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# Chlorothalonil in a Quartz Sand Soil: Wetting Effects on Sorption Capacity and Bound Residue

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Chlorothalonil has been found to persist but not leach in some quartz sandy soils. For this effect to be understood, it is necessary for the numbers of occupied and empty surface sorption sites to be known. This requires that the labile surface sorption capacity  $\theta_c$ , which is the total number of sites, be measured. Wetting effects might however, affect  $\theta_c$ . The measurement of  $\theta_c$  has been done only recently by very few laboratories, and the wetting effects have seldom been investigated. New analytical chemical methods are therefore required. On-line HPLC micro extraction has been used in the present work to develop a method for the titration of chlorothalonil onto the labile surface sorption sites. Two conclusions have been drawn from the measurements. The first is that  $\theta_c$  is one to 2 orders of magnitude greater than it is for the previously reported cases. Second, the effect of wetting on bound residue formation reported by Belliveau and Langford (9) has been confirmed. These effects help to explain the behavior of chlorothalonil in the quartz sandy soils.

## Introduction

The surface sorption sites of the previously described Simcoe sandy soil were titrated with chlorothalonil. The online HPLC microextraction method was used to ensure that labile surface sorption was clearly distinguished from total sorption. The titration did not saturate the surface sorption sites. The resulting isotherm did permit however, the calculation of both the labile sorption capacity  $\theta_c$  and the sorption equilibrium function  $\bar{K}_1$ . Although the  $\bar{K}_1$  value of  $(4.8 \pm 0.3) \times 10^4$  is within the range observed for other cases,  $\theta_c$  has the unusually high value of  $(23.8 \pm 0.4) (\mu\text{mol/g})$ . This explains why the relatively high solution concentrations used for the titration did not saturate the surface sorption sites. Estimated sorption and desorption rates show that these values are consistent with independently determined rate constants that are presented in a separate report. These equilibrium and kinetics parameters could be used together as input for predictive persistence and leaching computer models. The impact of wetting–drying cycles on pesticide interactions

with soils and sediments deserves greater attention. As a contribution to this, some evidence for the effects of water on both surface sorption and bound residue formation is examined. New experimental evidence is presented that supports the postulate that intraparticle diffusion of water is necessary for the intraparticle diffusion of dissolved organic compounds.

When chlorothalonil has been applied to crops on a sandy soil, its 4-hydroxy derivative is subsequently found mostly in the top 15 cm of the soil, although it has been detected in groundwater (1, 2). In order for the environmental fate of the 4-hydroxy derivative to be understood and predicted, the persistence and leaching of the parent compound must first be understood. For the interaction of chlorothalonil with a particular soil to be understood, it should be described in at least two conceptual dimensions. The first is that the total amount of chlorothalonil in the ground should be resolved into the three portions that can exist. They are the portion that is dissolved in the soil solution, the portion that can be recovered off labile surface sorption sites, and the bound residue portion (4–10). Chemical transformation, microbiological degradation, and transport by water are all influenced by the distribution among these three states. The second conceptual dimension can be considered in terms of the mass transfer among the three states, and any chemical transformation reactions that occur. This conceptual dimension is the interdependence between kinetics and equilibria. On one hand, even when they are not fully achieved in real soils, equilibria can provide useful limiting or reference baselines. It is more useful to know quantitatively just how far from equilibrium a system is at a given point in space or time, than it is to have only qualitative guesses that equilibria might not exist. On the other hand, equilibrium experiments can become more reliable if kinetics information is available with which the approaches to equilibria can be predicted. For cases in which reactions or processes are truly labile, equilibria and kinetics are tightly linked by the relationship between law of mass action equilibrium functions, and the forward and backward kinetic constants. In logarithmic terms, the standard Gibbs energy for an equilibrium can be the algebraic sum of forward and backward energies of activation. The point is that the occasional suggestion that because equilibrium conditions are frequently not found in environmental systems, equilibrium experiments are not very relevant is not fully realistic. The practical connection between equilibria and kinetics is reflected in the relationship between this report of equilibria and the preceding one on kinetics (3).

