Identification of the key factors affecting composting of a weathered hydrocarbon-contaminated soil

N. Beaudin, R.F. Caron, R. Legros, J. Ramsay & B. Ramsay*
*Department of Chemical Engineering, École Polytechnique de Montréal, C.P. 6079, Succursale Centreville, Montréal, Québec, Canada, H3C 3A7 (*author for correspondence, e-mail: ramsayb@chee.queensu.ca)*

Abstract

The effects of the C/N ratio, $CaCO_3$ and PO_4 addition, and temperature profile on reactor-based composting of weathered hydrocarbon-contaminated soil were evaluated in a series of 30-day tests in temperature-controlled mini-composters. Soil containing 17,000 mg (kg dry soil)$^{-1}$ mineral oil and grease (MOG) was composted with maple leaves and alfalfa. Although the leaves and alfalfa also contained MOG, degradation of contaminated soil derived MOG (total MOG degradation minus MOG degradation in a control with no soil) increased from 0 to 45% as the quantity of co-substrate increased from 0 to 63%. Simulation of biopile conditions (i.e., aeration and addition of mineral salts but no co-substrate) resulted in only 6% MOG degradation. Addition of $CaCO_3$ before composting increased total MOG degradation from 23% to 43%. Total MOG degradation increased with decreasing C/N ratio. At a molar C/N ratio of 17, 43% of the total MOG was degraded in 30 days, while at a C/N ratio of 40 there was no total MOG degradation. When temperatures ranging from 23 to 60 °C were investigated, 50 °C maintained for 29 days resulted in the maximum degradation which was 68% of total initial MOG.

Introduction

Composting can be used as a bioremediation technique by mixing contaminated soil with traditional composting substrates such as yardwaste and sewage sludge. This mixture may be treated in a windrow or in an enclosed reactor. Microorganisms consume the supplied substrates as well as the contaminants, possibly by co-metabolism. Many hazardous wastes have been converted to innocuous end-products in this manner. These include polynuclear aromatic hydrocarbons (PAHs), chlorophenols, and explosives such as 2,4,6-trinitrotoluene (Hogan et al. 1988; Valo et al. 1986; Williams & Myler 1990). Beaudin et al. (1996) demonstrated that composting resulted in degradation of 77% of the mineral oil and grease (MOG) of a weathered, petroleum-hydrocarbon, contaminated soil in 6 months while landfarming degraded less than 30% of the MOG in the same period.

While few studies have been published regarding the effects of composting conditions on contaminant degradation, many studies of traditional composting processes have been reported. Moisture content between 50 and 60% usually results in the highest degradation rate of the material to be composted (Suler et al. 1977) with 25 to 80% degradation. Composts operating at 45 °C have been shown to be more active (in terms of CO_2 production) than at 55 or 65 °C and became self-inhibiting around 60 °C (McGregor et al. 1981; McKinley et al. 1984). Maximum organic degradation rates (based on cumulative and peak CO_2 generation) have been reported to occur at C/N ratios of 22 (Nakasaki et al. 1992; Michel et al. 1993). N/P ratios of 2 to 5 are considered optimal in municipal composting. However, it is not known how these parameters affect hydrocarbon degradation in the composting of petroleum-contaminated soil.

The objective of the work presented in this paper was to evaluate the effects of the C/N ratio, temper-

ature and length of the thermophilic phase, and the addition of micro-elements on MOG degradation of a weathered, hydrocarbon-contaminated soil during composting.

Materials and methods

Soil

Two types of soil were used: a weathered, petroleum-hydrocarbon contaminated soil was provided by Imperial Oil, Sarnia, ON, and an uncontaminated soil obtained from Bomix Golden Sand, Daubois Inc., Montreal, PQ. Their characteristics are shown in Table 1.

Effect of leaf/alfalfa substrate

The additional substrate consisted of crushed leaves (mostly maple) with an approximate diameter of 1 cm, and alfalfa pellets measuring approximately 0.4 cm in diameter and 0.6 cm in length (5315 Purina Rabbit Chow, Ralston Purina Canada Inc., Woodstock, Ont.). Their characteristics are listed in Table 1. The contaminated soil to leaf/alfalfa ratio was varied to obtain a series of soil/amendment ratios (Table 2).

