Microbiological Degradation of Pesticides in Yard Waste Composting

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INTRODUCTION

The fate, biological degradation, and residual levels of pesticides in yard waste compost are essentially unknown, thereby posing both environmental and health concerns about the use of the composted product. In this article, the term "yard waste" is taken to mean leaves, grass clippings, brush, and other garden residues. The quantity of yard waste material generated by municipalities is considerable. Municipalities such as Montgomery County, Md., estimate that yard wastes make up 18% of the total solid-waste stream (2). In the metropolitan Columbus, Ohio, area, the amount of trash per household averaged 2,540 lb (1.15 metric tons) in 1989. Current trends in solid-waste legislation indicate the need to develop composting processes as alternative treatment technology for yard waste disposal as the landfill options are becoming extinct and prohibitively costly. In the United States, strong impetus for composting by municipalities will be provided through national incentives as part of the amended Resources and Conservation Act, currently pending federal legislation.

There are a number of possible routes of removal of toxic substrates from a compost environment, including mineralization (i.e., complete biodegradation), biotransformation (e.g., dehalogenation), assimilation as nutrient into microbial biomass, polymerization, volatilization, leaching, and sorption. The purpose of this review is to evaluate available information on the biotransformation of pesticides in yard waste. An attempt is made to summarize relevant studies conducted on various types of composts and soil samples and to extrapolate their relevance to yard waste composting.

Yard waste composting is a complex area of technology, encompassing many biological science and engineering disciplines. There is a paucity of technical and scientific information regarding the degradation of pesticides in composting systems, especially yard waste composting. Much of the

published information has been obtained from municipal solid-waste treatment processes or from studies on soil samples. For example, in a survey conducted in Portland, Oreg., a compost product was tested for 19 pesticides. Only 4 of the 19 pesticides were detected, and they were present at extremely low levels (14). With the exception of dicamba, MCPA, dichloroprop, and dinoseb (the chemical names are given in Table 1), all of the tested pesticides were below the detection level of 0.5 ppm. No effort was made to determine the respective concentrations of the pesticides initially present in the yard waste. These findings underline the need for development of analytical methodology for quantitative recovery and identification of pesticides present in complex environmental materials.

The initial concentrations and the fate of pesticides in compost systems remain unknown. Systematic studies of degradative pathways of selected pesticides have not been carried out on yard waste compost samples. Some degradative pathways are known to lead to dead-end metabolites, which may adversely influence the biodegradative abilities of the other microorganisms present. Recent examples of inhibitory interactions between concurrent pathways have been reported for 2,4-D and 2,4,5-T (15).

It is common practice to monitor the microbiological degradation of xenobiotic compounds by determining the residual concentration. However, a decrease in the concentration of the toxic compound does not necessarily mean that the environmental hazard is reduced; instead, it may be converted to other forms which may not be detectable by the standard analytical procedures employed. In a recent study by Racke and Frink (32), this point was aptly demonstrated. Between 2.6 and 4.2% of the initially applied [*naphthyl*-1-^{14}C]carbaryl (an insecticide) was recovered as the parent compound by dichloromethane extraction from the compost at the end of the process. The majority of the ^{14}C was not recoverable by standard extraction but was associated with a fraction from which the label was recovered as $^{14}CO_2$ via combustion. In general, compounds with partitioning coefficients in favor of organic solvents (i.e., hydrophobic com-

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TABLE 1. Listing of pesticides cited in the text

Use and common name	Chemical name
Herbicides	
2,4-D	2,4-Dichlorophenoxyacetic acid
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
MCPA	(4-Chloro-2-methylphenoxy)acetic acid
Mecoprop	2-(4-Chloro-2-methoxyphenoxy)propionic acid
Dichloroprop	2-(2,4-Dichlorophenoxy)propionic acid
Dicamba	3,6-Dichloro-o-anisic acid
Dinoseb	2-sec-Butyl-4,6-dinitrophenyl acetate
Benfluralin	N-Butyl-N-ethyl-2,6-dinitro-4-trifluoromethylalanine
Bensulide	S-2-Benzensulfonamidoethyl-O,O-diisopropyl phosphorodithioate
DCPA	Dimethyl 2,3,5,6-tetrachloro-1,4-benzendicarboxylate
Pendimethalin	N-(1-Ethylpropyl)-2,6-dinitro-3,4-xylidine
Trifluralin	2,6-Dinitro-N,N-dipropyl-4-trifluoromethylalanine
Fungicides	
Benomyl	Methyl 1-(butylcarbamoyl)benzimidazol-2-yl-carbamate
Triadimefon	1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butanone
Insecticides	
Carbaryl	1-Naphthyl methylcarbamate
Diazinon	O,O-Diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate
Lindane	1,2,3,4,5,6-Hexachlorocyclohexane
Malathion	Diethyl (dimethoxyphosphinothioylthio)succinate
Toxaphene	Polychlorocamphane (isomers of octachlorocamphane)

pounds) constitute environmental and health concerns and should be monitored to the level of their conversion to innocuous hydrophilic end products.

