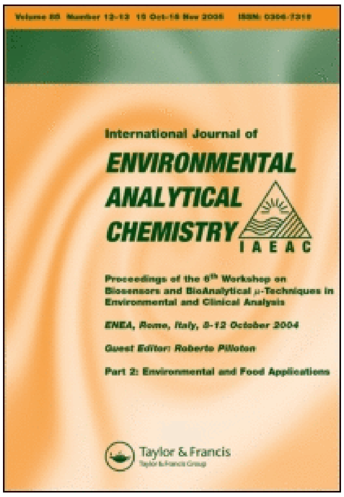

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SORPTION–DESORPTION STUDIES OF SIX PYRETHROIDS AND MIREX ON SOILS USING GC/MS-NICI

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Sorption–desorption equilibria of six pyrethroids (permethrin, cyfluthrin, cypermethrin, λ-cyhalothrin, deltamethrin and fenvalerate) and mirex were determined in soils possessing a range of organic content (1.15–2.46%). Solutions (in deionized water, pH 6.5–7.4) of the samples were shaken using a mechanical shaker for 24 h. The suspensions were centrifuged and aliquots of clear supernatant were passed through a C-18 column (SPE extraction). The eluates were concentrated to dryness before a volumetric standard was added. The analytes were determined by gas chromatography with negative ion chemical ionization mass spectrometry (GC/MS-NICI) either in SIR or SCN mode. Sorption isotherm parameters (n and k) were calculated according to the Freundlich equation. The values of n are around unity. Permethrin and cyfluthrin were the least sorbed pyrethroids, $k < 2$, mirex and fenvalerate the most. The effect of the pH on sorption was examined also (at pH values 2, 4, 6 and 9). Sorption behaviour on different soils and silica was also examined. Desorption studies were conducted on the same pyrethroid solutions. After sorption, the supernatant was replaced with a similar volume of deionized water. Desorption was achieved by removing all the supernatant from the centrifuged samples and then replacing it with deionized water. This equilibration process was repeated five times. Each time the suspension was centrifuged, concentrated and analyzed using GC/MS analysis. The residual amount of pyrethroid on the soil was calculated as the difference between the initial amount and the desorbed amount (mass balance).

Keywords: GC/MS-NICI; Pyrethroids; Soils; Extraction; Sorption–desorption; Isotherm parameters

INTRODUCTION

The pyrethroids represent a relatively new group of synthetic insecticides, although members of the group have been commercialized since the mid-1950s [1]. Their popularity has increased substantially in recent years, and new members are constantly being developed and commercialized. The naturally occurring compounds are collectively known as pyrethrins. Pyrethrins are obtained from the flower heads of members of the genus *Chrysanthemum* as a mixture known as pyrethrum or pyrethrum extract [2]. Synthetic pyrethroid insecticides, such as permethrin, cypermethrin, cyfluthrin,

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λ-cyhalothrin deltamethrin and fenvalerate, are esters of chrysanthemic acid with a range of alcohol moieties [3–6].

Contamination of fresh water ecosystems by pyrethroids occurs either by the direct discharge of industrial and agricultural effluents or indirectly through the discharge from sewage treatment works, where it is accumulated by the surrounding biosphere. However, pyrethroids have relatively low toxicity towards mammals and are of limited persistence in the environment compared with many other pesticide classes. The phase distribution of pesticides in a soil is determined by the nature of adsorptive soil colloids, the physicochemical characteristics of the pesticide, and a host of physical, chemical and biological factors which are determined by the particular soil environment [7–11]. Of the properties of the pesticide, the most important are the electronic structure and the water solubility. The soil components that control adsorption are the clay particles, amorphous mineral matter and soil organic matter. The adsorption (sorption) of pesticides by soil is governed by various intermolecular interactions including Van der Waals forces, hydrogen bonding, charge transfer, ligand exchange, direct and induced ion–dipole and dipole–dipole interactions and chemisorption [12].

