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Project 0239010 – Final report <u>Compost- a method for treatment of oil contaminants from agricultural</u> <u>activities</u>

Purpose of the project

The purpose of this project is to design a compost system that can degrade diesel oil and other mineral oils at the farms.

Background

It has been observed that the use of diesel oil at the farms causes contamination due to accidental spills. Due to the mobility of diesel oil the risk for contamination of groundwaters is very high.

A system for taking care of diesel oil spills has been design by Per Axelsson, Axon Miljöteknikk AB, Sala. The system consists in parking the tractor above a concrete platform. If accidental spills occur, the oil will be led to a well which contain a filter material that will absorbed the oil (Fig. 1).



Fig. 1 Concrete platform with a slope towards a well with filter material (heat-treated peat) where the diesel spills are absorbed.

The material in the filter consists on a heat-treated peat, very effective in absorbing diesel oil according to tests run at the Högskola in Luleå. Special IR equipment can detect when the filter material is saturated and has to be change by new one.

A problem still to be solved is what to do with the saturated filter material. Burning can be difficult if no authorized burning plants are located near the farm. A simple and effective solution could be the design of a compost system, which can degrade the diesel oil in the filter.

Composting is a known process and it is use often for the degradation of petroleum contaminated soils. The diversity of microorganisms which are present in the compost heaps can lead to the degradation of many types of organic pollutants, among them both the aliphatic and aromatic fractions of oils. The type of material to be composted, the C/N-ratio, temperature, are among the parameters that affects the efficiency of composting.

In order to accelerate the studies at lab scale we decided to use an active and already establish microbial community by using compost from the VAFAB installations at Sala and Västerås.

As already reported last year ("Lägesreport" 030930), the maturity of the compost had an effect on the degree of mineralization of the aromatic fraction of the oil. The 6-month mature compost gave a significant higher and faster degradation of phenanthrene during a period of 21 days of incubation. No such dramatic effect was observed for the aliphatic fraction for the same incubation period.

Further studies were recommended with longer incubation periods to confirm the overall effect of the compost maturity on the degradation of the aromatic and aliphatic fractions of the oil. The start of field studies were also recommended.

Results from the second year

Description of the treatments

New studies at laboratory scale were run using compost material from the installations of VAFAB from Sala and Västerås. The maturity of the compost was 2, 6 and 10 months old. Table 1 shows some physical and chemical characteristics of the compost materials used in this work.

Compost age	Dry matter	WHC	pН	Total-C	Organic-C	Total-N	C/N
(months)	(%)	(%)		(%)	(%)	(%)	
2	56.7	72.1	6.73	31.2	29.0	3.35	9.3
6	52.1	-	7.42	24.6	23.0	3.01	8.2
10	52.2	71.5	8.00	16.2	15.4	1.28	12.7

Table 1 Compost materials from VAFAB

The microbial ability of the compost for degradation of oil was tested by adding ¹⁴C labelled chemicals and the production of ¹⁴CO₂ followed. As in the studies in Year 1, phenanthrene and hexadecane were used as model substances representing the aromatic and aliphatic fractions of the oil, respectively. Additionally two other more persistent polyaromatic hydrocarbons (PAHs), pyrene and benzo(a)pyrene, were also included. Table 2 shows the structure of the chemicals used, their water solubility and the position of the ¹⁴C-carbons. The incubation time was of 60 days at 20 °C.

Besides the mineralization measurement of each of the studied chemicals, the degradation of a mixture of phenanthrene, anthracene, pyrene and benzo(a)pyrene (Table 2) was followed using cold chemicals and added to the three compost materials.