A diagrammatic representation and a flow sheet of yard waste composting are shown in Figure 1A and B, respectively. Two methods are widely used for commercial-scale composting of yard waste. These are windrows, in which aeration is controlled by periodic turning of the material, and aerated stati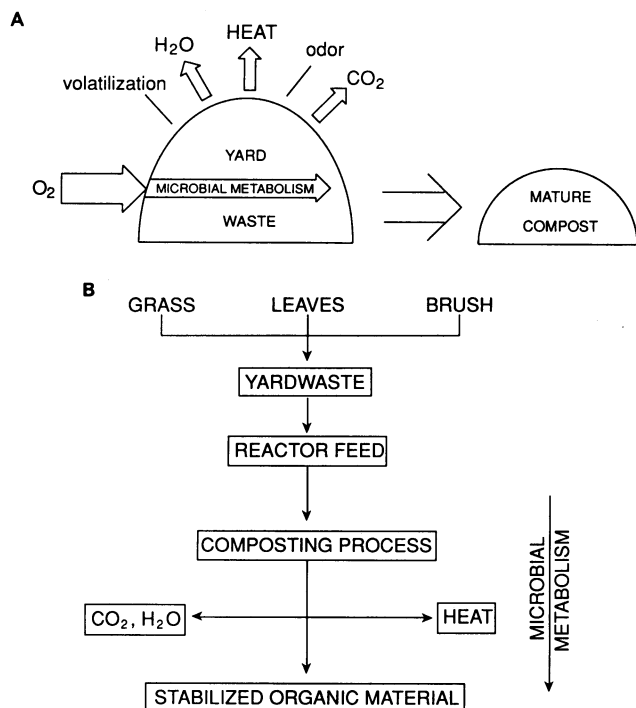c piles, in which air is introduced at controlled rates. The fate of pesticides in yard waste composting is difficult to evaluate because the mass balance and degradative pathways of pesticide residues remain unknown. It may be difficult to separate the microbiological degradation from the abiotic mechanisms of removal (adsorption, thermal conversion, radiation, and volatilization) of pesticides. Volatilization may account for a significant removal of pesticides from composted material, but this may not necessarily involve destruction of the molecule.

Ultimately, the success of composting is based on the microbial transformation of the waste into an environmentally acceptable end product. Current efforts appear to focus on mechanical and engineering optimization of the compost system with a limited appreciation of underlying microbial processes.

OCCURRENCE OF PESTICIDES

In the lawn care industry, herbicides are broadly divided on the basis of their mode of action and the timing of weed control application. They are divided on the basis of their mode of action into systemic herbicides, contact herbicides, and soil sterilants. Systemic herbicides are absorbed by vascular tissue and translocated throughout the whole plant. Treatment with contact herbicides kills plant tissues covered by the chemical. Soil sterilants render the soil toxic to all plant life. Herbicides are divided on the basis of the timing of application into preemergence and postemergence weed control agents (23). Pendimethalin, benfluralin, bensulide, DCPA, and benfluralin plus trifluralin are the most commonly used preemergence herbicides. Pendimethalin has the longest half-life in soil and is probably the most frequently used herbicide in this group. Postemergence broad-leaf control products such as 2,4-D, MCPA, mecoprop, dicamba, and dichloroprop are examples of the second group. The phenoxyherbicides, dicamba, and dichloroprop all have half-lives of up to several weeks in soil.

Insecticides commonly used in lawn care include diazinon, carbaryl, lindane, and malathion. Benomyl and triadimefon are commonly used to control plant-pathogenic fungi and nematodes.

FIG. 1. (A) Schematic diagram of the composting process. (B) Flow sheet of yard waste composting.

The degradative pathways of these target pesticides have not been completely characterized. The biochemical pathways for degradation of some of the above-mentioned pesticides have been concisely reviewed by Wallnöfer and Engelhardt (41).

DEGRADATION

The available information on biochemical pathways of pesticide degradation in composting is extremely scanty. Such information must be generated to determine whether the pesticide residue has been effectively eliminated and not just converted from one toxic form to another, which may not be detectable by the analytical method employed. The metabolites and degradative pathways of some pesticides have not been fully elucidated. Lack of detection of the parent pesticide may be a result of analytical constraints or the formation of intermediates not detectable by the method used. The majority of herbicides tend to be aromatic and hydrophobic, leading to their partitioning into plant tissue. Thus, the use of composted yard waste previously treated with a herbicide or an insecticide formulation is potentially unsafe for use on edible crops.

