

Adsorption—Desorption of Chlordimeform on Montmorillonite: Effect of Clay Aggregation and Competitive Adsorption with Cadmium

TOMAS UNDABEYIA,^{*,†} SHLOMO NIR,[†]
TAMARA POLUBESOVA,[†] GIORA RYTWO,^{†,‡}
ESMERALDA MORILLO,[§] AND
CELIA MAQUEDA[§]

Seagram Center for Soil and Water Sciences, Faculty of Agricultural, Food and Environmental Quality Sciences, P.O. Box 12, Rehovot 76100, Israel, Tel Hai Academic College, Upper Galilee, 12210 Israel, and Instituto de Recursos Naturales y Agrobiología, CSIC, Apdo 1052, Sevilla 41080, Spain

Effect of the aggregation state of montmorillonite clays of types SAz-1 and SWy-1 on the adsorption of the monovalent organic cation chlordimeform was studied. The shapes of the adsorption isotherms were related to the degree of dispersion of the clay, changing from S- to L-type by decreasing clay concentration. Unlike monovalent organic cations denoted dyes, chlordimeform adsorption did not exceed the cationic exchange capacity of the clay (CEC). At larger $\text{Ca}^{2+}/\text{Na}^{+}$ charge ratio (≈ 0.5), chlordimeform exhibited low apparent affinity for adsorbing to the SAz-1 clay, due to steric inhibition of its penetration between closely opposed clay platelets. The apparent affinity increased dramatically at smaller $\text{Ca}^{2+}/\text{Na}^{+}$ charge ratios (< 0.06) for Ca^{2+} -montmorillonite, or by switching to Na^{+} -montmorillonite. The desorption process of chlordimeform shows an apparent hysteresis in Ca^{2+} -montmorillonite. An adsorption model which combines electrostatic equations with specific binding in a closed system is able to account for part of this hysteresis by the reduction in the concentrations of the divalent cations Ca^{2+} and Mg^{2+} in the supernatant. Part of the hysteresis arises from a different state of aggregation of the Ca^{2+} -clay in the adsorption and desorption experiments. The model also yields good predictions for the competition between chlordimeform and Cd in adsorption processes and their consecutive desorptions.

Introduction

Adsorption—desorption reactions of pesticides in soils are affected by the physicochemical characteristics of the pesticide; the colloidal composition of the soil, humidity, and temperature; and the status of saturation of bases of the soil colloids (1, 2). Detailed knowledge of the behavior of pesticides requires a study of adsorption—desorption reac-

tions on the components of the soil, especially its colloidal fraction, which determines its reactivity (3, 4).

Hysteresis phenomenon frequently observed in adsorption—desorption processes of organic chemicals on both soils and their colloidal fraction has been partly attributed to artifacts of the experimental procedure. Bowman and Sans (5) observed that the dilution method, which involves addition of different distilled water volumes, strongly decreased the hysteresis of two organophosphate pesticides, in contrast with the consecutive desorption method, where a part of the supernatant is removed and replaced by the same volume of solution with no organic chemical. However, Horzempa and Di Toro (6) observed the opposite phenomenon for PCBs desorption from sediments. Hence, there is no definitive conclusion about the methodology used. Studies of the methods used have focused on the effect of the centrifugation step on pesticide desorption (consecutive method) and on the independence of partition coefficient on the solid:solution ratio, with no consideration of the influence of the background electrolyte (6, 7). Quantitative explanation for remaining hysteresis is scarce.

We present a study on adsorption—desorption reactions of a cationic pesticide, chlordimeform, on the clay mineral montmorillonite which also combines calculations with an adsorption model (8). We will also deal with the influence of the presence of the heavy metal cadmium on chlordimeform adsorption. Little quantitative information is available on processes taking place when heavy metals and pesticides are present together, such as competition on adsorption sites, precipitation, solubilization, complexation, or synergistic effects (9–11). This study deals with an environmental problem encountered by the growing use of herbicides and water from mines, sewage, industry, or sludge, which are rich in heavy metals.

Another aspect emphasized in the current study is the effect of the state of aggregation of clay platelets on the adsorption and desorption of a cationic herbicide, such as chlordimeform, in comparison with other monovalent organic cations.

Materials and Methods

Experimental. The clays used were standard montmorillonites from Arizona (SAz-1 montmorillonite) and from Wyoming (SWy-1 montmorillonite) supplied by the Clay Minerals Society. SAz-1 was used without further treatment, whereas carbonate content was eliminated of SWy-1 by using an acetic acid/sodium acetate buffer at pH 5.0. Their cationic exchange capacity (CEC) was determined by treating 1 g of clay with 25 mL of 1 M ammonium acetate at pH 7 during 24 h, collecting the supernatant, and repeating successively the process. The cations in the supernatant were analyzed. The CEC was determined to be 1.235 mol_c/kg for SAz-1 of which 1.0078 mol_c/kg corresponding to Ca^{2+} , 0.1916 mol_c/kg to Mg^{2+} , 0.026 mol_c/kg to Na^{+} , 0.096 mol_c/kg to K^{+} , and 0.76 mol_c/kg for SWy montmorillonite in which the exchangeable charges after carbonate elimination due to Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+} are 0.058, 0.022, 0.053, and 0.630 mol_c/kg, respectively.

