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Project Summary

Land Treatment of an Oily Waste—Degradation, Immobilization, and Bioaccumulation

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Land treatment of an industrial oily waste was investigated to determine the loss and immobilization of waste constituents and the impact of the waste and the application process on soil biota.

The waste was applied to field plots of a moderately to slowly permeable heavy silt loam in New York. The field plots consisted of four replicates each of natural controls, rototilled controls, and low, medium, and high application rate plots. Wastes were applied in June 1982, October 1982, and June 1983. In June 1983, the plots that had received the low applications received a high application and became the high application plots. During the study, the waste was applied to the test plots at seven waste application rates that ranged from 0.17 to 9.5 kg total oil and grease/meter^2 or from 0.09% to 5.25% oil and grease in the zone of incorporation.

The application of the wastes increased the pH and volatile matter of the soils. Over the period of the study, the half life of the total oil and grease in the field plots ranged from about 260 to about 400 days. Not all of the applied oil was lost from the plots. The refractory fraction ranged from 20% to an apparent 50% of the applied oil and grease. The refractory fraction did not appear to adversely affect the soil biota.

Napthalenes, alkanes, and specific aromatics were rapidly lost from the soil, especially in the warmer months. The half life of these compounds generally was less than 30 days.

The waste applications increased the concentration of several metals in the upper 15 cm of the soil. Except for sodium, all of the metals were immobilized in the upper 15 cm of the plots.

Earthworms bioaccumulated cadmium, potassium, sodium, and zinc. The accumulation could not be related to waste application rates and occurred in worms from the control plots as well as in worms from the plots that received the wastes. The land treatment of these wastes did not cause any unexpected bioaccumulation of metals in the earthworms. The earthworms did not accumulate napthalenes, alkanes, or specific aromatics that were in the applied waste.

Rototilling and waste application reduced the numbers and biomass of earthworms and the numbers and kinds of microarthropods in the field plots. Both types of soil biota were able to recover from the rototilling and waste application.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, 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

Land treatment is a managed waste treatment and ultimate disposal process that involves the controlled application of a waste to a soil. The wastes are applied to the surface or mixed with the upper zone (0-1 ft. (0-0.3m)) of soil. The objective of land treatment is the biological degradation of organic waste constituents and the immobilization of inorganic waste constituents. In this way, the assimilative capacity of the soil is utilized for waste management. Municipal wastewaters and sludges as well as industrial wastes can be treated with this process.

The land treatment of industrial wastes is receiving increasing attention as a cost effective and environmentally sound method of waste management. Land treatment has been used as a waste management technology by petroleum refineries in the United States for more than 25 years. The technology also has been used by the exploration and production sector of the petroleum industry and for the cleanup of oil spills.

The major concerns when land treatment is used for industrial wastes are the transformations, transport, and fate of potentially toxic metals and organics that may be in the wastes. Feasible waste application rates have been based on: (a) physical and chemical characteristics of the soil such as permeability, cation exchange capacity (CEC), and pH; (b) mobility and plant uptake of constituents in the applied wastes; (c) the characteristics of the waste; and (d) the degradation and immobilization of constituents in the wastes.

As identified in the Resource Conservation and Recovery Act (RCRA), land disposal methods are to be protective of human health and the environment. The factors to be taken into account in assessing such protection are the persistence, toxicity, mobility, and propensity to bioaccumulate hazardous wastes and their constituents.

Except as part of organic degradation, the soil biota rarely have been included in any research or full scale land treatment system or monitoring programs. However, the top layer of soil contains myriad microbes and invertebrates that degrade and transform the applied organics and that can affect the immobilization of the applied inorganics. Earthworms are active indigenous soil invertebrates that assist the dagradation of organic compounds. In addition, in the terrestrial food chain, earthworms represent one of the first levels of bioaccumulation that can occur when industrial wastes are applied to the land. It is appropriate to consider earthworms as a test organism for determining the impact of industrial waste on soil biota when land treatment is used for such wastes. Microarthropods, such as mites and springtails, are also biota found ih abundance in most soils and are secondary decomposers and detritus feeders. Studies have shown that they are affected adversely by insecticides and other chemicals added to the soil.

The overall purpose of this project was to determine: (a) the loss and immobilization of constituents of an oily waste when the waste was applied to the soil at different application rates, (b) the impact of the waste and the application process on soil biota, and (c) the general assimilative capacity of a soil when industrial wastes are land applied.

