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Study of the behaviour of azinphos-methyl in a clay mineral by batch and column leaching

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Abstract

Research efforts dealing with the processes affecting the transport of pesticides in soils are needed in order to prevent further damage of surface and groundwater reserves. Although organic matter has been recognised as the most important contributor to the adsorption of non-ionic organic pesticides in soils, in some cases clay minerals may have an important role in the retention of these compounds. The present study was designed to improve the knowledge of the behaviour of azinphos-methyl in soils. Coefficients from adsorption isotherms and HPLC analysis of soil column leachates were used in this work for predicting pesticide mobility in soils. The studied clay mineral was a Spanish bentonite with a predominant montmorillonite fraction. The results showed that azinphos-methyl was adsorbed on the clay mineral and demonstrated the catalytic effect of bentonite on the hydrolysis of the pesticide. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption isotherms; Clay; Soil; Azinphos-methyl; Pesticides; Organophosphorus compounds

1. Introduction

Pesticide contamination has become a world environmental concern because many pesticides have been used extensively for a number of years, and some of them are now found in surface and groundwater. So research efforts dealing with the processes affecting the transport of pesticides in soils are needed in order to prevent further damage to surface and groundwater bodies [1]. The risk of groundwater contamination is ultimately determined by the relative rates of percolation, sorption and degradation within the soil profile and it can be evaluated by different methods. Soil–water partitioning coefficients and coefficients from adsorption isotherm equations have been used for predicting pesticide mobility in soils. On the other hand, pesticide

mobility has been measured in the laboratory by using soil-leaching columns [2,3]. The soil organic matter has been recognised as the most important contributor to the retention of non-ionic organic pesticides in soils acting as a partitioning medium [4]. However, when the organic carbon content is low relative to the clay mineral content, the contribution of the clay to sorption may become more evident, especially for polar herbicides [5–7]. Besides that, some studies have demonstrated that clay minerals also have an important role in the adsorption of some non-ionic and sparingly soluble pesticides [8]. Moreover, by means of laboratory equilibrium processes the ability of clay minerals to catalyse the hydrolysis of adsorbed pesticides has been studied [9]. All these facts, besides the importance of the clay fraction of soils and sediments in contaminant transport, lead us to evaluate the behaviour of some pesticides in pure clay minerals. Agricultural chemicals have been detected with

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increasing frequency as contaminants in surface and ground waters [2,10,11]. Many of these compounds are non-ionic and only sparingly soluble in water, such as azinphos-methyl [12], which is a non-systemic and highly toxic organophosphorus insecticide mainly used in Spain [13]. So this pesticide has been selected for the present work, in which a Spanish bentonite has been used to investigate its capability of adsorbing azinphos-methyl by means of both equilibrium (batch) and dynamic (column) studies.

2. Experimental

2.1. Chemicals

Pure azinphos-methyl [*O,O*-dimethyl-*S*-(3,4-dihydro-4-keto-1,2,3-benzotriazinyl-3-methyl) dithiophosphate] from Riedel-de Haën (Seelze–Hannover, Germany) was used in all experiments. Baker (Deventer, Netherlands) supplied methanol (HPLC-grade) and Panreac (Barcelona, Spain) supplied CaCl_2 (analytical-grade).

The Centro de Investigaciones Energéticas y Medioambientales supplied the bentonite from a deposit in Cabo de Gata (Almería, Spain). Table 1 shows some properties of the studied bentonite [14]. Quartz, one of the more commonly minerals in natural geological media, was used as the supporting material.

2.2. Equipment

A Hewlett-Packard (Walbronn, Germany) UV–Vis spectrophotometer 8453 was used for the analysis of batch equilibrium solutions. A Waters (Milford, MA, USA) HPLC 2690 system with a Waters 996 photodiode array detector and a reversed-phase Kromasil 100 C_{18} (250×4.6 mm I.D.) was used for the analysis of column eluents.