Technical grade chlordimeform, (*N*-(4-chloro-2-methylphenyl)-*N,N*-dimethyl-methanimidamide), supplied by Schering Agro, S.A. (Berlin, Germany), was used. This pesticide is soluble in water (50% by wt) and is ionized completely (pH 3–7), giving the cation chlordimeform and chloride anion. Benzyltrimethylammonium (BTMA) (50 wt % in water solution) was obtained as chloride salt from Aldrich Chemical Co. (Milwaukee, WI, U.S.A.). Acriflavine (AF) (3,6-

* Corresponding author phone: 972-8-9481368; fax: 972-8-9475181; e-mail: undabeyt@agri.huji.ac.il.

[†] Seagram Center for Soil and Water Sciences.

[‡] Tel Hai Academic College.

[§] Instituto de Recursos Naturales y Agrobiología.

diamino-10-methylacridinium dihydrochloride) was obtained from Fluka Chemie AG (Buchs, Switzerland). Analytical grade salts NaCl and CdCl₂ were purchased from Merck (Darmstadt, Germany).

The adsorption experiments were done in triplicate in 50-mL polypropylene centrifuge tubes, by mixing 0.1 g of clay mineral with 20 mL of solutions containing various concentrations of organic cations and/or Cd. The concentrations used ranged from 100 to 1000 μM for chlordimeform and AF, from 1.0 to 20.0 mM for BTMA, and from 44.5 to 266.9 μM for Cd. Adsorption experiments for chlordimeform and BTMA were also carried out by adding aliquots of stock solutions of 100 mM of the organic cations to clay suspensions, the final clay suspensions being 0.66 g/L for chlordimeform, and 5.00 and 1.67 g/L for BTMA. Chlordimeform and BTMA concentrations were up to 20.0 and 4.0 mmol/g clay, respectively. All experiments were carried out in 0.01 M NaCl medium to keep the ionic strength constant. The samples were shaken for 24 h at 20 ± 1 °C. The solution concentrations of the organic cations were determined by UV-visible spectroscopy at 240 nm for chlordimeform and 262 nm for BTMA and AF. Chlordimeform adsorbed on the clay was also determined by adding an organic dye (crystal violet) as described in Rytwo et al. (12). The solution concentrations of Cd, Ca, and Mg were determined by atomic absorption spectrometry and those of K by flame photometry.

The desorption experiments with chlordimeform and/or Cd employed a clay concentration of 5 g/L. After equilibrium in adsorption was reached, half of the supernatant was removed after centrifugation and replaced by 10 mL of 0.01 M NaCl. This process was repeated twice more. The equilibrium pH for both adsorption and desorption processes was 6.5 ± 0.3.

Model Calculations

Model calculations followed the same procedure described by Nir (8) and Hirsch et al. (13). The three main elements in this model are (I) the adsorbed cations consist of (a) cations tightly bound to the surface (specific binding) and (b) cations residing in the double layer region; (II) the electrostatic Gouy-Chapman equations are solved for a solid/liquid system containing several cations of various valencies and particles whose surfaces are charged and partially neutralized by cation binding; and (III) the concentration of surface sites in the solid/liquid system is explicitly included in the computation, thus accounting for the concentrations of cations in solution during adsorption/desorption processes.

Let X_i⁺ denote a monovalent cation that binds to singly charged negative sites, P⁻, on the surface of the silicate:



The binding coefficient for such reaction, K_i, is

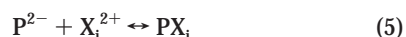
$$K_i = [PX_i]/([P^-][X_i(0)^+]) \quad (2)$$

in which [X_i(0)⁺] is the concentration of the cation at the surface. Divalent cations can form a 1:1 charged complex with a binding coefficient K₁ and a 2:1 neutral complex with a binding coefficient K₂. The 1:1 complexation is described by



$$K_{i1} = [PX_i^+]/([P^-][X_i(0)^{2+}]) \quad (4)$$

For the 2:1 complexation, we formally define a divalent site, P²⁻. The concentration of such sites is P⁻/2.



$$K_{i2} = [PX_i]/([P^{2-}][X_i(0)^{2+}]) = [PX_i]/((([P^-]/2)[X_i(0)^{2+}]) \quad (6)$$

