

Influence of Methods of Pesticide Application on Subsequent Desorption from Soils

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The amounts of fensulfothion [0,0-diethyl O-[p-(methylsulfinyl)phenyl] phosphorothioate] and its related sulfide [0,0-diethyl O-[p-(methylthio)phenyl] phosphorothioate] desorbed from three mineral soils with distilled water were greater when the compounds were spiked on the soil with either of two organic solvents (hexane–acetone, 95:5 v/v, or pure acetone) than when they were initially adsorbed from aqueous solution. For muck soil, the method of applying the two insecticides did not greatly alter their subsequent desorption behavior.

Desorption processes in soil–water systems have been traditionally studied by initially adsorbing the compound from aqueous solution and then successively desorbing it with distilled water increments (hereafter referred to as the "equilibrium adsorption method") (Bowman, 1979; Swanson and Dutt, 1973). Recently, Sharom et al. (1980) spiked (fortified) soil adsorbents with hexane solutions of insecticides (at 5 µg/g) and subsequently evaporated the solvent prior to adding distilled water to initiate the first desorption cycle. This approach offers the advantage of easily treating soil adsorbents with equal insecticide concentrations, facilitating comparisons of desorption tendencies among different insecticides on various soil adsorbents. In contrast, the equilibrium adsorption method requires prior knowledge of the adsorption isotherm in order to select a particular initial insecticide concentration on the soil for the first desorption cycle.

Table I. Properties of Soil Adsorbents

| adsorbent | % | | | | pH ^a |
|---------------------|------|------|------|----------------|-----------------|
| | sand | silt | clay | organic matter | |
| Plainfield sand | 91.5 | 1.5 | 7 | 0.7 | 6.9 |
| Big Creek sediment | 71 | 22 | 7 | 2.3 | 6.5 |
| Bondhead sandy loam | 77 | 15 | 8 | 3.9 | 6.9 |
| muck soil | 52 | 34 | 14 | 36.7 | 6.3 |

^a Measured in 0.01 M CaCl₂ (20 mL/10 g of soil).

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Table II. Adsorption Values for Fensulfothion Sulfide and Fensulfothion in the Four Soil Systems Using the Equilibrium Adsorption Method

| adsorbent | equilibrium adsorption values, $\mu\text{g/g}^a$ | |
|---------------------|--|---------------|
| | f. sulfide | fensulfothion |
| Plainfield sand | 34 | 5 |
| Big Creek sediment | 65 | 22 |
| Bondhead sandy loam | 64 | 24 |
| muck soil | 137 | 116 |

^a Initial solution concentration = 5.0 $\mu\text{g/mL}$.

The purpose of this study is to compare desorption of two insecticides of widely differing water solubility, fensulfothion [O,O-diethyl O-[p-(methylsulfinyl)phenyl]phosphorothionate] and its sulfide [O,O-diethyl O-[p-(methylthio)phenyl] phosphorothioate] to determine whether the manner in which insecticides are applied to soil can affect subsequent desorption processes.

EXPERIMENTAL SECTION

Reagents. Fensulfothion was purified according to previous methods (Bowman, 1973) and was >99% pure. Fensulfothion sulfide (f. sulfide) was 95.2% pure and was supplied by the Mobay Chemical Corp., Kansas City, MO.

Adsorbents. Two mineral soils, a stream sediment (hereafter included with the mineral soils) and a muck soil, the properties of which are shown in Table I, were used as adsorbents. After collection, the soils were air-dried, passed through a 2-mm sieve, thoroughly mixed, and stored in bulk containers until used.

Desorption Procedures. Two techniques were used to obtain initial starting concentrations of fensulfothion or f.sulfide on the adsorbents. For the first, the equilibrium adsorption method, triplicate 1.0-g soil samples (oven-dry basis) were equilibrated with 30 mL of an aqueous solution containing 5.0 $\mu\text{g/mL}$ insecticide (shaken for 6 h). Following centrifugation (8000g for 0.5 h), a 25-mL aliquot of the equilibrium supernatant was removed for analysis. The desorption process was initiated by replacing the aliquot with 25 mL of distilled water. For the second technique, the spiking method, an appropriate amount of insecticide was added to a bulk sample of the air-dried soil by using either (a) a hexane-acetone solvent mixture, 95:5 v/v, or (b) pure acetone as the carrier solvent. The treated soil was thoroughly mixed and the solvent was removed with a gentle airstream. Triplicate 1.0-g sub-samples of the treated soil (oven-dry basis) were weighed into 150-mL corex centrifuge bottles, and 30 mL of distilled water was added to initiate the first desorption cycle. With the hexane-acetone solvent mixture, two levels of spiking were used, one at 5.0 $\mu\text{g/g}$ (low spike), and the other (high-spike hexane-acetone) at the same level as the initial adsorption value (listed in Table II) obtained by the equilibrium adsorption method outlined above, so as to facilitate comparison between the two methods. With acetone as the solvent (high-spike acetone), soil adsorbents were spiked at the same level as that initially obtained by the equilibrium adsorption method. Desorption samples were shaken for at least 6 h before centrifuging at 8000g for 0.5 h prior to removing a 25-mL aliquot for analysis. This was replaced with 25 mL of distilled water to initiate the next desorption cycle. Four such desorption cycles were obtained for each treatment.

