



Project Summary

Fate of Selected Toxic Compounds Under Controlled Redox Potential and pH Conditions in Soil and Sediment-Water Systems

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A study was conducted to determine the effects of pH and redox potential conditions on the degradation of selected synthetic organics. Also, the effects of these physicochemical parameters as well as other physical and chemical properties of soils and sediment-water systems on the adsorption of selected organics were measured. Compounds used in degradation studies included methyl parathion, 2,4-dichlorophenoxyacetic acid (2,4-D), and Aroclor 1254 (a polychlorinated biphenyl formulation). Compounds used in adsorption studies included methyl parathion, 2,4-D, and pentachlorophenol. Soils and sediments used for both the degradation and adsorption studies were selected to include materials having a wide range of physical and chemical properties.

Degradation studies conducted on soil and sediment suspensions amended with the synthetic organics and then extracted and analyzed by gas chromatography showed important redox potential effects on the degradation of methyl parathion and 2,4-D, but not Aroclor 1254. Methyl parathion was removed much more rapidly under reducing conditions. Oxidized conditions contributed to more rapid degradation of 2,4-D. Degradation studies conducted with ^{14}C -labeled compounds also showed important effects of oxidation-reduction conditions on mineralization of the synthetic organics. If collection of the labeled carbon as evolved carbon dioxide was the criterion for measuring degradation, however, the rate of

degradation and the treatment effects, in the case of methyl parathion, were found to be very different compared to results of degradation studies using extraction and gas chromatography for analysis. Differences resulting from the analytical procedures used were discussed in terms of whether one was looking for initial modification of the parent molecule during degradation or for mineralization of the ^{14}C -containing portion of a labeled compound. The latter would usually involve a sequence of degradative steps before the label was converted to carbon dioxide.

Redox potential was shown to have a significant effect on the adsorption of pentachlorophenol as this compound was partitioned more with the solid phase under oxidized conditions than reduced conditions. Correlation coefficients between methyl parathion and 2,4-D adsorption and several physical and chemical properties of soil were determined. In particular, an effort was made to identify important properties contributing to adsorption in soils and sediments having a low organic matter content.

These degradation and adsorption studies demonstrated the importance of physicochemical properties on the persistence and mobility of selected synthetic organics in soils and sediments. Information of this type should improve the capability to predict the fate and potential impacts of synthetic organics in various environmental compartments. Additional work should be done,

however, to establish the effect of these physicochemical conditions on the rate of degradation under natural conditions.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, 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

The threat of adverse environmental impacts associated with organic pesticide residues or industrial waste depends on several factors. These include: (1) the particular compounds present, (2) the concentrations of the compounds present, (3) the environmental compartments in which the materials are found and the organisms exposed, (4) the persistence or rate of degradation of the material in various environmental compartments, and (5) the transport of the material in the environment.

A substantial amount of research has been conducted on the degradation and transport of synthetic organics in the last 20 years. Much of this work, however, has been limited to insecticides and herbicides in typical agricultural soil materials. Until recent years, little work had been done with sediment-water systems or with industrial organics. The sediment-water systems of streams, rivers, lakes, and coastal waters have been major recipients of pesticide residues, industrial organic wastes, and chemicals from transportation accidents (point and nonpoint sources). The physicochemical properties of sediment-water systems affecting the degradation and transport of synthetic organics are often substantially different from the properties of agricultural soils in an area. In deep or quiescent sections of a sediment-water system, the sediments will tend to have greater clay content, greater humic material content, and strongly anaerobic conditions prevailing in the bulk of the sediment material. The oxidation-reduction conditions of suspended particulates and the top few millimeters or centimeters of sediments are aerobic, however. The microbial and chemical processes occurring in oxidized sediments that may influence the degradation of synthetic organics are similar to processes occurring in typical upland soils. Thus sediment-water systems usually include a wide range of oxidation-reduction conditions.