The susceptibility of pesticides to biological degradation is extremely variable because of differences in molecular structure as well as in chemical and physical properties. Aromatic compounds such as 2,4-D, MCPA, mecoprop, and dicamba are halogenated, and their recalcitrance in the environment varies. High concentrations of pesticides may be inhibitory to the resident microbial community. The threshold concentrations of pesticides needed for induction of the degradative pathways have not been elucidated. Adsorption by soil particles and by other particulates decreases the effective concentration of halogenated organics and may therefore lower the residual concentration below the threshold for enzyme induction.

Factors influencing the microbiological utilization of the adsorbed fraction of organic compounds in soil and compost are largely unknown. Problems of analytical constraints contribute to a situation in which results of many published experiments are obscure and difficult to interpret.

Bellwick et al. (1) examined the degradation of [carboxy-^{14}C]2,4-D at different initial concentrations in prairie soil samples. After 56 days, about 90% of the initial 500 ppm of the substrate was detected, compared with 8% when 10 ppm of 2,4-D was initially applied. Parker and Doxtader (28) reported a direct correlation between the initial 2,4-D concentration (range, 1.3 to 134 ppm) and the length of the lag phase preceding active degradation in fine sandy loam. Measurement of the formation of $^{14}CO_2$ from [U-^{14}C]2,4-D showed that high concentrations (5,000 and 20,000 ppm) of 2,4-D inhibit the degradation of the parent compound in samples of various soil types (27). Thus, elevated levels of pesticides, higher than normally applied in the environment, retard the degradation by native soil microorganisms.

The position of the ^{14}C label is very important if the degradation is monitored by measuring mineralization of the labeled compound. Numerous studies show that the formation of $^{14}CO_2$ from the 1-^{14}C-labeled or the 2-^{14}C-labeled acetate group of 2,4-D is considerably faster than that from the ring-labeled ^{14}C of 2,4-D (34).

The degradation of a pesticide in compost involves biochemical conversions of pesticides by microbial consortia. In nature, microorganisms exist in consortia and seldom as pure or single cultures. These consortia display several interactions, with primary degraders being able to produce metabolites that are capable of supporting the growth of bacteria that cannot use the parent compound. It is a common trend that mixed cultures exhibit more rapid degradation than pure cultures. In some instances, as in the case of mecoprop (20), it is recognized that the degradation of the molecule, at least to the level of ring fission, necessitates mixed cultures. Ring fission occurs more readily under aerobic conditions with a supply of molecular O_2 for oxygenase activity. Composting passes through several stages in which microbial populations are greatly dictated by differences in prevailing temperatures, availability of oxygen, and other ambient environmental determinants (3, 8, 12).

It is common practice in current composting operations to incorporate a product recycle loop to provide an inoculum for the incoming reactor feed. The purpose of this practice, sometimes called natural seeding, is to shorten the time required to reach product maturity. This practice reduces the lag phase. Owing to constant selective pressure, the product recycle loop provides an active microbial community. It includes an inoculum for the thermophilic phase of composting, which otherwise might take a long time to develop from the yard waste.

The degradation of specific pesticides in yard waste by using laboratory-enriched mixed cultures derived from the same source material has not been evaluated. Comparative studies of degradation of recalcitrant materials by using laboratory-enriched cultures and naturally seeded inocula would provide valuable information on the perceived need by some in waste management to resort to bioaugmentation agents, a subject of much controversy and debate (10, 11). It has yet to be established whether microorganisms developed under laboratory conditions are able to compete in the compost environment. The use of enzymes such as cellulases is also highly contentious. Thus, the question of accelerating the composting process by using starter cultures and other bioaugmentation agents remains unanswered.

There is a wealth of information on the biodegradation of pesticides in soil systems (41). However, the degree to which studies carried out with soil systems are applicable to predicting pesticide degradation in the compost environment is not known. Soils typically have a high microbial species diversity. In compost piles, the distribution of microorganisms and the species diversity change in response to temperature.

