



Project Summary

Estimation of Parameters for Modeling the Behavior of Selected Pesticides and Orthophosphate

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A 3-year laboratory study was conducted to determine sorption and degradation of selected pesticides as well as sorption of orthophosphorus on several U.S. agricultural soils. The data obtained in the study permit the estimation of sorption and degradation parameters required in predicting nonpoint source loadings of pesticides and phosphorus from croplands. Nine pesticides (six herbicides and three insecticides) representing a broad range of chemical classes were studied. The pesticide studies were conducted with seven soil types; P-sorption was measured on 36 soils that are distributed widely across the United States.

Data collected during this project suggest that pesticide sorption coefficient (K_{oc}) based on soil organic carbon is not only independent of soil type but also of soil particle sizes within a soil type. Thus, each pesticide can be assigned a single K_{oc} value, and given the organic carbon enrichment of the sediment, partitioning of pesticide between solution and sediment phases during a given runoff may be estimated. For all pesticides studied, microbial degradation rates followed first-order kinetics. The rate coefficients (or half-lives) were not correlated with any of the following soil properties: soil organic carbon content, clay content, cation exchange capacity, pH, Eh, and total bacterial and fungal propagules. Temperature and soil-water tension (soil-water content) were the two soil environmental factors

that did show a significant effect on pesticide degradation rates. For temperatures in the range of 15-35°C and soil water tensions in the range of 0.1-1 bar, however, degradation rate coefficients for a given pesticide were essentially constant. Considerable amounts of non-extractable "bound" residues were formed for all soil pesticide combinations studied. Generally, larger amounts of bound residues were found in moist soils (incubated at soil water tensions less than 1 bar) than in drier soils (at 15 bar tension).

Phosphate sorption was measured using a standardized protocol. Measured P-sorption data were fitted to Freundlich, Langmuir, and Temkin equations. Phosphate sorption constants in the Temkin equations were better correlated with several soil properties than were the coefficients in Langmuir or Freundlich equations. Ammonium oxalate extractable Al, ammonium acetate extractable Ca, and clay content were the three soil properties most useful in estimating Temkin equation parameters.

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

Introduction

The use of pesticides, especially herbicides, has increased significantly during

the past three decades. These chemicals have contributed to increased crop yields and in many cases have decreased production costs. The use of pesticides, however, poses a potential threat to the environment and human health. Therefore, agricultural producers as well as environmental scientists are concerned with the fate of pesticides in agroecosystems. Consequently, information on pathways by which pesticides leave the site of application (i.e., croplands) and subsequently cause nonpoint source pollution will continue to be sought. Such data are essential to the development of appropriate controls and management technologies for minimizing nonpoint source loadings of pesticides from croplands

A major pathway for pesticide removal from croplands, especially in terms of pesticide movement to nontarget areas, is in runoff water and on sediment carried along with the runoff water. The amount of soil-applied pesticide that leaves the field in this manner depends primarily on the intensity and the duration of a rainfall event and on the time lag between pesticide application and the runoff event. The depth of soil layer (i.e., mixing zone) from which pesticides are removed during a runoff event is determined by the intensity and duration of the rainfall event. The amount of pesticide available within this mixing zone is determined by the extent of pesticide dissipation that occurs between application and a given runoff event. Various processes governing the fate of pesticides in soils are retention (adsorption-desorption), transformations (microbial and chemical degradation), and transport (overland flow, leaching, and volatilization).

Two approaches for estimating the edge-of-field nonpoint source loadings of pesticides are available. In the first, empirical relationships have been developed by correlating the quantities of pesticides available in the surface soil (0-1 cm) and the losses measured at the edge of the field. Obviously, such empirical relationships are developed based on extensive and often costly field measurements. Alternately, pesticide retention, transformation, and transport parameters can be used in several process-oriented nonpoint source simulation models that are presently available.

A 3-year laboratory study was conducted to measure sorption and degradation of selected pesticides and sorption of orthophosphate in U.S. soils. Seven soils from major agricultural areas in the U.S. along with nine pesticides were included

in this study. The pesticides were atrazine, cyanazine, metribuzin, diuron, propachlor, 2,4,5-trichlorophenoxyacetic acid, carbaryl, carbofuran and fonofos. These data were used to provide estimates of sorption coefficients and degradation rate coefficients for pesticides. Sorption of orthophosphate was measured on 36 U.S. soils. These data were used to determine soil factors influencing P-sorption on soils. The data may be used to estimate parameter values required in various process-oriented simulation models for describing nonpoint source loadings of pesticides and orthophosphate from croplands.

Conclusions

Based upon the data collected during this project, the following justifiable simplifications for estimating pesticide sorption parameters are proposed.

