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Biodegradation of petroleum-based oil wastes through composting

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Abstract

Composting of horse manure was used as a means of degradation of two oil wastes, oil sludge from petrol stations and petroleum residues from a refinery. Paraffin oil was chosen as a reference. Oil wastes decomposed to 78–93% during 4.5 months of composting. The degradation of the waste oils was higher than that of the reference paraffin oil and no difference was found between the two types of oil wastes concerning their decomposition. At the end of the experiment, most of the polyaromatic hydrocarbons had been degraded except pyrene, chrysene and dibenz(ah)anthracene. Gaseous losses of oil compounds through volatilisation from composts were found not to be significant.

Introduction

Petroleum-based oil wastes consist mainly of alkanes or paraffins with 1–40 carbon atoms per molecule, but a substantial amount of cycloalkanes may also be present in certain crudes (Overcash & Pal 1979). Such wastes come from petroleum industries, vehicle repair workshops, oil cleaning plants and oil water separators (Larry 1984) and are classified as hazardous wastes in Sweden (SNV 1980). A significant amount of the oil wastes can end up as contaminants in soil, sediment and water, and their remediation is being widely pursued to minimize negative environmental effects and risks for human health.

One of the technologies currently being developed for use in remediation of soil and sediment is composting (Williams & Keehan 1993). Composting has become increasingly popular during the past decade as an alternative to incineration or tipping of decomposable organic household waste. However, composting may also be a useful treatment process for hazardous biodegradable waste. Whereas the primary benefit from composting of household waste is the reduction of volume, hygienization and stabilisation for recycling or ultimate disposal, the objective of composting hazardous materials is solely to convert these substances into an innocuous end-product.

The objective of this study was to test the usefulness of composting as a means of biodegrading oil wastes. Horse manure was choosen because in a comparison between park waste and horse manure, horse manure decomposed faster.

Horse manure contained 45% DM, the pH value was around 7.4, total N content was 1.2% and the C to N ratio was 32. Simpkin et al. (1992) applied composting to the bioremediation of soil contaminated with diesel and motor gasoline in Alaska, showing the advantage over other bioremediation technologies in that it has the potential to generate and retain heat, which may be significant in cold climates. Doyle et al. (1986) investigated the degradation of ^{14}C-labelled trinitrotoluene (TNT) and ^{14}C-labelled hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in laboratory-scale composting and found that concentrations of both substances rapidly decreased during 6 weeks of composting.

Table 1. Characterisation of oil wastes used

Type and origin of waste	Dry matter (%)	Oil content on wet-basis (%)	Tot.extract. org. subst. (g kg^{-1} Dm)	Non- polar aliphatics (g kg^{-1} Dm)	Non-polar aromatics (g kg^{-1} Dm)	pH
Oil sludge (Petrol station)	44.4	20.0	499.0	441.0	16.8	6.1
Petroleum residue (Refinery)	47.4	32.0	972.0	608.0	78.5	6.6

Materials and methods

Composting and sampling

The oil wastes investigated were derived from waste water collected at petrol stations after oil separation, and from a petroleum refinery plant. The oil content in the separated oil sludge was 20% on a wet-weight basis and 32% in the petroleum residue (Table 1). Four garden compost bins, representing 4 treatments (see Table 2), with a volume of 280 L, equipped with a lid, insulation (3 cm rockwool) and a perforated bottom, were filled with horse manure and mixed with 1.8 to 7.1% of oil wastes in dry matter. Paraffin oil (light-fluent, purum, C-length 24–28) was used as a reference for comparison. Each bin was placed on wooden pallets in order to make the influx of air possible and to enable weighing of the compost mass.

On each sampling occasion, the composts were thoroughly mixed and four subsamples were collected from different locations in the compost bin. Subsamples were mixed, pooled and one sample was taken from the mixture, weighting about 150–200 grams. Prior to analysis, pooled samples were cut into small pieces with a pair of scissors, placed in a plastic bag and kept cool. Samples were analysed for oil constituents, dry matter, organic carbon and pH. Temperature was registered during composting.