Terrestrial soils and even some aquatic sediments undergo wetting and drying cycles. The important impact that this has on pesticide interactions with soils and sediments deserves more attention for both surface sorption and bound residue formation. Soil surfaces can simply be given a wetting period before measurements. At least two methods are now available for investigating the effect of water on bound residues. Langford and Belliveau have used magnetic resonance imaging methods for monitoring the diffusion of water into soil particles (11, 12). On the basis of the rates of diffusion of water and of dissolved organic compounds, they have suggested that the intraparticle diffusion of water is necessary for the intraparticle diffusion of organic compounds (12). Because the online HPLC microextraction method resolves total sorption into labile surface sorption and bound residue components, its application to the chlorothalonil titration of surface sites presented the opportunity of experimentally testing the postulated effect of water on bound residue

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formation. It is only necessary to change the wetting and spiking procedure of experimental samples.

## Theory

**(a) Labile Surface Sorption.** Equation 1 is the mass balance for labile sorption sites.

$$\theta_C = \theta_1 + \theta_0 \quad (1)$$

$\theta_C$  is the labile sorption capacity, defined and measured as a saturation limit.  $\theta_1$  and  $\theta_0$  are occupied and empty sorption sites, respectively. The customary distribution coefficient  $K_D$  is defined by eq 2.  $M_1$  is the solution concentration.

$$K_D = \theta_1 / M_1 \quad (2)$$

The sorption equilibrium is described in the usual way by eq 3, in which  $\bar{K}_1$  is the weighted average equilibrium function.

$$\bar{K}_1 = \theta_1 / M_1 \theta_0 \quad (3)$$

The distribution coefficient is consequently related to the equilibrium by eq 4 (5–7).

$$K_D = \bar{K}_1 \theta_C - \bar{K}_1 \theta_1 \quad (4)$$

There are seen to be two reasons why  $K_D$  is not inherently a rigorous constant. Even for the simplest cases in which there is only one type of sorption site so that  $\bar{K}_1$  becomes constant,  $K_D$  is a decreasing function of site loading,  $\theta_1$ . For natural mixtures such as soils and aquatic sediments,  $\bar{K}_1$  can become a weighted average of a mixture of equilibrium constants. This can be a second reason for the distribution coefficient to decrease with increasing loading of sorption sites. Under some circumstances however,  $K_D$  can seem to be approximately constant. For low coverage of sorption sites,  $\theta_1 \ll \theta_C$ .

$$K_D \approx \bar{K}_1 \theta_C \quad (5)$$

If only a small range of  $\theta_1$  values is scanned experimentally, the resulting small change in  $K_D$  can be less than the experimental error. The experimental error and numerical value obtained for  $K_D$  under one set of experimental conditions would not be valid for many other experimental conditions.  $\bar{K}_1 = f(\theta_1)$  would however provide a valid description of sorption equilibria. If the sorption sites are sufficiently similar, then  $\bar{K}_1$  will become approximately constant. There are at least two practical reasons for determining  $\theta_C$ . The first is that it is needed for the calculation of  $\bar{K}_1$ . The other is that it characterizes the capacity of a soil to retard leaching (13, 14).

Two methods have been used previously for the determination of  $\theta_C$  (7, 10). When it is experimentally convenient, the most direct procedure is the titration of a sample to a sorption plateau. The saturation limit is a titration end point. When this is not feasible, the titration data can be used for constructing a least-squares fit of  $K_D$  vs  $\theta_1$  according to eq 4. If a straight line indicates that  $\bar{K}_1$  is approximately constant, then  $\theta_C$  and  $\bar{K}_1$  are determined together from the slope and intercept. Another version of this method may be used when a numerical value of  $\bar{K}_1$  is available. It uses eq 6, which is a simple rearrangement of eq 4. Because of the limit in eq 6, a linear least-squares fit of  $(K_D/\bar{K}_1)$  vs  $\theta_1$  can be extrapolated to  $\theta_1 = 0$ .

$$\lim_{\theta_1 \rightarrow 0} (K_D/\bar{K}_1) = \theta_C \quad (6)$$

This has the advantage that the experimental errors in  $\bar{K}_1$

include those in  $K_D$ , and this calculation cancels them. The data can be made more internally self-consistent.

