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Characteristics of the Sorption of Chlorothalonil and Azinphos-Methyl to a Soil from a Commercial Cranberry Bog

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Insecticide and fungicide usage is a necessity in the production of an economically viable commercial cranberry crop (Marucci 1972). Maintenance of the water table in the cranberry bog at a level close to the soil surface (6 to 12 inches) is also required for the best and most productive growth of the cranberry plant. Given the close proximity of the ground water to the soil surface in the bogs and the fact that the bulk of New Jersey's commercial cranberry bogs are located in the Cohansey aquifer recharge area, the potential for contamination of sections of the aquifer by these pesticides is very real.

This paper describes the sorptive characteristics of 2,3,4,5 tetrachloroisophthalo- nitrile (chlorothalonil) and O,O-Dimethyl S-[(4-oxo-1,2,3 benzotriazin-3(4H)-yl) methyl] phosphorodithioate (Azinphos- Methyl) on soil of the Cohansey aquifer located in the southern New Jersey Coastal Plain.

MATERIALS AND METHODS

The soil used in this study was taken from a site at the Rutgers University Blueberry and Cranberry Research Center near Chatsworth, NJ. The Research Center is located on the Cohansey aquifer outcrop area. The specific site has no prior history of agricultural chemical applications although the organic top layer had been removed in preparation for cultivation. Sieve analysis of the soil indicated sand as the primary constituent, ranging from very fine to very coarse.

Soil properties were determined (Uchrin and Katz 1985a) and are listed in Table 1. Organic matter content was determined by the Walkley and Black modification of the

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Table 1. Physical properties of Cohansey soil.

Sand %	90.0
Silt %	8.0
Clay %	0.0
Organic Matter %	4.4
Porosity	0.55
Bulk Density g/cc	1.78

rapid dichromate oxidation technique (Nelson and Somers 1982), with organic carbon content being defined as 59 percent of the organic matter content.

Chlorothalonil, the active ingredient in the fungicide Bravo 500, and Azinphos-Methyl, the active ingredient in insecticide preparations commonly called Guthion were chosen for examination due to their use in the cranberry cultivation at the Research Station. Chlorothalonil is soluble in water in its pure form to approximately 0.6 mg/l at 25 C. Azinphos-Methyl is soluble in water in its pure form to approximately 29 mg/l at 25 C (Farm Chemicals Handbook 1987). Chlorothalonil is of special note since it was approved for use on cranberries in July of 1985 (40 CFR Part 180 1985).

Kinetic batch studies were performed by placing a predetermined mass of air-dried soil into a series of 50 ml screw cap centrifuge tubes, with empty tubes as controls. The soil was then saturated with 2.5 ml of deionized distilled water. One set of tubes was spiked with 25 ml of a saturated solution of chlorothalonil in water (approximately 0.7 mg/l). A second set of tubes was spiked with 25 ml of a solution of Azinphos-Methyl in water (approximately 15.01 mg/l). The tubes were immediately sealed with teflon-lined caps and agitated on a wrist action shaker. Tubes were withdrawn for analysis at intervals of 1,2,4,8,12,24, and 48 hours.

To determine the liquid phase concentration of the respective solutes, the tubes were centrifuged to separate the soil solids from the water. The supernatant was then carefully decanted and 5 ml aliquots were removed from each sample and extracted with 5 ml of pesticide grade n-hexane. The Chlorothalonil analysis was performed on a Varian model 3700 gas-liquid chromatograph with a 4 foot long by 2 mm I.D. column filled with 1.5% SP 2250 and 1.95% SP 2401 on 100/120 mesh Supelcoport. The Azinphos-Methyl was analyzed on a Tracor model 570 gas-liquid chromatograph with a 4 foot long by 4 mm I.D. column with 3% OV-101 on 80/100 mesh Chromsorb W.H.P. The concentration versus time plot for the adsorption of these compounds to the Cohansey soil, shown in Figure 1, indicates that equilibrium conditions were essentially reached for these systems within the