Soil sorption can be quantified in terms of a soil organic-matter–water partition coefficient, K_{oc}, where soil organic matter consists of humic and non-humic substances. Various relationship have been identified between soil sorption of different classes of compounds including pesticides and their octanol–water partition coefficient, K_{ow} [13]. Adsorption is generally measured by allowing the soil to react with aqueous solutions of the pesticide over a range of concentrations. At equilibrium the amount adsorbed is obtained as the difference between the amount added and the amount remaining in solution: the "difference method". Over a limited range of concentrations, there is often a straight-line relationship between the amount adsorbed, C_s, and the equilibrium concentration, C_w. The slope of the line is known as the adsorption coefficient, k, or the distribution adsorption constant, of the pesticide by the soil used in the experiment, and is a measure of the buffer capacity.

The equation $C_s = kC_w^{1/n}$, is a form of the Freundlich isotherm [14,15], which is often expressed in its logarithmic form:

$$\log C_s = \frac{1}{n} \log C_w + \log k$$

where C_s ($\mathrm{mg\,kg^{-1}}$) is the total chemical concentration associated with the sorbent C_w ($\mathrm{mg\,L^{-1}}$) is the total chemical concentration in the solution. Experimental data are often plotted in logarithmic form as a convenient way of determining whether removal of materials from solution is accomplished by adsorption and as a means of evaluating the constants k and n. Average values for k for commonly used pesticides vary greatly between weakly adsorbed and strongly adsorbed. Most partition/sorption studies have concentrated on relatively volatile compounds with simple chemical structures; little work has been done on more complex molecules, such as synthetic pyrethroids. This probably reflects the tremendous difficulties involved in studying these compounds as they are highly lipophilic and adsorb strongly to the surfaces of almost any experimental apparatus [16].

Sorption is one of the key processes controlling the fate of synthetic pyrethroids, which are rapidly and strongly sorbed by soil organic matter, and pyrethroids discharged to water bodies are present mainly in the adsorbed state. Sorption–desorption processes of pyrethroids in soil systems have been studied using ^{14}C-labelled analogues [17–19].

The objectives of this study were, therefore, to develop an appropriate and simple method to quantify the sorption isotherm parameters n and k, to study the sorption–desorption of pyrethroids by different soils (with different organic matter contents) and silica, and to study the pH effect on sorption. Chemical analysis of the soil solution to determine its pyrethroid concentration was performed using GC/MS-NICI for analysis.

EXPERIMENTAL

Chemicals and Solvents

Permethrin [3-phenoxybenzyl-(1*R*,*S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate], cyfluthrin [(*R*,*S*)-α-cyano-4-fluoro-3-phenoxybenzyl-(1*R*,*S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate], cypermethrin [(*R*,*S*)-α-cyano-3-phenoxybenzyl-(1*R*,*S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate], deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl-(1*R*)-3-(2,2-dibromovinyl)-2,2-dimethyl-cyclopropane carboxylate], λ-cyhalothrin [(*S*)-α-cyano-3-phenoxybenzyl-(1*R*)-3-(2, chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropane carboxylate] and fenvalerate [(*R*,*S*)-α-cyano-3-phenoxybenzyl-(*R*,*S*)-2-(4-chlorophenyl)-3-methylbutyrate] were all purchased from Promochem UK. Mirex and decachlorobiphenyl (DCBP) were obtained from British Greyhound. HPLC-grade hexane, dichloromethane, methanol, acetone, ethyl acetate and anhydrous sodium sulphate were obtained from Fisons, Loughborough, UK. C-18 columns (500 mg 2.8 mL) were from Alltech Associates. Silica gel (60–120 mesh) was obtained from BDH Chemical Ltd, Poole, UK.