Mineral salts medium

Each liter of mineral salts medium (MSM) was composed of (per liter): 2.45 g KH_2PO_4; 6.23 g K_2HPO_4; 18 g $(NH_4)_2SO_4$; 0.36 g $MgSO_4$; 0.108 g $CaCl_2$; 0.108 g $FeSO_4$ and 3.6 ml TES (trace element solution). The TES contained (per liter) 0.1 g $ZnSO_4 \cdot 7H_2O$; 0.03 g $MnCl_2 \cdot 4H_2O$; 0.30 g H_3BO_3; 0.20 g $CoCl_2 \cdot 6H_2O$; 0.01 g $CuSO_4 5H_2O$; 0.02 g $NiCl_2 \cdot 6H_2O$ and 0.03 g Na_2MoO_4.

Mini-composter design and experimental set-up

Mini-composters were 1-liter Mason jars, 18 cm in height with an internal diameter of 8 cm. Two openings were made in the cover of each jar through which 1/4-inch diameter stainless steel tubes were inserted to serve as air inlet and outlet ports. A perforated plate was placed 2-cm from the bottom to permit uniform air distribution. Air was pre-heated to composting temperature and humidified prior to being introduced under the perforated plate at a rate of 0.2 liter min^{-1}.

Soil mixed with leaves and alfalfa was loaded into these mini-composters and placed in a temperature-controlled oven. A temperature profile very similar to that obtained during an 8-liter temperature-autoregulated composting experiment (Beaudin et al. 1996) was imposed: one day at room temperature, followed by an increase to 50 °C in 30 minutes and maintained at 50 °C for 5 d, then gradually decreased over the next five days to room temperature at which it was kept for 19 d. This profile was used in all experiments except those in which the effect of temperature was being investigated. All experiments lasted 30 d.

The content of the mini-composters was mixed manually twice a week and water was added to maintain the moisture levels at 50–60% wt/wt except in experiments in which the substrate concentration was varied (Table 2) since the sandy soil cannot absorb as much water as leaves and alfalfa.

Effect of C/N ratio, temperature and length of the thermophilic phase and of $CaCO_3$ and PO_4^{-3} addition

To study the influence of the initial C/N ratio (from 17 to 49 (mol/mol)), parallel mini-composters with contaminated or with clean soil were set up with a corresponding amount of leaf/alfalfa substrate to determine the amount of total MOG degraded originating from the leaf and alfalfa. The compost consisted of 37.5% clean or contaminated soil, 1.3% KH_2PO_4, 2.5% K_2HPO_4, 4.9% of a 90-day-old compost as an inoculum, and 53.4% leaves and alfalfa. The ratio of alfalfa to leaves was varied to obtain different C/N ratios. For example at a C/N ratio of 17, there was 1 part alfalfa and no leaves (i.e. 1/0). Hence at C/N ratios of 20, 22, 30, 36 and 49, the ratio of alfalfa to leaves were 3.9/1, 2.35/1, 0.61/1, 0.29/1, and 0/1 respectively.

To determine the effect of temperature on total MOG degradation during composting, similar temperature profiles were imposed as described in the experimental set-up except that after the first day at 23 °C, the maximum temperature was kept at either 23, 30, 40, 50 or 60 °C for 5 days. Each mini-composter contained 37.3% soil, 37.3% alfalfa, 16.0% leaves, 4.0% $CaCO_3$, and 5.3% inoculum of a 90-day-old compost.

Either 4.2% $CaCO_3$ or PO_4^{-3} (as 1.5% KH_2PO_4 and 2.9% K_2HPO_4) or both were mixed at the start of the experiment with 38.9% contaminated soil, 38.9% alfalfa, and 17.7% leaves, and inoculated with 5.5% of a 90-day-old compost of the same contaminated soil.

Table 1. Characteristics of the soil and compost substrate

	Contaminated soil	Uncontaminated soil	Leaves	Alfalfa
Size distribution (%)				
Medium sand (2–0.416 mm)	26.9	19		
Fine sand (0.416–0.075 mm)	65.3	77.5		
Very fine sand (0.075–0.042 mm)	3.5	1.6		
Silt and clay (< 0.042 mm)	4.3	1.9		
Volatile matter (% wt/wt)	10.5	0	84.5	74.1
TOC (% wt/wt)	7	0	47	38
Total nitrogen (% wt/wt)	0.18	0	1.1	2.8
Orthophosphates (% wt/wt)	0	0	0.049	0.055
C/N (molar basis)	45.0 : 1		49.0 : 1	15.8 : 1
MOG (mg/kg dry soil)	17,000	<100	13,000	7,000
Aliphatic hydrocarbons (% wt/wt of MOG)	40			
Polar hydrocarbons (% wt/wt of MOG)	32			
Aromatic hydrocarbons (% wt/wt of MOG)	28			

