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Fate of Organic Contaminants during Sewage Sludge Composting

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Disposal of municipal sewage sludge in an environmentally sound manner has become increasingly difficult. Although most wastewater treatment sludge is now incinerated or landfilled, there is renewed interest in composting this organic waste as a means of recycling. Composting involves the aerobic degradation and stabilization of organic materials by thermophilic microorganisms under controlled conditions (Poincelot 1975). The Beltsville aerated-pile method, which is the most common technique in use, involves the construction of windrows of mixtures of sludge and woodchips through which air is drawn with blowers to maintain aerobic conditions during a 3 week to 3 month composting cycle (Willson et al. 1980). Over 100 municipalities are currently composting their sewage sludge and interest is steadily increasing (Goldstein 1987). The resultant compost products are used as soil conditioners for horticultural and agricultural purposes.

Municipal sewage sludge contains various pathogenic microorganisms and inorganic and organic chemical contaminants that raise concerns about land application of sewage sludge compost. A chemical survey of U.S. sewage sludges reported the routine occurrence of many of the priority pollutants (USEPA 1982). Some classes of organic chemicals commonly detected in this study were polyaromatic hydrocarbons (PAH), pesticides, halogenated hydrocarbons, phthalate esters, and industrial solvents. Although the fate of pathogens and heavy metals during composting of sewage sludge has received much attention (Nell et al. 1983; Lutz 1981), little research has focused on the fate of organic contaminants in compost.

The purpose of this investigation was to examine the fate of two representative organic contaminants, the polyaromatic hydrocarbon phenanthrene and the pesticide carbaryl, during composting of municipal sewage sludge. A laboratory composting apparatus was employed in order to control composting conditions and to facilitate complete recovery of the compounds studied.

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MATERIALS AND METHODS

A benchtop laboratory compost apparatus was used that has been found to accurately simulate Beltsville aerated-pile composting conditions (Sikora et al. 1983; Sikora and Sowers 1985). This apparatus consists of a water bath in which an airtight stainless steel chamber is immersed. Material to be composted is placed inside a stainless steel basket suspended within the immersed chamber. Compressed air is passed through the chamber at 60-70 cu cm/min and exhaust gas is passed through a condenser to remove water, through a polyurethane foam plug to trap volatile organics, and then scrubbed through a 3*N* NaOH trap for CO_2 collection. A differential temperature control unit monitors the temperature of the composting material and water bath via thermistors, and holds the temperature of the bath 1°C lower than the compost by means of a recirculating heater.

A dewatered mixture of primary and secondary digested sewage sludge (17-21% solids) was collected from the Bristol, CT wastewater treatment plant. The sludge was mixed with woodchips that had passed a 12 mm screen, in a 1:1.6 (v/v) ratio to an initial moisture content of 55-58%. The volatile organic compound content of the sludge was measured by loss of residue upon ignition at 400°C and ranged between 73 and 78%. The average pH of the sewage sludge was 5.8. Trapped CO_2 was determined after precipitation of $BaCO_3$ by titration of excess basicity with 1.2*N* HCl.

Radiolabelled 9-^{14}C-phenanthrene and naphthyl-1-^{14}C-carbaryl were obtained from Amersham Corporation and Sigma Chemical Company, respectively. Radiolabelled compounds were diluted with nonradioactive chemical prior to use, and were of greater than 98% radiopurity when used.

Initial sludge-woodchip mixtures of 1 kg were treated separately with either 1.3-1.6 ppm (dry wt) of ^{14}C-phenanthrene (5.0-5.4 μCi) or 1.8-2.2 ppm of ^{14}C-carbaryl (5.2-6.5 μCi) impregnated on 15 g of fine sand and incubated in the laboratory composters. Aliquots of initial mixtures were taken for determination of initial radiocarbon. In all experiments compressed air was drawn through the apparatus except experiment Car-3, during which air was replaced for 12 hours a day with O_2 for days 2-10 of composting. The maximum temperature of the water bath was set at 70°C except for experiment Phe-3, for which the maximum temperature was 55°C. In conjunction with experiments Car-2 and Car-3, 22 g of initial sludge-woodchip mixture was also incubated at a constant temperature of 25°C in a biometer flask in duplicate (Bartha and Pramer 1965).