Analyses and calculations

Organic carbon analyses were carried out on dried and ground samples with the help of a LECO CNS-2000 analyser. The total oil content to the Swedish standard method (SS 028 145-3) is based on the extraction of total organic substances and the determination of non-polar hydrocarbons (aliphatics and aromatics) with trichlorotrifluoroethane (TTE). Ten grams of compost sample were mixed with 400 mL deionised water, acidified to pH below 2 with HCI to prevent oil degradation and shaken with 50 ml TTE for 30 minutes. The quantity of total extractable organic substances in the TTE solution was determined by measuring absorption in the region of 3340–2507 cm^{-1}. In a further operation, polar hydrocarbons also present in the extract were separated through column chromatography with aluminium oxide. Thereafter the quantity of non-polar hydrocarbons was measured (aliphatic and aromatic) in the region 2915–2940 and 2950–2975 cm^{-1}, respectively. The quantity of aromatics was measured between 3015–3040 cm^{-1}. Calibration curves for aliphatic hydrocarbons were based on a 50/50 volume percent n-hexadecane and isooctane and for aromatic hydrocarbons on toluene.

For determination of polycyclic aromatic hydrocarbons (PAH) in compost samples, the same TTE extract was used. One ml extract was evaporated to dryness with hydrogen gas and the same amount of cyclo-hexane was added. The sample was transferred to a gas chromatography-vial (GC-vial) and PAHs were determined through a gas chromatograph coupled to a mass spectrometer (Hewlett Packard 5890, 5989A) (capillary column Restek, RTX-5, 0.25 μm film thickness, 30 m × 0.25 mm splitless injection with injection temperature of 275 °C, oven temperature 70 °C × 1 min., 7 °C/min. up to 300 °C for 15 min. and total time 49 min. interface temperature 300 °C, ion source 250 °C, quadrupole 100 °C).

Concerning hydrocarbon determination in compost air, a known amount of air volume from just above the compost surface was sucked through active coal samplers several times during the first month of composting. Samples were extracted by shaking with 2 mL CS_2 for 30 minutes. The extract was analysed directly by a gas chromatograph fitted with a flame ionisation detector (FID) (column DB Wax 30 m × 0.25 mm, thickness 0.5 μm, carrier gas-helium, split injection 30 ml/minute, start temperature 38 °C for 4 minutes, and 7 °C/minute up to the end temperature of 230 °C). Standard solution was prepared from a mixture of n-octane with $CS_2$with a ratio of 1:1000.

To be able to calculate the actual decomposition of carbon and oil in composts, mass losses during

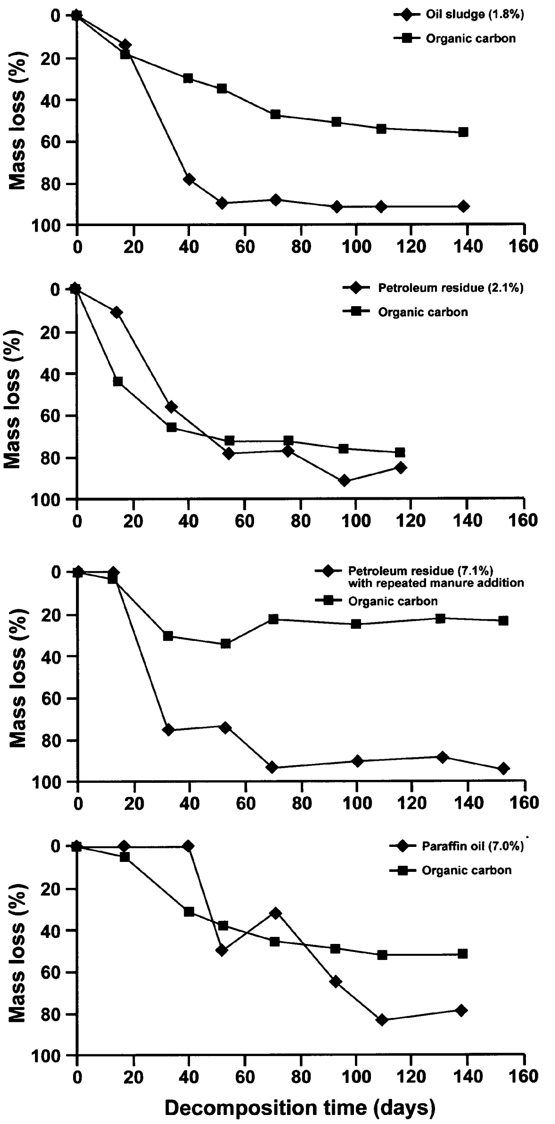

Figure 1. Oil and carbon mass decomposition in horse manure composts with different oil wastes.

composting had to be taken into consideration. Data on carbon and oil concentration in composts were multiplied with the corresponding remaining compost mass to derive the actual masses. The calculated masses were fitted to exponential decay functions by least-square technique using the SAS procedure NLIN (SAS Institute 1985).