**(B) Bound Residue Formation.** The amount of bound residue formed during 2 days of reaction time can be predicted for a case in which the soil has been soaked for 2 days before being spiked (3). Because the experiments being considered had 1 g of soil in 1 L of solution, the amounts of chlorothalonil per gram and the amounts per liter are both the same as the totals per sample. This simplifies the mass balance descriptions. Since surface sorption and desorption rates are both fast, the dissolved and surface sorbed chlorothalonil form a common labile pool that is depleted together by the rate determining intraparticle diffusion.  $Q_T$  defined by eq 7 is the labile pool total for a sample.

$$Q_T = M_1 + \theta_1 \quad (7)$$

Assuming that there are no losses other than bound residue formation, eq 8 gives the mass balance,  $M_0$ , for the whole sample, including the amount  $\theta_D$  that is trapped by intraparticle diffusion.

$$M_0 = Q_T + \theta_D \quad (8)$$

The rate of removal from the labile pool by intraparticle diffusion is described by eq 9. Equation 10 is another form of this, obtained by introducing the mass balance and equilibrium relationships.

$$-(dQ_T/dt) = k_D \theta_1 \quad (9)$$

$$-d\{[(\bar{K}_1(\theta_C - \theta_1) + 1)/(\bar{K}_1(\theta_C - \theta_1))]\theta_1\}/dt = k_D \theta_1 \quad (10)$$

Again for sufficiently low coverage of surface sorption sites,

$$\theta_1 \ll \theta_C$$

Equation 10 then reduces to a simple first order form, eq 11.

$$-[(\bar{K}_1 \theta_C + 1)/\bar{K}_1 \theta_C](d\theta_1/dt) = k_D \theta_1 \quad (11)$$

$\theta_b$ , the value of  $\theta_1$  after 2 days, can then be predicted from eq 12.

$$-\ln(\theta_b/\theta_a) = [\bar{K}_1 \theta_C/(\bar{K}_1 \theta_C + 1)]k_D(t_b - t_a) \quad (12)$$

In eq 12, the expression  $[\bar{K}_1 \theta_C/(\bar{K}_1 \theta_C + 1)]$  accounts for the fact that the labile pool of chlorothalonil  $Q_T$  is distributed between the solution and the surface sites according to the law of mass action. This distribution could not be properly described without the law of mass action and the labile sorption capacity. The use of  $\bar{K}_1$  and  $\theta_C$  makes eq 12 less location specific, if they can be calibrated for specific field sites. Once  $\theta_b$ , the value of  $\theta_1$  at 2. days reaction time has been calculated with eq 12, then the amount of bound residue,  $\theta_D$ , can be calculated from eqs 1, 7, 8, and 3. It is convenient to express the answer as  $(\theta_D/M_1) \times 100\%$ .

## Experimental Section

The experimental strategy consisted essentially of two procedures. A set of samples was prepared to represent the steps of a titration curve, with chlorothalonil being titrated onto surface sorption sites. Second, these samples were spiked before the two day preliminary soak instead of after as usual (3).

The analysis of the quartz sand soil from Simcoe, ON, Canada has been presented in a separate report (3).

Two standard stock solutions were used for the preparation of a series of samples all containing 0.4% acetone. The water solubility of chlorothalonil is about  $2.3 \times 10^{-6}$  M, and the acetone made the chlorothalonil sufficiently soluble. Stock

TABLE 1. Simcoe Soil Titration with Chlorothalonil for the Determination of  $\theta_c$  and  $\bar{K}_1$ <sup>a</sup>