Table 2. Composition and moisture content when additional amendment was added to the petroleum-contaminated soil

Soil (%)	Alfalfa (%)	Leaves (%)	KH_2PO_4 (%)	K_2HPO_4 (%)	$CaCO_3$ (%)	Moisture (%)	C/N (molar)	N/P (molar)
0	53.2	30.4	2.0	3.9	5.6	52	22.1/1	3.4/1
23.8	39.9	22.8	1.5	2.9	4.2	51	22.6/1	3.5/1
47.6	26.7	15.2	1.0	2.0	2.8	43	23.9/1	3.6/1
75.0	14.0	8.0	1.5	1.0	1.5	33	27/1	4.4/1
95.3	0.0	0.0	0.0	0.0	1.0	21	45/1	1/0

MOG analysis

A humid 15 g sample was mixed with 5 g Na_2SO_4 and 10 g $MgSO_4$ in a mortar (APHA et al. 1985). Once all the moisture had been absorbed by the $MgSO_4$, the mixture was pulverized and placed in a paper extraction thimble. The top of the thimble was filled with glass wool. The oil and grease were extracted in a Soxhlet apparatus using 1,1,2-trichloro-1,1,2-trifluorethane (Freon 113, Anachemia Science, Montreal, Que), at a rate of 20 cycles h^{-1} for 4.5 h. Fifteen grams of silica gel (Anachemia Science, Grade 12, 28–200 mesh, activated at 105 °C for 24 h) were added to the extraction solvent in a stoppered container and was mixed continuously for 10 min. The solvent was then filtered through glass wool, placed in a clean pre-weighed flask and evaporated. The flask was dried at room temperature for 24 h and weighed to obtain the amount of MOG extracted.

MOG fractionation

About 50 g of activated silica gel was packed in a 2-cm diameter column and covered in hexane. A hexane extract of the dried MOG sample was layered on the silica column. The hexane-insoluble fraction was then extracted in toluene and also added to the column. The aliphatic, aromatic and polar classes were eluted with 70 ml of hexane, then toluene, and then chloroform/methanol (1/1, vol/vol), respectively and quantified gravimetrically.

Soil-derived MOG

In all experiments in which the initial amount of leaves, alfalfa and soil was constant, degradation is reported as % total MOG degraded. However when investigating the effects of leaf/alfalfa substrate concentration and the C/N ratio, the ratio of leaf/alfalfa to soil was varied and consequently the amount of

plant-derived MOG was varied. To correct for this, soil-derived MOG was estimated by two methods. In the experiment investigating the effects of different initial concentrations of leaf/alfalfa substrate, it was assumed that the amount of plant-derived MOG degraded in each case was the same as a control in which there was leaf/alfalfa but *no* soil (and therefore no soil-derived MOG). In the C/N ratio study, it was assumed that the amount of plant-derived MOG degraded in each case was the same as the control in which *clean* soil was added (and therefore no soil-derived MOG). In both cases, the amount of plant-derived MOG degraded was subtracted from the total amount of MOG degraded (contaminated soil plus plant-derived MOG) to determine the soil-derived MOG degraded.

pH determination, dry weight and ash content of co-compost

A 10 g sample was mixed with 100 ml of distilled water for five minutes before the pH was measured with an electrode.

Approximately 10 g of sample was placed in a preweighed aluminum weighing dish and dried at 105 °C for 24 h. The dish with sample was weighed before and after drying to obtain the percent dry mass. The dried sample was then placed in a preweighed porcelain combustion dish, weighed and heated at 550 °C for 1.5 h. After cooling in a desiccator for 30 min, they were weighed to obtain the weight of ash. The ash content was used to calculate the mass of MOG per mass of initial dry compost from the measured MOG concentration. Since the dry mass of the compost decreased by a considerable amount (up to 32% in these experiments), the MOG content was calculated on an initial dry mass basis to determine the percent degradation at the time of sampling.

$$\begin{array}{cc} \text{MOG} & = \qquad \text{MOG} \\ \text{(mg/kg initial dry compost)} & \text{(mg/kg dry compost)} \end{array}$$
$\times$ Initial Ash fraction/Ash fraction at time of sampling

