

Effects of Soil Texture on Respiration and Metal Solubility in Heating Oil-Amended Soils

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The response of microorganisms to oily wastes applied to soil largely affects the rates at which these materials are degraded in soil. The short-term soil loading rate of oily-wastes is therefore mainly determined by microorganism responses. Conversely the total loading limit of a site will probably be determined by the metals or other toxic materials in the oily waste. Jobson et al. (1974) demonstrated significant increases in bacterial growth in soil to which crude oil had been applied, but fungal populations were not affected by oil amendment. The soil used was low in fertility and remained frozen for about half the year. Atlas (1981) reviewed aspects of microbial degradation of petroleum hydrocarbons and pointed out that supplemental fertilizer applications do not always promote oil degradation. Dibble and Bartha (1979) addressed questions regarding the influences of environmental parameters and soil fertility in a laboratory study of oil biodegradation. In their study an equal volume of sand-soil mix, inoculated with agricultural soil to ensure microbial diversity, was used to determine the responses of microbial activities associated with oil decomposition to soil fertilization (nitrogen, phosphorus, and potassium) and varied environmental parameters. Response to treatments was determined by monitoring microbial respiration and quantitative changes in oil residues in oil-amended, incubated soil. Oil decay and respiration were both found to respond to fertilization of the soil. Gudim and Syrett (1975) showed that microbial respiration in soils amended with different petroleum hydrocarbons increased when compared to unpolluted soils of the same description. Differences in respiration rates existed between differently treated soils. Soil texture seemed to be related to respiration response, although other dissimilarities in hydrocarbon pollutants used and site location preclude the valid testing of this effect. Atlas (1977) stated that increasing the surface area of oil exposed to the environment will promote biodegradation. Both soil fertility and soil pore size distribution are correlated with soil texture. Coarse-textured soils have a predominance of large pores, but low surface area and clay content, which are

not conducive to high inherent fertility. A comparison of oil transformations in soils of varying texture but similar fertility could reveal the effects of soil texture on oil decomposition. Differences in soil surface area may also cause differential responses to added metals in soils of diverse textures. The purpose of this experiment was to determine the effect of three different soil textures on rates of soil respiration and soil metal availability and content, following amendment with two types of heating oils.

MATERIALS AND METHODS

A moderately well-drained, fine sandy loam, Peru taxadjunct soil (coarse loamy, mixed, frigid Typic Haplorthods, 44% sand, 43% silt, 13% clay) was selected to represent medium-textured soils. Hereafter this type is referred to as fine sandy loam. Adams (sandy, mixed, frigid Typic Haplorthods, 83% sand, 9% silt, 8% clay) and Buxton (fine illitic, frigid, aquic Dystric Eutrochrepts, 12% sand, 68% silt, 20% clay) soils were selected to represent lighter and heavier textured soils. Hereafter these are referred to as loamy sand and silt loam, respectively. Bulk soil samples were collected and handled so as to preserve the biological components (Primer and Bartha 1972). Soils were placed in 5-liter trays and sufficient water to bring the soil to 60% of water holding capacity was mixed thoroughly into the soil. The experimental soils were amended with 193 mg N, 71 mg P, and 180 mg K/kg soil supplied as $\text{CO}(\text{NH}_2)_2$ and K_2HPO_4 . No. 6 and No. 2 heating oils were obtained from a local commercial distributor. The No. 6 oil conformed to the NBS standard (SRM 1634a) with the exception that vanadium content (356 mg/kg) was approximately seven-fold higher in the oil used for these experiments. Heating oils (15 ml of No. 2 or 13.4 ml of No. 6) were added to 500 g soil to approximate a 3% wt/wt loading rate of oil in soil. After thorough manual mixing, 100 g subsamples were placed into incubation vessels. The experimental units, representing three soils, two oil types, three replications, and two temperatures were incubated at 12°C and 25°C. During incubation soil moisture was maintained at 0.21, 0.15, and 0.28 kg H_2O /kg dry soil for the fine sandy loam, loamy sand and silt loam soils, respectively. Respiration in soil was measured as evolved CO_2 according to the method described by Bartha and Primer (1965). Determinations of CO_2 evolution were made at 0, 2, 4, 6, 8, 10, 17, 25, 33, 40, and 47 days. Soil samples were collected from incubation studies, sub-sampled and stored at 4°C until nutrient and extractable metal analyses were performed using pH 3.0 ammonium acetate extraction (Carpenter 1953) of dried samples at a 1:10 soil:solution ratio and a five minute shaking time. Analysis for potassium was performed by flame emission on an atomic absorption spectrophotometer. All other elemental analyses were performed with an inductively coupled argon plasma emission spectrograph.