no.	initial concn $M_0$ molarity	labile site $\chi_1$ mole fraction	coverage $\theta_1$ (mol/g)	in solution $M_1$ molarity	dist. coeff $K_D$ (mL/g)
1	0.00	0.000	0.000	0.000	$1.145 \times 10^{+3}$
2	$4.00 \times 10^{-6}$	0.095	$2.246 \times 10^{-6}$	$2.220 \times 10^{-6}$	$1.048 \times 10^{+3}$
3	$6.00 \times 10^{-6}$	0.131	$3.117 \times 10^{-6}$	$3.360 \times 10^{-6}$	$9.890 \times 10^{+2}$
4	$8.00 \times 10^{-6}$	0.179	$4.262 \times 10^{-6}$	$4.363 \times 10^{-6}$	$9.661 \times 10^{+2}$
5	$1.00 \times 10^{-5}$	0.206	$4.885 \times 10^{-6}$	$5.624 \times 10^{-6}$	$8.975 \times 10^{+2}$
6	$1.20 \times 10^{-5}$	0.243	$5.761 \times 10^{-6}$	$6.675 \times 10^{-6}$	$8.697 \times 10^{+2}$
7	$1.40 \times 10^{-5}$	0.266	$6.328 \times 10^{-6}$	$7.940 \times 10^{-6}$	$8.101 \times 10^{+2}$
8	$1.60 \times 10^{-5}$	0.308	$7.309 \times 10^{-6}$	$9.096 \times 10^{-6}$	$7.990 \times 10^{+2}$
9	$1.80 \times 10^{-5}$	0.340	$8.086 \times 10^{-6}$	$1.038 \times 10^{-5}$	$7.726 \times 10^{+2}$
10	$2.00 \times 10^{-5}$	0.365	$8.667 \times 10^{-6}$	$1.183 \times 10^{-5}$	$7.254 \times 10^{+2}$
11	$2.20 \times 10^{-5}$	0.387	$9.193 \times 10^{-6}$	$1.294 \times 10^{-5}$	$7.040 \times 10^{+2}$
12	$2.40 \times 10^{-5}$	0.413	$9.820 \times 10^{-6}$	$1.469 \times 10^{-5}$	$6.593 \times 10^{+2}$
13	$2.60 \times 10^{-5}$	0.439	$1.042 \times 10^{-5}$	$1.607 \times 10^{-5}$	$6.479 \times 10^{+2}$
14	$2.80 \times 10^{-5}$	0.460	$1.094 \times 10^{-5}$	$1.749 \times 10^{-5}$	$6.307 \times 10^{+2}$
15	$3.00 \times 10^{-5}$	0.478	$1.137 \times 10^{-5}$	$1.922 \times 10^{-5}$	$5.894 \times 10^{+2}$

<sup>a</sup> Solvent = 99.6% water + 0.4% acetone. Soil mass = 25.0 mg. Solution volume = 25.0 mL. Stock solution II aliquot = 0.100 mL.

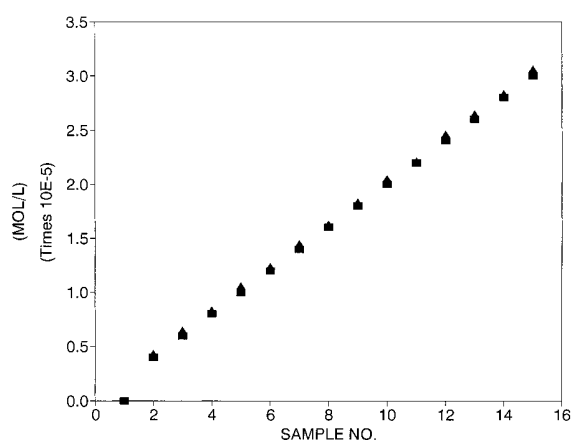


FIGURE 1. Chemical analysis by HPLC methods, of titration samples for chlorothalonil. ■, Added. ▲, Recovered.

solution I was prepared with 0.20008 g of chlorothalonil dissolved in 100 mL of acetone. The concentration was  $7.5219 \times 10^{-3}$  M. A set of stock solutions II was prepared in acetone by dilutions of stock I. Including stock solution I, this gave a set of 14 stock solutions in acetone covering the range of  $1.0 \times 10^{-3}$ – $7.5 \times 10^{-3}$  M. Samples corresponding to titration data points were prepared from the appropriate stock solutions II, as indicated in Table 1. The samples were maintained at 25.00 °C for 2 days before measurement, to allow water sorption. This differed from the practice that is followed for speciation kinetics experiments. Because wetting effects were being investigated, the spiking and wetting sequence was important. Dry portions of the soil sample were therefore spiked first, and then subsequently equilibrated with the chlorothalonil solutions for 2 days. The 0.2  $\mu$ m Nylon 66 filters used for offline filtration were calibrated for chlorothalonil sorption (3). The aqueous slurries in the titration samples were analyzed by online HPLC microextraction as previously reported (3–10).