Materials and Methods

This project was a cooperative agreement between Cornell University and the Robert S. Kerr Environmental Research Laboratory (RSKERL) of the Environmental Protection Agency (EPA). The research was conducted in laboratories of the Department of Agriculture Engineering, College of Agriculture and Life Sciences, Cornell University, and on land adjacent to the Cornell campus. The identification of the numbers and type of microarthropods in soil samples was done by Dr. Roy A. Norton of the Department of Environmental and Forest Biology, College of Environmental Science and Forestry (CESF), State University of New York, Syracuse, New York.

Wastes

The wastes were obtained on three separate occasions from a site in Oklahoma with the help of RSKERL personnel. The wastes were of unknown origin but were black, viscous, and collected from the bottom of a lagoon used to store wastes from oil refineries. Although the wastes were collected from a large holding lagoon on three different occasions and it was unlikely that the contents of the lagoon were homogenous, the characteristics of the wastes were reasonably similar, expecially when expressed on a moisture free basis (Table 1). The wastes were applied to the field plots to obtain a specific oil content in the soil of different plots. Samples of the wastes were analyzed before each application date, and the oil data was used to determine the volumes of a waste to be added to a specific plot.

These oily wastes had been contained in the holding lagoon for several years before the required quantities were removed and transported to the field site for application. Many volatile compounds may have been lost while the wastes were held in the lagoon.

Field Site

The site used for application of the waste was an old field in Tompkins County, New York. It had not been used for agricultural purposes and had not received applications of lime, fertilizer, pesticides, or herbicides for over 10 years before its use in this project. The site had been mowed annually to hinder growth of woody plants. The soil at the site was a Rhinebeck silt loam. It contained about one foot of moderately to slowly permeable heavy silt loam over slowly permeable silty clay loam or silty clay. The soil was somewhat poorly drained and existed on nearly level to moderate slopes in glacial lake areas.

The field site consisted of 20 plots, 4 meters by 4 meters, with 4 meters of border area surrounding each plot. Four waste application rates plus natural and rototilled controls were used at the site. Four replications were made for each waste application rate and type of control. All plots were mowed before each waste application. All plots, except the natural controls, were rototilled after each application of the waste. The four rototilled control plots had no waste applied but were nevertheless rototilled. The four natural control plots had no rototilling or oily waste applied and were used to separate the effect of the rototilling and the waste applications. The applied wastes were distributed over the plot surface as uniformly as possible and were rototilled into the soil to a depth of about six inches (15 cm) such that the zone of incorporation for these plots was the top six inches.

Each test plot (16 m^2) was marked with corner stakes to permit placement of a framed grid to define 400-0.04 m^2 (20 cm x 20 cm) sampling subplots. Three different subplots were sampled on each sampling date to determine changes in incorporation zone characteristics and in earthworm and microarthropod populations. To eliminate edge effects, the edge subplots were not sampled. The subplots that were sampled from among the 324 possibilities were determined using a random number table. Thus, different sampling locations were used at each plot each time samples were taken. No subplot was sampled twice during the study. An elevated plank platform was used to obtain the samples so that the plots were not disturbed or contaminated while the samples were taken.

Natural vegetation such as grass was allowed to become re-established on the plots after the waste applications.

nalytical Procedures

Soil samples were taken from each plot at approximately monthly intervals except during the winter. Hand sorting was used to determine earthworm numbers and biomass from each core. Before the physical and chemical characteristics of the soil were measured, the cores from each plot were composited. Residual soil was returned to the plots and used to fill in the core holes. The microarthropod samples were soil cores approximately 6 cm in diameter and 6 cm deep. The microarthropods were separated from the soil by inverting the soil core in a heat-gradient extractor for one week.

Metals and certain organics in the waste, soil, and earthworm samples were ınalyzed by personnel at the EPA Robert 3. Kerr Environmental Research Laborıtory (RSKERL). Cornell personnel anayzed the waste and soil samples for more 'outine parameters. Dr. Norton (CESF) ;ounted and identified the microarthroıods.

;pecial Studies

Two special studies were conducted to etermine the variability in the character;tics of the soil samples taken from ırious locations in the field plots, and e precision and accuracy of the ana/tical method used for oil and grease /hen used with soil samples. The spatial ariability study identified the extent to /hich the variability of the data was due to the non-homogeneity of waste application and rototilling. The results of the oil and grease analytical method evaluation established the extent to which this method extracted the oil and grease in the waste and soil samples.