A methanol–water mixture (70:30) at a flow-rate

of 1 ml/min was used as the mobile phase. The mobile phase and samples were passed through a 0.45- μm filter (Millipore, Bedford, MA, USA). For data processing, the chromatographic software Millennium 2010 (Waters, Milford, MA, USA) was used.

2.3. Adsorption studies

2.3.1. Batch experiments

Equilibrium adsorption isotherms were measured using the batch procedure at six azinphos-methyl concentrations ranging from 2.5 to 15 ppm. Equilibrium was achieved by shaking 1 g of duplicate samples with different soil compositions (5, 10 and 20% bentonite in quartz) with the aqueous pesticide solution (10 ml) at different pH values (3 and 7) during 24 h at 20°C. CaCl_2 (0.01 M) was used as background electrolyte in order to minimise ionic strength changes and to promote flocculation.

After the adsorption the suspension was centrifuged at 2000 rpm and the equilibrium concentration was determined in the supernatant by UV absorption at 226 nm. The adsorbed azinphos-methyl was calculated from the difference between concentrations in the aqueous phase before and after interaction with soil.

2.3.2. Column experiments

A glass cylinder (150×10 mm I.D.) was fitted with 10 g (90 mm) of the soil composed with 20% of bentonite in quartz. The column was saturated with the electrolytic solution (0.01 M CaCl_2). Different solutions with pesticide concentrations of 5 and 10 ppm at pH 3 and 7 in 0.01 M CaCl_2 were pumped with a peristaltic pump (Miniplus 3, Gilson, France) at a flow-rate of 15 ml/h. Column eluent was collected every 30 min with a fraction collector (FC 203B, Gilson, France), and it was analysed with the HPLC system previously described. Experiments were conducted at room temperature (20°C).

Table 1

Physico-chemical properties of the studied bentonite, cation exchange capacities (CEC) and specific surface area (S_{BET}) [14]

Sand (%)	Silt (%)	Clay (%)	Clay mineralogy (%)		CEC (mequiv./l)	S_{BET} (m^2/g)	d_{001} (Å)
			Illite	Montmorillonite			
6.7	13.3	80.0	15.0	85.0	107	62	14.8

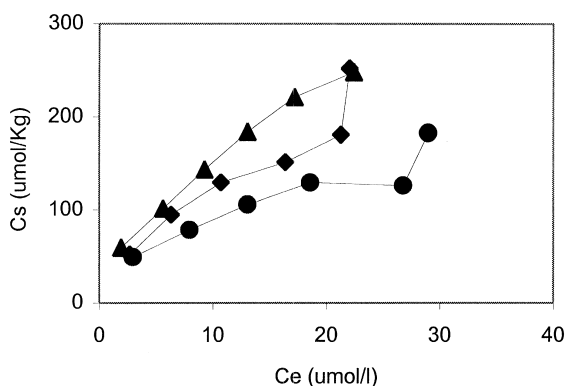


Fig. 1. Adsorption isotherms for different bentonite compositions at pH 7. ●, 5%; ◆, 10%; ▲, 20%.

3. Results and discussion

3.1. Batch experiments

Adsorption isotherms were obtained by plotting the amount of pesticide adsorbed (C_s in $\mu\text{mol/kg}$ soil) with respect to the equilibrium concentration (C_e in $\mu\text{mol/l}$).

Figs. 1 and 2 show the adsorption isotherms at different soil composition and at different pH, respectively. According to the classification of Gilles et al. [15], all the adsorption isotherms are of the L-type showing a convex initial curvature. This isotherm type indicates a decrease in specific adsorption sites when the concentration of pesticide increases. Otherwise, some isotherms (5 and 10%

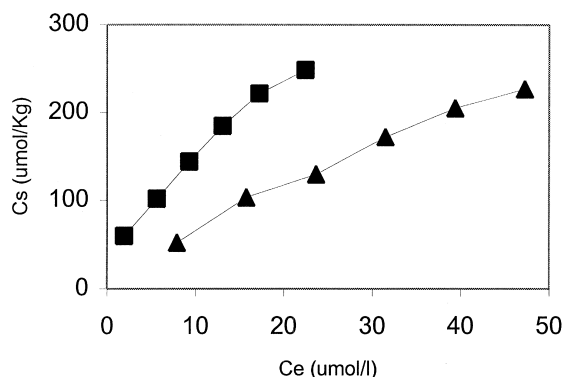


Fig. 2. Adsorption isotherms for different pH values at 20% of bentonite. ▲, pH 3; ■, pH 7.