In eqs 2–4, and 6 the concentration of the cations close to the silicate layer is needed. It is calculated by the relation

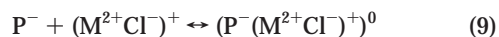
$$X_i(0) = X_i Y(0)^{z(i)} \quad (7)$$

where Y(0) = exp(-eΨ(0)/kT), e is the absolute magnitude of an electronic charge, z(i) is the valence of the given ion, Ψ(0) is the surface potential, k is Boltzmann's factor, T is the absolute temperature, and X_i is the molar concentration of cation i in its monomeric form in the equilibrium solution, far away from the surface. For a negatively charged surface Y(0) > 1, and the concentration of the cation at the surface, X_i(0), may be significantly larger than X_i.

In our calculations, only the 2:1 complexes were considered for the divalent cations. However, solution speciation of divalent cations, e.g.,



and adsorption to the clay of the type



were explicitly considered as in Hirsch et al. (13) and Rytwo et al. (14).

Results and Discussion

Chlordimeform Adsorption: Effect of Aggregation State of the Clay. We first investigated whether the adsorbed amounts of chlordimeform on Ca-montmorillonite could exceed the CEC of the clay and quantified the strength of this adsorption. The adsorbed amounts of organic molecules on clays can exceed the CEC of the clay, by interactions between the hydrophobic moieties (15, 16). Boyd et al. (17) and Sheng et al. (18) proposed that clay preadsorbed by large organic cations behaves as a partition phase. On the other hand, small monovalent organic cations such as tetramethylammonium (TMA) and BTMA do not adsorb beyond the CEC. Their adsorption up to the CEC required an excess of organic cation concentration from 3- to 5-fold of the CEC (19, 20). For chlordimeform adsorption, Hermosin and Perez-Rodriguez (21) showed that pesticide adsorption did not exceed the CEC by using chlordimeform concentrations up to 5-fold of the CEC for a clay concentration of 6.66 g/L. We examined chlordimeform adsorption on Ca-montmorillonite, by using 0.01 M NaCl solutions, for a clay concentration 10-fold lesser than the one used by the above authors, and a pesticide concentration that was up to 24-fold of the amount corresponding to the CEC. It can be seen in Figure 1 that chlordimeform adsorption reaches a plateau at 1.15 meq/g, which is slightly below the CEC, indicating the absence of hydrophobic interactions that will promote the adsorption beyond the CEC. Consequently, in our model calculations we avoided the introduction of another binding coefficient describing the formation of charged complexes.

The adsorption isotherms of chlordimeform on SWy-1 and SAz-1 montmorillonites at larger clay concentrations are given in Figure 2. The adsorption isotherm of chlordimeform on Ca-montmorillonite (SAz-1) shows an S-type shape, unlike the L-type isotherm in Figure 1, or the results reported in ref 21. The aggregation state of the clay platelets is largely determined by the charge ratio between Ca²⁺ and Na⁺ in the system (22, 23). In the presence of 0.01 M NaCl solutions the above charge ratio for SAz-1 in Figure 2 is about 0.5, whereas in Figure 1 it is about 0.06. The change in the

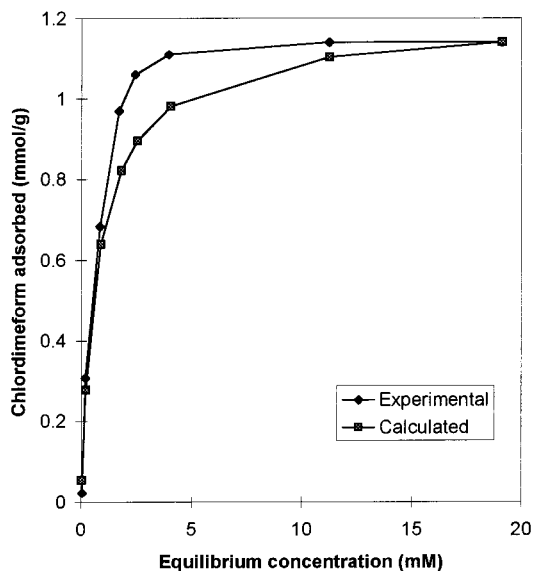


FIGURE 1. Adsorption isotherm of chlordimeform on Ca-montmorillonite. Clay concentration used was 0.66 g/L. Experimental errors smaller than the symbols.