Carbon dioxide

A quadrupole mass spectrometer (VG Quadrupoles, Middlewich, England) was used for on-line analysis of CO_2 and O_2 concentrations at the air inlet and outlet of the mini-composters. The flow rates of the gases entering the mass spectrometer were maintained between 100 and 150 ml min^{-1}, and the settling time for analysis was 60 s. The air flow rate and the difference
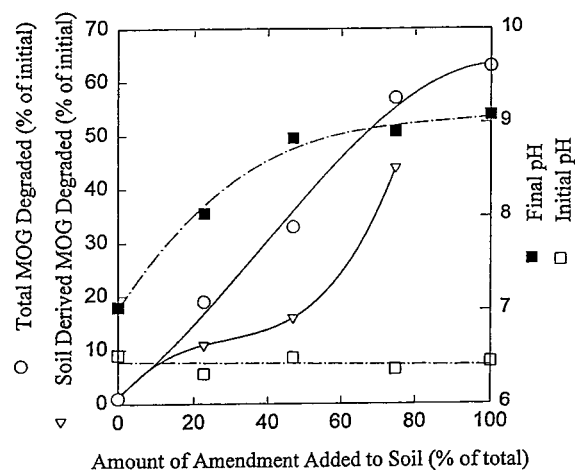

Figure 1. The effect of amendment addition on the apparent MOG degradation during soil composting.

in CO_2 and O_2 content between the inlet and outlet were used to calculate the total CO_2 produced and O_2 consumed.

Results

Abiotic loss

There was no decrease in MOG of an abiotic mini-composter (containing 3.89% $HgCl_2$) during 30 days of operation. Therefore, any reported MOG loss is not due to abiotic factors such as volatilization during aeration or related to the imposed temperature profile.

Effect of leaf/alfalfa substrate

The total amount of leaf/alfalfa added to the weathered, petroleum-contaminated soil was increased while the leaf to alfalfa ratio was kept constant (Table 2). There was an increase in both the total and soil-derived MOG degraded as the amount of leaf/alfalfa amendment was increased (Figure 1). At 0% amendment, only 1% of the total MOG had degraded after 30 days of treatment. Addition of 4.5 ml of MSM increased this to 6% (data not shown). The total MOG degradation increased almost linearly from 1 to 63% as the amount of amendment was increased to 100%. Soil-derived MOG degradation increased from 6 to 43% as additional substrate concentration increased from 0 to 63%. The final pH increased to a maximum of 9.0 as the amount of amendment was increased.
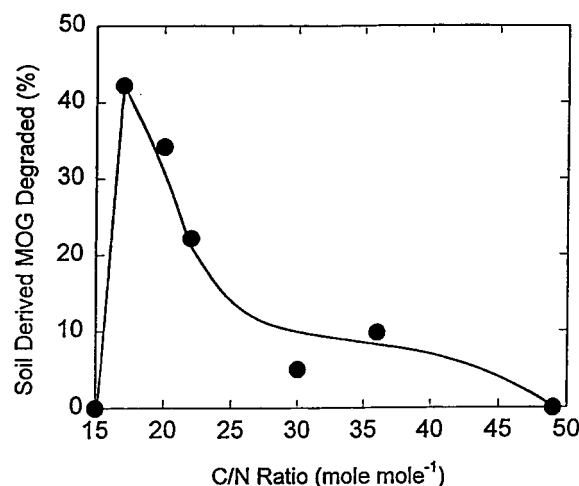
Figure 2. The effect of initial carbon to nitrogen ratio on the apparent MOG degradation during soil composting.

C/N ratio

After subtracting the corresponding MOG degradation of clean soil and the leaf/alfalfa substrate from the mixture of hydrocarbon-contaminated soil and the leaf/alfalfa substrate, the MOG degradation attributable to only the contaminated soil was found to decrease rapidly as the initial C/N ratio was increased to 30 and decreased more gradually as the C/N ratio was further increased to 50 (Figure 2). Composting activity did not always occur at C/N ratios of 17. The final pH reached a maximum of about 8.8 at low C/N ratios and decreased as the C/N ratio was increased probably due to decreased ammonia production.