bentonite) at high concentrations change from the L-shape to the S-type indicating the contribution of other sorption mechanisms [16]. Similar behaviours have been observed for the adsorption of polar pesticides in soils with high clay content and low organic carbon content [7,17]. On the contrary, a study about the adsorption of azinphos-methyl in natural montmorillonites with low organic carbon content [18] showed an S-type isotherm, where the adsorption increases with the concentration of the pesticide, giving n_f values of 1.18 and $\log K_f=2.17$.

Sorption parameters for our studies were calculated by fitting the obtained sorption data to the logarithmic form of the Freundlich equation: $\log C_s = \log K_f + n_f \log C_e$ where K_f and n_f are constants that are characteristic of the sorption, n_f indicates the extent to which the sorption is a function of concentration and K_f is the concentration of pesticide adsorbed for an equilibrium concentration equal to the unity and is considered to be a measurement of the adsorption capacity. Table 2 summarises the calculated values of K_f and n_f .

In general, the isotherms fulfil the Freundlich adsorption equation with correlation coefficients greater than 0.99. The highest value of r^2 corresponds to the continuous L-isotherm (subtype 1) [15]. By contrast, the lowest coefficients correspond to isotherms L, subtype 3, where the curvature changes from convex to concave. The values of n_f were found lower than the unity in all cases, as corresponds to L isotherms. Furthermore, it has been suggested that for pesticides n_f tends to less than 1 with a mean value of 0.87 [19]. The K_f values indicate that the adsorption of azinphos-methyl increases with the percentage of bentonite, showing a linear correlation between the adsorption of azinphos-methyl and the mineral clay content. The

Table 2
Adsorption coefficients (K_f and n_f) of azinphos-methyl on bentonite and correlation coefficient (R^2) calculated from Freundlich equation

Bentonite (%)	Solution pH	K_f	n_f	R^2
5	7	25	0.56	0.989
10	7	30.2	0.589	0.99
20	7	39.8	0.591	0.998
5	3	21.9	0.71	0.995
20	3	26.4	0.685	0.994

obtained K_f values for the studied insecticide is in the range of those obtained for other pesticides in different montmorillonites with no organic matter [7,20].

Adsorption coefficients at two different initial pH were also calculated (Table 1). The decrease in the initial pH of the pesticide solution results in a decrease of K_f that can be initially related to a decrease in the adsorption capacity of bentonite.

3.2. Column experiments

The movement of azinphos-methyl through the bentonite was studied by continuously applying aqueous solutions of the pesticide to the top of soil columns and monitoring its concentration in the effluent by HPLC. Because pesticide transport can not be separated from water movement, it was necessary to define the column hydraulic properties. In the present case, acetone was used to study the water movement along the column. Acetone is a good tracer because it is a conservative substance, which is subjected to transport with dispersion only [21]. Fig. 3 shows the representative breakthrough curve (BTC) for the acetone. From these results, an effective volume (i.e., the volume where the 50% of the input concentration is found in the output solution) of 5.5 ml was obtained. At this point, different column experiments with the azinphos-methyl solutions were carried out. Figs. 4 and 5 show the obtained BTC for the transport of azinphos-methyl at different initial pH and concentrations. A first look to those curves shows a similar behaviour of the pesticide transport at all the experimental conditions studied. An effective volume of approximately 120

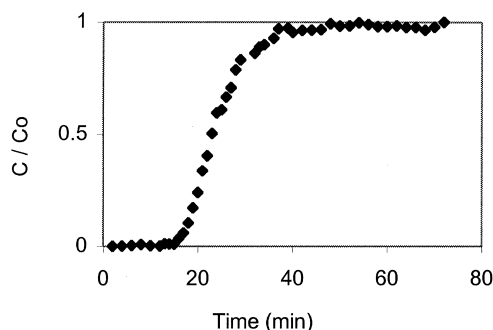


Fig. 3. Breakthrough curve of acetone.