Soil Preparation

Soils were collected from different sites representing a range of physical properties. Subsamples of homogenized soils were analyzed for moisture content, organic matter content, particle size distribution (texture) and pH. To determine moisture content, soils were dried at 105°C until a constant weight was achieved and were then heated to 500°C for 6 h to oxidize volatile organic matter content. Particle size distributions were determined by dry sieving. The soil pH was measured. Clean soil was prepared as follows: approximately 50 g soil was extracted with 1:1 (v/v) acetone:DCM for 6 h using a Soxhlet apparatus. The soil was oven dried to remove the excess solvent, a small amount of deionized water (approximately 2.5% by weight) was added to the soil and the soil was tumbled so that it was thoroughly mixed. The properties of the soils used in this study are summarized in Table I.

GC/NICI-MS Analysis

Analyses of the standards and extracts obtained from soil were performed on a Hewlett-Packard 5890A GC interfaced to a VG Trio 1000 quadrupole mass spectrometer (Fisons Instruments, Wythenshawe, Manchester, UK) and equipped with a Hewlett-Packard autosampler, operating in electron impact (EI) and negative ion

TABLE I Soil properties

Soil type	*Texture, %*	*Organic content, %*	*Moisture content, %*	*pH*
A	Loam coarse 68; silt 24; clay 8	2.1	12.5	6.5
B	Clay loam, coarse > 40	2.46	15	7.2
C	Sand loam, coarse > 75; clay < 4	1.71	9	7.3
D	Clean soil from A	1.67	15	7.4
E	Clean soil from B	1.15	9	7.3

chemical ionization (NICI) modes employing full scan and selected ion monitoring or recording (SIM/SIR). A DB-5MS capillary column of dimensions, 25 m × 0.25 mm i.d. × 0.25 μm film thickness with a helium head pressure of 5 psi was used to achieve separation employing the following temperature programme: initial column temperature, 100°C, hold for 1 min, increase at 35°C min^{-1} to 240°C, then increase at 8°C min^{-1} to 300°C, final temperature hold for 2 min; the total cycle time was 15 min. All spectra were acquired in the NICI mode (SCAN and SIR). The general mass spectrometer conditions were: ion source 250°C; electron voltage 70 eV; photomultiplier voltage 450 V; filament and source currents 4.4 and 345 μA, respectively. When operating in scanning mode, the scanned mass range was 50–550 u in 0.9 s while in SIR mode, the mass span was 0.02 amu in 0.02 s. The voltages of the filter parameters for NICI were periodically optimized using the ion at *m/z* 452 generated from the calibration compound, perfluorotributylamine (PFTBA). The linearity and dynamic range of the GC-MS using the SIR or SCAN mode was demonstrated by generation of standard curves for each analyte containing four, five or six levels of concentration, analyzed in duplicate. Standard deviations were calculated from five replicate injections of the daily calibration standard at 0.5 ng μL^{-1}, using response factors generated from the regression statistics. The limit of detection (LOD) was calculated as three times the standard deviation and this was used to calculate the minimum detection limit (MDL) for each analyte. A stock solution was prepared from each certified pesticide at 100 mg L^{-1} concentration. From the stock solutions, working calibration standards were prepared with mixtures of the pyrethroids and mirex at varying concentrations in hexane with the volumetric standard (DCBP) concentration held constant at 50 μg L^{-1}. Spiking solutions consisted of a mixture of the pyrethroids and mirex in acetone at different concentrations. A solution of DCBP (50 μg L^{-1}) was prepared in hexane to be added at the end of the analytical work-up and to act as the volumetric standard for the pyrethroids.

Sorption of Pyrethroids on Soils [11,18]

Tests were performed in 50-mL flasks. Samples (5 g) of dried soils and silica were equilibrated with 30 mL of pyrethroids solution (concentration levels 0.25, 0.5, 0.75, 1.0 and 1.5 μg mL^{-1}). The samples were shaken on a Stuart mechanical shaker for 24 h. The suspensions were centrifuged at 3000 rpm for 10 min. Aliquots of clear supernatant were passed through C-18 columns. The eluates were concentrated to dryness before the volumetric standard was added. The analytes were then determined by GC/NICI-MS in either SIR or SCN mode. The 500-mg C-18 cartridge was activated and conditioned with 5 mL acetone, followed by 5 mL each of methanol and methanol–water (35% v/v). The samples were applied at a flow rate of approximately

10 mL min^{-1}. Once the sample had passed through, the cartridge was dried for approximately 15 min. The analytes were eluted with 3 × 2 mL of hexane–ethyl acetate, 1:1 v/v. The combined extracts were then concentrated by nitrogen blowdown [20]. Sorption isotherm parameters were calculated according to the Freundlich equation. Sorption onto the glass walls of the flasks was determined through the mass balance (see Results and Discussion section).