Analytical. Automated gas-liquid chromatographs were used for analysis of equilibrium desorption solutions as reported previously (Bowman and Sans, 1979). Triplicate samples of each solution (triplicate injections) were injected in a water-methanol (70:30 v/v) mixture and compared with external standards in the same solvent mixture. Alkali-flame ionization detectors were used for detection of fensulfothion and f. sulfide which were separated on Pyrex glass columns, 0.7.6 m X 2 mm i.d., packed with 100-120-mesh AW DMCS Chromosorb W coated with 10% QF-1, and operated at 200 °C. The spiked soils, from which triplicate samples were taken for desorption studies, were extracted with 3 X 20 mL aliquots of ethanol immediately after the solvent (hexane-acetone) was evaporated. The ethanol extracts were centrifuged to remove traces of sediment before analysis.

RESULTS AND DISCUSSION

The desorption patterns of the four treatments of f. sulfide in the four soil systems were plotted as percent remaining adsorbed vs. desorption cycle (Figure 1). Least significant difference ($\text{LSD}_{0.05}$) values are shown on the

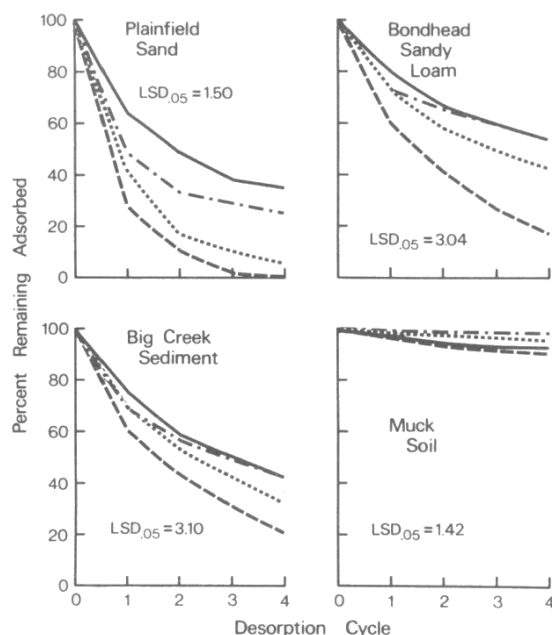


Figure 1. Desorption of fensulfothion sulfide from four soils. (-●-) Low spike; (●●●) high-spike acetone; (- - -) high-spike hexane; (—) equilibrium.

graphs for each soil system. In the three mineral soils, the amounts desorbed in the first cycle were less for the equilibrium adsorption method than for the same initial concentrations applied by the two high-spike treatments. Even the low-spike treatments on the mineral soils were desorbed to a greater extent in the first cycle than the equilibrium adsorption treatment, despite the 7-13-fold lower loading level. One might expect that for heterogeneous adsorbents such as soils, the lower the adsorbate loading level, the greater the adsorption energy (since the most energetic sites would be occupied first) and hence the greater the retention. This seemed to be true only in the comparison of the high- and low-spike treatments applied with hexane-acetone.

In all three mineral soils, f. sulfide desorbed less in the high-spike acetone treatments than in the high-spike hexane-acetone treatments. This suggests that the organic solvent played a role in the manner in which the compound was retained by the soil. Two possible explanations are that the more polar acetone permitted a more thorough penetration of the mineral soils by f. sulfide molecules, thereby exposing more adsorption sites, or the two organic solvents exhibited differential effects toward enhancing or hindering the adsorption of the sulfide molecules by the soil surface (i.e., interacted with hydration water of exchangeable cations).

There was a considerable difference in reactivity of the f. sulfide immediately following application to the soil surface in the two organic solvent systems. Within 1.5 h following application of f. sulfide to the soil using hexane-acetone (during the solvent removal period before distilled water was added), 10 and 20% of the f. sulfide had oxidized to fensulfothion in the muck and mineral soils, respectively. When acetone was used, less than 2% of the sulfide was converted to fensulfothion. Further conversion to fensulfothion appeared to cease upon addition of distilled water, which agrees with the minimal amount of conversion observed in the equilibrium adsorption method. The initial treatment levels for both the Low- and high-spike treatments using hexane-acetone (Figure 1) have been corrected for conversion to fensulfothion, since conversion occurred before the desorption process was initiated. It was also observed that f. sulfide was less susceptible to oxidation on glass surfaces when applied in an acetone solvent than in the hexane-acetone solvent.

Application methods did not appear to greatly influence the desorption pattern of f. sulfide in muck soil. After four desorption cycles, only 10% of the initial f. sulfide was desorbed with the high-spike hexane-acetone method, and slightly lesser amounts were desorbed with the other treatments. The low-spike treatment exhibited the least tendency to desorb, again presumably because of the energetics of the adsorption process.

