Simultaneous adsorption of chlordimeform and zinc on montmorillonite

Esmeralda Morillo and Celia Maqueda

Instituto de Recursos Naturales y Agrobiologia, Apartado 1052, 41080-Seville, Spain

ABSTRACT

The competitive adsorption of the cationic pesticide chlordimeform and the heavy metal zinc on montmorillonite was studied. For different concentrations of Zn used, chlordimeform decreases (in relation to Zn-free treatments) when the pesticide is adsorbed simultaneously with the metal, but increases when Zn is adsorbed previously to chlordimeform. When comparing the $K_D$ values chlordimeform is shown to have a higher affinity for montmorillonite when there is a previous adsorption of Zn than with the simultaneous adsorption of Zn and the pesticide. The adsorption of Zn decreases when chlordimeform concentration increases, in both cases, when the metal is adsorbed simultaneously with the pesticide and when chlordimeform has been previously adsorbed to Zn.

Key words: adsorption; pesticide; heavy metal; montmorillonite

INTRODUCTION

Phenomena of adsorption on clay minerals appear to be some of the most important factors affecting the behaviour and fate of pesticides in soils (Bailey and White, 1967; Mortland, 1975). At the same time the study of heavy metal reactions with the organic and mineral components of the colloidal fraction of soils has increased tremendously (Garcia Miragaya and Dávalos, 1986; Inskeep and Baham, 1983).

Although there are many works on the adsorption on clays of pesticides and heavy metals independently, little attention has been given to the phenomena which take place when both are present together. So, the aim of this paper is to contribute to the clarification of the competitive effects between the cationic pesticide chlordimeform and the heavy metal zinc when they are adsorbed on montmorillonite.

MATERIALS AND METHODS

The clay used was a montmorillonite from Arizona SAZ-1 (Van Olphen and Fripiat, 1979), supplied by the Clay Mineral Society.
Technical grade chlordimeform (99% purity), supplied by Schering Agro, S.A., was used. This pesticide is soluble in water (50% by wt) and ionizes completely, giving the chlordimeform cation and chloride anion. The adsorption experiments were done in triplicate in 50-ml polypropylene centrifuge tubes, by mixing 0.1 g of clay mineral with 0.01 N NaCl solutions containing various concentrations of chlordimeform and/or Zn. The samples were shaken for 24 h at 20 ± 1°C. The chlordimeform and zinc adsorbed were calculated as the differences between their concentrations before and after equilibrium. The concentration of chlordimeform was determined spectrophotometrically at 240 nm and zinc by atomic absorption spectrometry (AAS). The inorganic cation Ca\(^{2+}\) released during chlordimeform or/and zinc adsorption was determined by AAS using a Perkin Elmer apparatus model 703.

The successive adsorptions (Zn after chlordimeform or vice versa) were made by mixing 0.1 g of clay mineral with 0.01 N NaCl solutions containing various concentrations of chlordimeform or zinc. The samples were shaken for 24 h at 20 ± 1°C. After reaching equilibrium, the suspensions were centrifuged and the solid samples treated again with zinc, in the case of those previously treated with chlordimeform, or vice versa. The adsorption isotherms were obtained by plotting the amount of chlordimeform or Zn adsorbed \(C_s\) (\(\mu\)mol/g) versus the equilibrium concentration, \(C_e\) (\(\mu\)mol/l).

Chlordimeform and zinc concentration data are means of 3 replications. In the case of the pesticide the standard deviations range from 0.05 to 0.67 and in the case of the heavy metal from 0.08 to 0.46.

