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An Inquiry into the Phenomenon of Enhanced Transport of Pesticides Caused by Effluents

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AN INQUIRY INTO THE PHENOMENON OF ENHANCED TRANSPORT OF PESTICIDES CAUSED BY EFFLUENTS

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AN INQUIRY INTO THE PHENOMENON OF ENHANCED TRANSPORT OF PESTICIDES CAUSED BY EFFLUENTS

ABSTRACT

The objective of this collaborative research project was to determine the factors that may cause enhanced pesticide transport under effluent irrigation. For s-triazines, the potential for enhanced transport through association with effluent dissolved organic matter (OM) was shown to be small in batch and column studies and in numerical simulations. High alkalinity and pH of treated effluents increased soil-solution pH for selected soil-effluent combinations, promoting the dissolution of soil OM and mobilizing otherwise OM-retained pesticides. Evapotranspiration in column studies resulted in increased pore-water concentrations of dissolved OM and some pesticide transport enhancement with the greatest effect observed with OM-poor soils. For ionogenic pesticides, effluent-induced increases in soil-solution pH increased the mobility of pesticides with acid dissociation constants within 2 pH units of the initial soil-solution pH. Effluents high in suspended solids and/or monovalent cations resulted in blockage of soil pores reducing water-flow velocity and/or changing flow paths. Reduced flow resulted in an increase in desorption time of soil sorbed pesticides, increasing the amount available for further transport with the net effect being soil texture dependent. In terms of pesticide degradation in soils, effluents appeared to have only a minor effect for the few pesticides investigated.

CHAPTER I

INTRODUCTION AND OBJECTIVES OF THE ORIGINAL RESEARCH PROPOSAL

INTRODUCTION

Efforts to abate pollution and supplement available water resources in many parts of the world have resulted in the increased use of effluents for irrigation. In semiarid areas, where fresh water is limited, the use of effluents for agricultural purpose has been common practice over the last few decades (Rebhun *et al.*, 1987; Ronen and Magaritz, 1985). As reported by Miller (1990), treated effluent is one of the fastest growing sources of water for irrigating both agricultural and recreational facilities such as golf course, parks, school grounds and street medians in many parts of the United States. Wastewater reuse in both the U.S. and worldwide will inevitably increase as existing water supplies are incapable of meeting future demand brought about by increasing world populations and industrialization (Miller, 1990).

One potential side effect of reusing effluents is the long-term deterioration of groundwater quality by organic chemicals. Muszkat (1993) identified many toxic organic species at depths in the soil profile that have been irrigated with effluents for about 20 years, as compared with those irrigated with higher quality water. The organic pollutants found are composed both of the organic compounds originally present in the wastewater (Hutchins *et al.*, 1985) and the soil-borne organic pollutants such as pesticides. These compounds may leach down the soil profile to a greater extent when wastewater is used as the irrigant, because of the phenomenon termed facilitated transport. The enhanced transport of soil-borne pollutants is thought to be induced by complexation of the pollutants and surface-active components in the effluent. This hypothesis is supported by previous studies (Chiou *et al.*, 1987; Kan and Tomson, 1990) on the enhancement of apparent solubility of hydrophobic organics by surface active macromolecules, including commercial surfactants (alkyl polyoxyethylenes, alkyl phenol ethoxylates) or dissolved humic and fulvic acids. Hydrophobic contaminants tend to be retarded relative to the flow of water due to their interaction with soil and aquifer material. The interaction mechanism is hypothesized to be hydrophobic partitioning (Chiou *et al.*, 1983; Karickhoff *et al.*, 1979). Hydrophobic partitioning defined thermodynamically is the transfer of an organic compound from an

potential to a phase in which it has a lower chemical potential. The contaminant distribution between the two phases is defined when the chemical potentials are equal (i.e., equilibrium).