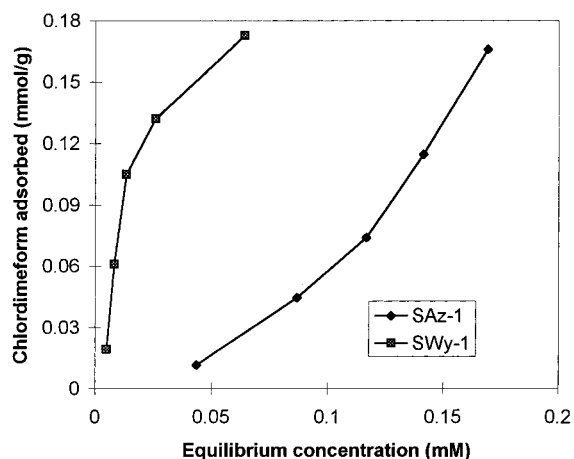


FIGURE 2. Adsorption isotherms of chlordimeform on Na-(SWy-1)- and Ca-(SAz-1)-montmorillonites. Clay concentration used was 5 g/L.

shape of the adsorption isotherm can be related to the degree of clay dispersion. For Ca-montmorillonite the clay particles are associated through face-to-face aggregation unlike Na-montmorillonite for which the clay plates would be largely dispersed in solution. It may be expected that the clay used in our experimental conditions shows an intermediate behavior because of the addition of 0.01 M NaCl in solution. For the lowest clay concentration used, the amount of Na adsorbed on the clay would be enough to disperse the clay plates, and the pesticide could access most of the exchangeable sites at low chlordimeform loading levels. The adsorption behavior should be expected to be the same as the adsorption on Na-montmorillonite (L-type, Figure 1). However, for the larger clay concentration used, the extent of clay aggregation would be higher for the Ca-clay.

Table 1 lists the experimental and calculated percentages of chlordimeform, calcium, and magnesium adsorbed as well as the calculated surface potentials for the adsorption data on Ca-montmorillonite shown in Figure 1. The calculated values are essentially predicted since the binding coefficients were taken from previous studies except for chlordimeform. We also considered the possibility that a fraction of calcium and magnesium exists in solution as CaCl^+ and MgCl^+ (14, 24), but the effect of such speciation was insignificant in our

TABLE 1. Calculated Surface Potentials ($-\Psi_0$) and Percentages of Chlordimeform, Ca, and Mg Remaining Adsorbed on Ca-montmorillonite as a Function of the Initial Amounts of Chlordimeform Added^a

chlord total (μM)	step no.	chlord (%)		Ca (%)		Mg (%)		$-\Psi_0$ (mV)
		exptl	calc	exptl	calc	exptl	calc	
101.5	adsorpt	55.0	60.9	83.7	81.3	78.1	79.1	80.9
	des#3	60.5	69.9	91.4	89.9	90.9	88.5	89.8
309.4	adsorpt	71.8	80.6	82.9	79.2	76.9	76.8	79.2
	des#3	81.9	86.2	90.0	88.8	90.4	87.3	88.4
714.0	adsorpt	80.3	78.5	82.5	75.4	76.0	72.8	76.7
998.8	adsorpt ^b	82.9	77.1	80.6	72.8	75.4	70.0	75.1
	des#3	88.4	84.6	89.4	86.4	89.9	84.6	85.8

^a The percentages are expressed with respect to the total amounts (adsorbed + in solution) of each cation for each step. Experimental and calculated values. The calculations employed the following values of binding coefficients: chlordimeform (90 M^{-1} and 30 M^{-1} for the lowest chlordimeform concentration), current work; Ca^{2+} (6 M^{-1}), Mg^{2+} (5 M^{-1}) (28); Na^+ (0.5 M^{-1}), K^+ (4 M^{-1}) as in Nir et al. (8). The total concentrations of Ca, Mg, K, and Na in the system (clay + solution) were 2.52, 0.479, 0.048, and 10.13 mM, respectively. The relative standard deviations obtained for chlordimeform adsorption ranged between 0.1 and 0.5%.

^b In this case, the fractions of the clay sites adsorbed by chlordimeform, Ca, and Mg were 0.13, 0.66, and 0.12, respectively.

case and could be ignored. It can be observed that there is a good correlation between the experimental and theoretical adsorption percentages except for the lowest chlordimeform concentration used. For this point, a perfect fit required to use a smaller binding coefficient of 30 M^{-1} (instead of 90 M^{-1}). This had little effect on the adsorption of Ca and Mg. According to Giles et al. (25), the S-type adsorption isotherms appear when the solute molecules encounter a strong competition on the substrate sites, from solvent or other species. The affinity for the clay will increase after some molecules would be adsorbed and increase the distances between closely opposed clay platelets.