1. Pesticide sorption on whole soils and soil size-separates is determined primarily by the soil organic carbon content. That is, the sorption partition coefficient based on soil organic carbon (K_{oc}) for a given pesticide is essentially independent not only of soil type but also of soil particle size. Thus, the problem of predicting pesticide sorption by soils or the partitioning of pesticides between the sediment and water phases of runoff reduces to a more manageable problem of a single K_{oc} value for a pesticide and the organic carbon enrichment for a given runoff event. This approximation is more likely to be in error for ionic and ionizable pesticides such as 2,4,5-T.
2. The extent of sorption isotherm nonsingularity may be specified quantitatively using the index $\beta = (N_a/N_d)$, where N_a and N_d are the Freundlich isotherm constants, respectively, for the adsorption and desorption isotherm loops. Large β values indicate extensive nonsingularity, while $\beta=1$ suggests singular isotherms. Based upon β values, it was concluded that isotherm nonsingularity increased with increasing soil particle size. For sand size-fraction ($> 50 \mu m$) β value was about 4, while for fine clay fraction $\beta=1$. Analysis of published sorption data for sediments supported this conclusion.

Two types of pesticide degradation rates were measured: mineralization rate

based on $^{14}CO_2$ evolution and disappearance rate based on the loss of solvent-extractable parent chemical. Using these data, the following conclusions regarding pesticide degradation are suggested:

1. Pesticide degradation rates in soils could be described using the first-order kinetics. For each soil-pesticide combination, the degradation rate coefficient (k , day^{-1}) or half-life ($t_{1/2}$, days) could be specified.
2. For all pesticides studied, the disappearance rate was greater than the mineralization rate. The differences between these two rates are due to accumulation of intermediate metabolites, assimilation into microbial biomass, and formation of "bound" residues. Of these, bound residue formation appears to be the major contributing factor.
3. Pesticide degradation rates were not correlated with soil organic carbon content, pH, cation exchange capacity, clay content, total bacterial propagules, and total fungal propagules. The two soil environmental factors that did influence pesticide degradation rates were soil-water content (or soil-water tension) and soil temperature.
4. Soil temperatures below $25^\circ C$ had a greater influence on pesticide degradation rates than did temperatures above $25^\circ C$. Hence activation energies (ΔE_a) for pesticide degradation between $15^\circ C$ - $25^\circ C$ were greater than those between $25^\circ C$ - $35^\circ C$.
5. Pesticide degradation rates in soils maintained at 15 bar soil water tension were substantially lower than at 1 bar or lower. At tensions between 0.1 and 1 bar, degradation rates were not significantly different.
6. Soil-water tension may influence oxygen tension and redox potentials in soils. As a result, the pesticide degradation pathway may be altered with changes in soil-water tension, and different types of metabolites may accumulate.
7. Bound residues, i.e., nonextractable ^{14}C -residues, were found during degradation of all pesticides in all soils studied. The extent of bound residue formation, however, was different for each soil-pesticide

combination. Generally, more bound residues were formed in moist soils (at 0.1, 0.33, and 1 bar tension) than in drier soils (at 15 bar tension).

Phosphate sorption isotherms were measured on 36 soils that were distributed widely across the United States and represented seven soil orders. The sorption isotherms were measured using a standard protocol and certain modifications, including the use of 0.03 M KCl as the background electrolyte (to more closely simulate natural conditions) rather than 0.01 M CaCl₂ and no disinfectant. Regressions analyses of the soil properties with the phosphate sorption parameters showed that soil properties were better correlated with the constants in the Temkin equation than the Freundlich or Langmuir equation constants. The equations that were used to estimate the Temkin constants with the best correlation coefficients were functions of ammonium oxalate Al and clay content or ammonium acetate Ca and clay. Calculated confidence limits around each calculated isotherm based on propagation of errors using the Temkin equation indicated that ammonium acetate, extractable Ca content, and clay content could be used successfully to predict 72% of the measured P sorption isotherms. Calculated isotherms were based solely on soil chemical and physical properties.

Recommendations

In this project a considerable amount of data were collected to characterize the nonsingularity in pesticide sorption isotherms for whole soils and soil size-separates. A number of earlier workers also have focused on an experimental investigation of isotherm nonsingularity. Despite such an extensive data base, a sound theoretical or conceptual basis for this phenomenon is still lacking. Efforts should be directed, therefore, towards a more systematic study of sorption isotherm nonsingularity using well-characterized sorbate-sorbent systems. While such information may not always be essential for predicting nonpoint source loadings of pesticides, these data will contribute to a better understanding of pesticide sorption on soils and sediments.

While a number of recent studies have focused on the spatial and temporal variability of soil physical properties, such data for various pesticide sorption and degradation parameters are essentially nonexistent. The data we obtained in this

project were for soils collected from a single random location within a single field for each soil type. This was justified because the principal objective here was to characterize sorption and degradation of pesticides in a broad spectrum of soil types. When it is of interest to predict pesticide losses at the edge of a single agricultural field or an entire watershed, however, the spatial and temporal variability of key properties (organic carbon

content, sorption coefficient, degradation rate coefficients, etc.) need to be measured. The impact of the variable model parameters on the model outputs (concentration with depth, mass emissions below the root zone, etc.) can then be evaluated. Thus, we recommend that studies be initiated at several locations in the U.S. to characterize the spatial and temporal variability of sorption and degradation parameters in a single field.

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The complete report, entitled "Estimation of Parameters for Modeling the Behavior of Selected Pesticides and Orthophosphate," (Order No. PB 84-148 774; Cost: \$17.50, subject to change) will be available only from:

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