Temperature of the thermophilic phase

Experiments were performed in which the temperature of the thermophilic phase was controlled at different maxima. The bimodal response in the amount of MOG eliminated was reproducible under the conditions used based on the relatively low standard deviations obtained (Figure 3). A maximum of 56% total MOG was degraded at 23 °C in 30 days. Degradation decreased with increasing temperature to 33% when the 5 day plateau was at 40 °C, and then increased to 47% at 50 °C. Much less total MOG was degraded (23%) when the plateau was at 60 °C. Further analysis of the compost at 120 days showed that total MOG degradation continued after the first 30 days increasing to 67% in the composts which had temperature plateaus of 23 and 50 °C. Separation of the residual total MOG into its aliphatic, aromatic and polar components found
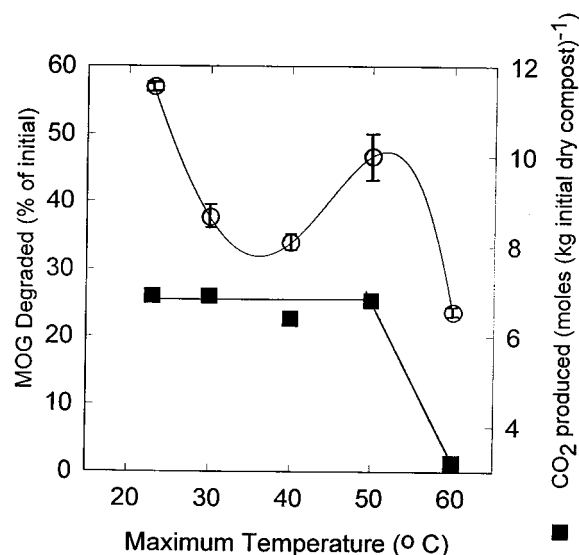

Figure 3. The effect of the 5-day maximum temperature plateau on the apparent MOG degradation during soil composting. The error bars indicate the spread in data of duplicate samples.

that each component had the same degradation trend as the total MOG. Approximately 6800 mmol of CO_2 per kg of initial dry compost was produced during 30 days of composting when the plateau temperature was at 23, 30, 40 or 50 °C, but declined sharply to 3200 mmol of CO_2 per kg of initial dry compost when the plateau was kept at 60 °C.

Length of the thermophilic phase

The length of the thermophilic phase (i.e., the length of time at which the temperature was maintained at 50 °C) was varied to determine the importance of the thermophilic phase on MOG degradation. The compost composition was identical to that used in the preceding experiment. After 30 days the total MOG degradation was found to be directly proportional to the length of the imposed thermophilic phase (Figure 4). Only 47% of the total MOG was degraded when the thermophilic phase was maintained at 50 °C for 6 days, whereas 70% was degraded when held at the same temperature for 30 days. The final pH was about 8.3 in all cases. When the compost was kept at 23 °C for an additional 90 days (i.e., a total period of 120 days), there was a further increase in MOG degradation. For the compost that had a thermophilic phase of 6 days, the total MOG degradation increased to 67% and while the compost whose thermophilic phase duration was 30 days had an 8% increase in total MOG degradation to 78%.
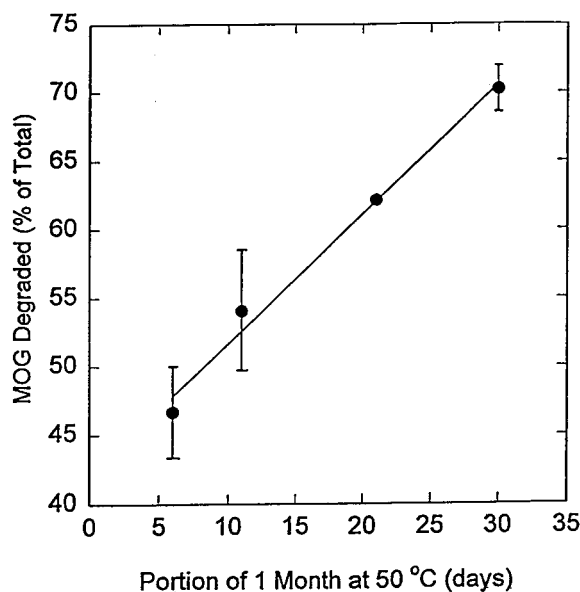
Figure 4. The effect of the length of a 50 °C temperature plateau on the apparent MOG degradation during soil composting. The error bars indicate the spread in data of duplicate samples.

