided on the proposal and the data from the NSSS, EPA decided not to establish numerical pollutant limits in the final Part 503 rule for certain pollutants which the Agency had proposed to regulate. The final sludge use and disposal regulations establish numerical pollutant limits for 10 metals (arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc) and an operational standard for total hydrocarbons emitted from sewage sludge incinerators. The proposed regulation would have established numerical pollutant limits for 28 inorganic and organic pollutants, as well as total hydrocarbons.

The Agency determined that it would not establish numerical pollutant limits for any pollutant meeting one of the following three criteria:

- (1) The pollutant is banned or restricted by EPA or no longer manufactured or used in manufacturing a product.
- (2) The pollutant is not present in sewage sludge at significant frequencies of detection based on data gathered from the NSSS.
- (3) EPA's risk assessment for the pollutants shows no reasonable anticipated adverse effects on public health or the environment at the 99th-percentile concentration found in sewage sludge from the NSSS.

Fourteen pollutants (previously scheduled to be regulated) met the above criteria and were omitted from the final Part 503 rule. They are: aldrin/dieldrin, benzene, benzo (a) pyrene, Bis(2-ethylhexyl) phthalate, chlordane, DDT (and its derivatives DDD and DDE), dimethyl nitrosamine, heptachlor, hexachlorobenzene, hexachlorobutadiene, lindane, PCBs, toxaphene, and trichloroethylene.

The final Part 503 rule is much more supportive of beneficial use practices. It covers three general categories of beneficial use and disposal practices: (1) application of sewage sludge to land - including farms, gardens, forests, and reclamation users, (2)

surface disposal on dedicated sites or in sewage sludge-only landfills, and (3) incineration at sewage sludge-only incinerators. Although states have the right to regulate sludge under their own authority, the minimum federal standards must be met (47).

The final Part 503 regulation contains ceiling concentrations, cumulative pollutant loading rates, pollutant concentrations, and annual pollutant loading rates. Any sewage sludge that does not meet the ceiling concentrations cannot be applied to land. Other pollutant limits also are included for bulk sewage sludge and for sewage sludge sold or given away in a bag or other container (e.g. compost). Bulk sewage sludge that is applied to the land is subject to cumulative pollutant loading rates if the sewage sludge does not meet the pollutant concentrations for high quality sewage sludge. Sewage sludge sold or given away in a bag or other container is subject to annual pollutant loading rates if it does not meet the pollutant concentrations for high quality sewage sludges.

The preamble to the final Part 503 rule explains that EPA created standards for those pollutants for which it had sufficient information to establish protective numerical limits, management practices, and other requirements. This first stage is identified as Round One. The agency had originally committed to identifying in May, 1993, the additional pollutants it will consider for regulation in Round Two and announcing its schedule for completion of the second stage effort. To date, the Round Two pollutants have not been disclosed.

3.2 Massachusetts Regulations

In the Commonwealth of Massachusetts, regulations for the land application of sewage sludge and septage are contained in the Code of Massachusetts Regulations (310 CMR 32) and are enforced by the Massachusetts Department of Environmental Protection (DEP). The regulations apply to municipalities, individuals, or businesses who desire to land apply sludge and/or septage for beneficial purposes, or to sell or distribute or offer for sale, distribution, or use sludge and septage. These regulations also

apply to compost products. The regulations are intended to allow the land application of sludge and septage for beneficial purposes in a manner that will protect public health and the environment from possible contamination which could occur from pathogens, metals, or toxic chemical compounds.

Concentrations of heavy metals and polychlorinated biphenyls (PCBs) largely govern the classification of sludges in Massachusetts and thus determine sludge disposal options (Table 3-1). Disposal of compost is dictated by the same classification scheme.

Type I sludge may be used, sold, or distributed without State approval and may be used for growing any vegetation. Type II sludge may be used, sold or land applied only with prior DEP approval and may also be used for growing any vegetation. Use, sale, or distribution for land application of Type III sludge requires prior DEP approval and may be used for growing any vegetation except for direct food chain crops. In addition, Type III sludge land application sites must be recorded in the registry of deeds in the chain of title for each site.

Table 3-1 DEP SLUDGE CLASSIFICATION CRITERIA

Component	Type I*	Type II*
Boron	< 300	< 300
Cadmium	< 14	< 25
Chromium	< 1000	< 1000
Copper	< 1000	< 1000
Lead	< 300	< 1000
Mercury	< 10	< 10
Molybdenum ¹	< 10	< 10
Nickel	< 200	< 200
Zinc	< 2500	< 2500
PCBs	< 2	< 10

* all values are mg metal/kg sludge

Sludge is classified as Type III if the concentration of any substance it contains exceeds any limit set forth for Type II sludge.

¹The molybdenum standard is 10 ppm when sludge products are applied to grazing land or on land where forage crops are intended to be grown, but is 25 ppm for other uses, e.g. horticultural.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

Based on the analysis of the information in the literature, the following may be concluded:

- 1) Very few trace organic compounds are found in either raw sludge or finished compost. Compounds which are detected are usually present at extremely low concentrations.
- 2) The concentrations of most trace organic compounds decrease during composting. However, the majority of the compounds are not completely degraded and a residual remains in the compost.
- 3) It is unclear which removal mechanisms account for the losses of individual trace organics during sewage sludge composting. However, the decrease in VOCs is usually attributed to volatilization. Many non-volatile organic compounds are susceptible to biodegradation during composting, although the extent of biodegradation depends upon the particular compound and the rate of metabolic activity in the compost mass.
- 4) Trace organic compounds are not widespread in composted sewage sludge and should not prevent the land application of composted sewage sludge.

