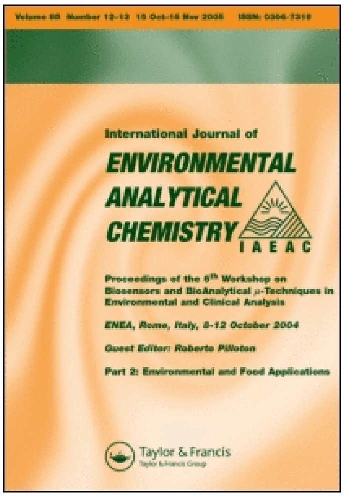

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Sorption of Cypermethrin Diastereoisomers to Quartz, Corundum, Goethite, Kaolinite and Montmorillonite

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SORPTION OF CYPERMETHRIN DIASTEREOISOMERS TO QUARTZ, CORUNDUM, GOETHITE, KAOLINITE AND MONTMORILLONITE

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Differential sorption and degradation of different pesticide stereoisomers in soil may result in accumulation of the most strongly sorbed and the slowest degradable isomers. In this work the pyrethroid cypermethrin (8 isomers) has been used for test of stereochemical interactions with surfaces of the minerals quartz, corundum, goethite, kaolinite and montmorillonite. The sorption of three diastereoisomeric fractions denoted *Cis* A, *Trans* C and *Cis* B + *Trans* D were quantified by use of GC-ECD in batch experiments with initial cypermethrin concentrations in the range 1–9 µg/L. Correction for cypermethrin sorbed to surfaces of the shaking flasks were accomplished to obtain net sorption isotherms for the minerals, all of which were well fitted by the Freundlich equation. Bonding affinities per unit surface area decreased in the order: corundum > quartz > kaolinite > montmorillonite > goethite. The isotherms for sorption of all diastereoisomeric fractions to quartz, corundum and goethite were all linear, whereas non-linear isotherms were found for sorption of *Cis* A and *Trans* C fractions to kaolinite and montmorillonite. Corundum, quartz and goethite showed a significantly stronger sorption of *Cis* A than the other fractions, while kaolinite sorbed *Cis* B + *Trans* D most strongly. The observed differences predict less leaching and slower degradation of the *Cis* A fraction in subsoils low in organic carbon.

Keywords: Chiral sorption; Cypermethrin; Diastereoisomers; Mineral surfaces; Gas chromatography

INTRODUCTION

Cypermethrin is a synthetic pyrethroid used against insects in agricultural crops at doses of 20–70 g a. i. /ha (Fig. 1). The highly hydrophobic character of this compound is reflected by its low solubility in water of 4–9 µg/L, an octanol–water partition coefficient (K_{ow}) of $10^{6.6}$, and an estimated partition coefficient normalised to organic carbon (K_{oc}) of 20×10^3 L/kg [1–4]. Pyrethroids are highly toxic to freshwater fish and to bees even at very low concentrations [5,6]. Moreover, pyrethroids when used as soil insecticides are not selective and may also kill beneficial soil microorganisms [7].

The hydrophobicity of cypermethrin causes strong sorption of the compound to soil particles, which makes the compound less bioavailable. This may retard

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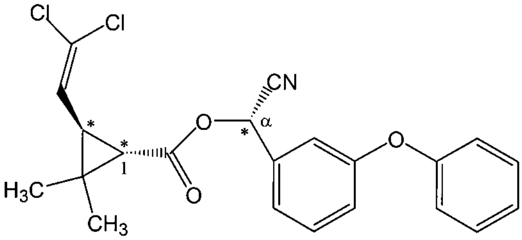

FIGURE 1 Molecular structure of cypermethrin [(*RS*)-α-cyano-3-phenoxybenzyl-(1*RS*, 3*RS*; 1*RS*, 3*SR*)-3 (2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate]. Chiral C atoms are marked with an asterisk.

degradation and cause build up of bound residues in soil and sediment with potential long-term effects on soil quality [8–14]. Formation of more polar and less strongly sorbed metabolites of cypermethrin may increase the transport of the metabolites to groundwater [15].