In a study with mixed compost substrates approximating municipal solid refuse, the microbiological degradation of 59 toxic organic chemicals was evaluated (37). The susceptibility of the toxic chemicals to biodegradation ranged from 83% for the herbicide trifluralin to 4% for the insecticide toxaphene. This study was based on the use of test cells of artificial compost mixture spiked with known concentrations of target pesticides. These test cells were of two designs, one for volatile toxic waste and the other for nonvolatile toxic waste. The cells were enclosed in fine plastic screens and inserted into the compost mixture. It was claimed that the conditions inside and outside the test cells were identical except for the target compounds of interest. Therefore, the contents of the test cells were claimed to be representative of the compost system. This claim has not been validated, and experimental artifacts due to variation in physical parameters such as aeration and moisture caused by the plastic screen are suspected to be present. Owing to the configuration of the pilot-scale compost, the system lost a substantial portion of heat through conduction and thus was not representative of a field-scale pile. In a field-scale compost pile, the major source of heat loss is vaporization. Although the
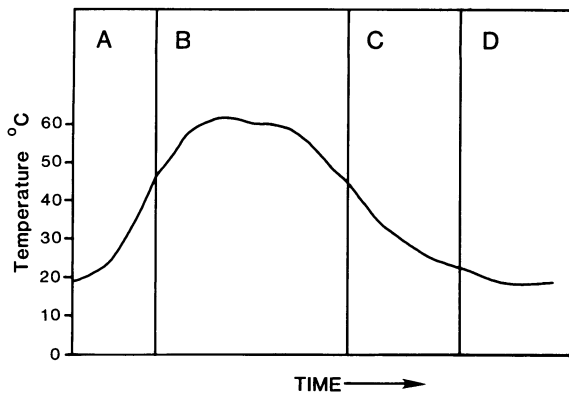
FIG. 2. Temperature-dependent phases of composting. (A) Mesophilic phase; (B) thermophilic phase; (C) cooling phase; (D) maturation phase.

TABLE 2. Distribution of active microorganisms at various temperature phases

Population	Distribution in[a]:			
	Mesophilic phase	Thermophilic phase	Cooling phase	Maturation phase
Eubacteria				
Mesophilic	↑	↓	↑	+
Thermophilic	−	↑	↓	−
Actinomycetes				
Mesophilic	↑	↓	↑	+
Thermophilic	−	↑	↓	−
Multicellular fungi				
Mesophilic	↑	↓	↑	+
Thermophilic	−	↑	↓	−

[a] The arrows indicate either an increase (↑) or a decrease (↓) in the population during each phase; −, no activity; +, slow or minor changes in the population.

biodegradation data presented in the report (37) are system specific and cannot be extrapolated to field-scale systems, the feasibility of composting materials containing hazardous chemicals has been demonstrated.

The distribution of pesticide degradation pathways among bacteria and fungi is varied (33, 41). Common pesticide-degrading bacteria include *Achromobacter*, *Arthrobacter*, *Pseudomonas*, and *Flavobacterium* spp. Fungi known to be able to degrade pesticides include *Aspergillus*, *Henderonula*, and *Penicillium* spp. A problem in investigating the fate of these compounds is that for many pesticides, the degradative pathways have not been elucidated. Some pesticides are known to degrade via several pathways. For example, the microbiological degradation of 2,4-D may proceed via *ortho*- or *meta*-cleavage of the ring, leading to the formation of different downstream intermediates (35). In single cultures, a degradative pathway may lead to a cul-de-sac, representing a partial, nonproductive transformation of the parent and resulting in metabolic constraints on the survival of the culture (5). It is not known whether dead-end metabolites can be subsequently utilized by mixed microbial communities.

COMPOSTING PROCESS

The composting process can be divided into four major microbiologically important phases, which are dictated by the temperature (Fig. 2). These phases may have considerable overlap based on temperature gradients and differential temperature effects on microorganisms. These are (i) the mesophilic phase; (ii) the thermophilic phase; (iii) the cooling phase; and (iv) the maturation phase. There is considerable overlap between the four phases. The composting process is initiated by the microbiological decomposition of organic material at the mesophilic temperature range. Upon active respiration, the temperature within the pile increases to a level which is prohibitive to mesophiles but suitable for thermophiles. This shift is also associated with a decrease in species diversity. The dominant bacteria of the thermophilic phase are spore formers (*Bacillus* spp.); thermophilic fungi have also been found (38). Most of the microbial decomposition and biomass formation take place during the elevated-temperature phase of composting. Compared with the initial mesophilic phase, the rates of degradation are relatively high during this second phase. This was substantiated by mea-

surement of CO_2 evolution rates during thermophilic composting (24). There is a considerable temperature gradient in a compost pile, with the temperature being highest at the center and decreasing toward the outer zones. The third phase of composting is a cooling phase as the amount of readily available organic carbon becomes a rate-limiting factor, causing the microbial activity and associated heat output to decline. During this period, mesophilic organisms become important again, but this time the recolonization is attributed to fungal invasion because their spores can withstand temperature extremes along with lower moisture levels and because of their ability to utilize lignin and waxy fractions. Bacterial reinvasion, including that by actinomycetes, of cooled compost zones remains to be explored. Associated with this question is the ability of mesophilic nonsporeforming bacteria to tolerate temperatures in excess of their own permissive maximum for prolonged periods. The thermotolerance of mesophilic bacteria in compost appears to involve the ability to withstand temperatures in excess of 60°C for several days (25). If the thermophilic phase has been relatively short, involving temperatures prohibitively high for thermophiles, a reheating period may occur after the cooling phase. At this time, a large amount of residual available organic material would still be available for mesophilic microorganisms.

