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Project Summary

Behavior of DDT, Kepone, and Permethrin in Sediment-Water Systems Under Different Oxidation-Reduction and pH Conditions

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A study was conducted to determine the effects of pH and oxidation-reduction (redox) conditions of soil and sediment-water systems on the persistence of three insecticide compounds. Three pH levels, ranging from moderately acidic to mildly alkaline, were studied for each compound. Four redox potentials (-150, 50, 250, and 450 mv) ranging from strongly reduced (anaerobic) to well oxidized (aerobic) were studied. The insecticide-substrate combinations included in the project were DDT in a Mobile Bay (Mobile, Alabama) sediment material, Kepone in the sediment material of a tributary of the James River (Hopewell, Virginia) and Permethrin in an Olivier soil material (Baton Rouge, Louisiana). Sample aliquots were removed from the laboratory microcosms to determine the recovery of the added compounds with time. A substantial redox potential effect was noted for DDT where recovery decreased from the spiking level of around 25 parts per million to less than 10 percent of the spiking level within a few days at -150 mv (strongly reduced condition). A less rapid loss of DDT was noted at 50 mv (moderately reduced condition), but the pesticide appeared stable under better oxidized conditions during the 45-day incubations. The levels of Kepone recovered did not change appreciably during 56 days of incubation under any of the combination of imposed pH and redox potential conditions. The recovery of Permethrin was affected by both pH and redox potential conditions over 25-day incubations. Unlike DDT, Permethrin was lost more rapidly under oxidizing conditions. Increasing pH enhanced the loss of this compound over the range of redox potential levels studied.

Information of the effects of physicochemical conditions on the persistence of pesticide residues such as demonstrated in this project should enable better prediction of the fate and potential impacts of residues in various environmental compartments.

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

Synthetic organic pesticides have been used extensively for almost three decades for controlling nuisance weeds, insects, and microbial organisms. Environmental problems sometimes arise, however, when non-target organisms are adversely affected either as a direct result of pesticide application or waste disposal, or as a result of pesticide residues that may be transported to sensitive ecosystems away from the point of application.

A substantial amount of environmentally related research has been conducted with pesticides, and especially insecticides, such that much is known about their fate and mobility under certain environmental conditions. Most environmental studies on fate and transport have focused on well-drained agricultural soils. Pesticide residues, however, are subject to a wide range of physicochemical conditions in the environment. Soon after typical agricultural applications, most residues become associated with medium textured, well-oxidized, near neutral pH soils. Subsequently, these residues may be transported in dissolved or adsorbed forms to surface waters and sediments of streams, rivers, lakes, or estuaries where the physical and chemical properties (physicochemical) as well as biological populations of the receiving environment are very different from the conditions at the point of application. For example, typical agricultural soils exhibit a wide range in texture (from sandy to heavy clay material), pH commonly ranges from 5 to 7.5, soils are nonsaline, and the organic carbon content of the plow layer typically ranges from a few tenths of a percent up to 2 percent. Compared to typical agricultural soils, sediments are characterized by finer texture (greater clay content), a narrower pH range (6.5 to 7.5), greater organic carbon content, moderate to strongly reducing (anoxic) conditions, and, depending on coastal proximity, sediments may have a higher salinity. These conditions have been shown to markedly affect the chemical mobility and biological availability of nutrients such nitrogen and phosphorus, trace metals, toxic metals, petroleum hydrocarbons, and certain pesticides. For pesticides, these differences are thought to affect the adsorptive capacity of the solid phase for pesticides and the chemical and especially microbial processes affecting pesticide degradation.

There is sufficient published information available on pH and redox potential effects on adsorptioin and degradation for selected pesticide compounds to document that these are important parameters to be considered in understanding the environmental fate of many pesticides. There is need for much more work to be done under carefully controlled pH and redox potential conditions, however, to improve understanding of factors affecting the environmental persistence and transport of pesticides. This is especially important as little is known of the physicochemical effects on the fate of most pesticide residues in some ecosystems, such as sediment-water systems, where residues have the greatest potential for biological accumulation and subsequent adverse effects. Such information should lead to development of improved predictive capability on the transport and fate of pesticide residues in various compartments of the environment.