Fensulfothion (water solubility = 2000 µg/mL) desorption was examined (Figure 2) by using the same treatment techniques as for f. sulfide (water solubility = 1.7 µg/mL) to determine whether a more water soluble compound exhibited the same differences between the spiking and equilibrium adsorption techniques. Only one spiking treatment with the hexane-acetone solvent was necessary for fensulfothion desorption from Plainfield sand (Figure 2) since coincidentally 5 µg/g was the amount adsorbed by the equilibrium adsorption method. The overall trend for fensulfothion desorption was similar to that for the sulfide, except that the total amount desorbed was greater, as might be predicted for the more water soluble fensulfothion. For the three mineral soils, considerably less fensulfothion was desorbed in the first desorption cycle when applied by the equilibrium adsorption method than was desorbed when applied with any of the three spiking methods. This difference was more distinct than it was for f. sulfide (Figure 1).

The differences in desorption patterns between the acetone and hexane-acetone spiking treatments for f. sulfide (Figure 1) were not observed with fensulfothion (Figure 2). Perhaps the more water soluble, more polar fensulfothion molecule (relative to f. sulfide) tended to minimize the differential effects that the two solvent systems had on the distribution and retention of the f. sulfide by the mineral soil surface. The low-spike treatments of fensulfothion were desorbed less than the comparable high-spike hexane-acetone treatments for the Bondhead and muck soils but showed no difference in the Big Creek sediment. In the muck soil, the spiking treatments resulted in fensulfothion desorption equal to (high-spike hexane-acetone) or less than that produced by the equilibrium adsorption method. With both f. sulfide (Figure 1) and fensulfothion (Figure 2), the high-spike acetone treatment desorbed slightly less than the equilibrium adsorption treatment in the muck soil.

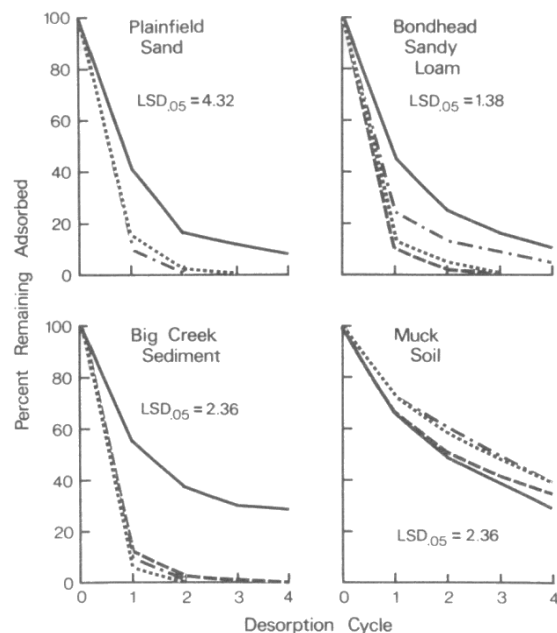


Figure 2. Desorption of fensulfothion from four soils. (-●-) Low spike; (●●●) high-spike acetone; (- - -) high-spike hexane; (—) equilibrium.

These results have shown that the method of application of insecticides to soil can have an important effect upon their subsequent desorption behavior. In the three mineral soils, insecticides adsorbed from aqueous solution were consistently desorbed to a lesser extent than if the soils were spiked with the insecticides in organic solvents. Consequently, desorption data obtained by the spiking technique are not directly comparable to desorption data obtained by the equilibrium adsorption method. With the exception of the fensulfothion–Big Creek sediment system, the higher treatment levels (high-spike hexane–acetone) were desorbed to a greater extent than the lower treatment levels (low spike). Peck et al. (1980) have also shown that the slope of the desorption isotherm increases with increasing initial concentrations. Clearly, the initial concentrations of insecticides on the soil must be comparable in order to make valid comparisons of desorption from various insecticide–soil combinations.

Although desorption data from the spiking and equilibrium adsorption methods are not directly comparable, both techniques have practical applications. The spiking technique simulates the manner in which insecticides are applied to and held by soil in field applications where the insecticide is physically deposited on the soil. The equilibrium adsorption method simulates more aqueous environments such as stream beds or waterlogged fields where the soil/solution ratio is relatively low. Further desorption studies need to be conducted using commercial formulations and application techniques to determine whether the spiking technique, in its present form, is a useful approximation of field conditions. Additional studies are also needed to describe insecticide desorption behavior in soil under nonwaterlogged, wetting- and drying-cycle moisture regimes.

ACKNOWLEDGMENT

We thank Dr. R. A. Chapman for his helpful suggestions in preparing the manuscript and Dr. D. G. R. McLeod for his assistance with statistical analysis of the data.

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Received for review January 27, 1981.
Revised manuscript received September 16, 1981.
Accepted September 16, 1981.