Retention by adsorption at solid/liquid interfaces depends on the structures and properties of both the sorbent and the solute [16], and on variables such as pH and temperature [17]. It is generally held that the principal sorbent for hydrophobic compounds in soils and sediments is the organic matter [18,19]. However, for soil and sediment materials low in organic carbon such as subsoils and aquifers, sorption to mineral surfaces may become important [20]. In such cases clay sized phyllosilicate and metal oxide particles are efficient natural adsorbents due to their large reactive surface areas [21]. The surfaces of clay minerals show large structural variations and they expose different types of active sites [17].

Technical standards of cypermethrin comprise a mixture of eight isomers owing to the three chiral centres in the molecule (cyclopropyl C-1 and C-3, and the benzylic carbon atom) (Fig. 1). In this paper a distinction is made between 4 diastereoisomeric groupings which are defined in the following way: *Cis* A = (1*R*-*cis*-α*R*; 1*S*-*cis*-α*S*), *Cis* B = (1*R*-*cis*-α*S*; 1*S*-*cis*-α*R*), *Trans* C = (1*R*-*trans*-α*R*; 1*S*-*trans*-α*S*), and *Trans* D = (1*R*-*trans*-α*S*; 1*S*-*trans*-α*R*). Stereoisomerism is an important factor influencing the reactivity of cypermethrin. For instance, only the 1*R*-*cis*-α*S* and 1*R*-*trans*-α*S* forms of the 8 stereoisomers are biologically active against target organisms, and furthermore degradation rates of cypermethrin may be different from one stereoisomer to another [22,23]. It appears that the trans cypermethrin isomers dissipate more quickly in soil than the cis isomers [12]. Other works consider that non-stereospecific hydrolysis and hydroxylation are the main initial pathways of cypermethrin transformation in soils and sediments [24]. Isomerization of cypermethrin (1*R*/1*S*, *cis*/*trans*), which so far has only been observed in aquatic systems [25–27], may stimulate degradation of otherwise slowly degraded isomers [12,28,29].

Stereospecific interactions between pesticide isomers and sorbent surfaces may result in some isomers being more strongly bound than others which may cause differences in the bioavailability and hence affect the rate of degradation of the different isomers. Thus, over time strongly bound stereoisomers may accumulate in soils and sediments. Stereospecific sorption has been observed for sorption of ortho- meta- and para-tricresyl phosphate isomers to kaolinite, alumina and montmorillonite [30]. *S*-enantiomers of two racemic herbicides mecoprop and dichloroprop have shown to be more persistent than the corresponding *R*-enantiomers in soils, an effect partly ascribed to preferential sorption of isomers [31].

There may be several reasons that stereoisomers interact differently with mineral surfaces. Diastereoisomers (i.e. stereoisomers not being mirror images of each other) normally show different physical properties such as solubility. Hence, it is also expected that they show different adsorption affinities. However, true chiral selectivity is observed when specific mineral surfaces show preference for one enantiomer over the other. For example, calcite ($CaCO_3$) crystals comprise mirror-related surfaces, which display chiral selectivity for D and L forms of asparatic acid [32]. In general any mineral with an asymmetric surface structure has the potential for enantioselective interaction and separation of racemic mixtures [32]. Hence, quartz, alumina, kaolinite and montmorillonite have the potential for chiral selectivity. The chiral minerals also promote asymmetric synthesis of chiral organic compounds [33–36].

The aims of the present work is to quantify the individual sorption of diastereoisomeric fractions of cypermethrin to typical mineral surfaces (quartz, corundum, goethite, kaolinite and montmorillonite), and to test if there is preferential sorption of one diastereoisomeric fraction over another. Batch sorption techniques have been used throughout and a technique for compensation of sorption to the surfaces of the shaking vessels used, is presented.

