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Project Summary

Determination of the Environmental Impact of Several Substitute Chemicals in Agriculturally Affected Wetlands

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Procedures have been developed for processing of anaerobic wetland sediments for pesticide recovery along with formulation of simulation models of anaerobic/aerobic soil and sediment environments to study pesticide degradation. Redox conditions of soils and sediment-water systems have a significant effect on *in situ* persistence of synthetic organic pesticides. Chemical and microbiological characteristics of wetland sediments have equally important consequences on mobility and degradation of toxic compounds.

The total invertebrate community of selected backswamp regions has been examined as affected by Guthion and other pesticides. Effect of xenobiotics on leaf litter decomposition in pesticide-supplemented field plots has been examined.

A system of continuous-flow and static microcosm systems have been developed for quantitative analyses of the effect of selected toxic substances, including Guthion, methyl parathion, and Kepone. Decomposition of ecologically significant substrates such as chitin is variously affected by different toxic substances as shown in microcosm investigations. Enzymatic tests, i.e., dehydrogenase and phosphatase, and ATP measurements, are sensitive indicators of biotransformation processes. Significant correlations are seen with microbial diversity indices and specific microbial groups such as filamentous fungi. Factorial analyses of physicochemical and microbial processes and xenobiotic interaction have demonstrated the application of the microcosm as a protocol or "tool" to simulate pristine and impacted *in situ* ecosystems.

This Project Summary was developed by EPA's Environmental Research Laboratory, Gulf Breeze, FL, 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

Increasing use of a variety of chemicals in agricultural practices presents potential environmental problems from the standpoints of use and danger to adjacent wetland systems. This problem is further complicated by the increased discharge of an array of toxic substances (xenobiotics) from industrial facilities and chemical disposal areas close to such sensitive wetland regions. An example of the complexity of the problem is evident in the coastal zone of Louisiana, comprising more than seven million acres of marshes and estuaries, and representing approximately 40% of the total coastal wetland area of the contiguous United States. The significance of this region as a fishery resource is well established. The ecosystem is close to major economically significant agricultural and industrial sites in the fertile Mississippi delta. A wide variety of organic materials, including potentially hazardous chemicals, are brought into the region by the gulfward movement of water. In spite of the widespread use of these chemicals, limited data are available on the fate of pesticides and other chemicals in such agriculturally affected wetlands.

Important chemical changes take place during passage of water through wetlands. Suspended sediment settles with decreased water flow, and inorganic nutrients, especially nitrogen and phosphorus, are utilized by plant growth. Major modification of xenobiotics, via abiotic hydrolysis and microbial degradation, in all likelihood, is most active in this area.

Degradation of xenobiotics in the environment occurs by abiotic as well as biotic processes. The degree of physical adsorption of compounds to colloidal mineral and humic materials strongly influences the susceptibility of soil- and sediment-bound pesticide residues to chemical or biological attack. Although there is considerable information on persistence and fate of pesticides in soils, limited data are available on the effects of pH, oxidation, and salinity levels and the combined interactive effects of chemical, physical, and biological conditions affecting degradation processes in wetland soil/sediment ecosystems.

Organophosphorus insecticides, the major class of compounds studied, generally are known to be less persistent in soils than many other chemical classes of pesticides, such as chlorinated hydrocarbons. However, some organophosphorus compounds have been shown to persist in soils for several months; furthermore, chemical and biological properties of soils and sediment-water systems affect such persistence.

The research summarized herein was undertaken to provide information on the fate and behavior of selected xenobiotics in the agriculturally affected coastal wetlands of Louisiana. An understanding of the biological, chemical, and physical conditions conducive to degradation of pesticides may enhance the predictive capability for assessment of potential environmental impact and aid development of management practices that minimize adverse effects.

The organization of this project involved linkages of research between three major components of our study: microbiology, *in situ* investigations, and physicochemical studies. The microbiological portion comprised both laboratory and *in situ* approaches involving correlation analyses and controlled simulation studies. The three field and laboratory approaches were designated as: Effect of Oxidation-Reduction Conditions on Pesticide Persistence, *In Situ*/Microcosm Investigations and Microcosm Evaluation and Validation, and *In Situ* Effects of Guthion on Backswamp Aquatic Invertebrates and Shallow Water Leaf Litter Decomposition.

Within this interrelated framework of research, several important component relationships among the individual projects need to be emphasized to provide a transition between major blocks of research data and to attenuate these major project results into a concise package.