Organic matter in soils and dissolved in a solution phase provide domains with high affinities for hydrophobic pollutants relative to pure water. The solubility of the compounds in the aqueous phase appears to increase as hydrophobic molecules associate with dissolved organic matter. The apparent solubility enhancement will be dependent both on the compound hydrophobicity and the concentration of the dissolved organic matter, also referred to as organic macromolecules. The dissolved macromolecules may be adsorbed to the surface of aquifer material or continue to move through the soil profile. Movement through the soil profile may be faster than water due to the large difference in molecular size (Enfield and Bengtsson, 1988; Enfield *et al.*, 1989; Magee *et al.*, 1991; Vinten and Nye, 1983). This phenomenon can be compared to exclusion chromatography where molecules are separated by size with the largest eluting first and each molecule flowing through a different portion of the total porosity. Therefore, organic contaminants associated with dissolved organic macromolecules may move faster than the unassociated organic contaminants.

Previous facilitated transport research has largely focused on strongly hydrophobic compounds such as PCBs (Chin *et al.*, 1990; Gschwend and Wu, 1985; Hasset and Anderson, 1982), PAHs (Kan and Tomson, 1990; Magee *et al.*, 1991), and hexachlorobenzenes (Enfield *et al.*, 1989). Also, most laboratory studies have centered on well characterized, and often times artificially high concentration of macromolecules, e.g. Triton X-100 (Kan and Tomson, 1990), Dextran (Enfield and Bengtsson, 1988), and humic acid (Barriuso *et al.*, 1992; Chin *et al.*, 1990; Chiou *et al.*, 1986; Lee *et al.*, 1990).

Recently, several studies have been conducted on the transport and fate of pesticides such as atrazine, prometryn, and napropamide (Graber *et al.*, 1995; Lee and Farmer, 1989). Graber *et al.* (1995) reported field observations suggesting that atrazine penetrated to a much greater depth in the effluent-irrigated cornfield than in high quality water-irrigated (Figure 1-1). The total quantity of atrazine in the effluent-irrigated profiles was higher than that in the control profiles. Due to the low hydrophobicity, i.e., low log K_{ow} , and moderately high aqueous solubility, weak basic or moderately polar pesticides do not have strong an affinity to dissolved organic matter (Karickhoff, 1981). Such data suggests that interactions of pesticide with soil components and dissolved organic matter other than simple hydrophobic partitioning into organic macromolecules must be considered. The involvement of specific

reaction sites and effluent parameters such as pH, ionic strength, and ionic composition should be examined to improve our understanding of effluent irrigation on pesticide transport.

Interactions of pesticide with the soil component and dissolved organic matter have been studied for the past few decades in an attempt to understand the behavior of pesticide in the soil environment. The main limitation in our understanding of these interactions is the complex nature of soil organic matter and the numerous processes in the soil environment that occur simultaneously. Additionally, the involvement of effluent parameters such as pH, ionic strength, and ionic composition may increase the complexity of interactions between the pesticides and the components of soil and effluent in the modified environment. In this study, the adsorption and mobility of triazine pesticide under effluent irrigation conditions will be examined. Therefore, it should be required to propose potential factors that would affect the mobility of pesticides in soil environment with effluent irrigation.

For pesticides with potentially reactive polar functional groups in which site specific interactions may be involved in the adsorption to soils, it could be hypothesized that dissolved organic matter may successfully compete for adsorption sites on soil surfaces, thus blocking the adsorption sites for pesticides. Continuous irrigation with effluent for a long period of time may especially modify the preference for adsorbed substances on the soil surface. It may change the total adsorption capacity and the reversibility of the adsorption processes. The modified properties may result in increased nonideality of pesticide adsorption. This includes nonlinearity of adsorption and nonsingularity of desorption.

