Bull. Environ. Contam. Toxicol. (2004) 72:276–282
© 2004 Springer-Verlag New York Inc.
DOI: 10.1007/s00128-003-8944-4

Environmental Contamination and Toxicology

Sorption-Desorption of Fenamiphos in Surfactant-Modified Clays

N. Singh,[1] M. Megharaj,[2] W. P. Gates,[3] J. Churchman,[3] R. S. Kookana,[3]
R. Naidu,[3] N. Sethunathan[4]

[1] Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110012, India
[2] Center for Environmental Assessment and Remediation, University of South Australia, SPRI Building W2-37, Mawson Lakes, SA 5095, Australia
[3] CSIRO Land and Water, PMB 2, Glen Osmond, SA 5064, Australia
[4] E-45A, 20th Street, Besant Nagar, Chennai 600090, India

Received: 31 March 2003/Accepted: 15 October 2003

Fenamiphos, ((ethyl 4-methylthio) *m*-tolyl isopropyl phosphoramidate) an organophosphorus systemic insecticide and nematicide, is used for the protection of golf courses and some herbaceous and arboreous plants. Leaching of soil applied nonfumigant nematicides to the deep soil layers is a topic of growing interest because of their potential for groundwater contamination. The need to protect and restore contaminated soils and aquifers is stimulating research to look for suitable materials to be used as sorbent, contaminant carrier and pollutant stabilizers (Jaynes and Vance 1996). Different pesticide carriers have been proposed for controlled release formulations to minimise the impact and load of pesticides in the environment (El-Nahhal et al. 1999, 2000; Fernandez-Perez et al. 1999, 2000; Undabeyta et al. 2000).

Clay minerals possess a net negative charge that is compensated for by exchange cations on their surface. Hydration of these cations imparts a hydrophobic nature to the clay surfaces. As a result natural clays are ineffective sorbent for non-ionic pesticides which frequently move from the contaminated site into the subsurface environment and ground water. However, the properties of the natural clay can be significantly modified by exchanging the metal cations with organic cations of the type $[(CH_3)_3N^+R]$ or $[(CH_3)_2N^+RR']$, where R and R' can be long alkyl chain or benzyl groups. In modified clays, the organic phase derived from the organic cations acts as the partitioning medium for the non-ionic pesticides. The organic phase of the organoclays has been shown to be 10 to 30 times more effective, on unit weight basis, than natural soil organic fraction in adsorbing pesticides (Boyd et al. 1988; Lee et al. 1989; Jaynes and Boyd 1991).

During past decade, there has been increasing interests in the use of these organoclays to remediate environmental contamination (Boyd et al. 1988; Xu et al. 1997; Celis et al. 2000). Before these organoclays can be used in the protection and restoration of soils and waters, information is needed on specific sorbent-pesticide interactions, including sorption-desorption behaviour. Studies indicate that fenamiphos is intercalated in the clay lattice (Rodriguez et al. 1988; Sanchez-Martin 2000; Singh et al. 2003), but data is lacking on the fenamiphos sorption capability of these clays. In the present study we have tried to evaluate the

---

Correspondence to: N. Singh

effectiveness of few montmorillonite organoclays to adsorb and retain highly water soluble fenamiphos, therefore sorption-desorption behaviour of fenamiphos was compared in natural and cationic-surfactant-modified clays.

MATERIALS AND METHODS

The sodium montmorillonite clay was obtained from Clay Repository of Clay Mineral Society, Columbia, MO, USA. Its cation exchange capacity was 100 cmol/kg. The analytical grade fenamiphos (96.4 % purity) was obtained from the Sigma Chemicals. The chloride or bromide salts of phenyltrimethylammonium-(PTMA), hexadecyltrimethylammonium (HDTMA) and benzylsterilatedimethyl-ammonium (BSDMA) were purchased from Sigma-Aldrich, Australia. Solvents and other reagents used were of analytical grade.

In the present study we have used the K-montmorillonite clay as standard natural clay. K-montmorillonite was prepared by replacing the sodium in Na-montmorillonite clay by potassium. Therefore, Na-montmorillonite clay (2 μ fraction) was equilibrated with 1M KCl solution for 24h. After equilibration clay suspension was centrifuged at 6000 rpm for 10 min and clay pellet was resuspended in fresh 1M KCl solution. The clay suspension was further equilibrated for another 24 h. Finally the clay was separated by centrifugation and was washed three times with distilled water and was dried at 60°C. The dried clay was ground to a fine power.