4.2 Recommendations

In order to better evaluate the fate of trace organic compounds during sewage sludge composting, the following are recommended:

- 1) Further studies are needed to better understand the intricate relationship between the physical, chemical, and biological processes which occur during composting.
- 2) Better methods to determine the exact routes of trace organic removal in a composting environment need to be developed.

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APPENDIX

EPA List of Organic Priority Pollutants

EPA List of Organic Priority Pollutants (Ref. 95)

Compound Name

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|-----|-------------------------------|-----|--|
| 1. | Acenaphthene | 42. | Bis (2-chloroisopropyl) Ether |
| 2. | Acrolein | 43. | Bis (2-chloroethoxy) Methane |
| 3. | Acrylonitrile | 44. | Methylene chloride |
| 4. | Benzene | 45. | Methyl Chloride |
| 5. | Benzidine | 46. | Methyl Bromide |
| 6. | Carbon tetrachloride | 47. | Bromoform |
| 7. | Chlorobenzene | 48. | Dichlorobromomethane |
| 8. | 1,2,4-Trichlorobenzene | 49. | Trichlorofluoromethane |
| 9. | Hexachlorobenzene | 50. | Dichlorodifluoromethane |
| 10. | 1,2-Dichloroethane | 51. | Chlorodibromomethane |
| 11. | 1,1,1-Trichloroethane | 52. | Hexachlorobutadiene |
| 12. | Hexachloroethane | 53. | Hexachlorocyclopentadiene |
| 13. | 1,1-Dichloroethane | 54. | Isophorone |
| 14. | 1,1,2-Trichloroethane | 55. | Naphthalene |
| 15. | 1,1,2,2-Tetrachloroethane | 56. | Nitrobenzene |
| 16. | Chloeoethane | 57. | 2-Nitrophenol |
| 17. | Bis (chloromethyl) Ether | 58. | 4-Nitrophenol |
| 18. | Bis (2-chloroethyl) Ether | 59. | 2,4-Dinitrophenol |
| 19. | 2-Chloroethyl Vinyl Ether | 60. | 4,6-Dinitro-o-cresol |
| 20. | 2-Chloronaphthalene | 61. | N-Nitrosodimethylamine
(Dimethyl Nitrosamine) |
| 21. | 2,4,6-Trichlorophenol | 62. | N-Nitrosodiphenylamine |
| 22. | Parachlorometa Cresol | 63. | N-Nitrosodi-n-propylamine |
| 23. | Chloroform (Trichloromethane) | 64. | Pentachlorophenol |
| 24. | 2-Chlorophenol | 65. | Phenol |
| 25. | 1,2-Dichlorobenzene | 66. | Bis (2-ethylhexyl) phthalate |
| 26. | 2,3-Dichlorobenzene | 67. | Butyl benzyl phthalate |
| 27. | 1,4-Dichlorobenzene | 68. | Di-n-butyl phthalate |
| 28. | 3,3'-Dichlorobenzidine | 69. | Di-n-octyl phthalate |
| 29. | 1,1-Dichloroethylene | 70. | Diethyl phthalate |
| 30. | 1,2-trans-Dichloroethylene | 71. | Dimethyl phthalate |
| 31. | 2,4-Dichlorophenol | 72. | Benzo (a) anthracene |
| 32. | 1,2-Dichloropropane | 73. | Benzo (a) Pyrene |
| 33. | 1,3-Dichloropropylene | 74. | 3,4-Benzofluoranthrene |
| 34. | 2,4-Dimethylphenol | 75. | Benzo (k) fluoranthrene |
| 35. | 2,4-Dinitrotoluene | 76. | Chrysene |
| 36. | 2,6-Dinitrotoluene | 77. | Acenaphthylene |
| 37. | 1,2-Diphenylhydrazine | 78. | Anthracene |
| 38. | Ethylbenzene | 79. | Benzo (ghi) perylene |
| 39. | Fluoranthrene | 80. | Fluorene |
| 40. | 4-Chlorophenyl Phenyl Ether | 81. | Phenathrene |
| 41. | 4-Bromophenyl Phenyl Ether | | |

82. Dibenzo (a,h) anthracene
83. Indeno (1,2,3-cd) pyrene
84. Pyrene
85. Tetrachloroethylene
86. Toluene
87. **Trichloroethylene**
88. Vinyl Chloride
89. **Aldrin**
90. **Dieldrin**
91. **Chlordane**
92. **4,4'-DDT**
93. **4,4'-DDE**
94. **4,4'-DDD**
95. a-Endosulfan-Alpha
96. b-Endosulfan-Beta
97. Endosulfan Sulfate
98. Endrin
99. Endrin Aldehyde
100. **Heptachlor**
101. Heptachlor Epoxide
102. a-BHC-Alpha
103. b-BHC-Beta
104. **Lindane**
105. d-BHC-Delta
106. **PCB-1242**
107. **PCB-1254**
108. **PCB-1221**
109. **PCB-1232**
110. **PCB-1248**
111. **PCB-1260**
112. **PCB-1016**
113. **Toxaphene**
114. 2,3,7,8-Tetrachlorodibenzo-P-dioxin (TCDD)