Desorption Studies

Desorption studies were conducted on the same pyrethroids and mirex solutions (0.25, 0.5, 0.75 and 1.0 μg mL^{-1}). After sorption, according to the sorption experiment, and centrifugation, supernatant was replaced with a similar volume of deionized water. Desorption was achieved by removing all the supernatant from the centrifuged samples and then replacing it with deionized water. This equilibration process was repeated five times. Each time the amount of pyrethroid that remained on soil was calculated as the difference between the initial amount and the desorbed amount. After the desorption steps, the flasks were allowed to dry for several days, then an extraction solvent was added (hexane : dichloromethane, 1 : 1 v/v, 20 ± 2 mL). The flasks were then submerged in an ultrasonic bath (Sonicor Instrument Corporation Copaique, NY) and sonicated for 30 min. The supernatant was decanted through a glass sinter (porosity 4) capped with anhydrous sodium sulphate (5 ± 1 g). The extraction procedure was repeated twice and the extracts combined. The extract was evaporated to about 5 mL by rotary evaporation under reduced pressure at 40°C, then transferred into a 15-mL conical vial with a 1-mL calibration mark, and evaporated just to dryness with a gentle stream of clean dry nitrogen. The residue was redissolved by adding 1 mL of volumetric standard DCBP. The final sample extracts were analyzed to determine the pyrethroid concentration using GC/MS-NICI [20,21].

RESULTS AND DISCUSSION

Representative NICI mass spectra and chromatograms for pyrethroids, mirex and DCBP have previously been reported [20–22]. Permethrin, fenvalerate and deltamethrin were totally resolved into two diastereoisomers while cyfluthrin and cypermethrin, which contain a third asymmetric centre, were partially resolved into envelopes of four and three diastereoisomers, respectively. *Cis* and *trans* isomers of permethrin and fenvalerate were quantified separately while the other pyrethroids were quantified using their base mass peak. In NICI mode using methane as the reagent gas, permethrin, cyfluthrin and cypermethrin, which are esters of dichlorovinylcyclopropane carboxylic acid (CPA), undergo dissociative electron capture to yield CPA$^-$ anions, for which m/z 207 is the primary quantitation ion and m/z 209 and 211 (two chlorine isotope pattern, 9 : 6 : 1) are used for diagnostic purposes. In spite of deltamethrin having a similar pyrethroid structure, the base ion is in the low-mass region at m/z 79 (81) resulting from the favoured fragmentation yielding Br$^-$ ions, where the ion background interference is greatest. The compound also has the characteristic ion at m/z 137 from the cyclopropane carboxylic acid unit after the loss of the two bromide ions, but the intensity ratio of m/z 79 (quantitation ion) to m/z 137 (diagnostic ion) is approximately 10 : 1. Fenvalerate undergoes similar dissociation to ion fragments at *m*/*z* 167 (169), the quantitation ion, and *m*/*z* 211 (213), the diagnostic ion, which correspond to the portion of the molecule containing the isopropyl group. For cyhalothrin the ion at *m*/*z* 241 arises from the splitting of the λ-cyhalothrin molecular anion to form the carboxylate ion. This is the base ion because of the inherent stability of the carboxylate ion, which supports the negative charge better than the molecular ion. The phenoxybenzyl moiety is undetected as a neutral fragment. Further loss of HCl from the base fragment ion *m*/*z* 241 yields the ion at *m*/*z* 205.