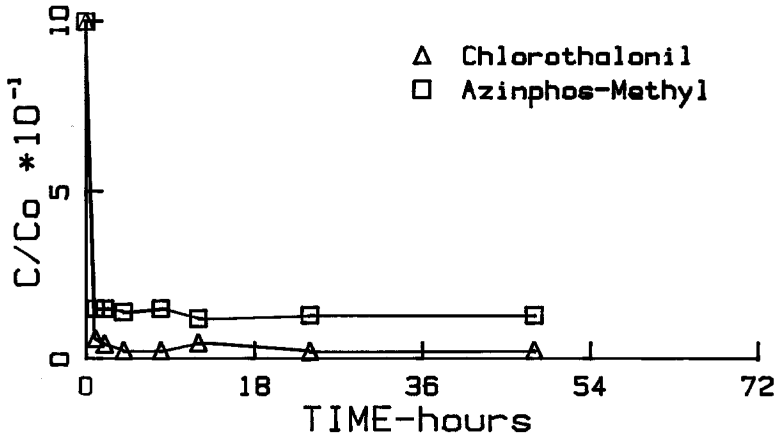

Figure 1. Batch Adsorption Rate Studies

first 5 hours. Analysis of the control centrifuge tubes indicated loss due to glassware to be negligible.

The procedure for the adsorption equilibrium study was identical to the kinetic study except that a matrix consisting of three soil masses (1,5, and 10 g) and five different pesticide spike concentrations was examined. The agitation of all samples on the wrist action shakers was carried out for 24 hours, which represented enough time for equilibrium to be reached.

Soil column studies were performed by placing soil into glass columns measuring four feet in length by two inches inner diameter which were sealed on both ends with teflon fittings and stood on end. The height of soil in the column was approximately 30 cm and a head of water was maintained on the soil surface to provide the driving force for the transport of the pesticides. Solutions of Chlorothalonil and Azinphos-Methyl containing 2.8 mg and 0.92 mg, respectively, in 100 ml of distilled water were applied to the tops of separate columns. Also added to each column at this time was 1 mg of lithium chloride, to be monitored as a tracer.

The column effluents were collected continuously and extracted every twelve hours. Analysis was performed as reported for the batch studies. The Chlorothalonil solution was a dilution of the commercial emulsion concentrate since solubility restrictions prevented the pure form from being applied in a 100 ml volume of water.

RESULTS AND DISCUSSION

The Freundlich Isotherm (Weber 1972), given as:

$$q_e = KC_e^{1/n}$$

where q_e is the solid phase equilibrium concentration [mass-solute/mass-adsorbent], C_e is the liquid phase equilibrium concentration (mass/volume), and n and K are constants indicative of the adsorption intensity and capacity, respectively, was fitted to the Chlorothalonil data (displayed in Figure 2.) and yielded a slope (1/n) of near unity indicating a linear adsorption relationship. With the equation reduced essentially to a linear adsorption model, K, computed to be 74.4 ml/g, becomes equivalent to the partition coefficient for Chlorothalonil on the Cohansey soil.

The BET Isotherm (Weber 1972), employed when multilayer adsorption is a consideration in the description of adsorption data, is given as:

$$q_e = BCQ/(C_s - C_e)[1 + (B - 1)(C_e/C_s)]$$

where q_e is the solid phase equilibrium concentration (moles-solute/mass-adsorbent), C_e is the liquid phase equilibrium concentration, C_s is the saturation constant of the solute, Q is the number of moles of solute adsorbed per unit weight of adsorbent forming a complete monolayer on the surface (adsorption capacity), and B is a constant expressive of the energy of interaction with the surface. The values of Q and B computed for the Azinphos-Methyl adsorption to the Cohansey soil are 191.7 ug/g and 5.064, respectively.

Results from the consecutive adsorption and desorption experiments for the Azinphos-Methyl system are shown in Figure 3.

A pronounced apparent hysteresis is evident between the adsorption and desorption traces. This phenomenon was also noted for the Chlorothalonil system. In all, very little (less than 22 percent) of the adsorbed mass of each chemical was recovered. This, of course, suggests that the sorptive processes are not totally reversible; an observation which will affect the modelling of the system as the theoretical model is predicated on the hypothesis that the sorptive processes are, in fact, reversible.

The column study employing Chlorothalonil was carried out for a period of 64 days at an average flow rate of 642 ml/day. Based on the flow rate and soil properties, a dispersion coefficient of 100 cm^2/day was found appropriate for this flow rate.

