

## METHOD OF REPEATED ADDITIONS FOR GENERATING PESTICIDE ADSORPTION-DESORPTION ISOTHERM DATA

An improved method is suggested for obtaining desorption isotherm data, which avoids problems associated with decanting supernatant solutions. This technique is also useful in obtaining adsorption isotherm data at equilibrium concentrations approaching the solubility limit of the adsorbate.

Pesticide adsorption isotherm data have usually been obtained using the batch technique, where various concentrations of pesticide solution were added either directly to dried adsorbent or to aqueous suspensions of the adsorbent. After equilibration, the concentration of pesticide remaining in solution was determined in the centrifuged supernatant. Desorption data have been obtained by several techniques, some of which have disadvantages discussed later in this communication (Adams and Li 1971; Gamar and Mustafa 1975; Grover 1975; Harris and Warren 1964). Yang (1974) generated one desorption point from each of four initial concentrations and mistakenly joined them to create a desorption isotherm, rather than generating a family of desorption isotherms, one from each initial concentration. The data of Yang have previously been discussed by Bowman and Sans (1977). Sharom (1977) generated desorption data using two methods, one using the same technique as Yang and the second using the method of repeated additions being recommended here. Desorption data have often been obtained by decanting the supernatant solution, adding an equal volume of water, equilibrating the system, then determining the pesticide remaining in solution. Several such "dilution steps" would generate a desorption isotherm.

There are several limitations and/or disadvantages to these traditional approaches:

(1) The upper limit of adsorption data obtainable is dictated by affinity of the adsorbent for the pesticide, pesticide water solubility, and soil/solution ratio. Some clay and organic matter adsorbents have shown great affinity for certain pesticides (>95% adsorption) making it difficult to generate an adsorption isotherm, since even the maximum solution concentration would be greatly depleted. Consequently it would be impossible to obtain adsorption data (i.e. equilibrium concentration) at or near the solubility limit of the pesticide, using this technique. However, in situations where this is not a problem, the conventional batch method for adsorption isotherms would be more expedient.

(2) In obtaining desorption data using the "decanting" method, there are two sources of error introduced: (a) it is difficult to decant all the centrifuged supernatant solution without losing some adsorbent, thereby affecting subsequent desorption steps; and (b) an indeterminate volume of solution is left behind, associated with the adsorbent when the supernatant is decanted. It is difficult to accurately account for this volume when adding subsequent aliquots of water in each desorption step.

The proposed method avoids the difficulties and limitations outlined above, and offers flexibility in selecting more evenly-spaced data points in the desorption isotherm. For the adsorption branch of the isotherm, repeated additions of pre-selected concentrations of pesticide solution are added to the adsorption system. After each addition and subsequent equilibration, an equal volume of centrifuged supernatant is removed (part of which is used for analysis). The volume and initial concentrations of pesticide solution are selected to produce uniformly distributed data points. Usually a single incremental volume is chosen for each isotherm although changing the incremental volume does not affect the positioning of the

isotherms (adsorption or desorption). The maximum incremental volume selected must not remove any of the centrifuged adsorbent at the bottom of the centrifuge tube. In the present study, it was impractical to remove more than 25 ml from the initial 30-ml volume, in the initial step.

Usually the pesticide concentration selected for the incremental additions is close to the solubility limit. Should the pesticide only have moderate affinity for the adsorbent, then lower pesticide concentrations should be used in the first one or two additions to better define the lower segment of the isotherm. Isotherms produced by this method are shown in Fig. 1. The soil used for both isotherms was 40-mesh Bondhead sandy loam, a portion of which was treated with H<sub>2</sub>O<sub>2</sub> to remove the organic matter. The treated soil was thoroughly washed to remove all H<sub>2</sub>O<sub>2</sub> oxidation products, freeze-dried and crushed to pass a 40-mesh sieve. To facilitate operations, 150-ml Corex centrifuge tubes with tinfoil-lined screw caps were used for both equilibration and centrifugation. For both adsorption isotherms, 30 ml of 1.92 µg/ml parathion were added to 1.0 g of soil. Twenty-five milliliters of equilibrated supernatant were removed and an equal volume of 4.80 µg/ml parathion added. The third and subsequent additions were 25 ml of 9.60 µg/ml parathion. In each successive addition, a diminishing amount of pesticide was removed, so logic will dictate where to terminate an experiment.