Results and discussion

Carbon and oil decomposition

In the four composts, between 30 to 60% of the dry matter was lost during the first month, indicating that horse manure was easily decomposable. The highest C mineralisation, 78%, was obtained after 4 months in the treatment with 2.1% petroleum residues (Figure 1). The extent of carbon mineralisation was in agreement with other compost studies (Hays 1973; Wilson 1971) and no lasting inhibitory effect of the oil wastes on the composting process was obvious, indicating that horse manure was a suitable material for the objective of this study. The decomposition of oil from composts was calculated as the product of concentration and corresponding remaining mass (Figure 1). After 4.5 months of composting, oil decomposition in the treatment with oil sludge was 90%, and in the treatment with petroleum residues about the same extent of decomposition was obtained. However, a somewhat lower degree of decomposition (80%) was measured in the treatment with paraffin oil. The most efficient oil decomposition (93%) was obtained in the treatment with petroleum residues where horse manure was repeatedly added. The period when the composting temperature was highest, between day 3 and day 7, did not coincide with the highest oil decomposition. The greatest portion of oil was decomposed between 3 and 5 weeks after the start. In the composts with 7 and 7.1% oil addition, a lag phase lasting between 2 and 4 weeks was measured, indicating that there is no effective decomposition of oil compounds in the period of higher temperature.

Aliphatic hydrocarbon concentrations increase significantly in three composts during the first couple of weeks (Table 2) and in a few cases also at other intervals. The initial increase in oil concentrations is explained by the fact that decomposition of the compost mass is more intensive than oil decomposition. As a result, oil concentrations increase in the remaining mass, although there is an actual breakdown of oil. Increases in oil concentrations at later intervals indicate that either the sampling or analytical procedure was not satisfactory. However, it is most probable that sampling of compost material, despite many subsamples, was the critical point, as straw particles, feces and oil wastes were not homogenously distributed.

Concentrations of aliphatic hydrocarbons decreased with time of composting, whereas aromatic hydrocarbons remained or decreased only slightly.

Table 2. Treatments, compost temperature, remaining mass, organic C and concentration of oil constituents in horse manure composts

Time of decomposition (Days)	Temp. (°C)	Remaining mass (%)	Organic C (%)	Hydrocarbons		Total oil conc. (g kg^{-1} DM)
				aliphatic	aromatic	
				(——g kg^{-1} DM——)		
Addition of 1.8% oil through oil sludge						
0	15	100	39.3	12.2	5.4	17.6
17	30	84	37.8	13.9	4.2	18.1
40	25	74	37.4	4.8	0.2	5.0
51	25	68	37.0	2.6	0.1	2.7
72	24	56	37.4	3.3	0.1	3.4
93	23	51	36.6	3.1	0.2	3.1
109	22	50	35.9	2.3	0.8	3.1
139	22	50	35.0	1.5	3.6	5.1
Addition of 2.1% oil through petroleum residues						
0	15	100	40.9	14.6	6.1	20.7
14	30	53	42.8	30.0	4.7	34.7
33	25	36	40.4	17.1	7.6	24.7
55	24	30	39.9	14.6	1.0	15.6
75	24	29	40.8	16.4	0.5	16.9
96	23	24	40.5	6.0	1.0	7.0
117	22	24	39.5	5.0	8.0	13.0
Addition of 7.1% oil through petroleum residues and repeated additions of horse manure						
0	15	100	41.4	70.5	1.0	71.5
12	30	86	46.8	81.1	1.0	82.1
33	25	66	43.8	26.1	1.0	27.1
54	24	64	44.6	32.2	1.0	33.2
61*	25	79	n.a.	n.a.	n.a.	n.a.
70	40	77	43.3	6.4	2.1	8.5
100	25	72	43.2	10.0	0.9	10.9
128*	25	80	n.a.	n.a.	n.a.	n.a.
131	35	75	44.5	10.3	2.0	12.3
154	25	71	44.7	5.9	1.0	6.9
Addition of 7.0% paraffin oil						
0	10	100	43.3	65.1	5.3	70.4
17	30	88	47.9	76.9	3.2	80.1
40	22	68	43.5	103.0	0.5	103.5
51	22	61	44.0	57.5	1.0	58.5
72	22	54	43.9	88.6	1.0	89.6
93	22	49	43.2	46.5	2.0	48.5
109	22	48	44.8	24.1	0.8	24.9
139	22	46	45.0	30.9	2.2	33.1

* Times when horse manure was added corresponding to 15% and 8% of the initial mass.