Aliquots of sludge-woodchip mixtures that had composted in the laboratory for 18-20 days and aliquots of initial mixtures were freeze-dried and subject to soxhlet extraction for 22 hr with 300 mL of dichloromethane. Unextractable ^{14}C residues in the mixtures were determined by combustion to $^{14}CO_2$ in a Harvey Biological Oxidizer. The dichloromethane extracts were concentrated and cleaned up for further analysis on a gel permeation column (GPC) (2.5 x 60 cm) containing Biobeads S-X3 (Lopez-Avila et al. 1981). At a flow rate of 5 mL/min of dichloromethane, high molecular weight humic substances and pigments eluted very quickly (20-35 min) while the low molecular weight fractions containing phenanthrene and carbaryl eluted at 43-45 and 37-39 min, respectively. The appropriate solvent fraction was again concentrated, transferred to acetonitrile, and then analyzed by HPLC using a Milton Roy CM4000 pump and UV detector set at 254 nm. Samples were injected at a flow rate of 1 mL/min onto a Spherisorb ODS-2 column (0.4 x 25 cm). The retention times for phenanthrene (85% acetonitrile: 15% water) and carbaryl (65% acetonitrile: 35% water) were 6.5 and 3.9 min, respectively. Radiocarbon in CO_2 traps, concentrated soxhlet extracts, GPC column eluent fractions, and HPLC column eluent fractions was determined by liquid scintillation counting.

RESULTS AND DISCUSSION

Laboratory composting experiments resulted in composting periods of from 18-20 days before return to ambient conditions. As shown in Figure 1, there was a rapid initial increase in compost temperature to thermophilic conditions in all experiments. All compost cycles except Phe-3, during which the maximum temperature was limited to 55°C, were characterized by a drop in temperature after 6-9 days, and a brief recovery to thermophilic temperatures before return to ambient temperatures. An explosive production of CO_2 was observed concomittantly with the initial rise in temperature to thermophilic conditions (Figure 1). Except in the experiment in which temperatures were limited to 55°C, secondary CO_2 evolution peaks coincided with thermophilic temperature recoveries. The temporary drop in temperatures during the composting experiments was preceded by a fall in CO_2 output. The cause of these temporary decreases in temperature and CO_2 output was probably a decline in microbial composting activity resulting from the excessively high initial composting temperatures, as was observed by Suler and Finstein (1977) and McKinley and Vestal (1985). Exhaust gas analysis revealed that anaerobic conditions were not experienced during laboratory composting, and less than 18% of the oxygen flowing through the compost was depleted. Approximately 75% of an added dose of 10 ppm of U-^{14}C-glucose was mineralized to $^{14}CO_2$ during an 18-day composting cycle, providing evidence of sufficient oxygen during composting for microbial activity. The finished compost was quite dry and odor-free, with loss of 1.6-5.7% of the initial dry weight and 30.9-43.0% of the initial wet weight. The composting parameters measured suggest that the laboratory compost apparatus provided a reasonable simulation of field composting conditions (Willson et al. 1980).

Analysis of the finished composts revealed that between 89 and 93% of the initially applied phenanthrene persisted unchanged. This is rather surprising because phenanthrene is the most biodegradable PAH, with a reported half-life in soil and sediment of 26 days and 28-126 days, respectively (Sims and Overcash 1983; Heitkamp and Cerniglia 1987). Previous work has shown that 93% of the less degradable PAH benzo(a)pyrene persisted through a municipal trash