The observed data appear in Figure 4. As can be seen there is a large degree of scatter in the data. A model

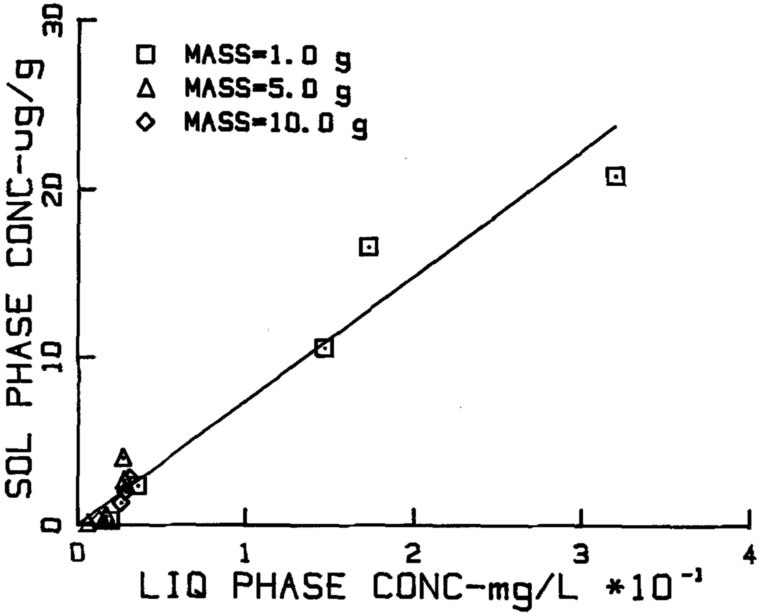

Figure 2. Adsorption Isotherm - Chlorothalonil on Cohansey Soil

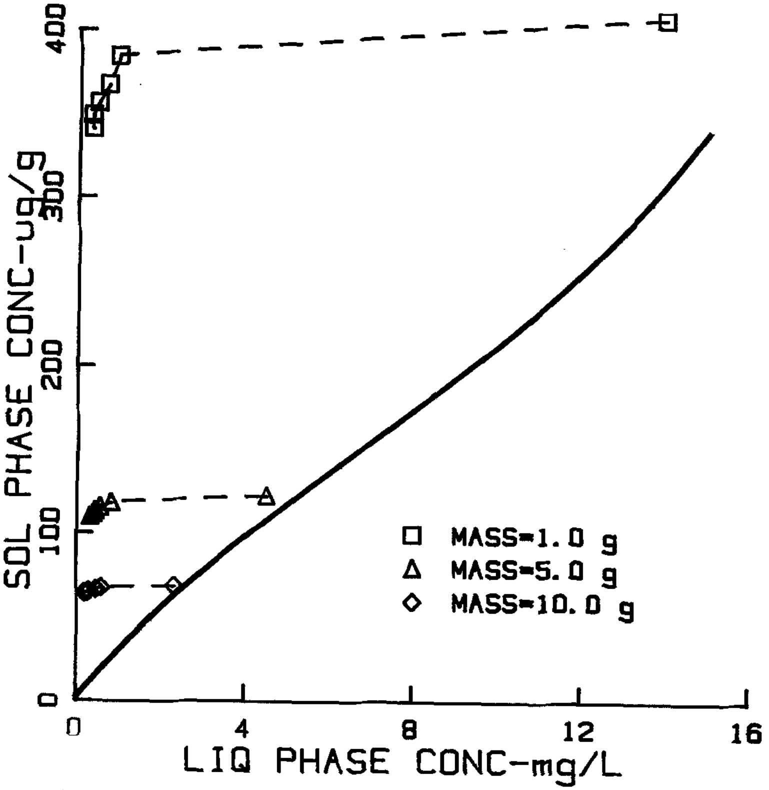

Figure 3. Consecutive Adsorption/Desorption Analysis Azinphos-Methyl on Cohansey Soil