COMPOSTING PARAMETERS

Temperature

Temperature is perhaps the most contentious of all the parameters controlling the rate of composting. Ultimately, the composting process is determined by the temperature profile. Changes in temperature are commonly used as a measure of microbiological activity underlying the composting process. Thus, the temperature profile of composting can be used to determine the stability of organic material.

The distribution of active microorganisms is dictated by the temperature in composting (Table 2). The benefit of elevated temperatures (>60°C) in promoting microbial activity and inactivation of pathogens has been a continual source of debate and controversy. The key period of the composting process is based predominantly on microorganisms which grow in the temperature range from 25 to 60°C, i.e., mesophilic (<45°C) and moderately thermophilic (40 to 60°C) organisms. Elevated temperatures (>60°C) lead to increas-
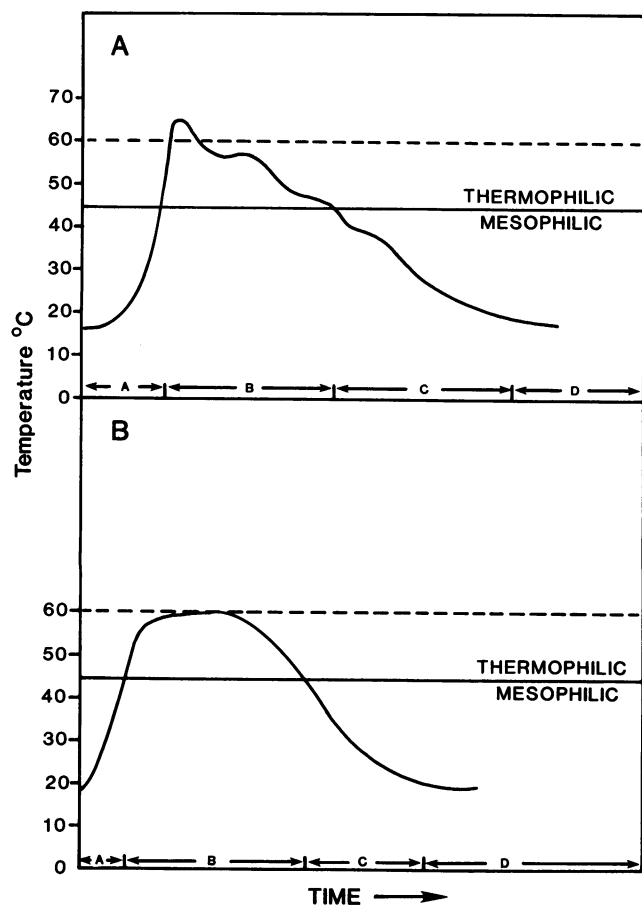
FIG. 3. Simplified temperature profile in a windrow composting process (A) and an in-vessel system (B). The time scale is arbitrary, demonstrating the relative time course of temperature change during composting.

TABLE 3. Relative distribution of microorganisms from plating of solid-waste materials during laboratory composting at five different temperature ranges[a]

Microbial group	% Distribution[b] of microorganisms among groups:				
	I (49–55°C)	II (50–57°C)	III (55–61°C)	IV (60–65°C)	V (65–69°C)
Fungi[c]	–	–	17	–	–
Actinomycetes	12	2	+	–	–
Bacillus spp.	23	77	78	100	83
Nonsporeforming bacteria					
Pseudomonas-type	17	21	–	–	–
Arthrobacter-type	47	+	+	–	–

[a] Data are summarized from previously published data (38, 39), with permission.
[b] Symbols: +, present in small numbers; –, not found.
[c] Based on Aspergillus fumigatus.

It is now generally agreed that the temperature of the composting process should not exceed 60°C to avoid rapid thermal inactivation of the desired microbial community. Nakasaki et al. (26) showed that the optimum temperature for microbial activity was below 60°C. This finding is in keeping with results of several other studies. The recommended temperature of <60°C is based on experimental data which demonstrate adverse changes in microbial activity (18, 21), amount of biomass (21), and species diversity (38) in response to elevated temperatures. Owing to the dynamic nature of composting process, nutritional fluxes continuously change concurrent with substrate depletion. Thus, it is difficult to evaluate the relationship between microbial activity and temperature at any given time point.