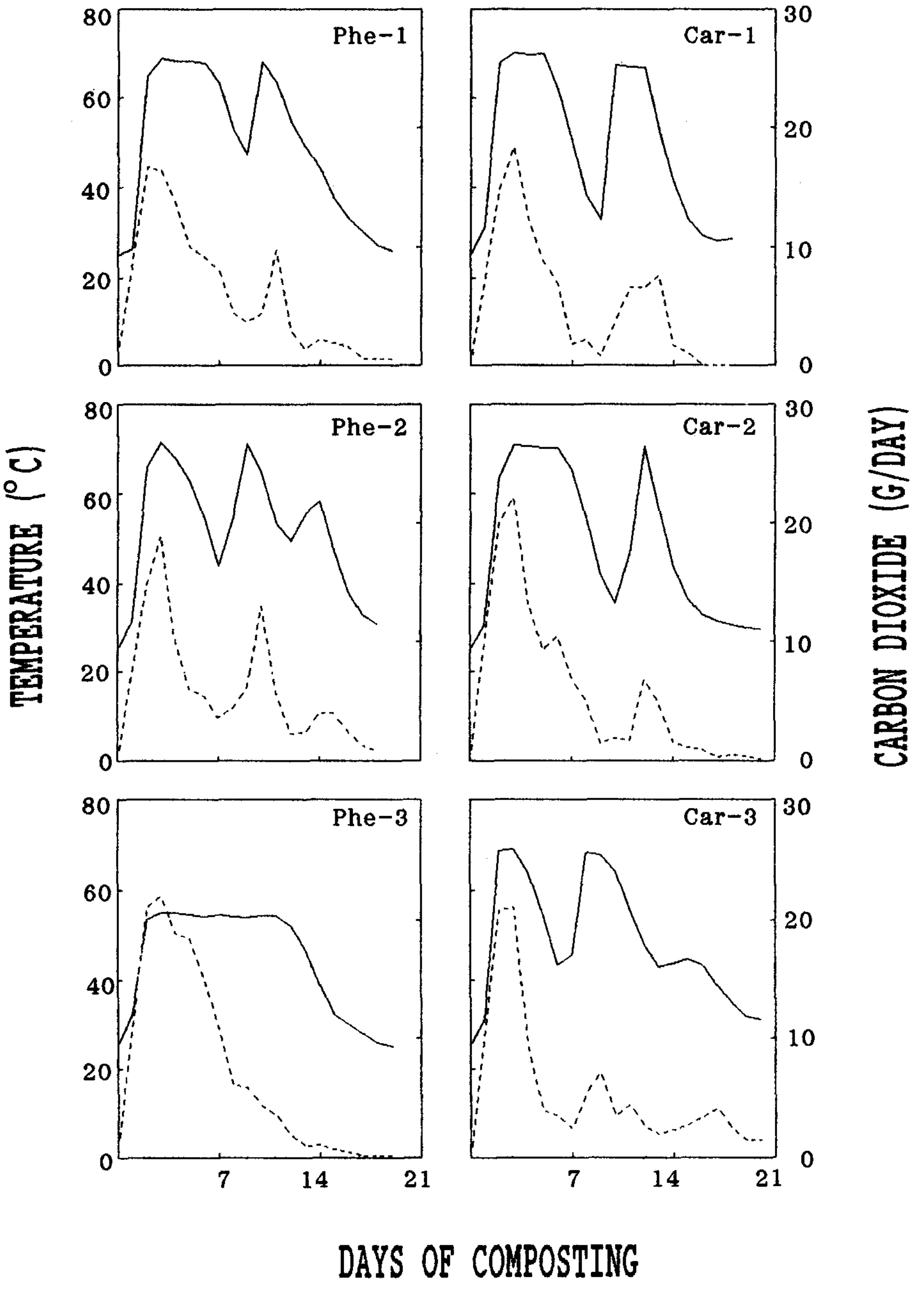

Figure 1. Laboratory composting temperature and carbon dioxide profiles. (__________) (--------)

Table 1. Composting conditions and the fate of ^{14}C-phenanthrene and ^{14}C-carbaryl during composting of sewage sludge.

PHENANTHRENE	Phe-1	Phe-2	Phe-3
composting conditions			
Phenanthrene ppm	1.3	1.6	1.5
Initial mix pH	6.3	6.2	6.2
Aeration gas	Air	Air	Air
Maximum temperature (°C)	69.0	71.4	55.0
% Dry weight loss	5.7	1.6	5.3
% Wet weight loss	37.2	34.2	43.0
CO_2-C evolved (g)	32.2	28.3	36.2
^{14}C recovered in % of applied ^{14}C			
Extractable Phenanthrene	92.8	90.9	89.8
Unextractable	14.7	15.1	16.9
$^{14}CO_2$	0.9	0.4	0.8
Total	108.4	106.4	107.5

