

Partitioning Behavior of Insecticides in Soil-Water Systems: II. Desorption Hysteresis Effects¹

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ABSTRACT

This investigation was undertaken to determine whether desorption hysteresis effects were dependent upon methods used in obtaining desorption data. Adsorption-desorption isotherms were obtained for two organophosphorus insecticides in aqueous suspensions of a clay, a sandy loam, and an organic soil. Desorption isotherms were obtained using both the consecutive desorption method and the dilution method. In the consecutive method, the same sample (after adsorption step) was put through a series of equilibration-centrifugation steps in which, following equilibration, the adsorbent was thrown down by centrifugation, and part of the supernatant pesticide solution was replaced by distilled water before reequilibration. In the dilution method a series of replicate samples (same adsorbent weight), after the adsorption step, were diluted to different volumes with distilled water, reequilibrated, then centrifuged to separate the phases. With the exception of one insecticide-soil system (where both methods produced minimal hysteresis), hysteresis effects were considerably reduced by using the dilution method. Repeated centrifugation appeared to be associated with the appearance of hysteresis effects observed using the consecutive desorption method. A short discussion is included on the improper use of desorption data to construct "single point desorption isotherms," which has created confusion in the literature.

Additional Index Words: irreversibility, non-singularity, isotherm, organic matter.

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The existence of nonsingularity, or hysteresis effects, in adsorption-desorption systems involving pesticides has been reported by numerous researchers (2, 5, 10, 17, 19). These effects manifest themselves when a desorption isotherm has a lesser slope than its respective adsorption isotherm, indicating a partial irreversibility. In pesticide-soil-water systems exhibiting hysteresis effects, significant over-estimates of pesticide desorption could be made if predictions were based only on the adsorption isotherm parameters.

Rao and Davidson (17) have identified three major possible sources of hysteresis effects as (i) artifacts created by the particular methodology, (ii) failure to establish complete equilibrium during the adsorption period, and (iii) chemical and/or microbial trans-formations of the pesticide during the experiment. Rao et al. (18) found that the centrifugation-resuspension step in the batch-type adsorption-desorption method might be responsible for at least part of the hysteresis, and instead suggested using a dilution method. However, Horzempa and DiToro (10), using a variation of the dilution method, reported that centrifugation did not appear responsible for nonsingularity effects in their studies.

Peck et al. (16) reported that as organic matter content of the adsorbent increased, hysteresis became more pronounced for diuron adsorption-desorption processes. This may be, in part, explained by a secondary slow adsorption process by organic matter. Khan (11) reported that 2,4-D and picloram adsorption by humic acid was slow in reaching equilibrium.³ We have noted (unpublished data) that chlorpyrifos exhibited a further 15% adsorption by an organic soil in a second 24-h adsorption period.

The entire issue of adsorption-desorption hysteresis has been unnecessarily complicated and confused by the improper presentation of desorption data in the form of "single-point desorption isotherms" (5, 7, 9, 10, 20). These graphical representations of desorption have been created by joining the first desorption points of separate systems (samples), not recognizing the thermodynamic singularity of the desorption process with respect to its initial starting point. This type of desorption representation can be easily spotted because the "desorption" branch has a steeper slope than the adsorption branch, implying that desorption occurred more readily (in a thermodynamic sense) than the adsorption process.

The purposes of this report are to describe our study of the effect of two desorption methodologies observed in several insecticide-soil adsorption-desorption systems, directed toward the elucidation of the causes of this phenomenon, and to discuss the graphical representation of desorption data.

MATERIALS AND METHODS

The chemical names of substances referred to are given in the Appendix. The purity of parathion was 98.8% and fensulfothion sulfone was recrystallized from methanol at -20°C. Air-dried samples (< 40 mesh) of Bondhead sandy loam (A horizon, 3.9% organic matter), a Ca-saturated Morris illite, and an organic soil (36.7% organic matter), the properties of which have been previously described (3), were used as adsorbents. Adsorption isotherms were constructed using the batch method and 30-mL volumes. Adsorbent weights for both adsorption and desorption isotherms were approximately 0.5, 0.75, and 1.0 g for the Ca-illite, organic soil, and Bondhead systems, respectively. All adsorption and desorption equilibration times were 24 h. For the initial adsorption step in both desorption procedures, triplicate 30-mL volumes of either a 10 or 30 µg mL⁻¹ solution of parathion or fensulfothion sulfone, respectively, were equilibrated with the appropriate amount of adsorbent. In the consecutive desorption method, samples were equilibrated in 150-mL Corexcentrifuge tubes. After centrifugation (6000 x g, 30 min) a volume of supernatant was removed, replaced by an equal volume of distilled water, and reequilibrated. This supernatant replacement procedure was repeated a total of four times, with the removed aliquot being re-centrifuged (43,500 x g, 10 min) to remove any remaining adsorbent traces. In the dilution desorption method, 15 samples were put through the adsorption step, using the 30-mL volume. After equilibration, one triplicate set was centrifuged (43,500 x g, 15 min) and the supernatant concentration was determined. The remaining 12 samples (four sets of triplicates) were diluted with different volumes (60 to 370 mL) of distilled water (final volumes, 90-400 mL), and reequilibrated. Appropriate aliquots of the suspension were centrifuged (43,500 x g, 15 min) and the supernatant concentration determined. All experiments were conducted at 20 ± 1.5°C. With both desorption techniques, desorption points at four equilibrium concentrations were obtained after the initial adsorption