## Results and Discussion

**(a) Labile Surface Sorption.** The possible causes of incomplete recoveries during surface sorption experiments are well-known (5–9, 15–19). When all of the other causes can be eliminated, bound residue formation is frequently a possibility that remains. If there were a negative systematic bias in the analytical chemical data, it would look like an incomplete recovery. Figure 1 is a test for possible losses and possible analytical chemical biases. In this case the recovery is complete to within the standard errors. Any bound residues

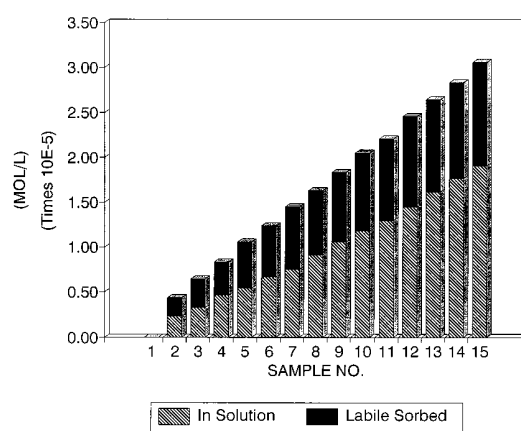


FIGURE 2. Chemical analyses by HPLC methods, of the equilibrium distribution of chlorothalonil between solution and labile surface sorption sites. See Figure 1.

that might have existed were smaller than the small random experimental error. The online HPLC microextraction method that produced the virtually complete recovery totals in Figure 1 also resolved the totals definitively into the solution phase and surface sorbed fractions illustrated in Figure 2. This permitted a titration curve to be constructed by plotting surface sorption against solution concentration. The titration curve did not have a plateau that would have indicated saturation of the surface sites. In some cases solubility limits prevent the attainment of a titration end point plateau. In other cases weak sorption might cause doubtful and point plateaus. In the present case, the labile sorption capacity seemed to be unexpectedly high compared to the previously reported cases (4–10).

$\bar{K}_1$  and  $\theta_c$  were simultaneously evaluated by the calculation method no. 1, which uses eq 4. This calculation requires the assumption that the titration had attained equilibrium because of its relatively high concentration range. This assumption has been tested with the rates estimated and listed in Table 3. The distribution coefficient  $K_D$  was first calculated from experimental data using eq 2. The linear least-squares fit was then made of  $K_D$  vs  $\theta_1$  to give  $K_D = C_0 + C_1\theta_1$ . Then from eq 4,  $\bar{K}_1 = C_1$  and  $\theta_c = -C_0/C_1$ . A linear least-squares fit shown in Figure 3 therefore produced the numerical values listed in Table 2.

It was then found possible to refine the numerical value of  $\theta_c$  by introducing the value of  $\bar{K}_1$  into calculation method no. 2. This method was used to refine the numerical values of  $\theta_c$  and  $\bar{K}_1$ . Using eqs 5 and 6, the linear least-squares fit

TABLE 2. Labile Sorption Capacity  $\theta_c$  and Equilibrium Function  $\bar{K}_1$  for Chlorothalonil in Simcoe Soil: Calculation Methods

type of parameter	calculation method 1	calculation method 2
	$C_0 = \bar{K}_1 \theta_c$ $C_1 = -\bar{K}_1$	$C_0 = \theta_c$ $C_1 = 1$
$C_0$	1.145	$23.76 \times 10^{-6}$
standard error	0.03	$0.4 \times 10^{-6}$
$C_1$	$-48.2 \times 10^{+4}$	-0.997
standard error	$0.3 \times 10^{+4}$	0.045
$R^2$	0.9592	0.9821
$\bar{K}_1$	$4.82 \times 10^{+4}$	
standard error	$0.3 \times 10^{+4}$	
$\theta_c$	$23.8 \times 10^{-6}$ (mol/g)	$23.76 \times 10^{-6}$ (mol/g)
standard error	$2.2 \times 10^{-6}$	$0.4 \times 10^{-6}$

TABLE 3. Chlorothalonil Titration of Simcoe Soil: Test for Equilibrium Sample 8<sup>a</sup>

data used	source experiment
$k_{B1} = 3.134 \times 10^3$ (g/mol $\times$ days)	kinetics
$\bar{K}_1 = 4.8 \times 10^4$	
$M_1 = 0.9096 \times 10^{-5}$	titration
$\theta_1 = 0.7309 \times 10^{-5}$	
$\theta_0 = 16.45 \times 10^{-6}$	
Mass Transfer Rates, Solution — Surface (mol/L)/day	
sorption	desorption
$0.469 \times 10^{-6}$	$0.477 \times 10^{-6}$

<sup>a</sup> Initial concentration =  $1.600 \times 10^{-5}$  M. Time after sample preparation = 2 days.