RESULTS AND DISCUSSION

The effects of soil texture on heating oil decomposition at 12°C can be seen in Figure 1. Respiration in soil treated with No. 2 heating oil was significantly higher in the fine sandy loam compared to both the loamy sand and silt loam soils. The lag period preceding the utilization of the No. 2 oil was longer in the silt loam soil (approximately 10 days) than in the coarser soils. Precautions were taken to prevent poor aeration in all incubated samples by allowing gas exchange at each CO₂ sampling time, but it is possible that oil and water in the silt loam soil impeded gaseous exchange between the soil and atmosphere. The smaller average pore diameter combined with the water content (0.28 kg/kg dry soil) in the silt loam soil may contribute to a reduction in gas diffusion, thus slowing oxidation of the oil. The fine sandy loam and silt loam evolved total CO₂ quantities approximately 5x and 2x that of the loamy sand. It is not likely that a deficiency of one of the major nutritional elements in the loamy sand soil limited biodegradation because all soils received nitrogen, phosphorus, and potassium. If the pore occlusion explanation stated previously applies, then a fertile, coarse-grained (i.e. sandy) soil should allow relatively high rates of activity. Since carbon evolved from loamy sand was significantly less than that from the fine sandy loam or silt loam soil, pore occlusion may not totally explain the results. Coarse-grained soils are characterized as having relatively low surface area-to-volume ratios. Fine-grained soils have larger surface-area-to volume ratios. A given amount of oil homogeneously distributed in soil would result in thick oil films on the particle surface of the coarse-textured soils and thin layers of oil on the particles of the fine-textured soils. Non-homogeneous oil distribution or gaps in oil coverage of soil particles will enhance aeration, but diffusion of oxygen through relatively thick oil layers would be slow and result in slower rates of decomposition. Oxygen and possibly nutrient diffusion through an oil layer may be more limiting to the biodegradation of oil in soil than the rates diffusion through soil pores. The reduction in decomposition rates that we observed in the loamy sand soil may have arisen because gases and nutrients were in contact with a smaller and relatively thicker surface oil layer. The silt loam demonstrated a restriction in CO₂ evolution compared to the fine sandy loam. This suggests the effective surface area-to-volume ratio is reduced (via occluded pores) in oil polluted, fine-textured soils. Therefore, the fine sandy loam soil used in these investigations may offer a compromise between soil surface area and percentage of large pores which allows good diffusion of gases and nutrients into the soil (through large pores) and enough surface area to ensure relatively thin oil layers. The fine sandy loam would then have a larger capacity to promote oil decomposition than either the loamy sand or the silt loam soil.

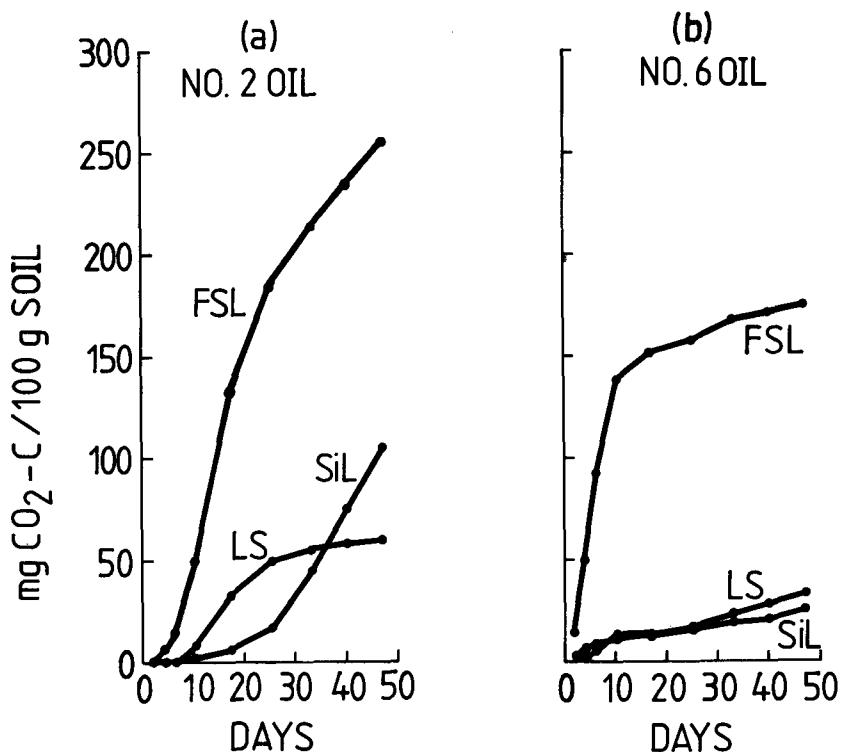


Figure 1. Cumulative CO₂ - carbon produced at 12°C in three oil-amended soils; a fine sandy loam (FSL), a loamy sand (LS) and a silt loam (SiL), which represent medium, coarse, and fine textured soils, respectively. Data have been corrected for CO₂ produced in control samples.