Sorption–Desorption Studies

The sorption of six pyrethroids and mirex is described by the Freundlich equation. The parameters *n* and *k* of the Freundlich sorption isotherms for soil A are given in Table II, which indicates that the values of *n* ranged from 0.906 to 1.046. The values of *n* for the adsorption of cyfluthrin, mirex, deltamethrin, and λ-cyhalothrin are less than one, while the values of *n* for the adsorption of cypermethrin, permethrin, and fenvalerate on the soil A are greater than one. The units of *k* are typically (mg organic sorbed/kg of solid) divided by (mg organic/L of water), or 1 L water/kg solid. Permethrin and cyfluthrin were the least sorbed pyrethroids, $k < 2$, mirex and fenvalerate the most. The value of *k* is considered to be characteristic of a given sorbate–sorbent system [23]. At present, it is not possible to compare *k* values in the literature since these parameters were derived from different units of C_w and C_s. Sorption in most surface water systems can be described by the Freundlich equation. For many pesticides at dilute concentrations (see Figs. 1 and 2) $1/n = 1.0$. Commonly, at low concentration, the values of *n* range from 0.7 to 1.2 [24].

The desorption sequence steps are summarized in Table III. Permethrin, cyfluthrin and cypermethrin were not detectable after two desorption steps, while mirex, deltamethrin, and λ-cyhalothrin desorbed after five steps. Fenvalerate was desorbed after four steps. In the case of soil A, permethrin, cyfluthrin, λ-cyhalothrin and fenvalerate were desorbed by 12–17%, while cypermethrin and mirex were desorbed by 4–7%; about 25% of deltamethrin was desorbed. The permethrin desorbed by about 8.28% after the first desorption step, the total desorption reaching 12.91% of an initial concentration of $1\,\mu g\,mL^{-1}$ after the second desorption step. The corresponding values for cyfluthrin and cypermethrin were 7.3 and 2.66% in the second desorption step and in total about 14.37 and 6.82% of the initial concentration. The desorbed amounts of λ-cyhalothrin, deltamethrin and mirex were 12.36, 24.35 and 4.68%, respectively,

TABLE II Freundlich parameters for pyrethroids and mirex in soil A

Compound	*Slope 1/n*	*n*	*k*
Cyfluthrin	1.1014	0.906	1.021
λ-Cyhalothrin	1.1000	0.909	7.603
Cypermethrin	0.9965	1.004	5.233
Deltamethrin	1.1000	0.909	2.443
Fenvalerate	0.9561	1.046	13.105
Permethrin	0.9927	1.007	1.874
Mirex	1.1018	0.907	12.705

RSD ± 2.5–4.6, $n = 3$.

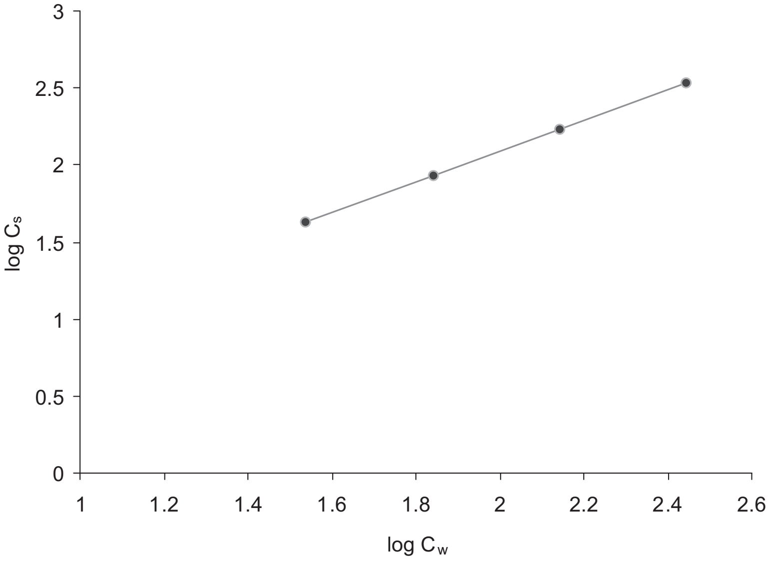

FIGURE 1 Sorption isotherm curve of cyfluthrin.