In summary the following treatments were run:

- a) mineralization of ¹⁴C-phenanthrene in 2-, 6- and 10-months old compost.
- b) mineralization of ¹⁴C-hexadecane in 2-, 6- and 10-months old compost
- c) mineralization of ¹⁴C-pyrene in 2-, 6- and 10-months old compost.
- d) mineralization of ¹⁴C-benzo(a)pyrene in 2-, 6- and 10-months old compost with and without unlabeled pyrene.
- e) degradation of a mixture of unlabeled phenanthrene, anthracene, pyrene and benzo(a) pyrene in 2-, 6- and 10-months old compost.

Table 2 Chemicals studied in this work

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Name	Structure	Solubility at 25°C			
		(g /l)			



* Position of the ¹⁴C-carbon

a) ¹⁴C-Phenanthrene mineralization

According to the preliminary results obtained in the first year, a 21-days incubation showed that phenanthrene was mineralized faster and more efficiently in the 6-months old compost compared to the 2- and 10-months old compost (Fig. 3). However, a longer incubation period showed that after a lag phase of approximately 25 days the mineralization of phenanthrene in the 2-months old compost starts to increase reaching almost the same levels as the 6-months old compost (80% mineralization) (Fig. 4). The mineralization of phenanthrene in the 6- and 10-months old compost showed almost no lag phase, however, at the end of the incubation period a 1.7-folded higher mineralization was observed in the 6-months old compost (Fig. 4). Phenanthrene degradation showed to be metabolic.



Fig. 4 Phenanthrene mineralization in 2-, 6- and 10-months old compost material.

b) ¹⁴*C*-*Hexadecane mineralization*

During an incubation period of 21 days (studies in Year 1) no clear relationship was observed between the mineralization of hexadecane and the maturity of the compost. However, the longer incubation period of 60 days showed that younger compost gives higher mineralization. A higher mineralization was observed in the 2-months old compost (72%) while no significant difference was observed between the 6- and 10-monthsold composts (58 and 57%, respectively) (Fig. 5). However, in all cases the degradation of hexadecane occurs immediately, i.e. there is no lag phase in any of the treatments (Fig 5).



Fig. 5 Hexadecane mineralization in 2-, 6- and 10-months old compost material.

c) ¹⁴C-Pyrene mineralization

The mineralization of pyrene was important in the 6- and 10-months old compost. No mineralization was observed in the 2-months old compost. After a lag phase of approximately 20 days the mineralization of pyrene started to increase and reached 35% at day 60 in the 6- months old compost. The lag phase in the 10-months old compost was larger, more than 20 days, but at day 60 a higher mineralization was observed (45%) compared to the 6-months old compost.



Fig. 6 Pyrene mineralization in 2-, 6- and 10-months old compost material.

d) ¹⁴*C*-*Benzo(a)*pyrene mineralization with and without the presence of unlabeled pyrene

The mineralization of benzo(a)pyrene alone was poor, less than 1% in all of the composts. The presence of pyrene did not enhance the mineralization (data not shown). However, at the end of the incubation period the chemical analysis of benzo(a)pyrene (extraction with solvents and analysis by GC-MS) showed that in the 2-months old compost benzo(a)pyrene was dissipated 88 –89 %. In the 6-months old compost no dissipation was observed and in the 10-months old the dissipation varied between 88 to 93 % depending on the presence or absence of unlabeled pyrene (Table 3). Hence, even that the mineralization was poor certain transformation of benzo(a)pyrene occurred in the 2-months old compost.

Table 3 Benzo(a)pyrene concentration in compost samples of different maturities with and without the presence of unlabeled pyrene

Compost treatment	Concentration (%)			
	in absence of pyrene	in presence of pyrene		
2-months old (-)	89	88		
6-months old (-)	100	107		
10-months old (-)	93	88		

e) Degradation of a mixture of unlabeled PAHs

The degradation of a mixture of unlabeled phenanthrene, anthracene, pyrene and benzo(a) pyrene gave different results depending on the maturity of the composts.



 $\begin{array}{c} 40 \\ 20 \\ 0 \\ 0 \\ \end{array}$

Fig. 7 Degradation of a mixture of phenanthrene (Phe), anthracene (Ant), pyrene (Pyr) and benzo(a)pyrene (B(a) P) in a) 2-months old compost, b) 6-months old compost and c) 10-months old compost.