In an experimental study of compost made from shredded paper and food scraps, Strom (38, 39) found that only few bacterial species remained active at temperatures above 60°C; those that survived were predominantly Bacillus spp. (Table 3). Fungi were found only in the narrow temperature interval from 55 to 61°C (Table 3), but the data were limited to the recovery of one Aspergillus species. Nonsporeforming bacteria were broadly categorized in two groups (Pseudomonas and Arthrobacter types), which were found at temperature intervals as high as 50 to 57°C. Colonies which did not grow upon subculture amounted to 17% of the total number of colonies at 63 to 69°C (38). These changes, although not documented for composted yard waste, serve to illustrate that major changes in microbial communities occur as the temperatures vary during the different phases of composting.

There is an appalling paucity of information available on the influence of temperature on the microbiological degradation of pesticides. Soil studies reported heretofore have utilized incubation temperatures at the mesophilic range; thus the role of thermophilic organisms in pesticide degradation remains obscure. Clearly there is an urgent need to investigate the influence of temperature on pesticide degradation in yard waste. Knowledge of the effect of temperature on pesticide biodegradation in yard waste materials would be an important step in disposing of yard wastes safely and efficiently. Moreover, the role of temperature in influencing the physical removal of pesticides via volatilization has yet to be investigated.

ingly rapid thermal inactivation of mesophilic microorganisms (42). Moderately thermophilic microorganisms are more thermotolerant to superoptimal temperatures. Although elevated temperature results in the destruction of pathogens, it also reduces the level and activities of desired microorganisms that are important in the composting process. It was only in the last decade that the role of heat and elevated temperature has been elucidated (6, 7, 18, 19, 21).

Figure 3 shows a simplified temperature profile of two composting processes, a windrow system and an in-vessel operation. Figure 3A represents the temperature profile of a windrow system that has not been turned. In this system, there is an initial burst of microbial activity and heat generation to a point at which the temperature becomes prohibitive to microbial activity, thereby causing a decline in activity and a concomitant decrease in the temperature. If the pile was turned, secondary peaks of microbial activity and heat output would be observed. However, the temperature profile would be similar to that depicted in Fig. 3A, with a cooling phase and a maturation phase. The in-vessel system represents a more controlled process as a result of an extended optimum thermophilic phase, as depicted in Fig. 3B. The in-vessel system is based on controlled temperature ascent, plateau, and descent, thereby effectively preventing excessive heat generation during the thermophilic phase.

Aeration

Composting is concerned primarily with the biological oxidation of organic waste material of recent origin via microbial metabolism to a stabilized organic residue. The process is associated with the production of heat, microbial biomass, CO_2, and H_2O. It is desired that the composting process be based on aerobic decomposition, and thus the availability of oxygen to the compost process is of prime importance.

The microbiological decomposition of pesticides in topsoils occurs largely via aerobic metabolism. For aromatic pesticides, ring activation and fission involve oxygenase activities to produce central metabolites. Mechanisms for anaerobic degradation of toxic organic compounds involve reductive dehalogenation before ring activation (33, 40, 41). Reductive dehalogenation in anaerobic microcosms in composts has yet to be documented.

Aeration has multiple functions: (i) it supplies O_2 to support aerobic metabolism (oxygenase functions and aerobic respiration); (ii) it controls the temperature; and (iii) it removes moisture as well as CO_2 and other gases. Insufficient aeration promotes the formation of anaerobic zones and the generation of foul odors, whereas excessive aeration limits microbial activity as a result of the reduced moisture and associated cooling.

According to De Bertoldi et al. (4), the O_2 content in the circulating air should not fall below 18% in windrows, although there are few experimental data to support this value. This value is the same as the regulated level of oxygen for operator safety as specified by the Occupational Safety and Health Act in the United States.

Jeris and Regan (17) suggested that 30 to 36% free air space is required to obtain adequate aeration for composting for a wide variety of materials. Free air space is a derived parameter, calculated on the basis of moisture. A study has yet to be reported to determine the rate of composting in relation to variation in the free air space of compost.

There have been some attempts to develop a mathematical relationship between oxygen consumption rates and the temperature for composting processes. The validity of these equations has been questioned (13) because the derivation of such relationships assumes constant rates under isothermal conditions. Because of the dynamics of composting, the oxygen consumption rates change during the process and therefore rate estimates may be valid only for limited periods. Because of the method of determining rates by instantaneous rate measurements, it is difficult to calculate rate constants for these systems.