Research Approach

Beginning with physical/chemical studies, the primary research objective, as noted, was to ascertain the effect of oxidation reduction conditions on pesticide persistence. An understanding of the underlying physical/chemical characteristics affecting pesticides in aquatic systems provides a framework for further studies within the microbiological/biological component and, in combination, provides an insight into pesticide effects within the general ecology of the target wetland system, an important consideration for coastal zone management. Specific objectives for the physical/chemical studies included:

- Development of efficient and reproducible extraction methodologies which eliminate problems associated with anaerobic sediments.
- Development of procedure for processing of anaerobic sediment samples to recover pesticides without introduction of degradation artifacts.
- Formulation of physical/chemical simulation studies, emphasizing oxidation reduction conditions, of anaerobic/aerobic soil and sediment environments to study pesticide degradation.

Microbiological investigations were two-fold in nature. The overall objective was to ascertain the effect and fate of a pesticide on the microbial component in an aquatic microenvironment. It was thought that an important linkage between biotic and abiotic factors impinging on pesticide effect and fate could be ascertained, providing further insight into pesticide effects in higher trophic communities. Thus, it was necessary to design and validate a laboratory/field protocol which would provide quantitative analysis of pesticide fate and effect. To do so, the following objectives were proposed:

- Development of laboratory/field protocol for pesticide analyses (including microbial/soil enzymatic activity and response, ^{14}C-respiration and bioaccumulation interaction, and complimentary residue analysis by GC methods established in physical/chemical studies).
- Development of laboratory/field protocol for *in situ*/laboratory analysis of key organic substrates, i.e., chitin and cellulose, as affected by xenobiotic addition under aerobic and anaerobic conditions.
- Development of selective media for *in situ*/laboratory sampling.

Earlier studies in this laboratory demonstrated the unique microbial composition of the salt marsh ecosystem and its extremely active chitinoclastic (chitin-decomposing) heterotrophic population. Significant rates of detrital turnover into the trophic food web have demonstrated the important role of the extant microbial biomass and the impact of stress factors on microbial ecosystems and specific transformation processes. With the completion of preliminary studies with the organophosphate, Guthion, two additional research objectives were proposed:

- The analysis of heterotrophic activity/enzyme activity profiles in several ecologically significant *in situ* soil microenvironments to correlate these observations with variations in controlled microcosms due to xenobiotic addition.
- Formulation of a statistical and computer-base program for data analysis of microbial and enzymatic activity variations.

Field studies of indigenous invertebrate populations primarily involved the analysis of *in situ* effects of the organophosphate, Guthion, on backswamp aquatic invertebrates, as well as providing indications of the effect of this pesticide on shallow water leaf litter decomposition. Specific objectives of our research group included:

- Development of total invertebrate community analyses of population dynamics with pesticide input.
- Development of laboratory cultures of selected wetland invertebrates and their possible use as indicators of environmental stress.
- Analysis of sampling errors in studies of *in situ* effects of pesticides in wetland communities.

Also included in the above research objectives were the analysis of techniques and problems associated with biochemical stress analysis (energy charge ratio) in pesticide affected food webs in estuarine ecosystems.

In all facets of the study, major attention has been given to the organophosphorus compound Guthion (0,0-dimethyl S-[4-oxo-1,2,3-benzothriazin-3(4H)-ylmethyl] phosphorothioate) used in control of the cane borer on sugarcane (*Saccharum officinarum* L.) in Louisiana. Guthion (azinphosmethyl) represents 80% of the total volume of insecticides applied to sugarcane, being substituted for Endrin over a decade ago because of problems in fish toxicity and insect resistancy. Other xenobiotics, such as methyl parathion, have been used to develop comparative data in terms of methodology and dose response.

In summary, the physicochemical experiments conducted during our investigation provided particularly useful information on the mobilization or immobilization processes occurring in soil environments. Implications as to the development, migration, and permanency of aerobic/anaerobic layers in both wetland flooded soils and adjacent agricultural soils with regard to pesticide environmental fate were presented. In recognization of the importance of oxidation-reduction conditions on the environmental chemistry of pesticide compounds, agricultural practices near sensitive wetland systems should be examined in terms of such physicochemical processes. Possible modifications should be designed to consider the following in overall agricultural practices:

(1) The implementation of draining vs. non-draining practices, particularly in rice growing regions, to take advantage of oxidation-reduction variations to regulate pesticide residence time.

(2) The monitoring of pH effects based on individual crop needs as well as pesticide environmental fate.

(3) The careful analysis of wetland soils adjacent to agricultural areas, with regard to their various physical and chemical properties to ascertain accumulation effects and residence time phenomena of pesticides.

Additional research is needed on mobility and degradation of toxic compounds, especially related to runoff activities. Incorporation of such data into appropriate data information bases, in an effort to further refine EPA's agricultural runoff model, is anticipated.