Results and Discussion

The oily waste was applied to specific test plots in June 1982, October 1982, and June 1983. In October 1982, the plots received larger application rates than those of June 1982. In June 1983, a very high waste application was made to the plots that had received the initial low application rates. The effect of seven application rates, ranging from 0.17 to 9.5 kg oil per meter^2 of surface area, was evaluated. The rates covered those likely to be used under actual field conditions.

Only the indigenous nutrients and trace elements in the soil and the waste were available to the micro- and macroorganisms as the wastes were degraded. No fertilizers or other amendments were added to the plots. The plots were only cultivated (rototilled) immediately before and after the wastes were applied. No subsequent cultivation occurred to aerate the zone of incorporation. The plots were undisturbed after the combined waste applications and rototilling and only natural aeration occurred in the plots. This is different from what would occur at most industrial land treatment sites, which are frequently tilled to promote mixing and aeration and to increase degradation and other losses. This approach was taken in order to approximate the changes that would occur under conservative and nonoptimum conditions such as when single or highly intermittent waste applications are administered or when a spill occurs. The approach also caused one less variable, the frequency and type of aeration (tilling), to be included in the study.

The pH of the plots that received the high applications of the oil waste increased. The increase was pronounced for the plots that received the very high applications in June 1983. With the very high application, the soil pH increased by more than one pH unit. After the waste applications, the pH stayed at above background levels for the remainder of the study.

The volatile matter in the soil was increased by applying waste. Until the waste applications in October 1982, the volatile matter in the plots was about 9% of the soil on a moisture free basis. After the October 1982 application, the volatile matter in the medium application plots was about 10% and in the high application plots, about 11%. After the application in June 1983, the volatile matter in the very high application plots was in the range of 14 to 15%. There appeared to be a slight decrease of the volatile matter in the very high application plots with time.

With time, the concentration of oil and grease in the soil decreased. However, the applied oil and grease was not lost completely. After each waste application, a new apparent background concentration in the respective plots resulted.

It was impossible to correlate statistically the oil and grease losses to the soil temperatures in the field plots. Temperature, however, should have an effect on such losses, since it affects the rates of biodegradation and volatilization, the most likely mechanisms of loss in the field plots. However, any effect due to temperature could not be discerned and separated from other parameters affecting the oil losses. The effect of temperature probably was masked by factors such as the variability in the oil and grease data, differences in soil moisture as the soil temperature changed, and differing oil and grease compounds in the soil at different times during the study.

The immobilization of metals in the soil was analyzed by comparing the metal concentrations of subsoil samples from the 15 to 30 cm depth taken in October 1983. The metal concentrations of subsoil samples from the plots to which the wastes were applied were analyzed statistically to determine if the deeper soils of

able 1. Average Characteristics of the Oily Wastes Applied to the Field Plots

	Application Date		
Parameter	*June 1982*	*October 1982*	*June 1983*
'ater, %WB[a]	*59.0*	*62.3*	*48.7*
sh, %MFB[b]	*26.9*	*30.1*	*30.2*
il & Grease, '/kg MFB	*660*	*614*	*470*
ɔtal Kjeldahl litrogen, mg/kg MFB	*2360*	*2320*	*2080*
ɔtal Phosphorus, ng/kg MFB	*2620*	*ND[c]*	*1760*
hemical Oxygen)emand, g/kg MFB	*1340*	*1250*	*1460*
I	*7.2*	*7.1*	*6.7*

NB = wet basis.
ИFB = moisture free basis.
) = not determined.

the controls and the waste application plots had differing metal concentrations. As of the October 1983 sampling date, the wastes had been applied to the medium and high application plots for about one year and had been applied to the very high application plots for about four months.

The statistical analysis indicated that sodium was the only metal with a significantly different concentration in the 15 to 30 cm depth between the control plots and any waste application plot. That difference only occurred for sodium in the soil of the very high plots.

Soil samples were extracted with methylene chloride and the extracts analyzed for organics. Time and personnel constraints made it impossible to analyze for the organic compounds in the oily waste. Rather, a smaller number of organic compounds were analyzed in selected soil samples to determine the loss of these compounds after application.

Soil samples from the very high application plots were emphasized since the concentration of organic compounds in these plots was expected to be well above detection limits and might remain so for a reasonable period of time. Soil samples from such plots were taken shortly after the application in June 1983 and monthly thereafter through October 1983. In addition, soil samples from a very high plot, a high plot, and a medium plot were analyzed at longer time intervals either to confirm the loss patterns from the very high plots or to identify the losses in the plots that had received lower waste applications. The organic compounds that were determined in the extracts included C_8 to C_{26} alkanes, napthalenes, and several other aromatics such as fluorene, anthracene, phenanthrene, and pyrene.