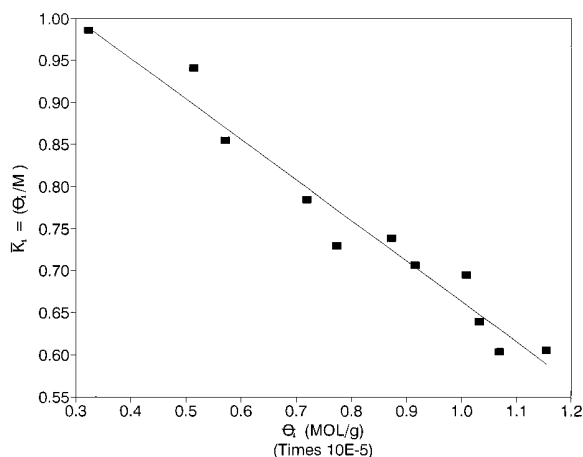


FIGURE 3. Chlorothalonil in Simcoe soil: titration data points. Calculation of the labile sorption capacity  $\theta_c$  and the equilibrium function  $\bar{K}_1$ . See Figures 1 and 2.

of  $(K_D/\bar{K}_1)$  vs  $\theta_1$  in Figure 4 gave an intercept that was an improved numerical value for  $\theta_c$ . This in turn improved the numerical values of  $\theta_0 = (\theta_c - \theta_1)$  and  $\bar{K}_1$ .

The estimation of the second-order rate constant  $k_{B1}$  has been reported for this particular case, in a separate report (3). To avoid sample mixing effects at the start of an experiment and interference from desorption later in the experiment, an initial rate calculation was done at a reaction time of 0.777 days. The rest of the data were obtained from the titration experiment. The sorption and desorption rates were estimated using the rate equations in that report. The titration experiment reported here and the previously described kinetics experiment (3) were conducted independently of each other. They have however produced together an internally self-consistent set of parameters. This not only

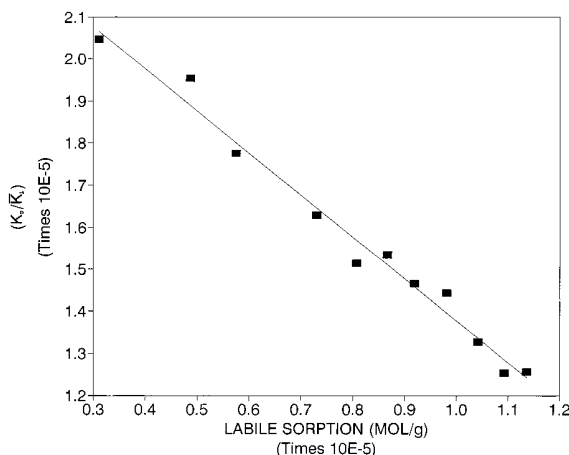


FIGURE 4. Chlorothalonil in Simcoe soil: titration data points. Refinement of the  $\theta_c$  value. See Figure 3.

indicates equilibrium in the titration experiment, but also demonstrates the validity in the higher concentration range of the rate constant that was measured in the lower concentration range.

A numerical value for the labile sorption capacity is important for several reasons (7). The first is that a soil with a large number of sorption sites per gram can retard leaching more effectively than one with fewer sorption sites per gram. Another reason is that  $\chi_1$ , the mole fraction of occupied sorption sites, can be calculated. This becomes significant especially for cases in which a mixture of chemically different sorption sites has a distribution of  $\bar{K}_1$  values. The average effectiveness with which sorption sites can retard leaching will consequently decrease with increasing site loading. Another reason for the importance of measuring  $\theta_c$  is that two soils with the same  $K_D$  might well have  $\theta_c$  values that differ by one or 2 orders of magnitude. A small number per gram of strong sorption sites might give a similar apparent  $K_D$  value as a larger number per gram of weaker sites. In addition, if the solution concentration exceeds that which would saturate the sorption sites, then the empirical distribution between solution and solids would give false  $K_D$  values. In contrast to some of the limitations of the distribution coefficient, the  $\bar{K}_1$  values made possible by a  $\theta_c$  measurement account directly for numbers of occupied and empty sorption sites per gram. Two soils could then be compared at the same mole fraction  $\chi_1$  of their sorption sites loaded. This would help to make experimental results less location specific.