We tested whether the apparent smaller affinity of chlordimeform for adsorption on Ca-montmorillonite might be due to delayed penetration between the clay platelets. The same adsorbed amounts of chlordimeform were obtained following 1, 3, or 7 days of incubation. Our suggestion is that energetically the interaction of chlordimeform molecules with the clay mineral platelets is less favored in Ca-montmorillonite where the planar faces are held together. This is particularly critical for low chlordimeform concentrations. However, it cannot be ruled out that part of the penetration of chlordimeform molecules into the interlamellar space is very slow and takes a longer time than 7 days. Another test for this suggestion was carried out by employing Na-montmorillonite. For chlordimeform adsorption on Na-montmorillonite, it can be expected that the apparent affinity of the herbicide for the clay would be higher since the clay mineral plates would be more dispersed in solution. Indeed, this is exhibited in Figure 2, or by using a higher binding coefficient (400 M^{-1}) for describing chlordimeform adsorption than for Ca-montmorillonite (Table 2). It is interesting to note that for Na^+ -montmorillonite the experimental values (Figure 2, Table 2) do not exhibit lower affinity of chlordimeform adsorption at the lower concentration added, unlike the situation with Ca-montmorillonite.

We deduce that the presence of organic molecules on the planar positions would increase the interlayer space, at least, in the positions closer to the edges, facilitating the interchange between the inorganic and organic cations. Xu and Boyd (26) also observed a different behavior for the adsorption of hexadecyltrimethylammonium (HDTMA) on Na- and Ca-montmorillonite. They related the degree of clay dispersion to the nonmonotonic and monotonic isotherms obtained

TABLE 2. Calculated Surface Potentials ($-\Psi_0$) and Percentages of Chlordimeform (Chlord) Adsorbed on Na-Montmorillonite as a Function of the Amount of Chlordimeform Added^a

chlord added (μM)	chlord (%)		$-\Psi_0$ (mV)
	exptl	calc	
103.7	97.6	98.8	115.8
294.8	97.7	98.6	113.5
515.7	97.7	98.4	110.8
720.7	97.1	98.2	108.1
1013.5	97.1	97.7	103.9

^a Experimental and calculated values. See Table 1 for binding coefficients used. The binding coefficient used for chlordimeform was 400 M^{-1} . The relative standard deviations obtained for chlordimeform adsorption ranged between 0.1 and 1.1%.

TABLE 3. Amounts of BTMA Adsorbed on Ca-Montmorillonite as a Function of the Amount Added

amount added (mmol_c/g)	amount adsorbed (mmol_c/g)	
	1.67 g/L^a	5 g/L^a
0.200		0.200
0.500	0.500	0.456
1.000	0.742	0.654
2.000	0.924	0.800
4.000	1.080	0.983

^a Clay concentration.

and to the inorganic/HDTMA distribution in clay interlayers at low loading levels.

We further tested the effect of the state of aggregation of the clay on the adsorption of monovalent organic cations, by employing BTMA and the dye acriflavine (AF) whose binding coefficients (to Na-montmorillonite) are larger than that of chlordimeform. In the case of AF whose binding coefficient is 10^9 M^{-1} (16), all the added dye was adsorbed (results not shown). Thus, the state of aggregation of the clay does not affect the adsorption of a monovalent organic cation whose binding affinity to the clay is extremely high. In the case of BTMA whose binding coefficient is 5000 M^{-1} (20), Table 3 shows complete adsorption at the low added concentration, in comparison with 55% for chlordimeform (Table 1). Model calculations (results not shown) indicate that the binding coefficients required to explain the adsorption of BTMA to Ca-montmorillonite are several-fold smaller than those used for Na-montmorillonite. Hence, in this case the state of aggregation of the clay does affect the adsorption, despite the fact that the shape of the adsorption isotherm is closer to an L-type.

Chlordimeform Desorption: Apparent Hysteresis. Figure 3 shows apparent hysteresis in the adsorption-desorption of chlordimeform on Ca-montmorillonite. The degree of desorption (relative to the amount adsorbed in the adsorption stage) is higher for the lower chlordimeform concentration, since in this case cumulative percent desorbed after three consecutive steps is 48.3%, unlike the values obtained for the initial (total) chlordimeform concentrations of 0.5 and 1.0 mM (25.6 and 26.4%, respectively). As discussed before, this can be a consequence of the lower affinity of chlordimeform adsorption by the clay at low loads, due to aggregation of the clay platelets.