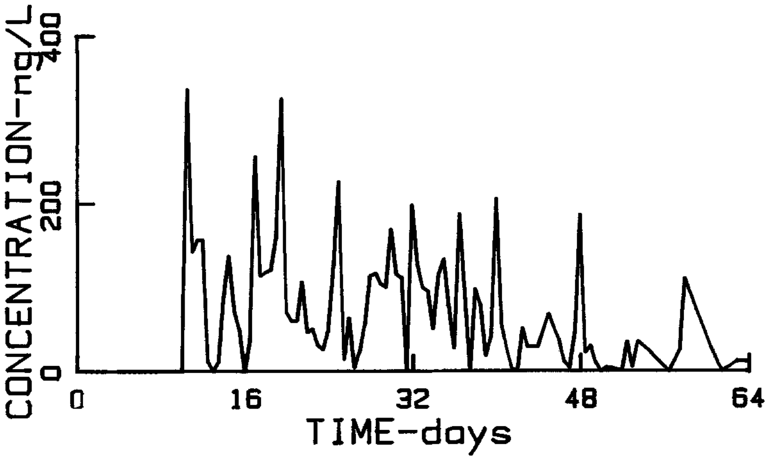

Figure 4. Column Study Raw Data
Chlorothalonil/Cohansey System

based on a non-dispersive system exhibiting linear, reversible partitioning and no degradation (Uchrin and Katz 1985b) was employed to describe the solute movement through the column. Figure 5, shows the expected model trace for this system. As is apparent, the model does not approximate the data well. This was not unexpected as the use of the emulsifying agent in the column study (which was not used in the batch study) obviously aided in the mobility of the compound. Nevertheless only a small percentage of the Chlorothalonil (less than 2.8 percent) was recovered from both the column effluent and the extracted column soil, suggesting that either irreversible adsorption or significant degradation had occurred. A similar model employing both partitioning and first-order degradation, developed by Ahlert and Uchrin (1986) was applied and a partition coefficient, Kd, and a decay rate coefficient, Kr, were calibrated to fit the data. In addition, the data were filtered using a 5-day average to eliminate random scatter. The resultant data/model traces are shown in Figure 6. and indicate good correspondance.

Table 2 summarizes the calibrated coefficients for both of the column experiments.

Table 2. Column parameters (calibrated)

Column	Q (L/day)	D (cm /day)	Kd (1)	Kr (1/day)
Chlorothalonil	0.642	100	25	19
Azinphos-Methyl	1.112	200	96.7	0