Table 3. Parameter values and coeffficents of determination for the decomposition of oil and organic carbon in horse manure compost

Treatments	Oil decomposition		Carbon decomposition		
	k (d^{-1})	R^2	k (d^{-1})	Mineralisable C_o (%)	R^2
1.8% oil through oil sludge	0.029 ± 0.005	0.90	0.020 ± 0.003	41.11 ± 3.34	0.98
2.1% oil through petroleum residue	0.021 ± 0.002	0.95	0.061 ± 0.004-	24.72 ± 1.21	0.99
7.1% oil through petroleum residue	0.025 ± 0.005	0.89	(no curve fit due to repeated manure additions)		
7.0% paraffin oil	0.010 ± 0.003	0.42	0.016 ± 0.005	37.04 ± 9.78	0.95

k = first-order rate constants, C_o = mineralisable C fraction.

Oil concentrations, regarded as the sum of aromatic and aliphatic hydrocarbons, decreased by 50 to 90% (Table 2).

The mass of carbon and oil, calculated from Table 2, were fitted to exponential decay curves (Table 3). However, carbon data of the compost with repeated manure addition could not be treated as a first-order decay. Concerning the lag-phase for oil decomposition in the composts with 7 and 7.1% oil, the end of this phase was regarded as the starting point for the curve fitting procedure. Rate constants describing decomposition of the oil wastes ranged from 0.010 to 0.029 d^{-1}, with the highest value for oil sludge and the lowest for paraffin. Rate constants for organic carbon decomposition ranged from 0.016 to 0.061 d^{-1}. The fact that k-values for carbon mineralization of the three composts consisting of the same horse manure varied so much, indicates that added oil wastes influenced the composting process.

At the start of the composting period, the dominant polycyclic aromatic hydrocarbon (PAH) was naphthalene, which accounted for more than 50% of the PAHs in the four composts. At the end of composting process, almost all PAHs were decomposed and values were close to or below the detection limit of $<$ 0.1 mg kg^{-1} dry matter. However, pyrene, chrysene and dibenz(ah)anthracene were still present at concentrations of 0.2–0.8 mg kg^{-1} dry matter, although this was 10 times lower than the initial concentration.

Oil evaporation

Sampling during the first month of composting when temperatures reached a maximum of 35–38 °C, showed that concentrations of hydrocarbon in compost air were very low, not excceeding 12 mg m^{-3} air. Only hydrocarbons with a carbon length of C_{10}-C_{15} were found in compost air. Based on the maximum concentration of 12 mg m^{-3}, the potential loss through evaporation was estimated. Carbon mineralisation during composting presupposes a minimum flow of air (oxygen) passing through the compost. For a loss of 1 kg carbon of the compost material, approximately 2.7 kg of oxygen are needed, which is equivalent to 83.3 mole O_2 (2249 L oxygen, 1mole $\approx$ 27 L at 25 °C). Oxygen constitutes around 20% of the air, and the calculated minimum air flow through the composts was 11–32 m^{-3}. This flow corresponds to a loss of less than 0.5 g hydrocarbons if the concentration in compost air is 12 mg m^{-3}, which is about 0.2% of the oil content. Thus, it can be concluded that volatilisation of oil was not a significant pathway for the disappearance from the compost.

The decomposition of oil in composts does not necessarily mean that oil is fully biodegraded into carbon dioxide and water. It may be partially degraded and converted into secondary organic substances and bound to the compost material as has been found for other substances (Doyle et al. 1986; Kaplan & Kaplan 1982; Rack & Frink 1989; Verstraete & Devliegher 1996).

Conclusions

Composting of horse manure together with oil wastes was found to be a suitable environment to achieve a microbial oil breakdown. The type of oil waste influenced the rate of carbon decomposition in composts, whereas the residual amounts of oils were similarly low in the four composts despite a lag-phase at initial oil concentrations of 7%. Repeated additions of horse manure to the composts enhanced oil decomposition. The extent of oil decomposition was higher than of organic carbon in the composts. Oil evaporation did not contribute significantly to its disappearance.

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