Together with the  $\theta_c$  and  $\bar{K}_1$  values in Table 2, Table 3, and Figure 5 fully characterize the titration experiment. It is important to note that the labile sorption capacity of the Simcoe soil for chlorothalonil is 1–2 orders of magnitude greater than the values reported to date for other soil – pesticide cases (3–10). Since quartz is expected to be relatively inert, the large labile sorption capacity of the Simcoe soil is likely caused by the small amounts of metal oxides and organic matter. The chemical structure of chlorothalonil is however expected to be an important factor. Labile sorption capacities measured for organic chemicals in the presence of water are generally much smaller than the surface coverage obtained by the “EGME” vacuum deposition method used for surface measurements (6). This is still the case here, even with the unusually large value of  $\theta_c$  obtained for chlorothalonil. This suggests the possibility that water competes with organic chemicals for surface sorption sites.

(b) Bound Residue Formation. A bound residue estimate for sample no. 2 has been used for testing the postulate by Langford and Belliveau and Henshelwood (11, 12) that the



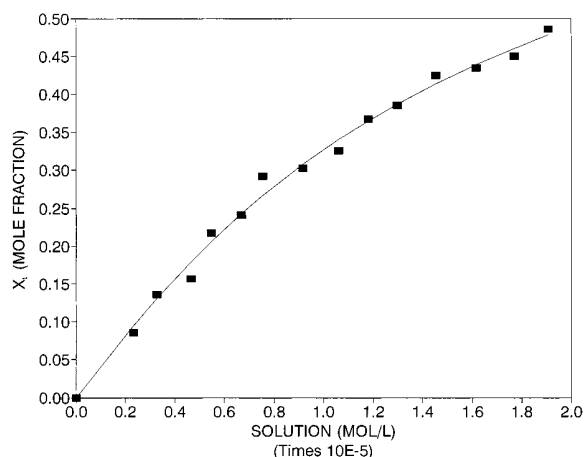


FIGURE 5. Chlorothalonil in Simcoe soil: titration data points. Coverage of labile sorption sites. See Figure 2.

TABLE 4. Data For Predicting Bound Residue in Sample 2<sup>a</sup>

parameter	value	units
$M_0$	$4.000 \times 10^{-6}$	(mol/L)
$K_1$	$4.82 \times 10^4$	(L/mol)
$\theta_c$	$23.76 \times 10^{-6}$	(mol/g)
$k_D$	0.374	day <sup>-1</sup>
$\theta_a$	$2.246 \times 10^{-6}$	(mol/g)
$(t_b - t_a)$	2.	day

<sup>a</sup> 2 days reaction time.

intraparticle diffusion of water is necessary for the intraparticle diffusion of a dissolved organic chemical. The calculation is most conveniently done for low loading of surface sorption sites, by entering the information from Table 4 into eq 12. The kinetics and equilibria then predict that after 2. days of water soak before spiking, there would have been a bound residue of  $\theta_D \approx 1.1 \times 10^{-6}$  (mol/g). This is about 27.0% of the total chlorothalonil in the sample. The prediction for this procedure is based on a substantial amount of experimental evidence (3–9). In particular, it is similar to the 30.5% bound residue in Figure 5 of the separate report (3), for chlorothalonil in prewetted Simcoe soil. In contrast to that, the titration samples that were spiked without a prior water soak showed no measurable bound residue 2 days after being spiked. In Figure 1, the data set for these samples without preliminary soak is remarkably definitive. They are direct experimental evidence for the Langford–Belliveau postulate that the intraparticle diffusion of water is prerequisite to the formation of bound residues by intraparticle diffusion.

(c) Conclusions. A general conclusion is that water strongly influences the interactions of organic chemicals with both the surfaces and the interiors of soil particles. There are also two conclusions about experimental requirements. One

is that bound residue experiments with dissolved organic chemicals should have preliminary water soaks. The other is that this is not necessary for the titration of an organic compound onto surface sites, but a post spiking surface equilibration period might be important.

In future work, the experimental methods now available should be used for a more systematic investigation of the impact of wetting and drying on pesticide interactions with soils and aquatic sediments. In addition, numerical integrations would permit eq 6 to be used for cases in which the loading of surface sorption sites is too high for the condition  $\theta_1 \ll \theta_c$  to be valid.

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