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Project Summary

Land Treatability of Refinery and Petrochemical Sludges

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The land disposal of API separator sludges was investigated with regard to decomposition rates of organic constituents and the possible impact of these materials on plants and surface water or groundwater quality. Two oily sludges (one from a petroleum refinery and one from a petrochemical plant) were studied as to their phytotoxicity, biodegradability in soils, water-soluble constituents, and field mobility.

Concentrations of refinery sludge of 5% v/v and above depressed ryegrass emergence and yield. The petrochemical sludge suppressed emergence and yield proportional to the amount of sludge applied, and the suppression lasted longer than that of the refinery sludge.

Biodegradation rates were greatest when small applications of sludge were made at frequent intervals. Optimum application rates for both wastes was 5% to 10% (wt/wt).

The water-soluble compounds in both sludges were low in degradability, potentially toxic, and extremely mobile in high concentrations. These results indicate a need for careful management of land treatment sites to avoid groundwater contamination. Gas-liquid chromatography (GLC) combined with column chromatography is recommended for effective monitoring of oily wastes applied to soils.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Soil disposal may prove to be the most economical and environmentally sound means of disposing of many of our complex industrial wastes. Such disposal can be effective provided that application rates and scheduling do not result in conditions that allow undesirable components or degradation products to run off or leach through the soil, and provided no materials accumulate to toxic levels in the soil.

Soil disposal of many wastes is effective because the soil has large surface areas in which to absorb and inactivate waste components. And if the soil is properly managed, it also presents an ideal medium for microbial decomposition because of the presence of oxygen, water, and the nutrients needed for degradation of organic constituents.

Oily wastes are often separated from reusable constituents or more easily disposed of materials by the use of API separators at petrochemical plants and depots. Certain fractions of the materials accumulate as sludge in these pits and must be periodically dredged or pumped out. These wastes have classically been disposed of by deep-sea dumping, deep-well injection, incineration, landfilling, and back-lot dumping. But all of these techniques have either economical or environmental drawbacks that limit their utility.

This report investigates the soil disposal of API separator sludges with regard to decomposition rates or organic constituents and the possible impact of these materials on plants and surface water or groundwater quality. Because of the complexity of the study, it was divided into four sections: phytotoxicity, biodegradation, water-soluble constituents, and field mobility of contaminants.

Phytotoxicity

In the phytotoxicity study, measurements were made of the impact of two oil-water separator sludges on the emergence and yield of ryegrass (Loluim multiflorum Lem.) grown on four diverse soils in the greenhouse. One sludge was from a petroleum refinery, and the other was from a petrochemical plant. Each was applied at rates of 0%, 5%, 10%, and 20% v/v to each of the four soils to determine the influence of application rates. After growth periods of approximately 6 weeks, the grass was harvested, and the soil-sludge mixture was air-dried, cultivated, and reseeded. Eight harvests were made in sequence. Soil wettability was measured twice to evaluate physical problems.

Concentrations of refinery sludge of 5% v/v and above depressed ryegrass emergence and yield through two mechanisms: phytotoxic constituents and impaired water relations. The phytotoxic constituents initially acted to retard plant growth. Several months were required for the sludge to degrade sufficiently to allow normal plant growth. Subsequent yield reductions resulted from the impaired water relations associated with residual hydrophobic hydrocarbons. This impairment was evidenced by the increased water adsorption times of the sludge-treated soils.

The petrochemical sludge had higher concentrations of both organic carbon and aromatics, and it suppressed emergence and yield proportional to the amount of sludge applied. The suppression lasted longer than that caused by the refinery sludge. Seedling emergence from soils treated with 20% refinery sludge did not differ from that in the unamended control by the second planting; but the corresponding treatments with the petrochemical sludge resulted in depressed emergence for the first five replantings. Grass yield from the 20% refinery sludge treatment required 13 months to reach control levels. The corresponding petrochemical treatment yield reaches only 47% of the control levels 17 months after application.