The overall purpose of these investigations has been to incorporate experimental data and overall experimental design, primarily developed for federal and state monitoring and management strategies, into environmental impact and hazard assessment of toxic chemicals in waterways and wetland systems. More information is needed on aquatic soil/sediment processes that are critical in productivity and food web dynamics. In continuing to pursue these aforementioned objectives, the overall conceptual approaches involved, and the ultimate use of information obtained, are illustrated in Figure 1.

The implementation of effective and optimal management practices for maintaining agricultural productivity must include an economic analysis of cost and energy use. Nevertheless, such practices should be deleterious adjacent to highly productive wetland areas. Development of economically efficient strategies for managing and monitoring agricultural pollution need to be based on use of the best agricultural and wetland environmental science and technology. Procedural wetland research efforts, such as presented here, must continue to resolve both compatibility as well as possible conflicts between hydrologically-linked habitats within a major aquatic ecosystem.

Conclusions

The procedural methodologies developed in this multidisciplinary tiered approach to analysis of the environmental effect and fate of selected xenobiotics in agriculturally affected wetlands provide a useful "tool" for further evaluation of other EPA priority-pollutant classes of compounds, i.e., phenols, phthalate esters, cholorbenzenes. In addition, information is contributed with regard to modifying current agricultural practices and to furthering development of coastal zone management strategies. The continuing formulation of valid predictive models will generate needed information on the fate (and effects) of a variety of toxic chemicals in fresh, brackish, and saline ecosystems. Furthermore, data should be obtained on microbial and related physicochemical transformation processes *in situ* and under laboratory conditions that affect the environmental fate of toxic chemicals.

In the projected evaluation of other EPA priority pollutants, the combination of field and laboratory methodology, the latter employing a variety of microbial,

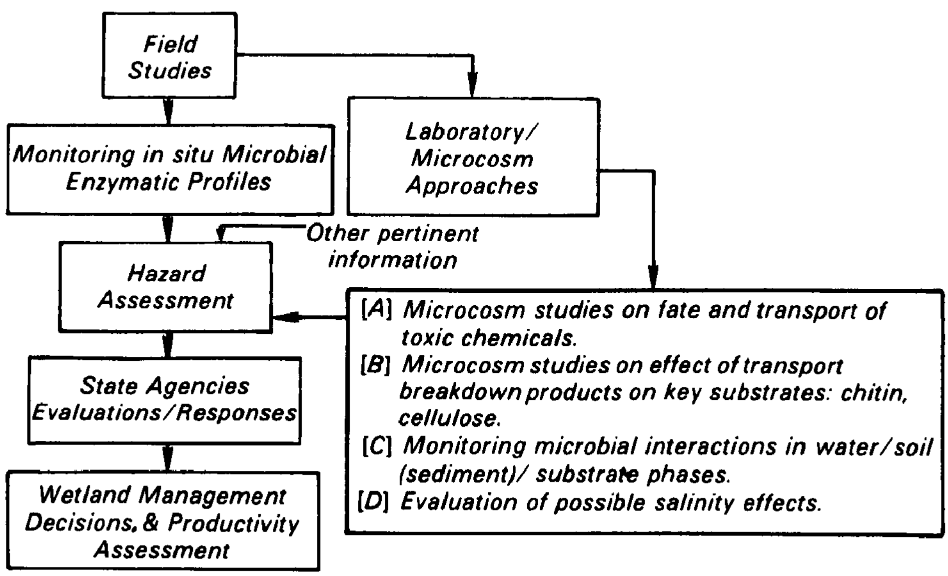

Figure 1. *Conceptual approaches and ultimate use of study information.*

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benthic, enzymatic, and physicochemical transformation activities, is the preferred approach. This allows for ongoing formulation of a valid computer data base program for statistical and numerical model analysis to standardize laboratory methods and to establish a ranking system for other classes of toxicants. In continuing these evaluations of xenobiotic impact in economically and biologically important wetland systems, we feel additional information should be garnered in the following areas:

(1) The further identification of relevant abiotic processes, particularly Eh/pH, which complement biotic transformations of "target" compounds.
(2) The role of ecologically significant metabolizable substrates, i.e., chitin, which provide an active microbial and enzymatic pool for both acclimation to, and subsequent enzymatic adaptation of, "target" xenobiotics.
(3) The ultimate bioavailability of selected xenobiotics to the aforementioned microbial pool and estimation of minimal, or threshold levels, at which biotransformation processes can proceed, and over what duration.

Biotransformation test protocols must include an evaluation of sorption reactions affecting rate(s) of microbial transformations. In addition, there needs to be a monitoring of microbial/benthos at varying Eh, pH, and salinity levels for comparative purposes.

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The complete report, entitled "Determination of the Environmental Impact of Several Substitute Chemicals in Agriculturally Affected Wetlands," (Order No. PB 82-242 017; Cost: $13.50, subject to change) will be available only from:
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