



Project Summary

Retention and Transformations of Selected Pesticides and Phosphorus in Soil-Water Systems: A Critical Review

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The current state-of-the-art for measuring or estimating pesticide retention and transformation parameters required in non-point source pollution models was reviewed. A data base of sorption partition coefficients, degradation rate coefficients, and half-lives for a broad spectrum of pesticides was compiled from a literature survey. Adsorption partition coefficients normalized with respect to soil organic carbon content were approximately constant across soils for a given pesticide. Octanol-water partition coefficients were "good" predictors of pesticide adsorption parameters. Chemical persistence in soils for a large number of pesticides has been measured under a variety of soil environmental conditions. These data were used to calculate first-order decay coefficients and half-lives. The variability of these parameters for a given pesticide across several soils was within a factor of two. Multiple regression properties could not be developed from the literature data because of inadequate information regarding the physical, chemical and environmental conditions of soil during the pesticide degradation studies. Seasonal losses by runoff from agricultural fields were generally less than 0.5% - 1.0% of the total amount applied. Although pesticide concentrations on the sediment phase of the

runoff are larger than those in the water phase, pesticide carried in the water phase accounted for more than 90% of the total mass emission during a given runoff event.

Phosphate sorption parameters (primarily Langmuir constants) were collected from the literature or computed from published adsorption isotherms. Statistical analysis showed that Langmuir sorption parameters S_{max} and k , each normalized with respect to extractable Fe and Al, were significantly correlated to the extractable metals. The correlations gave higher R^2 values and lower probability levels of significance for oxalate extractable Fe and Al than for citrate-dithionite-bicarbonate extractions. Correlations for other parameters with extractable Fe and Al were less significant. The composition and degree of crystallinity of Fe, Al oxyhydroxides appear to be the dominant factors in controlling phosphate sorption. Lack of uniformity in experimental methods used for determining Langmuir sorption parameters was noted during the literature survey. Development of standardized methodology (protocols) for this purpose appears essential for quantification of appropriate sorption parameters.

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 Federal Water Pollution Control Act Amendments of 1972, Public Law No. 92-500, specifies that the Administrator of the U.S. Environmental Protection Agency (EPA) shall, in cooperation with other agencies, provide guidelines for identifying and evaluating the nature and extent of nonpoint pollution sources. Because fertilizers and pesticides play such a major role in today's agriculture, runoff from fields involved with agricultural production has long been suspected of being a major nonpoint pollution source. Although it is difficult to conceive of a situation in which all possible environmental risks associated with the use of agricultural chemicals could be eliminated, management practices can be used that will significantly reduce these risks. Nonpoint agricultural pollutants of primary concern are sediment, nitrogen, phosphorus, and pesticides. The latter two pollutants can be transported from an agricultural field by both the water and sediment phases.

Several models (stochastic, empirical and deterministic) exist for estimating water and sediment transport from small fields and watersheds. More than 45 years of research on erosion by the U.S. Department of Agriculture in cooperation with state agricultural experiment stations has resulted in the development of numerical relationships for estimating annual soil losses from fields. Because of the success of these models and their previous calibration for specific regions, most agricultural chemical transport models were developed by "piggybacking" the components for chemical transport to the hydrologic and sediment transport models. The sediment and chemical transport models were developed in order to simulate the impact of agricultural production on water quality. The models also have the potential to be used by state and local agencies in developing and/or identifying land use management practices that will provide the least risk to the environment.

Many of the existing chemical transport simulation models have been calibrated to describe the behavior of a given plant nutrient or pesticide at a given location and for a specific cultural system. The feasibility of continuing to

calibrate these simulation models for a wide range of chemicals and management practices is not practical. Therefore, general relationships for estimating the basic coefficients required to describe adsorption and transformations of agricultural chemicals in the soil surface region subject to erosion are needed. Also the confidence that can be attached to the independently measured or estimated coefficients used in the chemical transport models for describing adsorption and transformation processes must be quantified.

Numerous equilibrium adsorption studies have been conducted using various pesticides and phosphorus sources as well as different soils. The validity of the equilibrium adsorption assumption based on relatively short-term experiments (less than 72 hours) and the reversibility of the adsorption-desorption process has been questioned by several researchers. Adsorption associated with short-term laboratory experiments may not be relevant for the long contact periods encountered under natural field conditions. Also, recent experiments involving "bound" pesticide residues point out the problem associated with assuming reversible adsorption, especially that occurring during sediment and water transport from an agricultural field or water shed. The bound pesticide residue question suggests that some of the pesticide transformation or disappearance data available in the literature may be in error and not suitable for estimating transformation rate coefficients of the original parent compound.

The primary emphasis of the present report was to present an extensive and reliable data base of the principal coefficients for describing adsorption and transformation characteristics of phosphorus and a broad spectrum of pesticides used across a range of soil types. This information was obtained from an extensive literature search using various computer information retrieval packages (data banks such as CANE, BIOSIS, etc.). The dependence of these retention and transformation coefficients on selected soil properties was evaluated. The information presented in this report should be helpful in estimating the values of the retention and transformation parameters required in various non-point source pollution models.