The cationic surfactants (PTMA, HDTMA and BSDMA) modified organoclays were prepared by dropwise addition of the aliquots of 0.1 M aqueous solution of chloride or bromide salt of PTMA (50% of CEC of clay), HDTMA or BDSMA (100% of CEC of clay) to a 10 g/L aqueous suspension of sodium-montmorillonite clay under continuos stirring. The clay suspension was equilibrated for 24h and centrifuged at 6000 rpm for 10 min. To replace remaining sodium with potassium the PTMA-montmorillonite clay was further equilibrated with 1M KCl solution. After 24 h equilibration the PTMA clay was separated by centrifugation. Finally all organoclays were washed with distilled water till free of chloride or bromide ions and were dried at 60°C. The dried clay pellets were ground to a fine powder. X-ray diffraction and surface charge measurements of modified clay showed that organic cation was present in the interlayer of the clay lattice (Singh et al. 2003).

Fenamiphos adsorption was studied by equilibrating 10 ml aqueous solution of fenamiphos (concentrations ranging from 2.5 to 10 μg/ml) to 50 mg clay/organoclay in 40 ml screw capped Teflon tubes. The clay suspension was equilibrated on rotary shaker for 16 h at room temperature. A blank control without clay was also maintained. After 16 h the clay suspension was centrifuged at 10,000 rpm for 10 min and fenamiphos was analyzed in the supernatant. The amount of fenamiphos sorbed by the clay was calculated from the difference of initial and final concentration of fenamiphos in the supernatant. There was no sorption of fenamiphos on Teflon tubes.

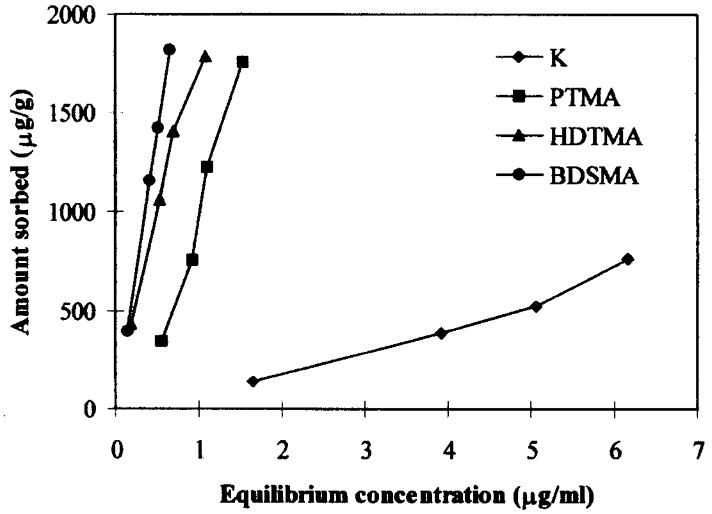

Figure 1. Sorption isotherms for fenamiphos in natural clay and organoclays.

Desorption of fenamiphos was estimated in the same tubes after adsorption. After adsorption the supernatant was decanted and was replaced with 5 ml distilled water and suspension was equilibrated for 16 h. After attaining equilibrium the clay suspension was centrifuged and fenamiphos was estimated in the supernatant. The clay pellet was subjected to another similar desorption cycle. Total of two desorptions were performed and total amount of fenamiphos desorbed was calculated by summing the amount of fenamiphos desorbed during each desorption. Hysteresis coefficient, H, for the sorption-desorption isotherms were calculated according to equation, $H = 1/n_{ads}/1/n_{des}$, where $1/n_{ads}$ and $1/n_{des}$ are the Freundlich constants obtained from adsorption and desorption isotherms, respectively.

Fenamiphos in aqueous solution was estimated by high performance liquid chromatography fitted with polychrome diode array (PDA) UV detector (model 9065), pump (Varian 9012), autosampler (Varian 9100) and star chromatograph work station for spectra processing. Fenamiphos was separated on Waters Radial Pack C18 cartridge (100 mm x 5 mm id, 4 μm particle size). A Novapak guard column (Waters) was used as precolumn. The operating conditions were: mobile phase – acetonitrile-water (30:70), wavelength - 210 nm, flow rate - 1 ml/min. Under these conditions the retention time for fenamiphos was 7.00 min.

RESULTS AND DISCUSSION

Adsorption isotherms of fenamiphos on K-montmorillonite and organoclays, PTMA-, HDTMA- and BSDMA-montmorillonite, are shown in Figure 1. K-montmorillonite clay was very poor absorbent of fenamiphos. An average of

Table 1. Sorption parameters of fenamiphos in modified clays.