For weakly basic pesticides such as the triazines, a change in soil solution pH due to the application of high pH effluents would influence adsorption mechanisms and the extent of pesticide adsorption. At low pH, a basic pesticide would be protonated forming a cation, resulting in cation exchange being a significant adsorption mechanism for the pesticides. Cation exchange mechanism is particularly important when trying to explain the high adsorption of methylthiotriazines such as prometryn with high pK_a values onto organic matter. At high pH values, hydrogen bonding and hydrophobic attraction would be the governing adsorption mechanisms, since the neutral species of the pesticide becomes dominant as pH increases. Due to the weaker attraction forces of the latter mechanisms, the total capacity of adsorption decreases with increasing pH. Therefore, the high pH of treated effluent may enhance the mobility of the pesticide.

The adjustment of pH also affects the release of soil organic matter into the soil solution and the adsorption of dissolved organic matter by soil. Jardin, *et al.* (1992) observed

that the maximum adsorption of dissolved organic carbon obtained from a surface stream by soil occurred at pH 4.5. The adsorption monotonically decreased at the higher and lower pH values. The increased soil pH may enhance pesticide concentrations in the solution phase as it is complexed with the dissolved organic matter released from the soil or supplied from the effluent, and thereby contribute to the greater mobility of pesticide in the soil solution.

Effluent irrigation can modify the degradation of pesticides in soil by means of several mechanisms directly or indirectly. They could include biotoxicity from components of effluent such as toxic organic compounds and heavy metals, changed bioavailability or distribution of pesticide with effluent irrigation, and increased alternative substrates for bacteria that would metabolize pesticides otherwise.

During infiltration of organic pollutants through the soil profile, one of the decisive factors regarding their distribution pattern is biodegradability. The detection of pollutants at deeper depth may suggest that the effectiveness of microbial communities in the deeper layers of soil profile might be quite limited. A low microbial population limited by lack of oxygen and supporting organic materials could constitute the key factors contributing to reduce biodegradability. The effectiveness of biodegradability could also be diminished if the adsorbed complexes were less accessible to microbial degradation than free species in the aqueous phase. Although adsorption may increase the amount of chemical degradation as in the case of surface catalyzed hydrolysis of triazine herbicides, Ogram (1985) showed that 2,4-D was not susceptible to microbial degradation when sorbed to the soil surface. Similar findings have been reported for organic acids and bases, and nonpolar chemicals (Ainsworth *et al.*, 1993; Guerin and Boyd, 1992; Scow, 1996; Smith *et al.*, 1992). Reduced bioavailability of sorbed organic solutes may result from the inaccessible region of sorption to the microorganism, a strong bonding of solute with the surface, or reduced solution activity of the solute to a level that will not support microbial utilization. The combined effects of low microbial mass and restricted biodegradability may be responsible for the higher concentration of organic compounds at depth.

Use of effluent can cause significant, unexpected subsurface pollution through enhanced transport of pesticides (Muszkat *et al.*, 1993). Pesticide transport out of the root zone and towards the groundwater system depends on the nature of treated effluents, on the chemical parameters of the pesticide selected, and on the characteristics of soil system. The main objectives of this study are to investigate the role of treated effluents in the transport of pesticides, and to identify the components of effluents and the types of soil and pesticides that

have a high potential for enhanced transport under treated effluent irrigation practices.

In order to achieve these objectives, three major hypotheses were proposed for examination. First, hydrophobic pesticides may bind with organic macromolecules in treated effluent, thus enhancing their solution concentration and mobility. However, complexation of weak hydrophobic triazine pesticides with DOM may not significantly impact the enhanced mobility of the pesticides. Secondly, treated effluent irrigation may result in changes of soil solution pH. Effluent-induced pH changes would shift speciation of weakly basic pesticides to the neutral species that have lower sorption affinities than protonated species involving cation exchange, thus enhancing mobility of pesticides under effluent irrigation. Third, it has been postulated that the long term application of treated effluents may change the chemical and physical properties of the soil particle surface, thereby impacting pesticide adsorption by soil.