Differences in biodegradation between oil types were observed (Fig.1), with the No. 6 treatments releasing less total CO₂ during incubation. Trends among soils show the fine sandy loam with the greatest amount of CO₂ release for both oils, while the silt loam and loamy sand released less CO₂ and in the case of the No. 6 oil, were not different from each other. The lower degree of biodegradation in No. 6 oil treatments may be the result of physical and chemical differences between oil types. The higher viscosity of the No. 6 oil prevented thorough mixing in soil and resulted in small lumps or balls of oil in the soil. The lighter No. 2 oil allowed a much more homogeneous distribution. We assume that the surface area of oil exposed to soil was much greater in No. 2 oil treatments than in No. 6 oil treatments. The degree of contact between oil surfaces and soil surfaces could account for the lower amount of carbon evolved from No. 6 oil-treated soil by the end of the incubation. Rates of CO₂ release were very rapid for both oil types in the fine sandy loam before the first 15 days. This similarity suggests

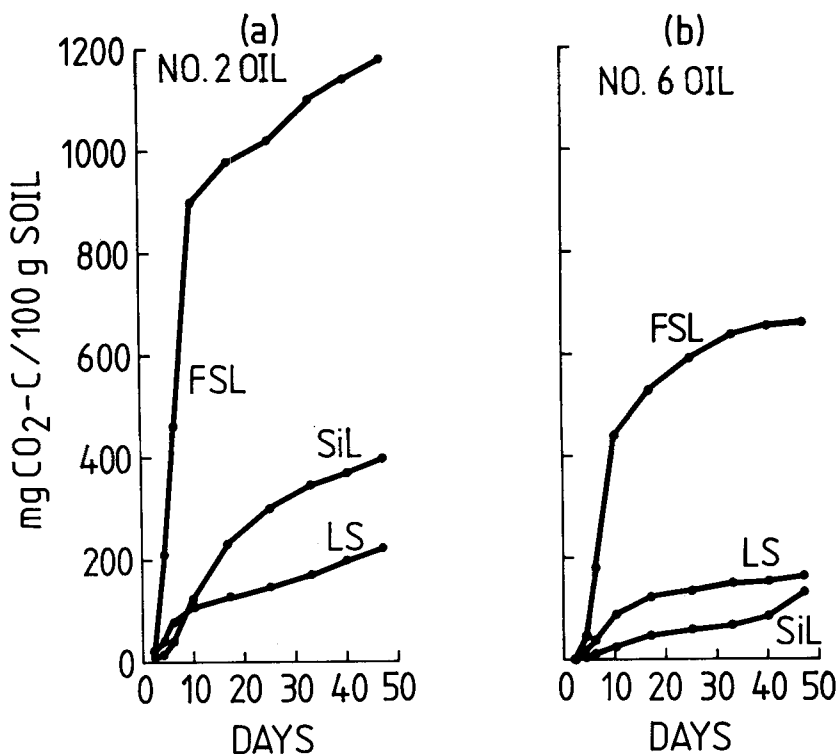


Figure 2. Cumulative CO₂ - carbon produced at 25°C in three oil-amended soils; a fine sandy loam (FSL), a loamy sand (LS) and a silt loam (SiL), which represent medium, coarse, and fine-textured soils, respectively. Data have been corrected for CO₂ produced in control samples.

the presence of readily decomposable substrate in the No. 6 oil that was apparently exhausted after 15 days. Rates of biodegradation at the end of the incubation remained high in the No. 2 oil-treated fine sandy loam samples, while the No. 6 oil treatments generated much lower CO₂ evolution rates.

Similar trends in CO₂ evolution rates were observed for both oil types in the loamy sand soil. Total CO₂ produced in the No. 2 oil treatments was greater than those in the No. 6 oil treatments, although the difference was not significant. Lower cumulative totals for CO₂ evolution from No. 6 oil-treated soils probably reflect the "balling-up" tendency of the heavier oil which substantially reduces the surface of oil exposed to soil.