EXPERIMENTAL

Chemicals and Sorbents

Technical cypermethrin (91%) [(*RS*)-α-cyano-3-phenoxybenzyl-(1*RS*, 3*RS*; 1*RS*, 3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate] was obtained from Dr. Ehrenstorfer (Augsburg, Germany). The cis/trans ratio of isomers in cypermethrin is in the order of 40/60 [37], and the relative distribution of the three isomeric fractions of cypermethrin analysed in this study was 28/27/45 of *Cis* A/*Trans* C/ *Cis* B + *Trans* D determined using the GC-ECD method. It is assumed that the 9% impurities contained in the standard solution are more polar than cypermethrin because they are eluted first along the SPB-608 capillary column with retention times in most cases less than 12 min (Fig. 2). Therefore, the competition for limited sorption sites on the surfaces of minerals between the two components is expected to be weak. Fenvalerate [(*RS*)-α-cyano-phenoxybenzyl (*RS*)-α-isopropyl-4-chlorophenylacetate], Pestanal quality (99.9% purity) was obtained from Riedel-de Haën (Seelze, Germany) and used as internal standard. Stock solution of cypermethrin (1000 mg/L) was made by dissolving cypermethrin in *n*-hexane (Unisolv for organic trace analysis; Merck). Working solutions were obtained by appropriate dilutions and calibration plots for each of the three-diastereoisomeric fractions *Cis* A, *Trans* C and *Cis* B + *Trans* D were made. Anhydrous sodium sulphate from Riedel-de Haën (Seelze, Germany) was baked at 500°C for 6 h before use as a drying agent.

Corundum, α-Al_2O_3, powder, extra pure and calcined at 1300°C was obtained from Riedel–de Haën (Seelze, Germany). Quartz, SiO_2, fine granular, washed and calcined was from Merck. The clay minerals KGa-2 kaolinite (Warren, Georgia) and SWy-1 montmorillonite (Crook, Wyoming) were supplied by the Clay Mineral Society (Source Clay Minerals Repository) [38]. Goethite, α-FeOOH, (goethite) was synthesised according to the procedure of Schwertmann and Cornell [39]. Infrared (IR) spectroscopy and X-ray diffraction (XRD) were used to test identity, purity,

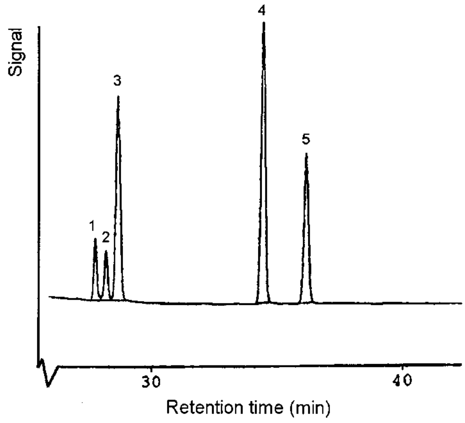

FIGURE 2 Example of GC-ECD chromatogram of hexane extract from sorption experiments. The peaks are identified as follows: 1–*Cis* A (0.028 µg/L); 2–*Trans* C (0.027 µg/L); 3–*Cis* B + *Trans* D (0.045 µg/L); 4 + 5–Internal standard of fenvalerate (two diastereoisomers).

and crystallinity of the sorbents. All minerals were found to be pure. The quartz and corundum were highly crystalline. Absence of trace organic carbon in the minerals was tested using an Eltra CS-500 carbon sulfur determinator analyser; no organic carbon was detected (< 0.002%). Specific surface areas as measured by the BET method (N_2 adsorption) were: quartz $0.10 \pm 0.01\,m^2/g$, corundum $0.17 \pm 0.01\,m^2/g$, goethite $31.6 \pm 0.3\,m^2/g$, montmorillonite $31.8 \pm 0.2\,m^2/g$, and kaolinite $23.5 \pm 0.1\,m^2/g$.