![Adsorption isotherms of chlordimeform (a) and Zn (b) on montmorillonite.](image)
RESULTS AND DISCUSSION

The adsorption isotherms for the pesticide chlordimeform and the heavy metal zinc on montmorillonite are shown in Fig. 1. The adsorption isotherm of the pesticide (Fig. 1a) shows a shape corresponding to the ‘S’ type of Giles et al. (1960). One of the conditions for S-class curve indicates an increased affinity for the adsorbate after a few molecules have been adsorbed. The data of isotherms of other authors for the same pesticide and clay mineral (Pérez-Rodríguez and Hermosín, 1979) contrast with those of this paper which showed adsorption isotherms of the conventional Langmuir type. This discrepancy can be attributed to the longer span of concentrations used by those authors, which masked the behaviour of the lower part of the isotherms. In addition in the previous paper no NaCl was added as background electrolyte, while in our case 0.01 N NaCl solutions are added together with the different concentrations of chlordimeform. Thus for low concentrations of pesticide the principal process is the interchange of Na\(^+\) from the background electrolyte, by Ca\(^{2+}\) cations which are saturating the planar positions on the montmorillonite and after that, the adsorption of chlordimeform by cationic exchange with Na\(^+\) ions is favoured by higher concentrations, thus showing an increased affinity for the adsorbate. As was shown in previous papers (Maqueda et al., 1986), the adsorption of chlordimeform by the clay fraction of soils takes place through a cationic exchange process.

Figure 1b shows the adsorption isotherm of Zn on montmorillonite. It has been suggested by several authors (Benjamin and Leckie, 1981; García-Miragaya et al., 1986; Madrid et al., 1991) that sorption of metal ions by layer silicates and other adsorbents may occur at several types of surface sites, with higher energy sites acting at the lower range of surface coverages. Retention of Zn ions by montmorillonite can be expected to occur through two different processes: by adsorption on variable charge edge sites and by exchange of the exchangeable Ca ions saturating the permanent charge planar sites.

A useful and simple parameter to measure the affinity adsorbent-sorbate is the distribution coefficient, \(K_D\), which can be defined as

\[
K_D \, M = \frac{(\text{Clay-M})}{(\text{sol-M})}
\]

Where (clay-M) is the concentration of sorbate \(M\) (Zn or chlordimeform) sorbed on the clay in mequiv./g and (sol-M) is the concentration of sorbate \(M\) in the equilibrium solution in mequiv./g. This parameter has been used by several authors (Turner et al., 1984). In the case of Zn, to calculate \(K_D\) it has been supposed that the metal is present in solution and may be on the clay as the Zn\(^{2+}\) and not as the ZnOH\(^+\) species, since, taking into account
the pH of our system (6.7) and the equilibrium constant for the reaction: 
\[ \text{Zn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{ZnOH}^+ + \text{H}^+, \quad K = 2.04 \times 10^{-8} \], the proportion of Zn$^{2+}$ species is 90% in relation to ZnOH$^+$.

It can be seen in Fig. 2a that the system with a very low proportion of adsorbed Zn gives large \( K_D \) values, and when adsorbed Zn increases \( K_D \) undergoes a strong decrease towards reaching a more constant \( K_D \) value. As was mentioned above, large values of \( K_D \) for small amounts of Zn adsorbed may be a consequence of the existence of sites in the clay surface with high preference for this metal. On the other hand, Madrid et al. (1991) have observed that the number of high-preference sites for Zn on montmorillonite increases with pH and it is suggested that they are located in variable charge edge regions. The 'more constant' value of \( K_D \) when the amount of Zn adsorbed is high suggests that the other possible sites for Zn adsorption, that is, the planar exchange sites, have no special preference for this metal.

The plot of \( K_D \) values of chlordimeform vs surface pesticide loading for montmorillonite (Fig. 2b), shows a different behaviour from that observed for Zn. It can be observed that if the chlordimeform sorbed on the clay is low, the \( K_D \) value is low and it increases as the sorbed pesticide is increasing. This seems to indicate that the adsorption of chlordimeform on montmorillonite takes place only through a cationic exchange process, in which the competition between the pesticide cations and the inorganic cations on permanent charge planar sites, and those from background electrolyte is very important. The fact that \( K_D \) value increases with the amount of chlordimeform adsorbed indicates that the sorbent-sorbate affinity increases, which is in agreement with the shape of the adsorption isotherm for this com-
pound on montmorillonite (Fig. 1), since the 'S'-type curve indicates an increased affinity for the adsorbate after a few molecules have been adsorbed. In this case the presence of some organic molecules on the planar positions of montmorillonite leads to a swelling of the interlamellar space of the clay facilitating an interchange between inorganic and organic cations.