In the 2-months old compost, phenanthrene was degraded completely after a lag phase of approximately 30 days. Anthracene was degraded 90% also after a lag phase of 30 days. Due to the relative high base line in the chromatograms no quantification of pyrene was possible. An important finding was a 70% degradation of benzo(a)pyrene after 60 days of incubation. (Fig. 7a).

In the 6-months old compost the degradation of phenanthrene occurred rapidly, no phenanthrene was found after 12 days of incubation. The remaining concentration of anthracene after 30 days incubation was 16% of the initial added and after 60 days of incubation no anthracene was found in the samples. Pyrene was also degraded completely after 60 days of incubation, while 57% of benzo(a)pyrene remained in the system at the end of the 60 days incubation period (Fig. 7b).

The degradation of phenanthrene, anthracene and pyrene was faster in the 10-months old compost. None of these chemicals were found after 60 days of incubation. However, benzo(a) pyrene was degraded poorly and 72% remained in the system at day 60 (Fig. 7c).

Discussion

The results obtained so far are of importance. To our knowledge, there is no information in the literature about the relationship between the compost maturity and the ability of degrading different types of chemical structures. The younger composts have the ability of degrading more efficiently aliphatic structures. Moreover, no lag phase is observed and the degradation starts immediately after addition of the aliphatic structures. Also, the microorganisms responsible for the degradation of aliphatic structures are present and active in composts of different levels of maturity.

The aromatic compounds are degraded faster in compost of middle or high maturity. In younger composts the ability takes some time to appear, approximately 20 to 30 days of lag phase while no lag phase is seen in older composts. However, at the end of the incubation period (60 days) the mineralization in younger composts can be as high as in the older ones.

A very interesting result was the mineralization of pyrene in older composts. Pyrene is a 4ringed PAH, with a very stable structure, which is difficult to degrade. Surprisingly, the older composts were able to mineralize around 40% of pyrene in 60 days. Another important result was the degradation of the even more recalcitrant benzo(a)pyrene. This compound was not mineralized when tested alone in compost materials of different maturities. However, when added together with other PAHs, 70, 40 and 30 % was degraded in 2-, 6- and 10-months old compost, respectively. The presence of the lower molecular weight PAHs contributed to the development of the right microorganisms and/or the right conditions for the degradation of benzo(a)pyrene, as for example formation of biosurfactants which can have increased the solubility of B(a)P.

Conclusions

- The degradation of hexadecane occurs immediately, without any lag phase, in composts of different maturities.
- The degradation of phenanthrene occurs with no lag phase in the 6- and 10-months old compost, while the degradation in the 2-months old compost occurs after a lag phase of approximately 30 days. However, at the end of the incubation period the percent of mineralization was 78, 85 and 50% in the 2-, 6- and 10-months old compost.
- Mineralization of pyrene was observed in the 6- and 10-months old compost but not in the 2-months old.

- Benzo(a)pyrene alone or in the presence of pyrene was not mineralized in neither of the compost materials of different levels of maturities. However, approximately 10% was dissipated in the 2-months old compost.
- Benzo(a)pyrene was degraded when added in a mixture together with phenanthrene, anthracene and pyrene. A 70, 40 and 30% degradation was observed in the 2-, 6- and 10-months old compost, respectively.
- The degradation of phenanthrene and pyrene was metabolic.

The results obtained so far are very encouraging and novel. A manuscript with the results is in preparation for submission to a scientific journal. The laboratory studies took more time than expected especially because of the importance to know more about the fate of the recalcitrant high molecular weight PAHs. Further studies are highly recommended to allow the design of a system that could be easily used at the farms for the treatment of diesel saturated filter material. High efficiency is expected.

Further studies of the ability of compost material to degrade other pollutants are also recommended.

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