Recovery from Aqueous Solution

The recovery of the cypermethrin diastereoisomeric fractions *Cis* A, *Trans* C and *Cis* B + *Trans* D from aqueous solution was tested in the following way: A volume of 40 mL water spiked with technical cypermethrin at concentrations levels of 0.25, 0.5 and 2 µg/L where *Cis* A = 28%, *Trans* C = 27% and *Cis* B + *Trans* D = 45% of the above concentrations was placed in a 100 mL amber flask and extracted twice with 20 mL *n*-hexane for 15 mins. An adequate amount of fenvalerate internal standard was added to the solution at the beginning of the extraction procedure. The combined extracts were dried with anhydrous sodium sulphate (2 g) for 1 h. After filtration on a 13 mm, 0.2 µm RC filter (Lida, Denmark), the extract was evaporated to approximately 1 mL using a rotary vacuum evaporator. The final extract was adjusted to 1 mL and placed in 1.5 mL vial and the cypermethrin isomer concentrations determined by the GC-ECD method described below.

Sorption to Centrifuge Tubes

Sorption of cypermethrin to the walls of the glass centrifuge tubes used in the mineral sorption experiments is expected to be relatively strong and therefore has to be accounted for in the mineral sorption experiments [40]. Hence, in order to be able to compensate for the sorption to the centrifuge tubes, experiments were carried out to produce isotherms for sorption of cypermethrin diastereoisomers to the tube walls. Fifty millilitre capacity Pyrex quality glass centrifuge tubes furnished with

Teflon caps (Kebo Lab) were used in all sorption experiments. The inner surface area of the glass tubes was estimated to 89 cm^2.

Cypermethrin stock solution was pipetted onto the walls of each of 9 centrifuge tubes resulting in 9 different initial concentrations ranging between 1 and 9 μg/L in 40 mL of aqueous solution. After the hexane solvent had been removed by flushing with N_2, 40 mL of water were immediately added to each tube, which were then shaken horizontally in the dark for 24 h. It was found that the mean time to reach equilibrium was typically between 16 and 20 h. Therefore, we concluded that shaking for 24 h was sufficient to achieve equilibrium. Light was excluded to prevent photodegradation. The aqueous solution was discarded, the remaining water in the tubes evaporated by flushing with N_2 and the amount of cypermethrin diastereoisomers sorbed to the centrifuge tubes extracted two times with 10 mL *n*-hexane. After drying, filtration and upconcentration of the combined extract cypermethrin isomers were determined by GC-ECD. The experiments were carried out as triplicates at room temperature ($22 \pm 2°C$).

Two tests were carried out to ascertain that sorption of cypermethrin to the centrifuge tubes and sorption to clay particles are additive in sorption experiments with clay minerals (cf. Eq. (1) below).

Test I

In this test the amount of cypermethrin diastereoisomers sorbed to the centrifuge tubes in presence of goethite or kaolinite was quantified and compared with sorption of cypermethrin diastereoisomers to the centrifuge tubes in absence of added mineral (see above). The test was carried out as a comparison of sorption isotherms. For this purpose, 0.4 g of goethite or kaolinite was weighed to each of a series of centrifuge tubes, and 40 mL of aqueous solution containing increasing amounts of technical cypermethrin stock solution was added. The hexane solvent was removed by flushing with N_2. The centrifuge tubes were capped and shaken in the dark at room temperature for 24 h after which the suspensions were centrifuged at 1600 g for 20 min. The sorbent and supernatant were discarded and the glass tubes were dried by flushing with N_2. Cypermethrin diastereoisomers were then extracted twice from glass tubes using 10 mL *n*-hexane, the combined extract dried, filtrated, upconcentrated and finally quantified using the GC-ECD method described below.

Test II

In this test cypermethrin diastereoisomers sorption to minerals quantified by use of Eq. (1) (see below) was compared with the sorbed amounts determined by direct extraction of the minerals corundum or quartz. A similar procedure as in test I was followed until termination of the centrifugation step. Now, the supernatant was discarded and the sorbent was dried by flushing with N_2. Once dried the sorbent was transferred to a 10 mL centrifuge tube, and extracted twice with 6 mL of *n*-hexane in an ultrasonic bath. After drying, filtration and evaporation of the combined extracts cypermethrin diastereoisomers concentrations were quantified using the GC-ECD method described below.