The loss rate constants for the specific organic compounds indicate that during the warmer months (June through October), the losses were rapid, with half-lives of generally less than 30 days. Because of the limited data, it was impossible to relate the loss rate constants to the soil temperature or other factors that might affect the loss of the organic compounds. The fact that some of the alkanes were detectable in the high application plot after seven months of cold weather suggests that the loss rates were lower during the winter months.

Soil Biota

The application of the wastes had definite effects on the earthworm numbers and biomass and on the microarthropods in the field plots, due to both the rototilling and the immediate impact of the waste. The soil biota were decreased by the rototilling and even more so by the wastes. However, with time, these soil biota did repopulate the field plots. The project results indicate that these soil biota can recover from the modest addition of oily wastes.

The data indicated that the earthworms accumulated cadmium, potassium, sodium, and zinc. Potassium and sodium are of physiological but not environmental importance in terms of bioaccumulation. The cadmium that accumulated in the earthworm tissue probably came more from the background cadmium in the soil than from the cadmium in the applied waste, especially since the cadmium had bioaccumulated at comparably high levels in the worms from the control plots. A comparison of the data from this project with data from the peer-reviewed literature indicates that the land application of these oily wastes did not cause any abnormal or unexpected bioaccumulation of metals in earthworms.

Conclusions

The objectives of this study were attained. The results indicated that the soil has the capacity to treat wastes such as those used in this study. Many of the organics in the applied waste were removed (lost) and the metals were immobilized when the wastes were applied to the soil intermittently and at varied rates. The soil cultivation method (rototilling) and the applied waste had an immediate adverse impact on the soil biota (earthworms and microarthropods), but the soil biota recovered with time. A fraction of the applied oil and grease was not removed during the study. The remaining organics and the metals did not appear to have any permanent adverse effect on the soil biota.

In addition, the application of these oily wastes to the field plots increased the pH of the acid soils (as much as one pH unit for the higher applications), increased the temperature of the soil in the field plots that received the higher applications by 1 to 5°C, and increased the organic matter of the soil by 1 to 5%.

The half-life of organics applied to the soil varied. The loss of specific organics (napthalenes, alkanes, and certain aromatics) in the field plots was rapid, especially in the warmer months. The half-life of these compounds was generally less than 30 days. In comparison, the half-life of the total oil and grease in the field plots ranged from about 260 to about 400 days. The oil and grease losses could not be correlated to the soil temperature, to other soil parameters, to the amounts of waste that were applied, or to the waste application rates.

All of the applied organics were not lost from the soil during the study. The separation and identification procedures used were not able to identify the type or structure of the residual organics that remained in the soil at the end of the study. However, based on laboratory studies using soil from the field plots and the fact that both earthworms and microarthropods could repopulate the soil of the plots receiving the wastes, the organics remaining in the soil did not appear to result in a permanent adverse impact to the soil biota.

As a result of the waste applications, the concentration of many of the metals in the waste increased in the top 15 cm of the plots. This increase was especially noticeable as a result of the high and very high applications. However, analyses indicated that, except for sodium in the very high application plots, all metals were immobilized in the top 15 cm of the soil.

The data indicated that soil biota such as earthworms and microarthropods can recover from intermittent applications of an oily waste. With time, the numbers and kinds of soil biota in the plots to which the wastes are applied can again become similar to those in the control plots, although at a rate not presently predictable. The land application of these wastes will not have an irreversible, adverse impact on earthworms and microarthropods.

The earthworms in the field plots did bioaccumulate several metals that were in the applied waste: cadmium, potassium, sodium, and zinc. However, when the level of bioaccumulation was compared to data from other studies and to bioaccumulation in worms found in the control plots, it was apparent that the land treatment of these oily wastes did not cause any unexpected bioaccumulation of metals in the worms. The earthworms did not bioaccumulate napthalenes, alkanes, or specific aromatics from the applied waste. Thus, the land treatment of these wastes did not lead to any bioaccumulation of apparent concern.

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***John E. Matthews** is the EPA Project Officer (see below).*
The complete report, entitled "Land Treatment of an Oily Waste—Degradation, Immobilization and Bioaccumulation," (Order No. PB 85-166 353/AS; Cost: $14.50, subject to change) will be available only from:
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