³ See the Appendix for a listing of the chemical names of pesticides used in this article.

point was established. Adsorbent weight variation among samples in any given dilution desorption experiment had to be kept to a minimum, because separate samples were used rather than repeatedly desorbing one sample as in the consecutive desorption method. The standard deviation of all sample weights within an experiment was < 1%. All samples were prepared as aqueous methanol mixtures and injected into a gas-liquid chromatograph equipped with an alkali flame ionization detector, as previously reported (3).

RESULTS AND DISCUSSION

The use of a dilution method to measure desorption as an alternative to the consecutive desorption method requires that the partition coefficient be independent of adsorbent concentration. In the preceding paper in this series (4), we demonstrated that partition coefficients of pesticides were independent of changes in the adsorbent, in direct contrast with results reported elsewhere (6,15).

The degree of desorption hysteresis exhibited by the various pesticide-soil (clay) systems was clearly related to the method used in deriving the data (Fig. 1). In all cases there was only a minimal amount of hysteresis in the desorption isotherms obtained using the dilution method, whereas all the systems (excepting FSO₂-Ca-illite) exhibited considerably more hysteresis with the consecutive desorption method. Differences in water solubility and partitioning tendencies of the two compounds produced isotherms in different concentration ranges, making direct comparisons among the different systems difficult.

The results in Fig. 1 concur with the proposals of Rao and Davidson (17), that the centrifugation-resuspension step in some way was responsible for the observed hysteresis effects. Perhaps a partially irreversible compaction of the adsorbent by centrifugal forces greatly increased the time required for desorption processes to reestablish equilibrium, thereby creating the impression that partitioning had shifted in favor of the adsorbent. We have observed (unpublished data) that a single centrifugation does not appear to affect partitioning of pesticide-soil suspensions during batch-type adsorption studies, where equilibrium has been reached prior to centrifugation. Using presaturated glass microfiber filters to separate the two phases, we achieved essentially the same equilibrium concentrations as with centrifugation.

Evidence would seem to suggest that centrifugation can be used only once to separate the water and adsorbent phases, and that any additional adsorption or desorption steps might produce erroneous results. However, in an earlier study (1), we found that the repeated-additions method (at equilibrium, phases were separated by centrifugation, a portion of the supernatant was replaced with fresh pesticide solution, and then the system resuspended — the process was repeated several times to generate the isotherm) produced the same adsorption isotherm as did the standard batch-type method, where several pesticide-adsorbent suspensions were centrifuged only once. Thus, it appears that repeated centrifugation steps do not affect partitioning when involved in adsorption processes, but do for desorption processes.

Horzempa and DiToro (10) found that using their variation of a dilution method for desorption actually produced greater hysteretic effects for hexachlorobiphenyl (HCBP) adsorption-desorption by a lake sediment or by montmorillonite clay