Project

This research was conducted to determine the effects of physicochemical conditions on the persistence of three pesticides in soil and sediment-water systems. Soil and sediment suspensions were incubated at selected pH and redox potential levels which include the range commonly found in these systems.

Three insecticides were studied. DDT [1,1-*bis*-(*p*-chlorophenyl)-2,2,2-trichloethane] was included because it is still widely distributed in the environment though its use has been eliminated or greatly restricted in recent years. Also, there is considerable published information for DDT on different degradative pathways and products dependent upon oxidation conditions. A Mobile Bay (Mobile, Alabama) sediment material was used in the laboratory microcosms for DDT studies.

Kepone [decachloro octahydro-1,3,4-metheno-2H-cyclobuta [*cd*]pentalen-2-one] was included in these studies using a sediment material from a tributary of the James River (Bailey's Creek, Hopewell, Virginia) to determine whether its persistence in the environment is influenced by physicochemical conditions. The known environmental problems with this compound are confined to the James River area. Because essentially nothing was known of factors affecting Kepone persistence in soils and sediment-water systems, this compound was included to de mine whether studies of physi chemical effects on its persiste might suggest something about its f in the James River and perhaps sugg management practices that could used to minimize adverse envir mental impacts.

The persistence of Permethrin, phenoxybenzyl (±) *cis-trans*-3-(2 dichlorovinyl-2,2-dimethylcyclopropar carboxylate] a synthetic pyrethr was also studied under control physicochemical conditions using Olivier soil material (Baton Rou Louisiana). The synthetic pyrethro are a relatively new class of insectici that are highly effective against tar insects, exhibit low mammalian toxic and are far less persistent in t environment than many chlorinat hydrocarbon insecticides. The hi susceptibility of larvae and juven crustaceans to certain of these co pounds and the expected increasin important role of the synthe pyrethroids in insect control prograr suggest it is important to exami factors affecting the persistence these residues in the environment.

Conclusions

The effects of oxidation-reducti conditions on the persistence and tran formations of DDT were studied in Mobile Bay sediment material at pH 6. 7.0, and 8.0. The recovery of DDT fro the spiked Mobile Bay sedime material decreased very rapidly und strongly reduced conditions (-150 m such that 90 percent could not b recovered after as little as 5 days. Th apparent rapid degradation rate und strongly reducing conditions was som what greater than reported in mo published studies on the effects reducing conditions on DDT persistenc

Various explanations for the rapi decrease in DDT recovery were cor sidered, including experimental art facts. Although the levels of measure degradation products (DDD and DDE measured did not totally account for th loss in DDT, DDD levels were greatl increased where DDT was disappearin rapidly at -150 mv providing evidenc that a substantial amount of DDT wa actually degrading within a matter of to 3 days. It was concluded that DD was indeed degrading very rapidl under very strongly reduced condition in the Mobile Bay sediment materia compared to moderately reduced o oxidized conditions. It is probable the chemical properties and possibly the microbial activity of the strongly reduced Mobile Bay sediment material are very different from most soils and sediments used for DDT studies and that these differences contribute to very rapid losses of DDT from this material compared to most published degradation rates for DDT. Another factor may be that the -150 mv potential included in this study was a more intense reducing condition than is achieved in other studies of DDT degradation in flooded soils or soils equilibrated in the absence of air.

A less rapid loss was noted at 50 mv (moderately reduced conditions) while DDT appeared fairly stable under better oxidized conditions. Where recovery of DDT decreased rapidly (strongly reduced conditions) both DDD and DDE levels were elevated, but DDD predominated. Only at 50 mv was there any indication that a degradation product was accumulating in the Mobile Bay sediment material. The small increase in DDD levels noted with time was not equal to the rate of DDT loss, indicating that DDD was also not stable where conditions were conducive to rapid DDT degradation.

The results of these DDT studies were in general agreement with other published reports on the environmental fate of DDT with the possible exception that DDT may degrade more rapidly under strongly reduced conditions in Mobile Bay sediment material than in most anaerobic soils and sediments.