Table 3. Effect of $CaCO_3$ and PO_4^{3-} addition

	% MOG degraded	pH	
		Initial	Final
None	23	5.75	8.37
PO_4^{3-}	35	6.42	8.79
$CaCO_3$	43	6.56	8.37
PO_4^{3-} and $CaCO_3$	25	6.39	8.74

The effect of $CaCO_3$ and $PO_4{}^{3-}$ addition

When either $CaCO_3$ or PO_4^{3-} or both was(were) added, the initial pH increased from 5.8 to 6.4 (Table 3). PO_4^{3-} addition also changed the initial N : P ratio from 99 to 3 (molar basis). When neither $CaCO_3$ nor PO_4^{3-} was added, only 23% of the total MOG was degraded. When both were added, there was no effect as 25% of the total MOG was degraded. Adding $CaCO_3$ or PO_4^{-3} individually enhanced degradation to 35 and 43% respectively. It is likely that adding both at the same time resulted in $CaCO_3$ combining with KH_2PO_4 and K_2HPO_4 to produce $Ca_3(PO_4)_2$ precipitate, making neither bioavailable.

Discussion

Both composting (Beaudin et al. 1996) and the addition of finished compost (Rosenbrock et al. 1997) have been shown to aid in bioremediation of specific contaminated soils. The possible beneficial effects are numerous and include improvement of soil structure, addition of key nutrients, increased sorption of contaminants such that they are no longer extractable, provision of a bulking agent to increase oxygen transfer, provision of an inoculum and, especially in the case of active composting, increased cometabolism. Some studies have attempted to identify the relative contribution of these phenomena but their conclusions vary depending on the particular system studied.

In the present study it is clear that, composting greatly decreases the extractable soil-derived MOG. The increase in MOG degradation after addition of MSM to the soil demonstrates that nutrient provision is an important factor. Low C/N ratios should favour carbon utilization and thus enhance the total MOG degradation. This proved to be the case as the apparent degradation of soil-derived MOG increased substantially as the C/N ratio was reduced from 49 to 17 (Figure 2). Similar results have been obtained in landfarming where a C/N ratio of 18 (lowest ratio tested) resulted in maximum oil decomposition (Rasiah et al. 1991).

Maintenance of thermophilic conditions in traditional composting is generally considered to be necessary to achieve a final product of high quality. Little is known about the effect of thermophilic conditions on hydrocarbon degradation although a previous composting study showed that polyaromatic hydrocarbon (a major MOG fraction) degradation was higher at 35 °C than at 50 °C (Hogan et al. 1988). In our study, more total MOG was degraded when the temperature profile was maintained at 23 °C rather than imposing a 5-day plateau at 50 °C (Figure 3). However, when thermophilic conditions were maintained for 30 days, much more total MOG was eliminated than at 23 °C for 6 days (Figure 4). In reactor-based composting, temperature can be controlled by a variety of factors such as the aeration rate and the organic load. In windrow composting, the length of the thermophilic phase is controlled by the amount and type of degradable organic material.

Due to variability in soil structure, hydrocarbon composition and available amendment, optimal conditions may be very difficult to predict. For example, it is known that PO_4^{-3} availability to microorganisms is

dependent on pH and the presence of divalent cations such as Ca^{2+} and Mg^{2+} which can bind PO_4^{-3}. PO_4^{-3} and Ca^{2+} concentrations, and the pH of the environment have had dramatic effects on the extent of mineralization of contaminants such as phenol when pure cultures have been used (Robertson & Alexander 1992). However, due to the complexity of PO_4^{-3} solution chemistry, there is no clear explanation for this, making it difficult to predict which nutrients should be added in composting. In this case, nutrient optimization studies may be necessary. These should incorporate small-scale units (minicomposters) and the specific soil to be remediated

Few scientific studies have investigated composting as a bioremediation process. Apart from the obvious importance of pH, this study has shown that the amount of organic amendment, the C/N ratio and the temperature profile are key factors affecting composting of this particular weathered, hydrocarbon-contaminated soil. Phosphate and calcium addition also play a role. Future work should focus on the mechanisms responsible for the positive effects of temperature and organic amendment in the hope that general principles may be developed for composting of hydrocarbon contaminated soils. In particular, physical factors such as increased bioavailibility due to changes in soil structure must be studied. These factors need to be separated from the effects of the amendments on biological components such as the composition, size and activity of the microbial population.

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