Although modern composting systems are designed for aerobic processes, anaerobic zones inevitably exist, regardless of the aeration system used, as a result of microsites and the nature of the reactor feed. An understanding of the aeration requirements leading to optimal pesticide destruction is critical. The porosity of the reactor feed, i.e., the free air space and the ability to withstand compaction, dictates aeration rates. It was recently reported (43) that if grass clippings are composted alone, they rapidly become anaerobic. When grass is mixed with leaves, anaerobiosis is effectively prevented by the increased air space of the reactor feed. However, in practice this observation is not necessarily true, as matting of the leaves tends to occur. Research is needed to determine optimum proportions of components in yard waste to attain the best composting rates.

pH

Optimal pH values for composting range from pH 5.5 to 8.0. Bacteria favor a near-neutral pH, whereas fungi favor an acidic pH range. The pH of the yard waste composted in the Portland, Oreg., study ranged between pH 5.8 and 7.2 (14). 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.

The pH changes in yard waste are sequential. Initially the pH is acidic as a result of degradation of the cell sap of the plant residues. The pH drops further as a result of acid-forming bacteria. It then increases and becomes alkaline and finally drops back to near neutral as a result of humus formation. The pH-buffering capacity increases as a result of humus formation (31).

Moisture

The moisture content of compost varies depending on the porosity of the reactor feed, free air space, aeration, temperature, and other related physical factors. Moisture in this context is defined as weight loss after the sample has been dried to constant weight at 100 to 110°C. Water activity, which specifically addresses the available water for microbial activity and for chemical reactions, is not commonly used to describe water relationships in composting. The optimal moisture in composting also depends on the strength of the reactor feed to withstand compaction which changes physical characteristics of compost layers, ultimately resulting in decreased aeration and microbial activity.

Excessive moisture inhibits aerobic metabolism as a result of oxygen diffusion limitations; conversely, a lack of water also impedes composting. The optimal moisture content in composting has been empirically determined to range between 50 and 60% for bacteria (9, 30). Bacterial metabolic activity is severely inhibited when the moisture content drops below 40%. Fungi have a lower moisture threshold. Snell (36) showed that oxygen uptake during composting at moisture levels below 30% was approximately 15% of that at 55% moisture. Miller (22) used water potential to characterize the composting process. He stated that at water potentials below −20 kPa (about 60% moisture), bacteria progressively failed to colonize the compost mass. However, the term "water potential" was ill defined, and its significance remains obscure. Furthermore, the conclusion was not supported by the experimental data presented in the paper. Above 60% moisture, a compost pile tends to become anaerobic and hence emits foul odors (31).

C/N Ratio

The optimal carbon/nitrogen ratios for the microbiological decomposition of organic material in composting processes has been reported to be in the range of 26 to 35 (30). In general, this range is similar to that reported for agricultural soils. The underlying biological basis of the optimal ratio is obscure. Microbial biomass, on a dry weight basis, contains approximately 50% C and 10 to 14% N. Allowing for respiration (i.e., carbon substrate as the electron donor), the optimal ratio may reach values as high as 30 as reported for composting. Grass clippings have an elemental C/N ratio of about 20, and leaves have a ratio between 40 and 80 (30). If the C/N ratio is low, as is the case for grass clippings, the microbiological degradation leads to excess ammonia formation, which increases the pH and thereby enhances ammonia

volatilization. Conversely, if the C/N ratio is too high, the process becomes nitrogen limited. Nitrogen limitation and its effects need to be better documented for composting systems. Besides 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 thereby retard the microbial activity. The C/N ratio is not constant during composting because of the removal of carbon as CO_2 upon microbial respiration. It is not clear whether nitrogen fixation contributes to the nitrogen mass balance, especially under high C/N conditions. The effect of C/N ratios on pesticide degradation in soils and composting systems has not been elucidated.

VOLATILIZATION

This environmental factor is frequently overlooked as a route of removal of substrates. In bench-scale studies, volatilization has been shown to represent a major route of substrate removal for certain pesticides. In many instances it is extremely difficult to single out the role of volatilization as a route of removal of the test compound owing to the lack of carefully controlled experimental conditions. The volatility of parent pesticides differs from that of their degradative intermediates. The question also remains whether the mere decrease in the concentration of a compound in the sample material is sufficient evidence that the environmental hazard has been effectively eliminated. An alternative possibility is that the compound is translocated to another environmental compartment, in this case air, thereby contributing to air pollution and potentially posing a health hazard in a confined working space. Detailed analysis of volatilized products must be performed to determine whether they constitute a health risk.

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 (37), 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 absorption 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 volatile compounds must be improved.

In a study of a mixture of cattle manure and sawdust carried out by Petruska et al. (29), about 50 and 21% of the insecticides chlordane (^{14}C labeled) and diazinon (^{14}C-labeled), respectively, were recovered as volatile organic material by entrapment in polyurethane foam during 3 weeks of composting under aerobic conditions. In this study, the temperature of the compost was maintained at 35°C for the first 24 hours and then raised stepwise over 6 days to a final temperature of 65°C, which was maintained for the rest of the experiment. Attempts to characterize the volatile organic material by thin-layer chromatography indicated that little transformation of chlordane had taken place. In contrast, transformation of diazinon was substantial during the composting process.