ORIGINAL OBJECTIVES OF THE RESEARCH PROPOSAL AND DIGRESSIONS

Enhanced transport of pesticides out of the rootzone and towards the groundwater zone depends not only on organic matter content, but on the nature of the dissolved organic material itself, the characteristics of the inorganic suspended and dissolved material, and on the water solubility and acid dissociation constant of the pesticides in use. The purpose of the proposed research is to determine the specific factors which cause enhanced transport of pesticides in the presence of treated effluent. The ultimate goal is to match pesticides with soil type and effluent quality to help minimize the enhanced transport phenomenon. The specific objectives are:

1. *To screen selected effluents for their ability to enhance the transport of pesticides of varying water solubilities in important agricultural soils using both batch and column experiments.* Based on previous results (Muszkat et al. 1993a; Muszkat et al. 1993b; Graber et al., 1995), we assumed that enhanced transport or increased solubility of pesticides in the presence of effluent would be observed in laboratory batch experiments. As such we intended to differentiate between effluents which caused this phenomenon versus those which did not. This assumption was not borne out, however, in sorption, complexation, and solubility trials with different effluents performed by both the Israeli and American teams (Chapters 1-3). The results for these batch experiments contrasted with results from large container experiments (Chapters 3, 12) and the previous field trial.

In an attempt to understand these differences, new experimentation was devised (Chapters 4,6,7, 11,12).

2. *To characterize the nature and composition of the dissolved and suspended organic and inorganic materials in the effluents that resulted in significant enhanced transport of pesticides in (1).* Because Objective 1 was in part unsuccessful, objective 2 was not relevant. However, two effluents were fractionated according to the scheme described in the proposal for use in batch and column experiments. These results of these fractionation experiments are reported in chapter 3.
3. *To determine the relative impact on enhanced transport of the different components identified in (2) as a function of concentration.* The fractions were not subsequently used in batch and column experiments for several reasons: (a) several fractions were not water soluble after freeze drying; (b) there was concern that the use of specific fractions as opposed to the whole effluent would not result in a representative response; (c) replacement experimentation was devised using artificial effluent (Chapters 1,2,4,6,10,11).
4. *To investigate the nature and rate of the complexation reaction between the pesticides and the organic and inorganic components determined in (2) to be primarily responsible for transport enhancement.* Because batch and column experimentation resulted in some unexpected results that were suspected to be related to organic compound complexation with organic matter (both solid and dissolved), this objective was expanded to include more basic studies into the nature of organic compound-organic matter (OM) interactions. The expanded objective was directed towards improving our basic understanding of the types of interactions responsible for sorption and towards understanding the effect of OM structure on organic compound sorption (Chapters 5,8,9,13).
5. *To develop a preliminary assessment tool that incorporates the identification of components and their concentrations which have a high potential for resulting in enhanced transport.* A model for enhanced pesticide transport under irrigation with effluent has been proposed (Chapters 4,13). Additionally, a model for organic matter structure as affecting organic compound sorption has been developed (Chapter 9). These models are based on the research performed in the framework of the BARD grant.

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CHAPTER 14

DESCRIPTION OF THE COOPERATION

The Israeli and American teams maintained a high degree of contact and consultation throughout the course of the BARD project. In the first year the American PI visited the Israeli laboratories for project design and development. In the second year the Israeli PI visited the American laboratories for mutual progress reporting and to discuss findings. Deviations and digressions in the original workplan as a result of the first year's work were proposed and jointly developed. Regular contact between the two teams was maintained through electronic mail communication. The two PIs met a third time in the final year at a conference in Boston, and planned the last stages of work and report and manuscript writing. Some of the results of this study will be published as a collaborative effort. The PIs have plans for future cooperation as this cooperation was fruitful, productive and enjoyable, and high degree of mutual respect was created.