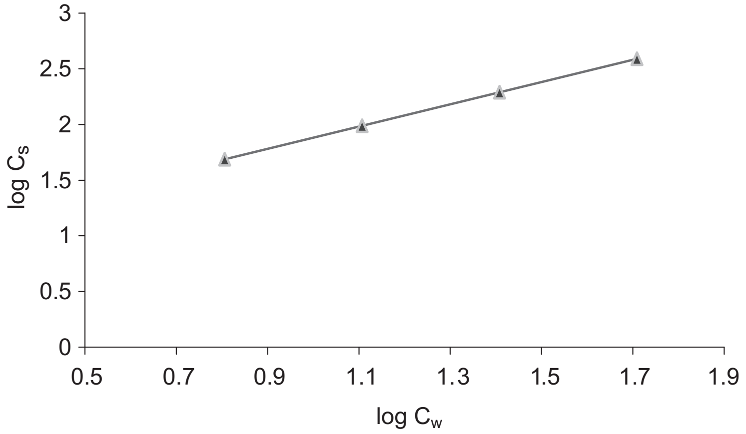

FIGURE 2 Sorption isotherm curve of cyhalothrin.

after the fifth desorption step. Fenvalerate desorbed by about 6.52% after the first, 4.34% in the second, the total reaching 10.86% of the initial concentration spiked, 16.19% of the total was desorbed after the fourth step.

Desorption steps observed in this experiment were related to the *k* values. The apparent *k* values of sorption of pyrethroids showed that the values for fenvalerate and mirex were larger by a factor of two than the values obtained from spiked soil for cypermethrin and λ-cyhalothrin, while the sorption distribution constants, *k*, for deltamethrin, permethrin and cyfluthrin were, respectively, about two, three or four orders of magnitude smaller than those for cypermethrin and λ-cyhalothrin. Desorption isotherms show hysteresis for cyfluthrin, cyhalothrin and deltamethrin,

TABLE III Desorption steps with sorption results for pyrethroids and mirex

Compound	*Desorption steps*, μg L^{-1} ± *RSD*, *n* = *3*					*Total*[a]	*Sorption*[b]
	*1st**	*2nd*	*3rd*	*4th*	*5th*		
Permethrin	82.80 ± 3.1	46.2 ± 3.8	–	–	–	0.1291 ± 3.45	0.834 ± 2.3
Cyfluthrin	70.70 ± 2.9	73.0 ± 4.1	–	–	–	0.1437 ± 3.5	0.858 ± 7.6
Cypermethrin	41.60 ± 2.6	26.6 ± 3.4	–	–	–	0.0682 ± 3.0	0.916 ± 4.8
λ-Cyhalothrin	88.00 ± 4.5	11.8 ± 3.6	07.8 ± 4.1	07.9 ± 4.3	08.2 ± 3.0	0.1236 ± 3.9	0.942 ± 5.6
Deltamethrin	74.30 ± 2.5	71.0 ± 2.7	95.0 ± 4.0	28.0 ± 2.9	13.0 ± 2.8	0.2613 ± 2.98	0.851 ± 7.4
Fenvalerate	65.20± 4.6	43.4 ± 4.4	29.9 ± 2.8	23.4 ± 3.7	–	0.1619 ± 3.87	0.869 ± 4.9
Mirex	10.90± 2.8	12.6 ± 2.5	09.2 ± 3.2	08.0± 2.9	06.1± 4.2	0.0468 ± 3.12	0.978 ± 4.5

[a] Total desorption steps (mg L^{-1}).
[b] Sorption (mg L^{-1}).
*Desorption steps (μg L^{-1}).

confirming that a redistribution process took place continuously through the desorption experimental period.