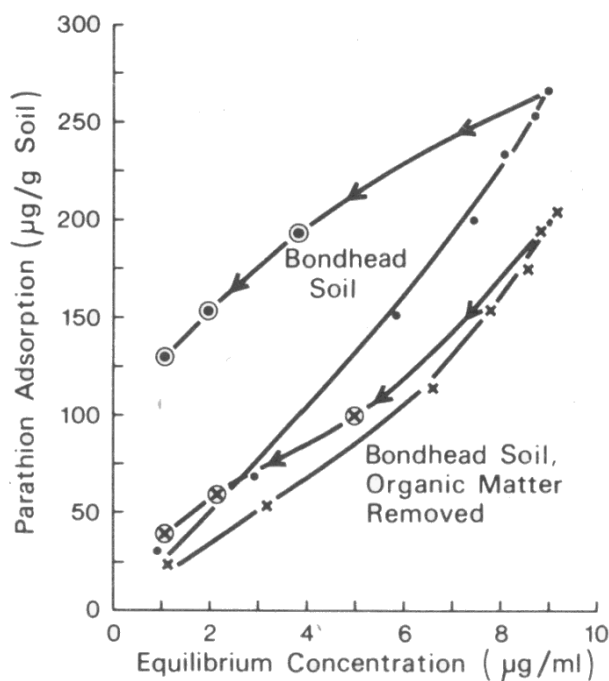
At this point the desorption branch of the isotherm can be initiated by adding a distilled water increment rather than another pesticide increment. The process is then repeated in the same fashion that the adsorption phase was completed, but using water rather than pesticide. In the present study only three desorption steps were carried out, and it can be seen that successive desorption points become more closely spaced as in the upper adsorption branch. The first desorption step removed considerable parathion (Fig. 1) and resulted in a large gap in the isotherm. In such cases where the adsorbent only has moderate affinity for the pesticide, the initial desorption steps should employ smaller dilution increments (i.e. in this case 10, 15 or 20 ml rather than 25 ml).

Unpublished data from this laboratory have shown that adsorption isotherms produced by this method are virtually identical to those generated by standard techniques, except that isotherms produced by the method of repeated additions extend to higher concentrations. As an example, the isotherm constants for parathion adsorption by Bondhead sandy loam obtained by the conventional method were:  $K = 29.1$ ,  $1/n = 0.947$ , compared with  $K = 29.6$ ,  $1/n = 0.977$  for the same soil shown in Fig. 1. The isotherm constants were derived from the logarithmic form of the Freundlich equation,

$$\log x/m = \log K + 1/n \log C \quad (1)$$

where

$x/m$  = nanomoles parathion adsorbed per gram adsorbent.



**Fig. 1.** Parathion adsorption-desorption isotherms for Bondhead sandy loam, with and without organic matter, by the method of repeated additions (arrows indicate desorption isotherm).

$K$  = Freundlich intercept, when  $\log C = 0$ ,  $C = 1$ ,  $x/m = K$ .

$1/n$  = Freundlich slope.

$C$  = equilibrium concentration of parathion, nanomoles/ml.

The slight differences in slope of the two isotherms may have been due to the unequal equilibrium concentration ranges of the two sets of data; for the conventional isotherm the range was from 2.3 to 15.1 nanomoles/ml compared with 3.2 to 31.0 nanomoles/ml for the repeated additions isotherm. As far as could be ascertained, this method of repeated additions for obtaining desorption isotherm data was first reported by Swanson and Dutt (1973), but they did not point out the advantages discussed here. The intention of this communication is to show the definite advantages of this technique applied to desorption studies, and to further demonstrate situations where it could be useful in generating adsorption data.

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