Clay	Freundlich parameters			Linear regression	
	K_f	1/n	r^2	K_d	r^2
K	69.8	1.27	0.997	135.1	0.974
PTMA	976.6	1.63	0.930	1502.2	0.980
HDTMA	1763.0	0.93	0.996	1534.0	0.974
BSDMA	2804.7	1.00	0.999	2796.9	0.974

33.5% of fenamiphos was sorbed by the K-montmorillonite. However, exchanging the K with organic cation significantly enhanced the fenamiphos sorption capability of the montmorillonite clay. PTMA-, HDTMA- and BSDMA-montmorillonite clays removed 82, 87 and 93%, respectively, of the fenamiphos initially present in the aqueous solution. The distribution coefficient (K_d), which is the measure of the affinity of fenamiphos to clay/organoclays, is listed in Table 1. The K_d values for organoclays were several times higher than the value obtained for K-montmorillonite. The highest K_d was obtained for BSDMA-montmorillonite (20 times) followed by HDTMA and PTMA (11 times). These results indicate that compared to natural clay, organically modified clays are highly effective in absorbing fenamiphos from the aqueous.

Fenamiphos sorption data was subjected to Freundlich adsorption equation.

$$\log\ x/m = \log K_f + 1/n \log C$$

where, x/m is the amount of fenamiphos sorbed (μg) per gram of clay, C is the equilibrium concentration of fenamiphos (μg/ml) and K_f and 1/n are the empirical adsorption constants. Constant K_f (intercept) represents the amount of fenamiphos sorbed at an equilibrium concentration of 1 μg/ml and is the measure of fenamiphos sorption. Constant 1/n (slope) represents the dependence of sorption on the initial concentration of fenamiphos in aqueous phase. The fenamiphos sorption was very well explained by the Freundlich adsorption isotherms ($r^2 >$ 0.974). Similar to K_d value the K_f value for fenamiphos sorption was higher in BSDMA-montmorillonite indicating that fenamiphos was sorbed to maximum extent in this clay.

The values of $1/n_{ads}$ varied between 0.93 and 1.63. The slope values nearly equal to unity for HDTMA- and BSDMA-montmorillonite clays indicate that the sorption of fenamiphos in these clays was independent of initial concentration of fenamiphos and there is minimum competition from water molecule for sorption sites on these sorbents. Fenamiphos sorption isotherms were S-type for K-montmorillonite and PTMA-montmorillonite (Giles et al. 1960). This type of isotherm is characterized by lesser sorption of pesticide at low equilibrium concentration and sorption increases at higher equilibrium concentration.

The organoclays used in the present study belong to adsorptive (PTMA) and organophillic clay types (HDTMA and BDSMA) and different sorptive mechanisms have been proposed for them (Jaynes and Boyd 1991). The organophillic clays have 2-paraffin-like layer of the cation, which is fixed in the interlayers of the clay lattice and this phase acts as the partition medium for the nonionic pesticides. However, organic cations in adsorptive clays act as the nonhydrated pillars that prop open the clay layers exposing the abundant silioxane surfaces. The nonionic pesticides are sorbed by the mineral surfaces between the organic pillars.

Table 2. Desorption parameters of fenamiphos in modified clays.

Clay	Parameter	Concentrations (μg/ml)			
		2.5	5.0	7.5	10.0
K	% D	39.6	47.8	52.0	63.8
	1/n	0.16	0.18	0.21	0.38
	H	7.93	6.83	5.85	3.23
PTMA	% D	32.4	24.6	19.6	17.0
	1/n	0.50	0.38	0.28	0.23
	H	3.26	4.39	5.82	7.08
HDTMA	% D	10.4	12.7	13.3	12.8
	1/n	0.15	0.17	0.19	0.18
	H	6.20	5.47	4.89	5.16
BSDMA	% D	9.2	9.2	9.5	10.8
	1/n	0.14	0.14	0.14	0.16
	H	7.14	7.14	7.14	6.25

D- Amount desorbed.
H- Hysteresis coefficient.

The types of adsorption isotherms obtained in this study, also prove the suggested sorption mechanism. Fenamiphos sorption isotherms in natural and PTMA-montmorillonite are nonlinear. This type of isotherm corresponds to surface adsorption mechanism. At low equilibrium concentration, fenamiphos has to compete with the water molecule for sorption sites. But as the concentration of fenamiphos in aqueous solution increases its sorption also increases. This results due to an increase in solute molecules on the clay surface and is generally explained by a side-by-side association process between sorbed molecules that help to hold them to the surface (Weber and Miller 1989). Greater sorption of fenamiphos in PTMA-montmorillonite compared to K-montmorillonite was the result of more availability of silioxane surfaces, which were created due to prop opening of the clay lattice by PTMA moiety. Lee et al. (1989) have shown that adsorptive clays show nonlinear uptake of benzene and small aromatic molecules. However, adsorption of fenamiphos in organophillic clays is affected through a partition interaction and we get linear sorption isotherms extending from low to high relative concentrations.