The overall recovery of added pyrethroids (aqueous + soil + glass-sorbed) were between 84 and 98% for all seven pesticides. The mass balance equation shows that

$$x = s + c + q$$

where x (μg) is the initial pyrethroid added to the soil, c is the aqueous concentration of analyte detected (total desorption steps, μg), s is the soil-sorbed pyrethroid and q is pyrethroid on glass walls. The sorption results are summarized in Table III. Calculations were performed by measuring the total pyrethroid sorbed on the soil using the sonication technique. The results showed that permethrin was the least sorbed (about 83.5% of 1 μgmL^{-1} applied), mirex the most (97.8%). The proportion of pyrethroids adsorbed on the apparatus walls was measured after the desorption steps. The results showed that an average of 48% (0.48 μg) of the pyrethroids applied on the four soils were adsorbed to the glass walls by the end of the experiments [18]. The results also showed that around 75% (0.75 μg) of the pyrethroids applied on silica were recovered from the surfaces of the experimental apparatus.

Effect of Organic Content on Pyrethroid Sorption

Other results of pyrethroid sorption on four soils of varying organic content indicate that sorption is associated with organic content. Sorption of pyrethroids and mirex was greater in soil B with high organic matter content (2.46%) than in soil A (2.1%). In the case of clean soils (D and E), sorption of pyrethroids was not significantly changed, compared to soils A and B. In the absence of an organic coating, pyrethroid sorption on silica was significantly decreased (see Figs. 3 and 4).

Adsorption is a surface phenomenon and is very much dependent on the surface area and the organic content of the adsorbent. Adsorption of pyrethroids was low on the pure mineral particles (silica). The sorptive capacity of all soils with different organic content were much higher than that of pure mineral particles, suggesting that pyrethroids had partitioned into the organic carbon phase rather than adsorbed onto

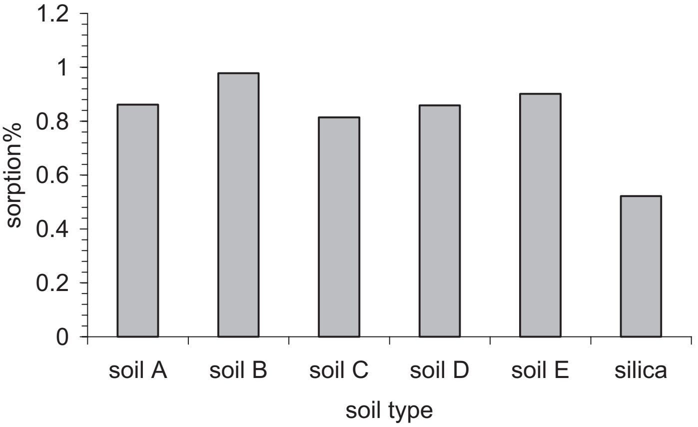

FIGURE 3 Sorption studies on different soils and silica.

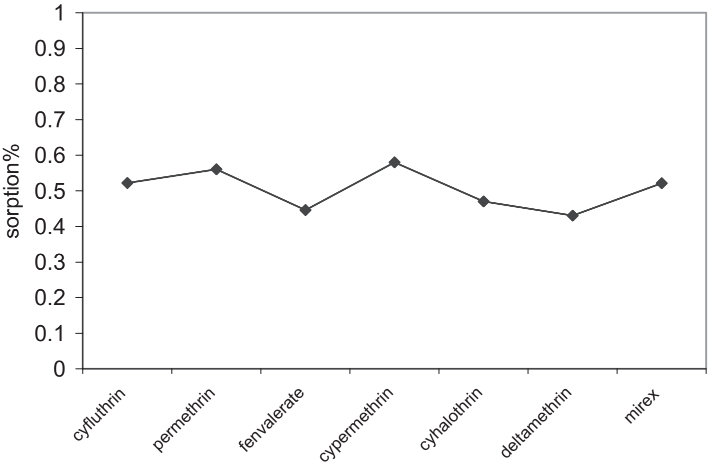

FIGURE 4 Sorption studies of pyrethroids and mirex on silica.

the particle surfaces [25,26]. The sorption of pyrethroids and mirex was a function of the organic carbon content for heterogeneous soil materials and their components.