Conclusions

A large data base exists for estimating partition coefficients for pesticide

retention in soils. An analysis of these data indicated that errors associated with various simplifying assumptions (e.g., linear and singular isotherms; instantaneous equilibrium) appear to be within a factor of 2 or 3. Such errors may be tolerable for most nonpoint source pollution modeling applications. For a given pesticide, adsorption partition coefficients based on soil organic carbon were fairly constant regardless of soil type. Furthermore, octanol-water partition coefficients were good predictors of pesticide adsorption partition coefficients.

The persistence in soils of a large number of pesticides under a broad range of soil environmental conditions has been reported. A data base was compiled for first-order decay constants (k) and half-lives ($t_{1/2}$) for pesticide disappearance in soils from these reports. Over the wide range of soil and environmental conditions under which degradation was measured, the coefficient of variation of the average k and $t_{1/2}$ values for a given pesticide was surprisingly small ($<100\%$). Thus, pesticide disappearance rates can be estimated within a factor of 2 to 4 for most pesticides using presently available data. In most cases, observed half-lives of pesticides under field conditions were shorter than those measured in laboratory incubation studies. This was attributed to the fact that under field conditions a multitude of factors and processes contribute to pesticide disappearance, while laboratory studies are performed under controlled conditions and therefore measure fewer, if not a single process.

Efforts to develop multiple regression equations correlating degradation rates with soil properties were unsuccessful. Part of the problem arises because many reports reviewed failed to give soil physico-chemical properties and incubation conditions (temperature and soil-water tension). Pesticides were placed into the following three groups based upon their half-lives in soils: non-persistent ($t_{1/2} \leq 20$ days), moderately persistent ($20 \leq t_{1/2} \leq 100$ days) and persistent ($t_{1/2} \geq 100$ days). Pesticides in the first group are 2,4-D, 2,4,5-T, dicamba, dalapon, methyl parathion, malathion, and captan. Moderately persistent pesticides are atrazine, simazine, terbacil, linuron, TCA, glyphosate, parathion, diazinon, fonofos, phorate, carbofuran, carbaryl, aldrin, dieldrin, endrin, heptachlor and PCP. Persistent pesti-

cides are trifluralin, bromacil, picloram, paraquat, DDT, chlordane, and lindane.

A broad range of langmuir isotherm parameters were compiled for phosphate sorption by soils and other solid adsorbents. Based upon the limited amount of data available, the sorption parameters were found to be significantly correlated with extractable "active" Fe and Al. A lack of uniformity in experimental methods used in determining the Langmuir sorption parameters or phosphate sorption indices was noted. Development of standardized methodology (or protocols) for this purpose appears to be essential for quantification of phosphate sorption parameters. "Active" Fe and Al appear to be measured by oxalate extraction rather than by citrate-dithionite-bicarbonate extraction. Crystallinity of Fe and Al oxyhydroxides play a dominant role in determining inorganic phosphate sorption. A "universal" partition function for inorganic phosphorus retention in soils can be developed provided proper input parameters are measured. These parameters include the measurement of "active" Fe and Al, time-dependence of phosphate adsorption-desorption and phosphate sorption isotherm parameters.

Recommendations

Measurement of octanol-water partition coefficients for a broad spectrum of pesticides should be continued. Special emphasis should be given to recently developed high-pressure liquid chromatography (HPLC) methods for estimating octanol-water partition coefficients. Also, this concept should be extended for ionic and ionizable organic compounds. The relative contributions of various particle-size fractions of soils to pesticide retention should also be measured. Such particle size partitioning data are now available for only a limited number of organic compounds and not for a wide-range of soil-pesticide combinations. This information is needed to evaluate the significance of runoff sediment "enrichment" by fines in estimating total pesticide losses.

The disappearance rate of solvent-extractable parent compound should not be used as the only measure of pesticide degradation rate in soil-water systems. The potential for significant accumulations of toxic metabolites (especially under anaerobic conditions) and formation of "bound residues" must be taken into account. Mineralization rate (i.e., total breakdown of pesticides to carbon dioxide, water, and

inorganic ions) should be used as an index of pesticide degradation rate because it represents total detoxification of the pesticide. Because mineralization rates are generally smaller than parent compound disappearance rates, the former provides a more conservative estimate of the pesticide degradation rate. The rates and mechanisms of bound pesticide residue formation in soils as well as the release characteristics and environmental toxicity of these residues should be characterized. Special attention should also be given to rates of formation and release of bound residues under anaerobic environments (encountered by sediment-bound pesticide residues in streams, rivers, lakes, etc.).

Standardized methodology (protocols) should be developed for measuring phosphate sorption parameters, "active" soil components (Fe and Al oxyhydroxides and solubilized Ca) involved in phosphate retention, and the time-dependence of phosphate sorption-release in soil-water systems. Further testing of various phosphate sorption models is required in order to develop appropriate sorption parameters. A quantitative index needs to be defined for the "crystallinity" of the Fe and Al oxyhydroxides in soils. Such an index will be used in developing a "universal" partition function for phosphate retention by soils, similar in concept to pesticide partition coefficients based on soil organic carbon.

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The complete report, entitled "Retention and Transformations of Selected Pesticides and Phosphorus in Soil-Water Systems: A Critical Review," (Order No. PB 82-256 884; Cost: \$25.50, subject to change) will be available only from:

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