Desorption of fenamiphos showed hysteresis from all clays. In general, fenamiphos sorption was more reversible in K- and PTMA-montmorillonite clays (higher % D) compared to HDTMA- and BSDMA-montmorillonites (Table 2) In K-montmorillonite clay fenamiphos sorption was more irreversible at low concentration adsorbed (2.5 μg/ml), showing high hysteresis coefficient (H). However, modifying the montmorillonite clay with cationic surfactants significantly decreased fenamiphos desorption and greater amounts of fenamiphos was retained in the clay matrix. In PTMA-montmorillonite fenamiphos sorption was more irreversible at higher sorption concentration of 10 μg/ml. This indicates that in this organoclay, fenamiphos was more strongly sorbed at higher interlayer coverage and is difficult to remove. Fenamiphos desorption from HDTMA- and BSDMA-montmorillonite was nearly independent of sorbed phase concentration and only 10-13% and 9-11% of fenamiphos was desorbed from the respective clays. This study indicates that fenamiphos desorption in these clays depends not only on the nature of organic cation but also to some extent on the sorbed phase concentration of fenamiphos.

The results of the present study indicate that modifying the natural clays with organic cations significantly enhances the fenamiphos sorption capability of the clay. The organophillic clays, HDTMA and BSDMA, were superior to adsorptive clay (PTMA-montmorillonite) in retaining the sorbed fenamiphos. The organoclays may find application in soil and water decontamination and as carrier for controlled released formulation of fenamiphos.

Acknowledgment. Neera Singh was supported by a BOYSCAST Fellowship from the Department of Science and Technology, Government of India, New Delhi, India. The Remediation of Contaminated Environments Program, CSIRO Land and Water, Adelaide, Australia funded this work.

REFERENCES

Boyd SA, Lee J-F, Mortland MM (1988) Attenuating organic contaminants mobility by soil modification. Nature 333:345-347

Celis R, Koskinen WC, Hermosin MC, Ulbarri MA, Cornejo J (2000) Triademefon interaction with organoclays and organohydrotalcites. Soil Sci Soc America J 64:36-43

El-Nahhal Y, Nir S, Polubesova T, Margulies L, Rubin B (1999) Movement of metolachlor in soil: effect of new organoclay formulation. Pestic Sci 55:857-864

El-Nahhal Y, Nir S, Polubesova T, Margulies L, Rubin B (2000) Montmorillonite-phenyltrimethylammonium yields environmentally improved formulation of hydrophobic herbicides. J Agric Food Chem 48:4791-4801

Fernandez-Parez M, Villafranca-Sanchez M, Gonzalez-Pardas E, Flores-Cespedes F (1999) Controlled release of diuron from an alginate-bentonite formulation: water release and soil mobility study. J Agric Food Chem 47:791-798

Fernandez-Parez M, Villafranca-Sanchez M, Gonzalez-Pardas E, Flores-Cespedes F (2000) Mobility of isoproturon from an alginate-bentonite controlled release formulation in layered soil. Chemosphere 41:1495-1501

Giles CH, MacEvan TJ, Nakhawa SM, Smith D (1960) Studies in adsorption. Part II. A system of classification of sorption-desorption isotherms and the diagnosis of adsorption mechanism and specific surface areas of solids. J Chem Soc 3:3973-3993

Jaynes WF, Boyd SA (1991) Clay mineral type and organic compound sorption by hexadecyltrimethylammonium exchanged clay. Soil Sci Soc America J 55:43-48

Jaynes WF, Vance GF (1996) BTEX sorption by organoclay cosorptive enhancement and equivalence of interlayer complexes. Soil Sci Soc America J 60:1742-1749

Lee JF, Crum JR, Boyd SA (1989) Enhanced retention of organic contaminants by soil exchanged with organic cations. Environ Sci Technol 23:1365-1372

Singh N, Megharaj M, Gates WP, Churchman J, Anderson J, Kookana RS, Naidu R, Chen Z, Slade PG, Sethunathan N (2003) Bioavailability of an organophosphorus pesticide fenamiphos sorbed on an organo-clay. J Agric Food Chem 51:2653-2658

Rodriguez JM, Loopez AJ, Bruque S (1988) Interaction of fenamiphos with montmorillonite. Clay Clay Min 36:284-288

Sanchez-Martin M (2000) Adsorption of carbofuran and fenamiphos by montmorillonite. Fresenius Environ Bull 9:582-589

Undabeyta T, Nir S, Rubin B (2000) Organoclay formulations of the hydrophobic herbicide norflurazon yield reduced leaching. J Agric Food Chem 48:4767-4773

Weber JB, Miller CT (1989) Organic chemical movement over and through soil. In: Sawhney BL, Brown K (ed) Reactions and movement of organic chemicals in soils, SSSA Special Publ 22, SSSA and ASA, Madison, WI, p 305

Xu S, Sheng G, Boyd SA (1997) Use of organoclays in pollution abatement. Adv Agron *59*:25-62