Effect of pH on Sorption

The effect of the pH on sorption was examined by carrying out the same experiments as described earlier over a range of four different pH values. The pH of each sample was adjusted with HCl or NaOH to pH 2, 4, 6 or 9. The results showed that over this range, pH did not have a significant impact, although soil-sorbed pyrethroids and mirex concentrations at pH < 4 are slightly higher than at pH 9 (see Figs. 5 and 6).

Pyrethroids are examples of non-ionizable compounds. The experiments show a constant sorption of pyrethroids over the range of pH values tested. Thus, the results

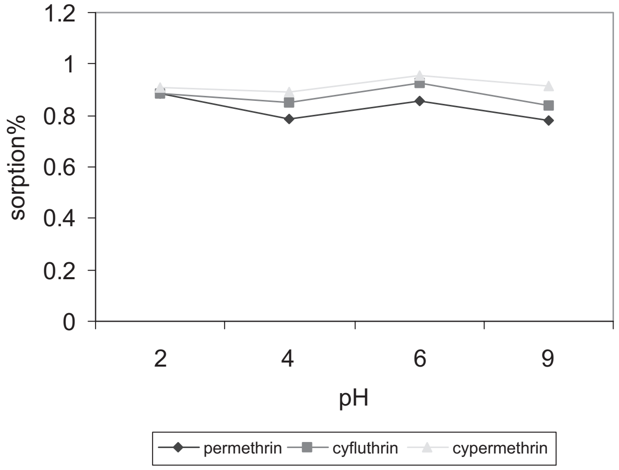

FIGURE 5 Effect of pH on sorption.

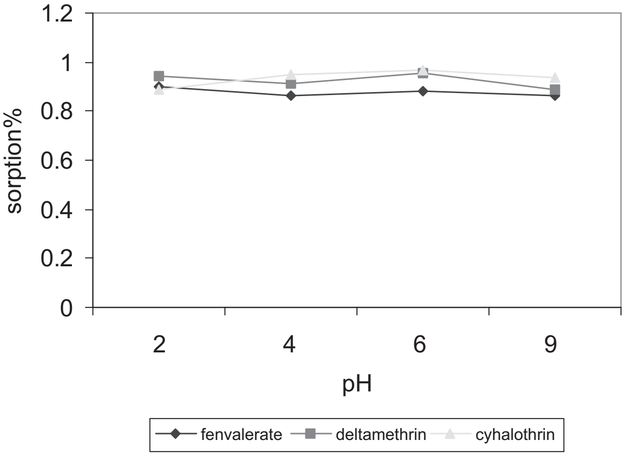

FIGURE 6 Effect of pH on sorption.

support the assumption that sorption is not significantly affected by changing pH, even though the charge density of soil organic matter might vary with pH [27].

CONCLUSIONS

An understanding of the sorption mechanism is fundamental to predicting the fate and distribution of many pyrethroid contaminants. Sorption measurements allow the evaluation of these pyrethroids in relation to their capacity to remain in the soil solution. The *n* and *k* constants for pyrethroid sorption on soil have been estimated. Results presented here show that the values of *n* are near unity. The close similarity in molecular structure of permethrin and cyfluthrin (esters of dichlorovinylcyclopropane carboxylic acid) may be responsible for the values of *k* being of similar magnitude, 1.876 for permethrin, 1.021 for cyfluthrin. Structural features, hydrophobicity, organic matter content of soil, and solubility are the main factors for the *k* values of other pyrethroids being significantly higher. In the desorption experiments, the solid-phase extraction technique allowed measurement of the aqueous phase concentrations, while in the sorption experiments, the ultrasonic extraction yielded information for the soil-sorbed concentrations. The experiments were designed to develop a reproducible and simple method suitable for the study of the sorption–desorption of pyrethroids from soil, which has largely been achieved.

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