BIOAVAILABILITY OF PESTICIDES

Pesticide residues in reactor feed may not be readily available for microbiological attack for a variety of reasons. Exoenzymes involved in pesticide degradation have not been reported to date. Active degradation of a pesticide molecule is an intracellular event, and thus the entry into the cell is a necessary prerequisite for degradation. 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 are characteristic for each pesticide. Active uptake systems associated with the microbiological degradation of pesticide molecules with aromatic rings have not been described.

As a rule, pesticide-degrading bacteria exhibit preferential utilization of sugars and organic acids which are readily metabolized through common intermediate pathways to yield tricarboxylic acid cycle metabolites. It is commonly observed that the ability to degrade pesticides is mediated by plasmids and possibly other mobile genetic elements (e.g., transposons). Therefore, the inability to degrade pestides may be due to physical loss of the plasmid or transposon because of the lack of selective pressure when the organisms are presented with an alternative substrate. The possibility of catabolite repression has yet to be elucidated. It has yet to be established which carbon substrates in an active composting phase exert regulatory control over the enzymes of relevant pathways for the degradation of pesticide residues.

Pesticide concentrations in free solution may be low, although total concentrations may reach high levels as a result of sorption of pesticide residues and their metabolites by soil particles. Sorption may render these compounds unavailable for microbiological degradation or at least slow the rate of degradation. In general, sorption isotherms of pesticides in relation to their availability to microorganisms are poorly understood and have yet to be experimentally addressed in the context of composted material. Associated with these problems is the physical entrapment of pesticides in sites which are effectively protected from microbial invasion and colonization, thereby providing microsite protection. Compost provides a large surface area which displays various surface-catalytic effects that influence microbiological processes. In nature, bacteria readily colonize surfaces and form biofilms which actively take part in bioconversions through fluxes with the surrounding media. The investigation of these interplays should also shed some light on the importance of operational parameters such as particle size and morphology of the reactor feed.

RESEARCH NEEDS

The extrapolation of results from laboratory- and pilot-scale composters to demonstration- and commercial-scale systems awaits validation. Commonly, conditions in bench- as well as pilot-scale operations are maintained at near-optimal level. Such levels of control are seldom available in commercial-scale systems. Controlled demonstration-scale experimentation is difficult and expensive to perform, especially if accurate mass balances are required. Consequently, there is a need for a bench-scale composter that can accurately simulate the pilot- and demonstration-scale environment. A major technical problem in reproducing large-scale conditions is the simulation of the thermal profile.

Numerous bench-scale systems have been developed (16, 29). One fundamental difference between bench- and large-

scale systems is the route of heat loss. In a bench-scale compost system, most of the heat is lost by conduction because of the large surface-to-volume ratio, and by minimization of the role of ventilation-induced vaporization. In a commercial-scale pile, heat is lost predominantly via ventilation vaporization of water. Since conduction does not remove water vapor, whereas ventilation vaporization does, a bench-scale system should be designed to shift the mechanism of heat loss from conduction to ventilation. This goal can be partially achieved by placing the bench-scale composter in a controlled-temperature environment. An associated problem is that it has not been possible to maintain the conductive heat flow at reasonably constant levels (16).

An inherent problem with all the bench-scale compost systems developed to date is the compression of a 2- to 3-m-high field-scale pile into a roughly 0.5-m-high laboratory-scale system. Thus, the validity of accurate simulation of the vertical field scale gradient is questionable. Although this has not experimentally validated, it may be possible to overcome this problem by operating laboratory-scale composters in tandem. The first system would represent the lower part of the pile, and the second would represent the high-temperature top half of the pile.

Standardization of experimental and analytical approaches is needed to evaluate composting technology for the treatment of hazardous waste. A related problem is the lack of a standardized reactor feed which would enable experimental data to be verified accurately in different laboratories. Without standardization and calibration, attempts to determine pesticide mass balances in yard waste will be difficult. The level of analytical methodology used in yard waste composting studies is insufficient to meet the scientific criteria of reproducibility, and the scientific principles underlying the composting process have yet to be fully recognized.

Compost reactor feed is not homogeneous and poses several analytical problems in representative sampling and recovery of pesticides from the material matrix. Yard waste composting represents an exciting and viable option for reducing the burden on rapidly diminishing landfill space. Treatment of waste materials by composting is also attractive in hazardous waste management. It is obvious that the research and development effort in composting requires an integrated multidisciplinary approach. Without an insight into the microbiological, chemical, and physical complexity of these processes, advances in this area of waste treatment are likely to remain at the level of phenomenological observations instead of endeavors to optimize and control the process.

ACKNOWLEDGMENTS

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