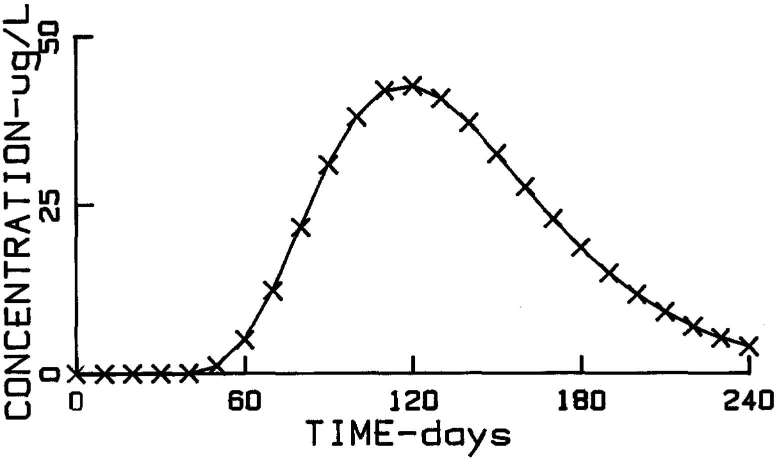

Figure 5. Model Predicted Column Trace
Chlorothalonil/Cohansey System

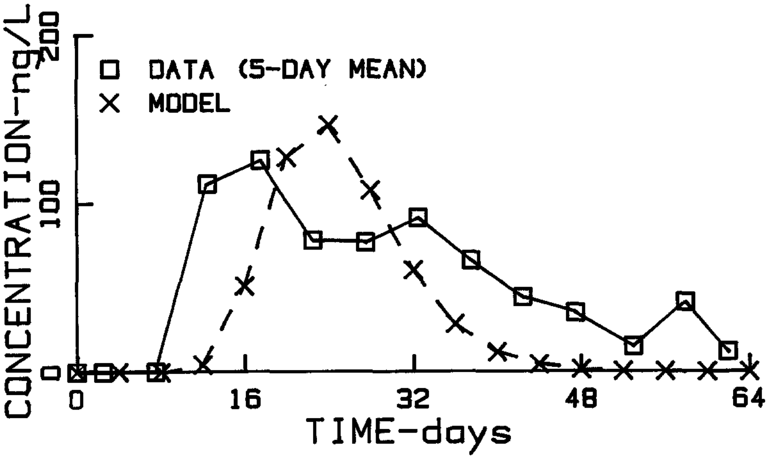

Figure 6. Flow-Through Column Study
Chlorothalonil/Cohansey System

The flow-through column experiment examining Azinphos-Methyl was carried out for a period of 64 days at an average flow rate of 1.112 L/day. Using the partition coefficient obtained from the batch experiments, the model predicted the effluent trace shown in Figure 7. No Azinphos-Methyl was detected in the column effluent over the experimental period. The soil matrix material was then removed from the column, partitioned into one inch segments, and extracted for analysis. The data are shown in Figure 8. together with a recalibrated model trace focusing on the solid phase mass balance (Uchrin and Katz 1985).

A good correspondance to the data is apparent. Again, the fact that a new partition coefficient had to be

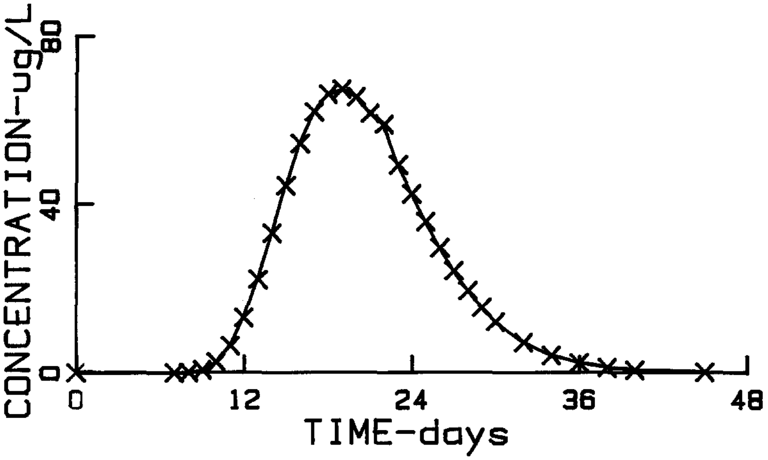

Figure 7. Model Prediction
Azinphos-Methyl/Cohansey Soil

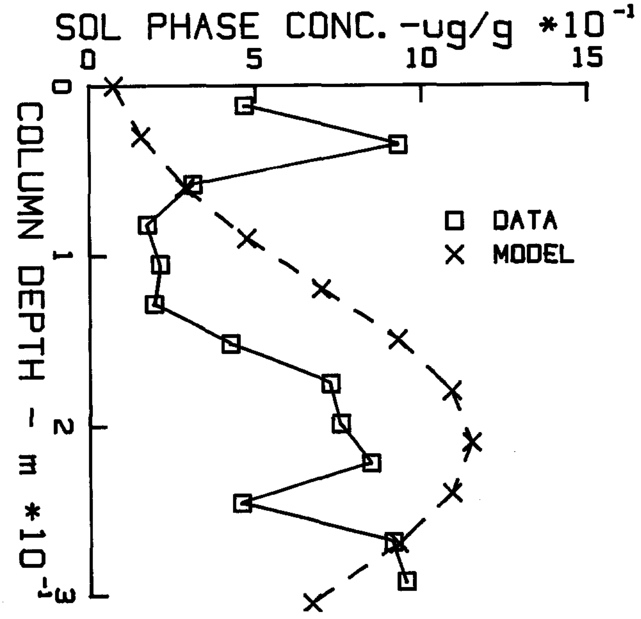

Figure 8. Column Study - Azinphos-Methyl

calibrated is not unexpected since the original was predicated on the hypothesis that the sorptive processes were reversible, which was shown to be incorrect by the batch consecutive desorption experiments and by the column experiment which showed the system to be quite resistant to desorption.

Although simplified models are available for describing the transport of organic substances in groundwater systems, their appropriateness is a function of their ability to accurately describe prototype situations. Simplified models, available in the literature, were tested for their ability to predict the observed data. In general, the models had serious difficulties in matching the data with the result that significant parameter modification had to be performed in order to obtain acceptable correspondance.

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