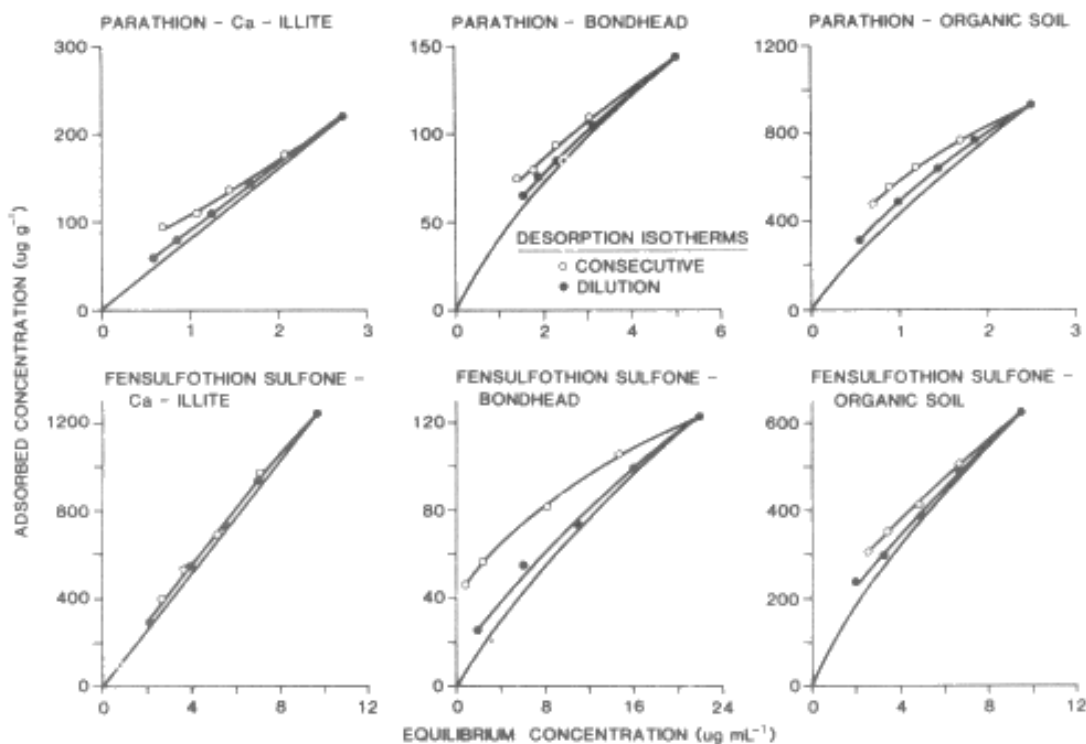


Fig. 1. Adsorption (solid lines) and desorption isotherms for parathion and fensulfothion sulfone in aqueous suspensions of Ca-illite, Bondhead sandy loam and an organic soil.

than did the consecutive desorption method — just the opposite of our results. They attributed the considerable scatter of their successive desorption data to experimental variability at low concentrations, but it is puzzling that, with numerous consecutive dilutions (at least six), the solution concentration did not simply drop below detectable limits rather than remaining at approximately the same concentration. These data would suggest a very substantial desorption of HCBP in order to maintain a relatively constant solution concentration after each desorption step. This seems quite at variance with the very minimal desorption they reported for another experiment on the same system using their dilution method.

Their variation of the dilution method involved successively removing portions of the whole system suspension and replacing these aliquots with equal volumes of distilled water. Since it is difficult to maintain completely homogeneous suspensions, one should have an independent means of confirming the amount of adsorbent removed. Since this method does not maintain a constant adsorbent concentration (if this is of concern), it might be preferable to use the dilution method, in which there is no removal of adsorbent, but instead only various volumes of distilled water added.

Although the dilution-desorption data presented in Fig. 1 minimize the observed magnitude of hysteresis, it should be kept in mind that there are situations where "true" hysteresis effects (as opposed to method-created artifacts) can have an important bearing on predicting pesticide behavior in soil-water systems. There has also been an increasing amount of attention devoted to "bound residues" in soil organic matter (12). In adsorption-desorption systems where the adsorbent contains significant amounts of organic matter, observed hysteresis effects could be expected to slowly increase with the period of time allowed for the system to equilibrate. Peck et al. (16) reported that apparent hysteresis effects increased for diuron adsorption-desorption with increasing organic matter content of the adsorbent. As noted earlier, we have observed a further adsorption of chlorpyrifos (up to 15%) during a second 24-h adsorption period. Khan (12) has shown an example of prometryn, a herbicide whose binding increased over a 150-d period, until it accounted for more than 40% of the applied material. However, "mass balance" problems arise because of the definition of "bound," since much of the bound residue data depends on radioactive labels, which do not distinguish degradation products from the original compound. Compounds that have been degraded and are retained by organic matter would create the appearance of increasing desorption hysteresis, when in fact the true amount of retention of the intact compound by the soil would be less than reported.

It is interesting to note that the more persistent pesticides (DDT, dieldrin) exhibit less binding tendencies than do the relatively non-persistent pesticides such as methyl parathion and fonofos (9, 13, 14). Large apparent hysteresis effects reported for compounds such as methyl parathion or fonofos may in fact be a consequence of their relative instability in soil-water systems, quite unrelated to true hysteresis.

It was earlier noted that confusion has been created in the literature through presentation of desorption data using so-called "single-point desorption isotherms." This has arisen because of the ease in establishing one desorption equilibrium from each of the adsorbent-adsorbate systems used in producing an adsorption isotherm and joining these points to produce a line. Although there is nothing mathematically incorrect about this graphical representation (any two points define a line), it is rather meaningless from a scientific viewpoint, as the line produced does not accurately represent the partitioning behavior of the system as the variables (i.e., solution concentration) change.