It has been reported for more than a decade that the degradation rate of some synthetic organics is affected by physicochemical conditions of their environment, such as pH, oxidation-reduction intensity, and salinity. Relatively little research,

however, has been done on this topic. Some researchers have made the generalization that the degradation of synthetic organics is faster under anaerobic conditions. The research conducted by the Laboratory for Wetland Soils and Sediments over the last few years indicates that the effect of oxidation-reduction conditions on degradation rates is very compound specific. Because of the recent emphasis on modeling the fate of synthetic organics in the environment and the wide range of physical, chemical, and microbial properties encountered in soils and sediment-water systems that may affect the persistence of synthetic organics, it is important to understand the effects of physicochemical conditions on the degradation of pesticide residues and industrial organic wastes.

It is well established in the literature that soil and sediment humic material is a primary component associated with the adsorption of synthetic organics. Humic materials are also qualitatively and quantitatively affected by oxidation-reduction conditions. Recent literature has clearly demonstrated that the partitioning of hydrophobic organics between bound and dissolved forms is associated with the amount of humic materials present. The possibility also exists, however, that oxidation-reduction conditions affect the chemical properties of humic materials affecting adsorption of synthetic organics. Other soil components such as hydrous iron oxides that may influence the adsorption of synthetic organics are also affected by oxidation-reduction conditions.

The objectives of this research were to: (1) determine the effects of pH and oxidation-reduction conditions on the degradation rate of selected toxic synthetic organic compounds, (2) examine the effects of oxidation-reduction conditions and other soil properties on the adsorption of the selected synthetic organics, and (3) demonstrate an experimental approach for evaluating the effects of physicochemical conditions of soil and sediment-water systems on the environmental chemistry of synthetic organics.

Project

Two types of degradation studies were conducted. In one, soil and sediment suspensions amended with either methyl parathion, 2,4-D, or Aroclor 1254 were maintained under controlled pH and redox potential conditions. The loss of these compounds with time was measured by extraction and gas chromatographic analysis as an indication of degradation. In the second type of degradation study conducted, methyl parathion and 2,4-D uniformly labeled with

^{14}C in the aromatic ring were incubated under air and oxygen-free nitrogen conditions in several soil and sediment materials. Collection of labeled carbon dioxide was used as a measure of degradation in these studies.

Adsorption coefficients for 2,4-D and methyl parathion were determined using batch equilibrium methods on 19 soil and sediment materials selected to give a wide range in physical and chemical properties. These properties were measured and regression values calculated to indicate which properties or combination of properties were important in influencing adsorption coefficients. Also, adsorption coefficients were determined on some soil and sediment materials pretreated under controlled pH and redox potential conditions.

These degradation and adsorption studies were conducted to examine the role of physicochemical properties on the persistence and mobility of selected organics in soils and sediments. Information of this type should improve the capability to predict the fate and potential impacts of synthetic organics in various environmental compartments.

Conclusions

In studies using stirred suspensions under controlled pH and redox potential conditions, salinity effects on the loss of methyl parathion from an estuarine sediment were minimal. Soil and sediment differences, pH, and redox potential levels had a greater effect on the loss of methyl parathion. Sediments tended to give more rapid degradation than soils. In the two materials studied at different pH levels, methyl parathion loss was greater at near neutral pH levels compared to moderately acid conditions. Of the experimental parameters examined, redox potential had the greatest effect on the loss of methyl parathion. Methyl parathion levels decreased much more rapidly under reducing than oxidizing conditions. Generally, there was a sequential increase in degradation rate for every incremental decrease in redox potential over the four pH levels studied.

The apparent very rapid degradation of methyl parathion under strongly reduced conditions is believed to be due to processes other than direct microbial metabolism. In one case, a complete loss of the compound was observed within hours. Plots of the log of concentration versus time were nearly linear, as indicated by high correlation coefficients in most cases. Careful examination of these plots, however, revealed a slight upward curve indicating some deviation from first order degradation kinetics.

One degradation study using stirred suspensions and controlled pH and redox potential conditions was conducted with 2,4-D. As observed for methyl parathion, redox potential conditions greatly affected the loss of 2,4-D, but, unlike methyl parathion, 2,4-D was removed much more rapidly from oxidized than reduced soil material.

Aroclor 1254 was incubated at two pH and four redox potential levels for six weeks. Although recovery decreased to about half of initial levels after six weeks in the stirred suspensions, there was no apparent effect of pH or redox potential on the recovery of this PCB formulation.