Table 1 also lists the experimental and calculated percentages of chlordimeform, calcium, and magnesium, remaining adsorbed after desorption steps on Ca-montmorillonite. No additional parameters were employed in the calculations. The model yields a good prediction for the fractions of Ca and Mg remaining adsorbed. The hysteresis

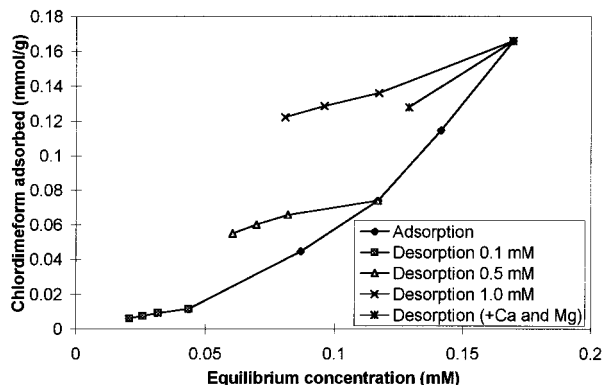


FIGURE 3. Adsorption-desorption isotherms of chlordimeform on Ca-montmorillonite. Clay concentration used was 5 g/L.

observed is explained as partly due to the reduction in total concentrations of the divalent cations Ca and Mg in suspensions after each desorption step, when removing half of the supernatant and replacing it by the same volume of NaCl 0.01 M. The reduction in the concentrations of the main cations competing with chlordimeform upon desorption results in its enhanced adsorption in all the desorption cycles. The reduction in the concentration of the divalent cations also results in an increase in the magnitude of the surface potential for each desorption process, which promotes the adsorption of chlordimeform. Calculations (8) indicate that similar hysteresis but somewhat smaller would also occur with Na-montmorillonite, as was indeed observed (results not shown).

However, the state of aggregation of the clay platelets also plays a role in the hysteresis observed. When we supplemented in the desorption experiments the concentrations of Ca^{2+} and Mg^{2+} removed and left the system to incubate for 7 days, the amount of chlordimeform adsorbed still remained higher than in the corresponding adsorption cycle (see Figure 3). Reducing the incubation time in this experiment to 1 day resulted in a higher adsorbed amount. A similar procedure abolished the hysteresis in the case of Na-montmorillonite. Hence, part of the hysteresis can be anticipated from the S-shape of the adsorption curve, which implies an apparent larger affinity of chlordimeform for adsorption to Ca-montmorillonite at larger chlordimeform concentrations. Apparently the Ca-montmorillonite-chlordimeform system still yields higher affinity for chlordimeform adsorption despite the lower concentration of chlordimeform in the desorption stage. In contrast, in the adsorption process the added chlordimeform encounters more clay platelets in aggregates that pose some more steric inhibition for chlordimeform adsorption. It appears that some changes in the state of aggregation of Ca-montmorillonite-chlordimeform system take much longer times than 7 days.

Simultaneous Adsorption of Chlordimeform and Cadmium. The presence of other cations, such as the heavy metal Cd, is expected to affect chlordimeform adsorption on the clay. The adsorption of Cd on the clay has been described by the use of two binding coefficients, Cd^{2+} (10 M^{-1}) and CdCl^+ (30 M^{-1}) (13). The speciation of Cd in solution as Cd^{2+} , CdCl^+ , and CdCl_2^0 has been included in our calculations. These model calculations might be expected to underestimate the adsorption of the heavy metal at lower metal loading, since we only consider adsorption to one type of sites (interlayer sites), without including the effect of adsorption of the heavy metal to the edge sites, which are usually considered sites of higher affinity for heavy metals than the planar sites (22, 27). According to Undabeytia et al. (28), the predicted values are not expected to deviate more than 8% from the experimental value for the lowest Cd concentration

TABLE 4. Calculated Surface Potentials ($-\Psi_0$) and Percentages of Chlordimeform, Cd, Ca, and Mg Remaining Adsorbed on Ca-montmorillonite as a Function of the Initial Amounts of Chlordimeform and Cadmium Added^a

chlrd added (μM)	Cd added (μM)	step no.	chlrd (%)		Cd (%)		Ca (%)		Mg (%)		$-\Psi_0$ (mV)
			exptl	calc	exptl	calc	exptl	calc	exptl	calc	
100.0	44.5	adsorpt	51.2	60.5	82.9	79.6	84.5	80.5	79.7	78.5	80.4
1000.0	44.5	adsorpt	79.1	76.5	75.0	70.4	76.9	71.8	71.3	68.9	74.4
		des#3	91.4	84.4	93.8	84.8	87.6	86.2	88.1	84.5	85.6
300.0	89.0	adsorpt	70.0	79.8	76.4	76.7	81.0	77.8	78.1	75.4	78.3
		des#3	86.1	86.6	86.1	88.3	89.3	89.4	88.0	87.9	89.1
1000.0	177.9	adsorpt	79.5	76.0	66.2	69.4	75.6	70.7	70.1	67.9	73.8
100.0	266.9	adsorpt	48.6	57.6	76.1	76.0	78.8	77.2	76.1	74.7	77.8
500.0	266.9	adsorpt	69.9	77.6	71.7	72.2	76.7	73.5	70.8	70.7	75.4
		des#3	87.9	85.7	89.5	86.8	88.0	88.0	88.2	86.4	87.5
1000.0	266.9	adsorpt	79.0	75.0	64.0	67.4	74.8	68.7	69.4	65.7	72.6

^a The percentages are expressed with respect to the total amounts (adsorbed + in solution) of each cation for each step. Experimental and calculated values.

used, for which the importance of the edge sites may be more emphasized. This is partially due to the fact that the adsorption to the sites of lower affinity starts before fully saturating the edge sites (10).