Fig. 3. Adsorption isotherms of Zn on montmorillonite from chlordimeform-free solutions (○) in comparison with simultaneous (●) and successive (□) Zn adsorption, at various chlordimeform concentrations: 0.1 (a), 0.5 (b) and 1.0 (c) mmol/l.
Reaction of montmorillonite with solutions of both adsorbates: Zn and chlordimeform

(a) Simultaneous and successive adsorption of Zn in the presence of chlordimeform

Figure 3 shows the adsorption isotherms on montmorillonite of Zn from chlordimeform-free solutions in comparison with simultaneous and successive Zn adsorption when the concentrations of chlordimeform used were 0.1 mmol/l (Fig. 3a), 0.5 mmol/l (Fig. 3b) and 1.0 mmol/l (Fig. 3c). It can be seen that the adsorption of Zn decreases when chlordimeform concentration increases in both cases, that is, when the metal is adsorbed simultaneously with the pesticide and when chlordimeform is adsorbed before Zn.

In the case of Zn adsorption on interlamellar positions of montmorillonite it can be due to competition between Zn and chlordimeform for those permanent charge positions; in the case of the Zn fraction adsorbed on the edges of the mineral variable charge surfaces Zn adsorption is more difficult due to physical adsorption of pesticide molecules on the external surfaces of montmorillonite (Pérez-Rodríguez and Hermosin, 1979) and so, the approach of Zn to the clay is impeded.

On the other hand, differences can be observed if Zn adsorption is in the simultaneous or successive form. In the case of a low chlordimeform concentration, Zn adsorption is higher in the simultaneous than in successive form (Fig. 3a); but if the chlordimeform concentration is high, more Zn is adsorbed in the successive than in simultaneous form (Fig. 3c). The possible reason may be that, if the pesticide concentration used is high, a greater part is adsorbed on planar positions in the clay, opening the layers and facilitating the subsequent penetration of Zn. This behaviour is possible only in a range of concentrations of chlordimeform much lower than the cationic exchange capacity (CEC) of the mineral, and so a very small fraction of interlamellar positions are occupied by the pesticide, the other positions being available for Zn adsorption.

When chlordimeform concentration is low, a great part is adsorbed physically on the external surfaces of montmorillonite. Thus, the approach of Zn to the variable charge positions on the clay is not easy if the clay has been previously treated with the pesticide. But, if treatment is simultaneous with Zn and chlordimeform, the high affinity of Zn for superficial positions makes it the first species to occupy those positions. Therefore adsorption is higher than in the successive form.

The same behaviour is also observed in the differences of the $K_D$ value of Zn adsorption on montmorillonite in the presence of chlordimeform (Fig. 4), in which $K_D$ values have been graphically represented as a function of the amount of Zn adsorbed, in the cases of simultaneous (Fig. 4a) and successive
advised (Fig. 4b). In both cases, a decrease in $K_D$ value can be observed when chlordimeform concentration increases, so, Zn affinity for the clay decreases in the presence of chlordimeform.

In general, the $K_D$ values obtained, over the whole ranges of chlordimeform concentrations used and amounts of Zn adsorbed, are lower in simultaneous than in successive adsorption, that is, the affinity of Zn for montmorillonite is higher in successive adsorption.

