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Use of Urea as a Nitrogen Fertilizer in Bioreclamation of Petroleum Hydrocarbons in Soil

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Recently there has been increased concern over the spillage and underground leakage of refined petroleum hydrocarbons into soils. Deposition of these petroleum products may occur as a result of storage tank and pipeline leakage, and transport accidents. As a means to clean up such a spill, soil biochemists have recommended bioclamation with amendments consisting of fertilizers, in particular nitrogen and phosphorus. Petroleum hydrocarbons are highly carbonaceous in nature and often lack the necessary nutrients (N and P) to promote biodegradation. Hydrocarbon-oxidizing organisms require nitrogen and phosphorus to degrade hydrocarbons at a ratio of approximately equal to their cellular tissue. A common C:N:P ratio used in reclamation techniques is 10:1:0.1. However, in most cases, nutrient amendments are made with multiple loading rates to prevent high accumulation of salts. This investigation focuses on a particular nitrogen fertilizer, urea, which can be used as a bioamendment in reclamation of oil spills. It should be kept in mind that upon contamination, a readily available nitrogen source should be accessible to the microorganisms in degrading the contaminant. This study reveals that urea, although having a high nitrogen content, may not be the best choice to optimize biodegradation of petroleum hydrocarbons.

MATERIALS AND METHODS

The soils used were surface samples (0- to 15-cm) selected to obtain a range in pH (6.45 to 8.55), organic C (0.91 to 1.52%) and texture (23 to 46% clay and 21 to 61% sand). Field-moist soil samples (<6 mm) of 5 g each (oven-dry basis) were placed in 50-mL Erlenmeyer flasks and subsequently treated with three rates of leaded gasoline (Shell Oil), kerosene (UCR), diesel oil (Texaco) and motor oil (Shell Fire and Ice All Season [10-40W]). The petoleum hydrocarbons were applied at 0, 5, 10 and 25% loading rates (wt. of oil/wt. of soil) to account for levels that might be found in spillage or leakage situations. The flasks were stoppered and incubated for 14 days at 25°C.

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The method of Tabatabai and Bremner (1972) was used to assay urease activity. Triplicate samples were assayed by treating the soil with 0.2 ml toluene, 9 ml tris-H_2SO_4 buffer (pH 9.0) and 1 ml of 0.5 M urea. The flasks were incubated at 37°C for 2 h, then 35 ml of 2.5 M KCl containing 100 μg ml^{-1} Ag_2SO_4 were added and mixed, and a 20-ml aliquot of the soil suspension was taken for NH_4-N analysis. Controls were performed to assay urease activity without the influence of petroleum hydrocarbons by incubating the soils with deionized water instead of the oils on an equal volume basis. Preliminary experiments revealed that the oils did not interfere with determination of NH_4^+.

RESULTS AND DISCUSSION

Table 1 indicates that the presence of various refined oils can severely inhibit the urease reaction in soils. The degree of inhibition ranged from 23 (kerosene) to 61% (leaded gasoline). The greater the loading rate, the less effective urea becomes as an amendment. In ranking the inhibition of each of these refined oils, it appears that leaded gasoline is the most inhibitory at all three loading rates to the urease reaction. Because inhibition of urease activity is so high, urea should not be recommended as a nitrogen fertilizer to reclaim petroleum spills. A more readily available source of N to the hydrocarbonoclastic population in soil would be ammonium nitrate or perhaps ammonium

Table 1. Effects of refined oils on urease activity in soils

Refined oils	Loading rates (%)	Percentage inhibition of urease activity in soil specified		
		Altamont	Kitchen Creek	Pico
Diesel fuel	5	28	24	27
	10	36	35	31
	25	47	39	44
Kerosene	5	24	23	27
	10	28	31	28
	25	32	35	33
Motor oil	5	23	31	29
	10	27	38	34
	25	38	45	48
Leaded gasoline	5	34	48	40
	10	46	51	46
	25	55	67	61

sulfate providing both a nitrogen and sulfur source. Urea is often employed in landfarming operations where petroleum oils are purposely deposited onto soil for disposal of waste. In many landfarming operations, oily sludge materials containing heavy metals could possibly inhibit urea catalysis in soils (Frankenberger et al., 1983). Tabatabai (1977) showed that certain heavy metals inhibited the urease reaction, particularly Cd^{2+} (49%), Cu^{2+} (51%), Hg^{2+} (75%), and Ag^{+} (84%). With increased popularity of landfarming operations in disposal of waste oils (Mauder and Waid, 1973) and *in situ* biodegradation of hydrocarbons contaminating the subsoil, it is highly recommended that an inorganic nitrogen source be used rather than urea, simply because the availability of the NH_4^+ derived from urea would be greatly delayed by providing a source of nitrogen as urea. Refined oils can inhibit urea catalysis in soils to such an extent that the incorporation of urea fertilizer would do little benefit in the immediate bioreclamation of petroleum hydrocarbons.

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