Sorption Experiments with Minerals

The sorption isotherms for bonding of cypermethrin diastereoisomers to the different minerals were determined in sorption experiments using 9 different initial concentrations in the range from 1 to 9 µg/L in 40 mL water where the concentrations of *Cis* A, *Trans* C and *Cis* B + *Trans* D are equal to 28, 27 and 45% of the total concentrations, respectively. Sorbent amounts of 0.4 g were weighed to each of a series of centrifuge tubes followed by addition of 40 mL of aqueous cypermethrin solutions. The hexane solvent in the aqueous solution was removed by flushing with N_2 for 5 min. The centrifuge tubes were capped and shaken in the dark at room temperature for 24 h. After equilibrium, the suspensions were centrifuged at 1600 g for 20 min. Then the supernatant was transferred to a 100 mL amber flask, an appropriate amount of the internal standard added, and extracted twice with 20 mL *n*-hexane for 15 min. The hexane phases were combined and dried with anhydrous sodium sulphate (2 g) for 1 h and filtered using a 13 mm, 0.2 µm RC filter. The extract was evaporated to approximately 1 mL using a rotary vacuum evaporator at 30°C. The final extract was adjusted to 1 mL and placed in 1.5 mL vial and the cypermethrin diastereoisomer concentrations quantified using the GC-ECD method described below. Three replicates of each level of concentration were made.

The mass of diastereoisomers sorbed by the minerals (M_{Min}) was calculated according to the following formula:

$$M_{\mathrm{Min}} = M_{\mathrm{Init}} - (M_{\mathrm{Sol}} + M_{\mathrm{Tubes}}) \tag{1}$$

where M_{Init} denotes the initial mass of sorbate added to solution, M_{Sol} the mass of sorbate remaining in solution at equilibrium, and M_{Tubes} the mass of sorbate sorbed to the centrifuge tubes at a specified equilibrium solution concentration. In praxis M_{Tubes} were calculated from the expressions fitting the sorption isotherms of the centrifuge tubes.

Gas Chromatographic Analysis

The gas chromatographic determinations were carried out using a Shimadzu Model GC-17A equipped with ^{63}Ni Electron Capture detector ECD-17 ver. 2 system operated at 300°C and a current intensity of 1 nA. The GC was connected with a Shimadzu Model AOC-20i auto-sampler equipped with a split-splitless injector operated in the splitless mode (270°C, 60 s, 0.5 µL). Nitrogen (99.999% purity) was used as carrier and make-up gas with flows of 1.4 and 12 mL/min, respectively. A Supelco SPB-608 fused silica capillary column 30 m × 0.25 mm with a 0.25 µm film thickness was used. Separation of diastereoisomeric fractions were achieved with the following oven temperature programme: 90°C, hold 1 min; 25°C/min to 250°C, hold 1 min; 5°C/min to 270°C, hold 20 min. By this method three peaks with retention times of approximately 27.7, 28.2 and 28.6 min were obtained (Fig. 2). In correspondence with previous GC work on cypermethrin [41,42] the first peak was assigned to *Cis* A, the second peak to *Trans* C and the third peak to *Cis* B + *Trans* D mixture. Hence, the GC method allows for distinction of three-diastereoisomeric fractions. Standard curves covering the concentration range from 0.03 to 100 µg/L were prepared for the three fractions by plotting the integrated area of the corresponding peak divided by the integrated area of the internal standard *vs*. the concentration of the isomeric fraction.

The cypermethrin standard contained about 9% impurities. These impurities are observed in Fig. 2 at retention times up to 12 min. As the impurities are more polar than cypermethrin and no decrease was observed in the concentrations of the "impurity peaks" for the solution analysed after sorption it is assumed that sorption competition with the cypermethrin isomers is insignificant.

Statistical Analysis

Analysis of variance was performed using a generalised linear model (GLM) at the $p < 0.05$ level (SAS Institute, 1999). The isotherms for sorption of the different diastereomeric fractions to the same mineral were compared by least squares analysis of the logarithmic form of the Freundlich equation fitting the sorption isotherms. The model used consisted in presenting the amount of isomer sorbed to a mineral as a function of its concentration in solution, the type of isomer fraction (*Cis* A, *Trans* C or *Cis* B + *Trans* D), plus the interaction of the concentration in solution with the isomer fraction.