In simultaneous adsorption (Fig. 4a) the decrease in affinity is observed for both low and high amounts of Zn adsorbed. But, in successive adsorption (Fig. 4b) the behaviour of $K_D$ curves is different in the case of high amounts of Zn adsorbed, since $K_D$ converges towards a constant value in each concentration of chlordimeform used. The reason may be that when the surface metal loading on the clay is high, the high affinity sites have been occupied, so only the interlamellar positions are accessible. In such conditions, when the adsorption is simultaneous, the chlordimeform concentration in the equilibrium solution provides strong competition for the Zn, whose affinity decreases. But, in successive adsorption, the chlordimeform concentration
present in equilibrium solution is very low, since there is only a small fraction of pesticide desorbed from the clay. The competition with Zn for adsorption is practically zero and the affinity of Zn for the planar surfaces is the same for all the concentrations of chlordimeform used previously, including when no chlordimeform had been used.

(b) Simultaneous and successive adsorption of chlordimeform in presence of Zn

Figure 5 shows the adsorption isotherms on montmorillonite of chlo-

![Graph showing adsorption isotherms](image-url)

**Fig. 5.** Adsorption isotherms of chlordimeform on montmorillonite from Zn-free solutions (O) in comparison with simultaneous (●) and successive (□) chlordimeform adsorption, at various Zn concentrations: 5 (a), 15 (b) and 30 (c) ppm.
SIMULTANEOUS ADSORPTION OF CHLORDIMEFORM AND Zn ON MONTMORILLONITE

dimeform from Zn-free solutions in comparison with simultaneous and successive chlordimeform adsorption when Zn concentration was 5 ppm (Fig. 5a), 15 ppm (Fig. 5b) and 30 ppm (Fig. 5c). For all concentrations of Zn used, chlordimeform adsorption decreases (in relation to Zn-free treatments) when the pesticide is adsorbed simultaneously with the metal, but increases when Zn is adsorbed previously to chlordimeform. This may be due to the fact that the cationic exchange between chlordimeform and Zn adsorbed on planar positions is easier than between the pesticide and interlamellar calcium. Some experiments with Zn-montmorillonite (not shown) indicate that the adsorption is higher than with Ca-montmorillonite.

Figure 6 shows $K_D$ values of chlordimeform adsorption on montmorillonite as a function of the amount of chlordimeform adsorbed in the cases of simultaneous (Fig. 6a) and successive adsorption (Fig. 6b).

In simultaneous adsorption, $K_D$ values are very similar for each Zn concentration used and also to $K_D$ values in the case of Zn-free solutions; however, it can be observed that all the $K_D$ curves of solutions containing

![Fig. 6. Chlordimeform $K_D$ values as function of the amount of chlordimeform adsorbed in simultaneous (a) and successive (b) adsorption, at various Zn concentrations: 0 (O), 5 (■), 15 (■) and 30 (□) ppm.](image-url)
Zn are over those of Zn-free solutions, so it can be concluded that in simultaneous adsorption of Zn and chlor-dimeform the affinity of chlor-dimeform for montmorillonite is very similar, but always a little higher, to the affinity without Zn in solution. This appears to contradict facts observed previously (Fig. 5) where the absorption of chlor-dimeform, simultaneously with Zn, is lower than its adsorption in Zn-free solutions.

On the other hand, in successive adsorption of Zn and chlor-dimeform (Fig. 6b) a great difference can be seen between $K_D$ values of chlor-dimeform adsorption corresponding to solutions with both adsorbates and those values corresponding to Zn-free solutions, the former being higher than the latter. This is in agreement with the results observed in Fig. 5 showing the higher adsorption of chlor-dimeform for montmorillonite previously treated with Zn solutions.

Another interesting point to observe is that the affinity of chlor-dimeform for Zn-treated montmorillonite is very similar for all the different Zn concentrations used, above all when the amount of chlor-dimeform adsorbed is low.

In conclusion, comparing the $K_D$ values in Figs. 6a and 6b, a higher affinity of chlor-dimeform for montmorillonite is observed when there is a previous adsorption of Zn, than in the simultaneous adsorption of Zn and the pesticide.

REFERENCES