In selected studies, carbon dioxide production and evolution was measured from microcosms incubated under controlled redox potential conditions. The data indicated greater microbial activity with increasing redox potential. It was not possible to relate the degradation rate of any of the compounds studied directly to microbial activity levels. With methyl parathion in particular, it was obvious that factors and processes other than microbial respiration rates were involved with the rate of degradation.

In degradation studies using labeled compounds in unstirred soil materials and the collection of labeled carbon dioxide as a measure of degradation, oxidation-reduction conditions had substantial effects on the rate of mineralization of methyl parathion and 2,4-D.

Carbon-14 labeled methyl parathion was incubated for two to three months in six soil and sediment materials under air and nitrogen atmospheres. A very large and statistically significant oxidation treatment effect was observed in all six materials. In every case, 10 to 20 or more times of the labeled carbon from the aromatic ring was evolved as labeled carbon dioxide under oxidizing conditions compared to reducing conditions. Recovery of the ring-labeled carbon in 2,4-D as carbon dioxide was also much greater under oxidized conditions. For the one soil material studied using both ring- and chain-labeled 2,4-D, no difference was noted in the rate of mineralization of the aromatic ring or the alkyl chain portion of the molecule.

Comparing the results of the extraction/gas chromatography studies with the biometer flask studies revealed major differences in the conclusions one might draw on the effects of oxidation conditions on degradation rates. One difference is that the observed degradation rate of methyl parathion is much slower in the unstirred soil and sediment materials (biometer flasks) compared to the stirred suspensions (extrac-

tion/gas chromatography analysis). Another more striking difference is that oxidation-reduction treatment effects are opposite for methyl parathion using the two degradation study techniques. These observations must be addressed.

For the degradation studies, the biometer flasks were maintained at about 23°C whereas the stirred suspensions were kept at about 28°C. The temperature difference would be expected to contribute to some increase in degradation rate in the stirred suspension, but it is unlikely that temperature differences accounted for most of the degradation differences observed.

The rate of degradation may be enhanced in stirred suspensions compared to unstirred conditions. Other literature reports have noted a stirring effect in laboratory studies of toxaphene degradation under both aerobic and anaerobic conditions, and it was suggested that stirring some soils provides additional available carbon to microorganisms to sustain rapid degradation of toxaphene.

Next, the apparent opposite treatment effects, depending on the type of degradation study, must be addressed. In the biometer flask studies, the labeled carbon was located in the aromatic ring of the methyl parathion molecule. Other studies discussed in the report suggest that several other modifications to the molecule may occur before degradation of the aromatic ring (i.e., hydrolysis of the ester group and reduction of the nitro group on the benzene ring). Thus recovery of the label as carbon dioxide represents very substantial modification (degradation) of the parent compound. The rate of recovery of the label as carbon dioxide does not say anything about the rate of initial or partial degradation of the parent compound as several sequential intermediate degradation products are probably involved before mineralization of the aromatic ring to carbon dioxide occurs. Thus, it is highly probable that modification of the parent molecule occurred at a greater rate than indicated by the rate of recovery of the label.

Extraction of the soil or sediment material and analysis by gas chromatography more accurately indicates the rate of loss of the parent compound but, unless intermediate degradation products are identified and quantified, does not reveal much about the rate of total mineralization of the parent molecule. Both ¹⁴C labeled and extraction/specific compound quantification methods are used extensively in degradation studies of synthetic organics. The comparison of results by the two methods in this study, which indicates opposite treatment effects, clearly demonstrates that a researcher should carefully consider the compatibility of

a particular experimental approach with the research objectives.

Organic matter content of the soil and sediment materials was generally indicated to be the most important property affecting adsorption. As expected, 2,4-D was less strongly associated with the sediment phase than methyl parathion, and pH was more closely associated with the adsorption of 2,4-D than with methyl parathion.

One objective of this study was to examine soil properties that may be important in immobilizing synthetic compounds where the soil organic matter content is low. Data were presented indicating that in these low organic matter content soils, the association between adsorption and oxalate extractable Mn and Ca may be an important relationship. Additional work should be done in low organic matter soil material to better quantify the relationship between adsorption and soil geochemical properties.