RESULTS AND DISCUSSION

Recoveries of Cypermethrin Diastereoisomers from Aqueous Solution

Liquid–liquid extraction using hexane as the organic solvent proved to be an efficient and reproducible method for the extraction and determination of cypermethrin diastereoisomers in aqueous solution (Table I). Using this method, recoveries of all diastereoisomers from aqueous samples were higher than 95% with a standard deviation lower than 2.9%.

Sorption to Centrifuge Tubes and Sorption Tests

The sorption isotherms of the three cypermethrin diastereoisomeric fractions are linear within the concentration range tested, indicating constant partitioning between the aqueous solution and the surfaces of the centrifuge tubes. The sorption affinity constant K_a is here defined as the ratio between the amounts of cypermethrin sorbed per unit glass surface (μg/cm^2) and the equilibrium concentration of sorbate in water solution (μg/cm^3); K_a is determined as the slope of the regression lines in Fig. 3. The values

TABLE I Mean recovery values of cypermethrin diastereoisomers from aqueous solution spiked at three concentration levels

Cypermethrin diastereoisomers	*Spiking levels* μg/L	*Recovery* (%) ($n = 6$)	
		Mean	*STDev*
Cis A	0.07	95.2	2.9
	0.14	96.2	1.6
	0.56	97.4	1.6
Trans C	0.07	97.7	1.9
	0.13	97.6	1.4
	0.53	97.1	1.3
Cis B + *Trans* D	0.11	97.2	1.3
	0.23	97.1	1.2
	0.91	96.8	0.9

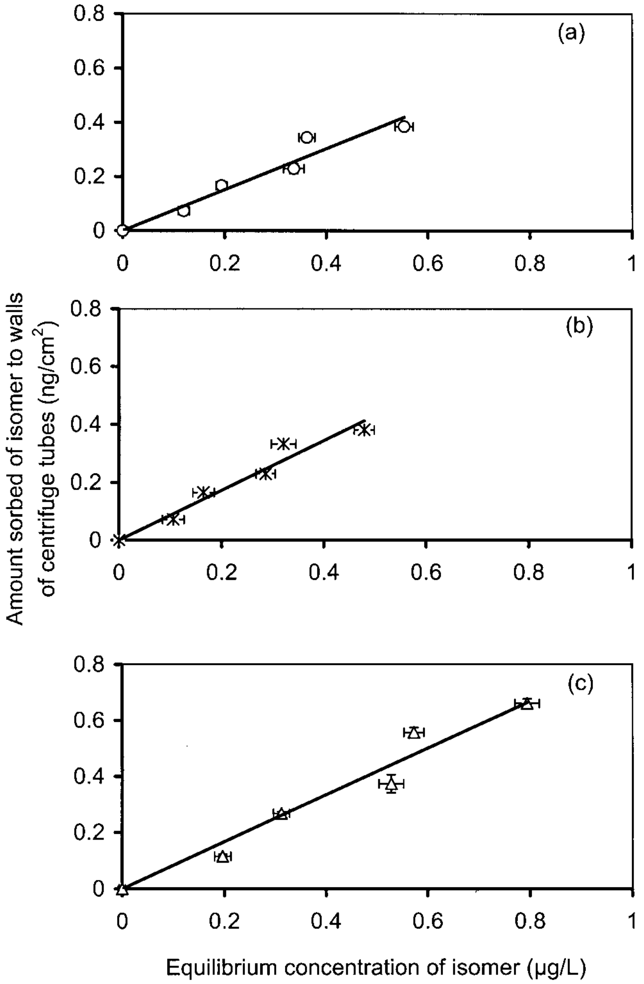

FIGURE 3 Isotherms for bonding of diastereoisomers to centrifuge tubes: (a) *Cis* A, (b) *Trans* C and (c) *Cis* B + *Trans* D. Straight lines are due to regression analysis with *Cis* $A_{sorbed} = 0.76$ *Cis* $A_{solution}$ ($R^2 = 0.92$); *Trans* $C_{sorbed} = 0.86$ *Trans* $C_{solution}$($R^2 = 0.94$); (*Cis* B + *Trans* D)$_{sorbed} = 0.83$ (*Cis* B + *Trans* D)$_{solution}$ ($R^2 = 0.96$). Error bars represent standard deviations.