Figure 2 shows cumulative CO₂ emission from soils amended with No. 2 or No. 6 oil and incubated at 25°C. The fine sandy loam allowed the highest respiration rates under either oil treatment. Almost 1200 mg of CO₂-C had been released from the

fine sandy loam at 47 days after No. 2 oil treatment. This total was greater than amounts in either silt loam or loamy sand soil. Emission of CO_2 was significantly greater ($P>.05$) in the silt loam than in the loamy sand soil at all times after 8 days of incubation. Respiration rates for fine sandy loam samples treated with No. 2 oil were greater than similar samples incubated at 12°C (Fig. 1a). The fine sandy loam treated with No. 2 oil demonstrated maximum decomposition rates prior to 20 days of incubation in either temperature regime (Figs. 1a and 2a). When each soil by oil combination is compared across temperature, similar patterns, but with significantly higher CO_2 release and shorter lag times at 25°C , are observed. No influence could be attributed to an interaction of soil texture and incubation temperature.

The CO_2 release trends for silt loam and loamy sand treated with No. 2 oil were similar to those for fine sandy loam, having longer lag periods and lower total CO_2 release at 12°C than at 25°C . The fine sandy loam differed in having higher total CO_2 release at both temperatures than the other soils.

Biodegradation of No. 6 oil at 25°C was significantly greater ($P>.05$) than at 12°C (Figs. 1 and 2). A similar lag period for all soil textures was followed by high rates of decomposition in the fine sandy loam soil and significantly lower ($P>.05$) rates in the silt loam and loamy sand soils.

Cumulative carbon evolution data for both temperatures show decomposition was greatest in fine sandy loam, followed by silt loam and loamy sand soils with No. 2 oil treatment. Reasons for the inversion of the curves for silt loam and loamy sand soils before 33 days are unknown. In samples treated with No. 6 oil and incubated at both temperatures, the fine sandy loam had the highest rate of activity followed by significantly lower ($P>.05$) rates in the loamy sand and silt loam soils. Rates of CO_2 emission were not significantly different ($P>.05$) between the loamy sand and silt loam soils before 40 days. The trend was for higher rates of activity in the loamy sand soil after 40 days.

The pH 3.0 ammonium acetate extraction showed differences through time for several metals, the most significant of which are iron and manganese. Other elements analyzed in the ammonium acetate extraction, but not reported here, include Ca, Mg, K, P, and Al. The extractable Mn and Fe levels compared by single degree of freedom contrast statements are shown in Table 1.

These levels reflect the reduced species of Fe and Mn, both of which are more soluble in acidic extractants than the corresponding oxidized species (Cotton and Wilkinson 1977). For each soil studied, the extractable Fe and Mn levels were greater in the No. 2 oil-treated samples than for the control samples. The levels of extractable Fe and Mn appear to be related to the

level of microbial activity in the soil. The enhanced activity of microorganisms on the soil surfaces of No. 2 oil-treated samples should contribute to localized anaerobic conditions.

The loamy sand soil also showed significantly greater extractable amounts of Mn at 25°C than at 12°C (data not shown). Significantly higher levels of extractable Mn were found for No. 2 oil amendments compared to No. 6 oil treatments.

Table 1. pH 3.0 ammonium acetate metal levels in three soils

Treatment	FSL		SiL		LS	
	Fe	Mn	Fe	Mn	Fe	Mn
	---mg/kg--		---mg/kg--		---mg/kg--	
Control	5.7	17	1.5	45	9	5.0
3% No. 6	4.8	18	1.3	47	9	7.2
3% No. 2	7.6	30	3.3	88	11	13.8
Significance						
Control vs.						
Treatments	ns	*	*	*	ns	*
3% No. 6 vs.						
3% No. 2	*	*	*	*	*	*

FSL = fine sandy loam SiL = silt loam LS = loamy sand

This difference mirrors differences found by carbon dioxide release determinations on the loamy sand soil. The interrelated combination of reduced oxygen partial pressure and high levels of microbial activity presumably contributed to the greater extractable amounts of Fe and Mn.

The No. 6 oil contained significant amounts of vanadium and nickel (350 and 55 mg/kg, respectively). Analysis of soils for total metal content following incubation showed a significant increase in vanadium (43 to 60 mg/kg V), a non-significant increase in nickel content and no changes in As, Cd, Cr, Cu, Hg, Mn, Pb and Zn when compared to control treatments. Although V and Ni levels may slow biodegradation, the types of hydrocarbons in oil and oil distribution in the soil should be more important for determining decomposition rates with single applications of No. 6 oil to soil. Metal levels in No. 2 oil were found to be quite low. No significant effects from No. 2 oil addition were found by soil analysis for total metal content.

These results suggest that soil texture is an important factor to consider in management practices designed to promote biodegradation of oil in soils. Loam and other medium-textured soils may offer the best opportunity for the biooxidation of oily wastes.

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