Consider the graphical representation of an adsorption-desorption system as depicted in Fig. 2, simulating a typical "family" of desorption isotherms (A-A2, B-B2, C-C2) associated with the adsorption branch (A-B-C). We have demonstrated, using the repeated-additions method (1), that an adsorption system at point A will follow the isotherm to B and to C with successive additions of higher concentrations of pesticide solution. This corresponds to an influx of pesticide to a natural system, and the system response would be along pathway A-B-C. From a desorption standpoint, because of hysteresis effects, systems at points A, B, or C are unique; if the equilibrium concentration of pesticide were lowered (an influx of fresh water), each system will follow its own desorption pathway (A-A1, B-B1, C-C1). Further reductions in solution concentrations will eventually produce the systems represented by A2, B2, and C2, respectively. The "single-point" curve, A1-B1-C1, which is commonly represented as a desorption isotherm (5, 7, 8, 10, 20), does not represent the desorption behavior of any real system (having a greater slope than the real desorption isotherm and often having a greater slope than the adsorption branch). It is impossible for system C to alter its desorption pathway at C1 and proceed to A1 (along C1-B1-A1) instead of to C2. The points forming these "single-point" lines are not usually shown with their singular connections (A1-A, B1-B, C1-C) to their source points (A, B, C). It is virtually impossible to reconstruct a proper desorption isotherm from "single-point" data, since only one point on a single-point line belongs with a particular starting adsorption point. The continued presentation of these "single-point lines" only creates unnecessary confusion for a topic that already is sufficiently complex, especially since (i) some newcomers to the field may not realize the difference between these irrelevant lines and the true isotherms, and (ii) these "single-point isotherms" are often not labeled as such (7, 8, 10, 20).

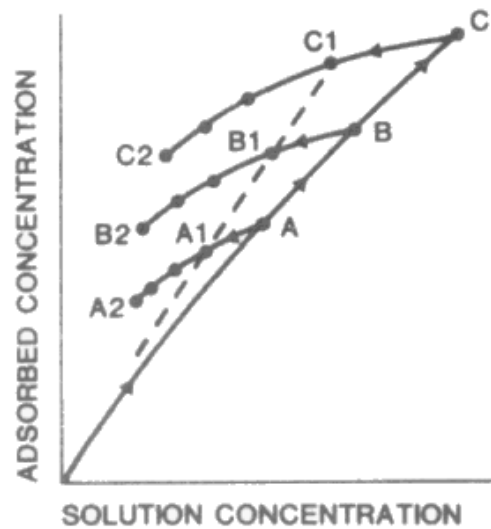


Fig. 2. Graphical representation of an adsorption-desorption system.

CONCLUSIONS

These studies have demonstrated that in some pesticide-soil (clay) systems, a substantial amount of the observed hysteresis is caused by centrifugation of the suspension. The dilution method for desorption isotherms produced less apparent hysteresis in the systems studied and is preferred over the centrifugation-resuspension method. An added advantage is the shorter period of time required to complete the isotherm since all desorption points can be obtained simultaneously, rather than in several repeated steps. However, with the dilution method it is important that the adsorbent weights for each of the replicates be kept as close to the same value as possible, and that the adsorbent be as homogeneous (thoroughly mixed) as possible. The small amount of observed hysteresis in the dilution method may be ascribed to a combination of true hysteresis and/or small adsorbate losses due to degradation, glass adsorption, and volatility, which occurred during the equilibration period. Since soil organic matter has been reported to slowly bind pesticides, observed hysteresis effects would probably increase with exposure time. It is possible that the relatively short equilibrium periods (up to 24 h), such as used here and by most researchers, may be inadequate to fully observe these irreversible processes.

In order to lessen the confusion regarding graphical representation of desorption data, it is recommended that "single-point" desorption curves no longer be used. Since they do not accurately represent partitioning of pesticides in either experimental or in naturally occurring soil-water systems, they create false impressions of adsorption-desorption behavior.

APPENDIX

Nomenclature of Pesticides Mentioned in Text and Figures

<u>Common Name</u>	<u>Chemical Name</u>
Chlorpyrifos	O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate
DDT	1,1,1-trichloro-2,2-bis(p-chloro-phenyl)ethane
Dieldrin	1,2,3,4,10,10-hexachloro-exo-6,7-epoxy,4,4a, 5,6,7,8,8a-octahydro-1,4-endo, exo-5,8-dimethanophthalene
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Fensulfothion sulfone	O, O-diethyl O-[p-(methylsulfonyl)phenyl] phosphorothioate
Fonofos	O-ethyl S-phenylethylphosphonodithioate
Hexachlorobiphenyl	2,4,5,2',4',5'-hexachlorobiphenyl
Parathion	O, O-diethyl O-p-nitrophenylphosphorothioate
Picloram	4-amino-3,5,6-trichloropicolinic acid
Prometryn	2-methylthio-4,6-bis(isopropylamino) s-triazine
2,4-D	2,4-dichlorophenoxyacetic acid

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