of K_a (cm) for the three-diastereomeric fractions are: K_a(*Cis* A) = 0.76 ± 0.2 cm, K_a (*Trans* C) = 0.86 ± 0.2 cm and K_a (*Cis* B + *Trans* D) = 0.83 ± 0.2 cm. The diastereoisomeric fractions have equal bonding affinities as the K_a values are not significantly different at the $p < 0.05$ level. These K_a values are close to those reported previously by Zhou *et al.* [40], for lambda-cyhalothrin (0.82 cm) and tefluthrin (0.88 cm) pyrethroid analogues of cypermethrin.

From these experiments it is clear that sorption of cypermethrin isomers to the centrifuge tubes is important and should be taken into consideration when carrying out sorption batch experiments with the mineral sorbents. For the three-diastereoisomeric fractions, the retention to the centrifuge tubes is relatively high with sorption of approximately 30–50% of the amounts initially added. Similar results have been reported by House and Ziqing [43] and Hinckley and Bidleman [44] for pyrethroids like permethrin and fenvalerate where up to half of the initially added amounts were sorbed to glass tubes in the concentration range of 0.01–0.07 μg/L.

The validity of using Eq. (1) for calculation of cypermethrin sorption to minerals was evaluated in two test experiments. In test I the sorption of cypermethrin diastereoisomers to the centrifuge tubes was determined in presence or absence of goethite or kaolinite. Almost similar isotherms for the sorption of the *Cis* B + *Trans* D fraction to the centrifuge tubes was obtained irrespective of the presence of goethite (Fig. 4a). Similar results were found with the other isomeric fractions and in the experiments with kaolinite (data not shown). These results demonstrate that cypermethrin sorption to centrifuge tubes determined in absence of added mineral can be used to estimate sorption to centrifuge tubes when mineral sorbents are present, and hence that Eq. (1) can be used for calculation of sorption to minerals. The slightly higher amount of cypermethrin sorbed in presence of mineral can be explained by cypermethrin sorption to mineral particles adhering to the centrifuge tubes which are then coextracted with the centrifuge tubes.

In test II the sorption of cypermethrin diastereoisomers to corundum or quartz found by use of Eq. (1) was compared with cypermethrin sorption determined by direct extraction of the sorbents; an example is shown for sorption of *Cis* B + *Trans* D to