Table 4 gives the experimental and calculated, i.e., predicted percentages of chlordimeform, cadmium, calcium and magnesium adsorbed as well as the calculated surface potentials, for the simultaneous adsorption of the pesticide and the heavy metal, on Ca-montmorillonite. The experimental adsorption of the heavy metal decreases as much as 12% for 10-fold increase in chlordimeform concentration, whereas the amount of herbicide adsorbed decreases by about 2% for an increase of 6-fold in cadmium concentration. The model is able to predict the competitive adsorption of the pesticide and the heavy metal, yielding a good agreement between the experimental and calculated values.

The binding coefficient that is a measure of the affinity between the cation and the charged surface can be affected by several factors such as electrostatic interactions and steric effects and is strongly dependent on the size of the hydrated cation (8). The chlordimeform molecule lies flat in the interlayer space of the clay, holding the aromatic ring parallel to the layers of the silicate. This cation will not be hydrated due to its size and hydrophobic nature (21). The interaction of the positive charge of chlordimeform with the ditrigonal cavities of the montmorillonite will be more favored than for Cd, despite its higher positive charge, since the metal will be hydrated, and its charge will be screened by water molecules. Moreover, van der Waals forces will be responsible for an increase in the magnitude of the value of the binding coefficient for the organic cation. In comparison with Cd^{2+} the CdCl^+ species has a relative high binding coefficient, because of its lesser hydrated size.

For the lowest chlordimeform concentration, the competition of the pesticide with the heavy metal might be expected to reduce the pesticide adsorbed amounts due to steric effects exhibited by the aggregated platelets. However, the percentage of chlordimeform adsorbed only decreases 2% for a 6-fold increase in Cd concentration. Our calculations predict that high ionic strength (100 mM) may have a more significant effect on the adsorption of both cations than their competition under the conditions presented in Table 4, which include upper bounds on their concentrations in general polluted areas.

Desorption of Chlordimeform and Cadmium. Table 4 also shows that the model yields good predictions for the amounts of chlordimeform, cadmium, calcium, and magnesium, remaining adsorbed after desorption steps. The total experimental desorption percentages (relative to the amounts adsorbed in the adsorption stage) after three desorption steps are higher in the case of the pesticide than for the heavy

metal. For example, for the initial concentrations of 44.5 μM Cd and 1000 μM chlordimeform, the total experimental desorption percentages deduced are 6.3 and 12.4%, respectively. This can be due to the fact that the concentrations of the divalent cations are higher than those of the pesticide in the double layer (see eq 7), being about 9.0 and 1.7%, respectively, for cadmium and chlordimeform. This is also the explanation for the increase in the fraction of Cd remaining adsorbed as Cd^{2+} , from 44.9% for the adsorption to 61.2% after three desorptions, at the expense of the species CdCl^+ , whose fraction decreases from 23.6 to 14.1% after three desorptions (complete set of results not shown).

General Discussion. The model used is able to explain qualitatively and fairly quantitatively adsorption-desorption processes for complex systems, in which there are six cations, including speciation and adsorption of solution complexes, whereas adsorption-desorption processes have usually been studied for binary systems with certain exceptions for ternary systems (29, 30). In our study, the hysteresis observed is partly explained by interchange equations that take into account the complexation of the cations with the negatively charged sites on the surface of the clay, and in part it is related to the state of aggregation of the Ca-montmorillonite-chlordimeform platelets which yields higher affinity at the higher adsorbed amounts of chlordimeform. Previous explanations for the observed hysteresis of inorganic cations invoked mechanisms such as differential hydration of the interchangeable cations, dehydration of the clay or soil, swelling crystalline expansion, or inaccessibility of sites caused by the formation of quasi-crystals (31). Except for the binding coefficient of chlordimeform, the binding coefficients in the model used in the current work were taken from previous studies and for a different montmorillonite clay. These binding coefficients could yield reasonable predictions for the adsorbed amounts of all the inorganic cations or a monovalent organic cation, such as AF, and also for chlordimeform except for the case where low chlordimeform concentration was added to a relatively high $\text{Ca}^{2+}/\text{Na}^+$ ratio in the system, which was interpreted to reflect steric hindrance of penetration of chlordimeform cations between clay platelet aggregates. In the case of chlordimeform whose binding affinity is rather small in comparison with that of the dyes, the state of aggregation of the clay affects the apparent affinity and contributes to the hysteresis observed in sorption-desorption experiments.