CHAPTER 15

CONCLUSIONS AND EVALUATION OF THE RESEARCH ACHIEVEMENTS

For s-triazines of moderate aqueous solubility and relatively weak hydrophobicity, the potential for enhanced transport through association with effluent DOM was shown to be minimal through various batch and some kinds of column studies as well as using numerical simulations. However, the high pH, alkalinity, suspended solids, and monovalent-rich electrolyte matrix often characteristic of treated effluents may result in enhanced pesticide transport for some pesticide-soil combinations. High alkalinity and pH of treated effluents relative to clean water were shown to result in increases in soil-solution pH for selected soils. Increases in soil-solution pH can promote the dissolution of soil organic matter (SOM) where pesticides may be sorbed thereby mobilizing contaminants otherwise retained by the soil surface. For ionogenic pesticides, sorption mechanisms are pH sensitive within ranges defined by the acid dissociation constants (pK_a) of both the pesticide and soil. Many earlier studies showed that at low pH values, triazine molecules can protonate and adsorb to soil through cation exchange mechanisms (Talbert and Fletchall, 1965; Weber *et al.*, 1969). As pH increases, adsorption decreases due to the speciation shift from the protonated to the neutral species of the triazine. Effluent induced increases in soil-solution pH will impact mobility of pesticides that have pK_a values that fall within 2 pH units of the initial soil-solution pH. The pH and buffer capacity of both soil and effluent, and the pK_a of the pesticide govern the magnitude of enhancement in pesticide mobility. Long-term irrigation with treated effluents high in suspended solid content will result in the blockage of soil pores reducing water-flow velocity or changing flow paths. A similar result may occur from enhanced dispersion of soil particles caused by effluent matrices high in sodium. Reduced flow will increase the contact time of the pore-water with the soil sorbed pesticide allowing additional time for pesticide release, thus increasing the amount available for further transport. The potential for any of these processes to significantly enhance transport in the field will most likely increase with repeated treated effluent irrigation. Evapotranspiration, was shown to have an effect on enhanced transport of pesticides under effluent irrigation, mainly due to strong increases in dissolved organic matter content of soil solution. This effect is expected to be small in soils which naturally have soluble organic matter contents which

are similar to the organic matter content of irrigation water. The greatest effect may be expected in organic matter poor soils which are marginally useful for agriculture.

The effect of effluents on pesticide degradation was also considered. Effluents appeared to have only a minor effect on degradation of selected pesticides in soils. Results indicate that effluent-induced increases in soil-solution pH for low pH soils may enhance degradation through hydrolysis by a few per cent. On the other hand, high DOM concentrations may retard degradation due to limited bioavailability especially for soils where degradation is normally more favorable. This study suggests that effluent irrigation will have a minimal affect on degradation of selected pesticides in soils; however, changes in soil properties and microbial ecology after long-term effluent irrigation in the field may result in significant changes in degradation and subsequent mobility. The preferred use of effluent carbon and nitrogen sources for energy by microbial populations may reduce pesticide degradation subsequently enhancing the pesticide mass available for further transport; however, this was not investigated in our research project.

Specifically interacting organic compounds such as pesticides were seen to undergo specific interactions with organic matter, thus increasing their potential for sorption over similarly sized, non specifically interacting compounds. Hydration of soil organic matter was shown to have an important effect on sorption of hydrogen bonding compounds, increasing significantly their sorption as compared with anhydrous systems. The increase in sorption for hydrogen bonding compounds was contrasted with no hydration effect for non polar compounds, thus demonstrating that polar crosslinks in organic matter play an important role in compound sorption.

CHAPTER 16

LIST OF PUBLICATIONS

Publications in Reviewed Journals

- Borisover, M. and Graber, E.R. (1997). Specific interactions of nonionic organic compounds with soil organic carbon. *Chemosphere* 34 p.97-113.
- Borisover, M. and Graber, E.R. (1997). Comment on "Competitive Sorption Between Atrazine and Other Organic Compounds in Soils and Model Sorbents". *Environmental Science and Technology* 31 p. 1577.
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Manuscripts in Submission to Reviewed Journals

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