The persistence of added Kepone was studied in James River sediment materials incubated at three pH (5.0, 7.0, and 8.0) levels and four redox potential levels (-150, 50, 250, and 450 mv). There was no clear indication that redox potential had any effect on Kepone recovery with time, though a very gradual reduction in Kepone recovery was noted at all redox levels at pH 8.0 in the stirred suspensions.

The persistence of Permethrin, a synthetic pyrethroid, was studied in an Olivier soil suspension amended with this compound under a range of redox potential conditions at pH 5.5, 7.0, and 8.0. Both pH and redox potential strongly influenced the degradation of this compound. Unlike DDT, Permethrin was lost more rapidly under oxidizing conditions. Increasing pH enhanced this loss under both moderately reduced (+50 mv) and weakly oxidized (+250 mv) conditions. In well oxidized suspensioins, Permethrin recovery decreased from the approximately 17 ppm spiking level to less than 0.5 ppm in about 3 weeks. Under strongly reducing conditions, recovery of the added Permethrin ranged from near spiking levels to around 1/3 of spiking levels (depending on pH) during the 26-day incubations.

The results of this study indicate Permethrin is more persistent under reducing conditions typical of sediments that are a habitat for many important benthic organisms, which, according to the literature, are highly sensitive to some synthetic pyrethroids. Permethrin cannot be considered a persistent pesticide compared to most chlorinated hydrocarbons. However, its somewhat greater stability in reducing sediments that may receive residues in runoff, and the potential for adverse effects to organisms associated with sediment-water systems, make physicochemical effects on Permethrin degradation an important environmental consideration.

The results of this study demonstrated that the physicochemical conditions of the soil and sediment-water systems studied (pH and redox potential) substantially influenced the environmental chemistry of two of three synthetic organic pesticides included in this project. The results of this study and the very limited information available from the literature indicate that the persistence, degradation pathways and products, and the mobility of many or most synthetic organics may be affected by the physicochemical characteristics of the environmental compartments with which these residues become associated. Because of the apparent important effects of physicochemical conditions on the environmental chemistry of synthetic organics, and the wide range in these properties found in the various environmental compartments that may receive residues, it is important to understand the influence of physicochemical conditions on the environmental chemistry of pesticides before an accurate assessment can be made of the fate and potential impact of pesticide residues in all affected areas of the environment. For example, biometer flask studies of a compound such as Permethrin in a typical aerobic soil may not indicate the potential for persistence and accumulation in anaerobic lake and wetland sediment-water systems where there is considerable potential for adverse impacts on benthic organisms.

Recommendations

Because of probable physicochemical influences on the environmental chemistry of most pesticides, additional work should be done to characterize these effects for existing compounds where this information is lacking. Of particular importance are those compounds thought to be relatively persistent, compounds known to be especially toxic, particularly to non-target organisms, and comounds that are released into the environment in relatively large quantities. The nonvolatile organics of the EPA priority pollutant list should be considered as prime candidates for studies of this type.

As part of the information the chemical industry is required to furnish when applying for registration to label and market a new pesticide product, testing should be done to determine persistence and pathways of degradation in soils and sediments under a range of physicochemical conditions. Also, the information should be obtained for a number of typical soils and sediments under their indigenous physicochemical conditions that should include a wide range of these properties.

Though the laboratory suspension studies of the type conducted in this project should accurately indicate the effects of physicochemical conditions on the environmental chemistry of the compounds studied, there is a need to systematically examine physicochemical effects under more natural conditions to more accurately reflect the rate of the processes.

The activity of microbial populations, either directly or indirectly, plays a major role in the fate of pesticide residues in the environment as well as in regulating the physicochemical conditions of the various environmental compartments. Studies should be done to characterize the relationship of the activity of microbial populations to the transformations observed for synthetic organics under various physicochemical conditions.

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The complete report, entitled "Behavior of DDT, Kepone, and Permethrin in Sediment-Water Systems Under Different Oxidation-Reduction and pH Conditions," (Order No. PB 81-213 266; Cost: $11.00, subject to change) will be available only from:
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