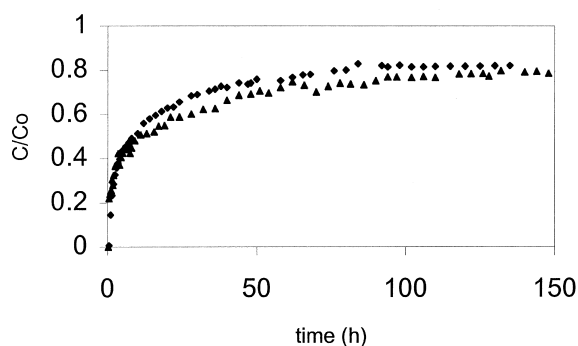


Fig. 4. Breakthrough curves for different initial concentrations of azinphos-methyl at pH 7. \blacktriangle , 10 ppm; \blacksquare , 5 ppm.

ml was obtained in all cases. The difference between this result and that obtained for acetone means that the pesticide is retained in the soil column [22]. So, according to the results obtained in the equilibrium experiments, there is an adsorption process of azinphos-methyl on the bentonite. The curves in Figs. 4 and 5 also showed a reversion after 400 ml of the pesticide solution had been applied to the soil columns, in such a way that the recovered azinphos-methyl in the effluent resulted in the order of 80%. Such behaviour can be attributed to a degradative process [23] that takes place at both the studied pHs, although the degradation was greater at pH 3 giving a lower percentage recovery (approximately 70%) than at pH 7 (approximately 80%).

These results suggest that the decrease of K_f , obtained at the low pH in the batch experiments, could probably be due to degradation processes, instead of being due to changes in the adsorption

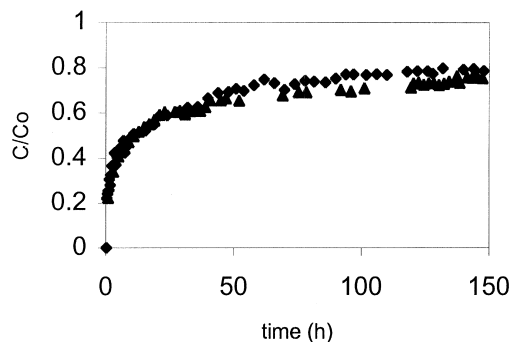


Fig. 5. Breakthrough curves for different pH values at an initial concentration of 10 ppm. \blacktriangle , pH 3; \blacksquare , pH 7.

capacity. It has been suggested [9] that when the pesticide is hydrolysed some degradation products may occupy adsorption sites in the solid, although other ones may pass into the solution. Provided that some of the degradation products of azinphos-methyl have chromogenic groups [24], the net effect would be an increase in the UV signal giving an increase in the measured equilibrium concentration (C_e) and so a decrease in K_f .

The fact that no degradation was observed in a pesticide solution free of clay kept at the same conditions as the suspensions suggests that bentonite can affect pesticide degradation. This effect has been already observed in other studies [25,26], where the results obtained at normal and sterilised conditions demonstrate the significance of clay minerals in the hydrolysis of organophosphorus pesticides.

4. Concluding remarks

Results obtained in the present work show that, although the positive correlation between the organic matter content and the soil adsorption of pesticides is well known [2], for soils with low amounts of organic matter the contribution of clay minerals to sorption becomes more evident. Both equilibrium and column experiments demonstrated the adsorption of azinphos-methyl in the studied bentonite that increases with the percentage of bentonite in the soil and is little affected by pH. The different K_f values obtained in the batch experiments at the studied pHs are not due to adsorption differences but due to degradation processes. So, care must be taken when using adsorption isotherms and Freundlich constants to describe the behaviour of azinphos-methyl in soils.

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