The method of processing sediment materials before conducting the adsorption procedures (testing wet sediment materials versus aliquots that had been dried and ground) did make a difference in the 2- and 24-hour adsorption coefficients measured for pentachlorophenol. Sample preparation methods did not affect the relative oxidation treatment effects. Pentachlorophenol was more tightly bound to oxidized estuarine sediment solids than to reduced sediment solids.

Recommendations

Many scientists now recognize that oxidation conditions affect the persistence of synthetic organics in soil and sediment-water systems, although there is relatively little published information on the role of oxidation-reduction conditions on the degradation rate of specific synthetic organics. Where information is available on oxidation-reduction effects on degradation of synthetic organics, the effect of this parameter is often great enough such that soil and sediment oxidation conditions should be considered in evaluating the persistence and potential impacts of the compounds in the environment. Where suitable information is available, it should be incorporated into modeling efforts to predict the fate of synthetic organics in the environment.

Work done in the Laboratory for Wetland Soils and Sediments and by a very few other laboratories has clearly demonstrated the importance of redox potential conditions in soil and sediments on the rate of degradation of many compounds as well as the fact that different compounds respond differently to redox conditions. Unfortunately, the information available to date generally does not permit one to quantify redox potential effects

on degradation rates under natural conditions. For example, it appears that stirred suspension studies may indicate an artificially high rate of degradation.

On the other hand, most degradation studies using ¹⁴C-labeled compounds in unstirred soil materials make conclusions on degradation rates based on recovery of the labeled carbon as carbon dioxide. In most cases, depending on the molecular structure of the compound and the position of the label, recovery of the label as carbon dioxide certainly indicates the compound has degraded such that nothing of environmental consequence remains. This approach, however, tends to be overly cautious as labeled carbon dioxide is collected only after substantial modification of the parent compound, usually through a series of many degradation products.

For many compounds, modification of the molecule has proceeded beyond the point where it presents an environmental threat long before the label is recovered as carbon dioxide. Also some of the label, transformed to harmless decomposition products, may be incorporated into the humus fraction of the soil and retained as soil organic matter for extended periods of time. The two methods used for degradation studies, particularly those examining physicochemical effects, have been successful in documenting the importance of redox potential but probably are unreliable in indicating effects of physicochemical conditions on the rate of degradation.

We have conducted degradation studies using both methods in this project to demonstrate how the experimental approach can affect the results and conclusions of degradation studies. Thus, one recommendation coming from this project is that more be done to alert environmental organic chemists doing degradation research to the importance of matching experimental techniques to the research objectives such that

erroneous conclusions on treatment effects and degradation rates are minimized.

The sequence of research findings to date have led to the conclusion that physicochemical conditions do substantially affect the degradation rate of many compounds, but research methods should be devised and employed to provide information on how physicochemical properties of soils and sediments affect the degradation rate of compounds under natural conditions. This information would be most useful to modelers for predicting the persistence of synthetic organics in various environmental compartments. The technique developed should be relatively inexpensive and capable of including a wide range of physical and chemical properties of soil and sediment.

These degradation studies should be placed in the field so that the experimental units

are subjected to natural climate, microbial, and hydrologic conditions. Soil and sediment materials should be characterized for most of the commonly measured properties, much as was done in the adsorption study included in this report using 19 soil and sediment materials.

One important difference in the degradation studies would be that the soils should be characterized for certain parameters in their natural condition, not after sampling, drying, and grinding. Then degradation rates and soil properties should be evaluated using appropriate statistical procedures to determine the relationship between degradation rate and the measured soil properties. If a large number of soils were included, statistically valid prediction models could be developed for degradation rates under natural conditions based on soil and sediment properties.

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H. W. Holm is the EPA Project Officer (see below).

The complete report, entitled "Fate of Selected Toxic Compounds Under Controlled Redox Potential and pH Conditions in Soil and Sediment-Water Systems," (Order No. PB 84-140 169; Cost: \$13.00, subject to change) will be available only from:

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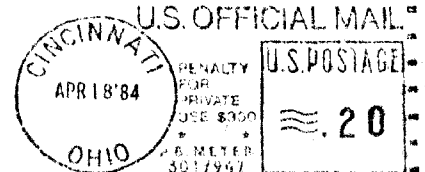
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