Acknowledgments

This research was supported in part by a Grant G-045-95 from G.I.F., the German-Israeli Foundation for Scientific Research and Development. Dr. Undabeytia acknowledges

the Spanish Government for a postdoctoral fellowship (ref. PF9633975424) at the Seagram Center.

Literature Cited

- (1) White, R. E.; Dyson, J. S.; Gerstl, Z.; Yaron, B. *Soil Sci. Soc. Am. J.* **1986**, *50*, 277.
- (2) Wietersen, R. C.; Daniel, T. C.; Fermanich, K. J.; Lowery, B.; McSweeney, K. J. *Environ. Qual.* **1993**, *22*, 819.
- (3) Weber, J. B. and Swain, L. R. *Soil Sci.* **1993**, *156*, 171.
- (4) Maqueda, C.; Morillo, E.; Martin, F.; Undabeytia, T. *J. Environ. Sci. Health* **1993**, *B28*, 655.
- (5) Bowman, B. T.; Sans, W. W. *J. Environ. Qual.* **1985**, *14*, 270.
- (6) Horzempa, L. M.; Di Toro, D. M. *Water Res.* **1983**, *17*, 851.
- (7) Singh, R.; Gerritse, R. G.; Aylmore, A. G. *Aust. J. Soil Res.* **1989**, *28*, 227.
- (8) Nir, S. *Soil Sci. Soc. Am. J.* **1986**, *50*, 52.
- (9) Stadler, M.; Schindler, P. W. *Clays Clay Miner.* **1993**, *41*, 680.
- (10) Undabeytia, T.; Morillo, E.; Maqueda, C. *Clay Miner.* **1996**, *31*, 485.
- (11) Morillo, E.; Undabeytia, T.; Maqueda, C. *Environ. Sci. Technol.* **1997**, *31*, 3588.
- (12) Rytwo, G.; Serban, C.; Nir, S.; Margulies, L. *Clays Clay Miner.* **1991**, *39*, 551.
- (13) Hirsch, D., Nir, S.; Banin, A. *Soil Sci. Soc. Am. J.* **1989**, *53*, 716.
- (14) Rytwo, G.; Banin, A.; Nir, S. *Clays Clay Miner.* **1996**, *44*, 276.
- (15) Margulies, L.; Rozen, H.; Nir, S. *Clays Clay Miner.* **1988**, *36*, 270.
- (16) Rytwo, G., Nir, S. and Margulies, L. *Soil Sci. Soc. Am. J.* **1995**, *59*, 554.
- (17) Boyd, S. A.; Mortland, M. M.; Chiou, C. T. *Soil Sci. Soc. Am. J.* **1988**, *52*, 652.
- (18) Sheng, G.; Xu, S.; Boyd, A. *Environ. Sci. Technol.* **1996**, *30*, 1553.
- (19) Jaynes, W. F.; Boyd, S. A. *Soil Sci. Soc. Am. J.* **1991**, *55*, 43.
- (20) Polubesova, T.; Rytwo, G.; Nir, S.; Serban, C.; Margulies, L. *Clays Clay Miner.* **1997**, *45*, 834.
- (21) Hermosin, M. C.; Perez-Rodriguez, J. L. *Clays Clay Miner.* **1981**, *29*, 143.
- (22) Morillo, E.; Maqueda, C. *Sci. Total Environ.* **1992**, *123/124*, 133.
- (23) Lagaly, G. *Applied Clay Sci.* **1989**, *4*, 105.
- (24) Sposito, G.; Holtzclaw, K. M.; Charlet, L.; Jouany, C.; Page, A. L. *Soil Sci. Soc. Am. J.* **1983**, *47*, 51.
- (25) Giles, C. H.; MacEwan, T. H.; Nekhwa, S. N.; Smith, D. *J. Chem. Soc.* **1960**, 3973.
- (26) Xu, S.; Boyd, S. *Environ. Sci. Technol.* **1995**, *29*, 3022.
- (27) Madrid, L.; Diaz-Barrientos, E.; Contreras, E. *Aust. J. Soil Res.* **1991**, *29*, 239.
- (28) Undabeytia, T.; Nir, S.; Rytwo, G.; Morillo, E.; Maqueda, C. *Clays Clay Miner.* **1998**, *46*, 423.
- (29) Morgun, Y. G.; Pachepskiy, Y. A. *Sov. Soil Sci.* **1987**, *19*, 1.
- (30) Datta, S. C.; Sastry, T. G.. *J. Indian Soil Sci.* **1990**, *38*, 201.
- (31) Verbug, K.; Baveye, P. *Clays Clay Miner.* **1994**, *42*, 207.

Received for review August 13, 1998. Revised manuscript received December 7, 1998. Accepted December 11, 1998.

ES980822K