Biodegradation

The biodegradation rates of the two sludges were studied using a soil respirometer as a model for field studies. Biodegradation rates were measured by CO_2 evolution and residual hydrocarbon analysis. The microbial population was determined after 6 months of incubation of the waste-soil mixture. Parameters studied included soil texture, soil moisture, mineral nutrient amendments, application rates, application frequency, and temperature. Maximum degradation rates were achieved with Norwood sandy clay at a temperature of 30C. The greatest rate of biodegradation per unit of waste applied occurred when small applications were made at frequent intervals. Addition of mineral nutrients effectively increased the biodegradation rates of both the refinery and the petrochemical sludges. The soil microcosm was stimulated by small applications of waste, but reduced numbers of microorganisms were found when the application rates exceeded 5 g/100 g of soil for either sludge. Thus a comparison of degradation rate and the microbial population indicates that the optimum application rate for both wastes is 5% to 10% (wt/wt).

Water-Soluble Constituents

A study of the water-soluble constituents of the refinery sludge was performed using Bastrop sandy loam, Nacogdoches clay loam, and Norwood loam. The sludge was extracted with water, and the water-soluble fraction (WSF) was partitioned into benzene. Concentrated extracts were applied to soil thin-layer chromatographic (soil TLC) plates and eluted with deionized water. Soil column leaching studies supplemented the soil TLC, and the analyses of column leachates and soil TLC were performed using gas-liquid chromatography.

Analysis of the WSF yielded largely mono- and diaromatic hydrocarbons such as phenols and naphthalenes. Most of the WSF was highly mobile as a group on soil TLC plates where the solutes moved with the wetting front. Since the waste constituents were concentrated to achieve resolution, the mobility may have been a result of concentrations in excess of the adsorption capacity of the soil. No significant mobility differences occurred among the three soils because of the extreme mobility of the WSF. Compounds of increased polarity and molecular weight exhibited decreased movement in all soils. Soil column results were inconclusive because of confounding by soluble soil organic matter.

The low degradability and the potential toxicity of the soluble compounds in conjunction with their extreme mobility when applied at high concentration suggests that careful management of land treatment sites will be needed to assure that groundwater contamination does not occur.

Field Mobility Study

The field mobility study was conducted to evaluate the fate of two land-treated oily wastes under conditions that duplicated field conditions as nearly as possible. Controlled applications were made of the refinery sludge and the petrochemical sludge to large undisturbed soil monoliths under field conditions. Soil samples were taken periodically to determine degradation and residual organics, and leachate was collected and monitored for potential groundwater contaminants. The same four soils were used as in the phytotoxicity study.

Degradation rates for neither sludge were measurably influenced by soil pH or cationic distribution.

Soil texture profoundly affected the depth of migration. Depth of penetration was inversely related to the degradation rates observed when fertility was not a limiting factor. The deeper the migration, the slower the decomposition. Withholding nitrogen fertilizer reversed the trend and retarded decomposition in the zone of incorporation. This observation is an anomaly attributed to nutrients leached from the surface profile and to the attendant nutritive requirements related to the material balance within a given depth interval. Hydrocarbon levels within surface horizons were materially greater than subsurface horizons requiring a greater nutritive level.

Climatic factors were normalized over soils because of the juxtaposition of the field-installed lysimeters. Degradation rates were diminished for both refinery and petrochemical sludges over the winter months corresponding to the lowered soil temperatures.

Gas-liquid chromatogrphy (GLC) analysis together with column chromatography was an effective means of monitoring the fate of complex waste hydrocarbons applied to soils.

Significant amounts of water moved through all the soil profiles during the study period, buy hydrocarbons were not found in detectable concentrations in leachate from any of the lysimeters. Leachate collected as long as 2 years after waste application remained free of hydrocarbons.

Conclusions and Recommendations

Though oily sludges applied to land may initially be phytotoxic and reduce the yield of the vegetation that manages to emerge, the toxicity diminishes with time. Thus soils used for land treatment of oily sludges can eventually be revegetated.

A comparison of degradation rate with the microbial population indicates that the optimum application rate for both the refinery and petrochemical sludges is 5% to 10% (wt/wt).

The water-soluble compounds in both sludges are potentially toxic, low in degradability, and extremely mobile when applied at high concentrations. Thus careful management of land treatment sites is recommended to prevent groundwater contamination.

The mobility of waste organics and their degradation products in soil are not well understood. GLC analysis combined with column chromatography can be effectively used to monitor these wastes in soils. Additional information should be developed on the fate and mobility of organic wastes in the soil so that land treatment facilities can be designed and managed to protect our groundwater resources.

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***Robert E. Landreth** is the EPA Project Officer (see below).*
The complete report, entitled "Land Treatability of Refinery and Petrochemical Sludges," (Order No. PB 83-247 148; Cost: $19.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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