CARBARYL	Car-1	Car-2	Car-3
composting conditions			
Carbaryl ppm	2.2	1.8	1.9
Initial mix pH	6.4	6.3	6.3
Aeration gas	Air	Air	Air/O_2
Maximum temperature (°C)	70.3	70.9	69.0
% Dry weight loss	1.8	2.7	3.4
% Wet weight loss	30.9	35.5	31.0
CO_2-C evolved (g)	24.5	30.4	46.2
^{14}C recovered in % of applied ^{14}C			
Extractable	4.2	2.8	2.6
Carbaryl	<0.1	<0.1	<0.1
Unextractable	92.5	97.3	96.0
$^{14}CO_2$	1.6	4.9	4.6
Total	98.3	105.0	103.2

composting cycle (Muller and Korte 1975). Very little mineralization of phenanthrene occurred in the present composting experiments, and $^{14}CO_2$ formation represented <1% of applied phenanthrene. However, quantities of unextractable metabolites remaining in compost ranged from 14.7-16.9% of applied ^{14}C. These unextractable residues were reported by Heitkamp and Cerniglia (1987), who noted their formation from phenanthrene in sediment, to "represent residues which were either irreversibly bound to organic matter or permanently incorporated into sediment microorganisms".

Phenanthrene was just as persistent in the compost from the experiment in which temperatures were limited to 55°C (Phe-3). Hogan et al. (1988) reported >87% 'disappearence' of three PAH, phenanthrene, fluoranthene, and pyrene, during 35 days of laboratory sewage sludge composting at 50°C. However, the object of their study was the destruction of hazardous wastes not the fate of environmental contaminants, and they therefore used an unusually high aeration rate of 5,000 cu cm/min/kg compost, a high initial PAH concentration of 1000 ppm, and a microbial compost inoculum that had been acclimated to these PAH for up to 7 months.

In the case of carbaryl, only 2.6-4.2% of the initially applied ^{14}C could be extracted from the compost at the end of the composting cycle (Table 1). In all cases, less than 0.1% of the applied carbaryl was recovered in this extract. Nearly all of the extractable ^{14}C residues eluted from the GPC cleanup column with the high molecular weight humic material, indicating that this residue represented covalently bound ^{14}C incorporated into the soil organic matter. Between 1.6 and 4.9% of the applied carbaryl was mineralized to $^{14}CO_2$ during composting. The great majority of applied ^{14}C was recovered as unextractable residue remaining in the compost. Previous studies have demonstrated that the hydrolysis product of carbaryl, 1-naphthol, can become covalently bound to soil organic matter (Sjoblad and Bollag 1977). In most soils, however, only 5-11% of applied carbaryl becomes unextractable, with between 23 and 81% completely mineralized to $^{14}CO_2$ (Racke and Coats, 1988). The much greater proportion of organic matter in compost may encourage the formation of these unextractable residues.

To determine whether oxygen limitation played a role in the lack of complete mineralization of carbaryl, one composting experiment was conducted (Car-3) with air containing elevated levels of oxygen. Although this resulted in much greater production of CO_2 compared to experiments in which compressed air was used, there was no significant increase in the production of $^{14}CO_2$ (Table 1). It is also possible that the microorganisms active in mineralization of carbaryl are not active at the elevated temperatures experienced during composting. Incubation of sludge-woodchip mixtures treated with ^{14}C-carbaryl at 25°C resulted in the recovery of 18.6% of applied ^{14}C as carbaryl, 48.2% as unextractable residue, and 16.9% as $^{14}CO_2$. Thus, mineralization of carbaryl was much greater at ambient temperatures than at composting temperatures. Finstein et al. (1983) reported that at composting temperatures above 61°C microbial species diversity drastically decreased. The microorganisms involved in mineralization of carbaryl may be members of the compost community that cannot withstand or remain active at extremely high temperatures.

The pathway of degradation may determine which compounds are degraded during composting and to what extent they are mineralized. Phenanthrene was very persistent during sewage sludge composting, and it has been shown that its microbial metabolism is initiated by an oxidative reaction (Cerniglia 1984). In contrast, carbaryl was very non-persistent during composting, the first reaction in its microbial metabolism being a hydrolytic one (Rodriguez and Dorough 1977). Diazinon, a pesticide that is also subject to an initial hydrolysis during microbial metabolism, was reported to be extensively degraded during composting of dairy cow manure (Petruska et al. 1985). Future research is needed to discern the types of degradative reactions that readily occur during composting, and also to differentiate between biological and chemical routes of degradation.

In conclusion, it appears that some pollutants will persist through the composting process to appear in finished composts that are applied to soil. Martens (1982) treated finished trash composts with several PAH and found that extensive mineralization of these pollutants occurred at ambient temperatures. Thus, it may also be important to consider the fate of organic contaminants in compost-amended soils.

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