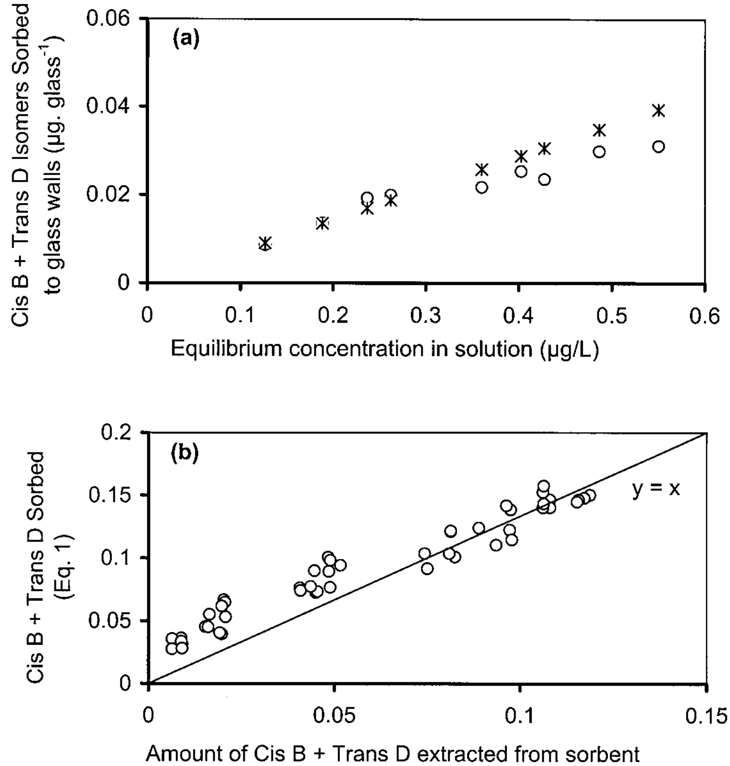

FIGURE 4 Tests of the validity of Eq. (1). (a) Test I: Comparison of the amount of cypermethrin (*Cis* B + *Trans* D fraction) sorbed to centrifuge tubes in presence (*o*) and absence (*x*) of goethite. (b) Test II: Comparison of the amount of cypermethrin (*Cis* B + *Trans* D fraction) sorbed to corundum calculated by use of Eq. (1) with the amount of the same cypermethrin fraction determined by direct extraction of the mineral.

corundum in Fig. 4b. Except at low concentrations the sorbed amounts found by the two methods are almost equal; a similar result was obtained for the other isomeric fractions and with quartz as the sorbent (data not shown). This again is a proof of the validity of Eq. (1) for compensation of the amounts of cypermethrin sorbed to the centrifuge tubes. The slightly lower values for cypermethrin sorption found in direct extraction is probably an effect of mineral particles adhering to the surfaces of the centrifuge tubes, a similar effect as observed in test I. In conclusion the two test experiments justifies the use of Eq. (1) for calculation of cypermethrin sorption. Hence, this method has been used in all further sorption experiments.

Sorption Isotherms of Cypermethrin Diastereoisomers to Mineral Sorbents

Sorption isotherms for bonding of diastereoisomers to quartz, corundum, goethite, kaolinite and montmorillonite were produced. The sorption data of the diastereoisomeric fractions were fitted by the Freundlich equation:

$$Q_{\mathrm{eq}} = K_F C_{\mathrm{eq}}^{n} \tag{2}$$

where Q_{eq} is the quantity of sorbate retained per unit mass of sorbent (μg/g), C_{eq} is the equilibrium concentration of the sorbate in aqueous solution (μg/L), and K_F and n are empirical constants. The exponent, n is dimensionless and is a measure of the non-linearity involved, whereas the Freundlich constant K_F is related to the affinity of bonding.

All five minerals sorbed the cypermethrin diastereoisomers. The sorption isotherms of diastereoisomers to goethite and kaolinite are presented as examples in Figs. 5 and 6, respectively. The Freundlich parameters and regression coefficients of the different diastereoisomers with corundum, quartz and goethite are presented in Table II, while those for kaolinite and montmorillonite are listed in Table III. Sorption isotherms describing sorption of the three diastereoisomeric fractions to quartz, corundum and goethite were found to be almost linear since the exponent n was close to 1. For the clay phyllosilicates kaolinite and montmorillonite sorption isotherms were linear for the *Cis* B + *Trans* D fraction whereas non-linear isotherms were observed for sorption of the *Cis* A and *Trans* C fractions (Figs. 6a and b). When the sorption isotherms of the different diastereoisomeric fractions are compared, it is clear that the sorption to quartz, corundum and goethite is lower than the sorption to montmorillonite and kaolinite on a mass basis. Among the first three minerals corundum and goethite show a significantly stronger sorption of all isomer fractions than quartz (Table II).

Adsorption is highly dependent on the surface area of the sorbent. Hence, another way to compare the adsorption properties of the different minerals is to compare the Freundlich affinity constants, K_F^s, after they have been normalised to specific surface areas (Tables II and III). The K_F^s values of the three diastereoisomer fractions varied in the following order: corundum > quartz > kaolinite > montmorillonite > goethite. Although goethite, kaolinite and montmorillonite have higher affinity constants than corundum and quartz on a mass basis, their sorption affinities on a specific surface area basis are lower.

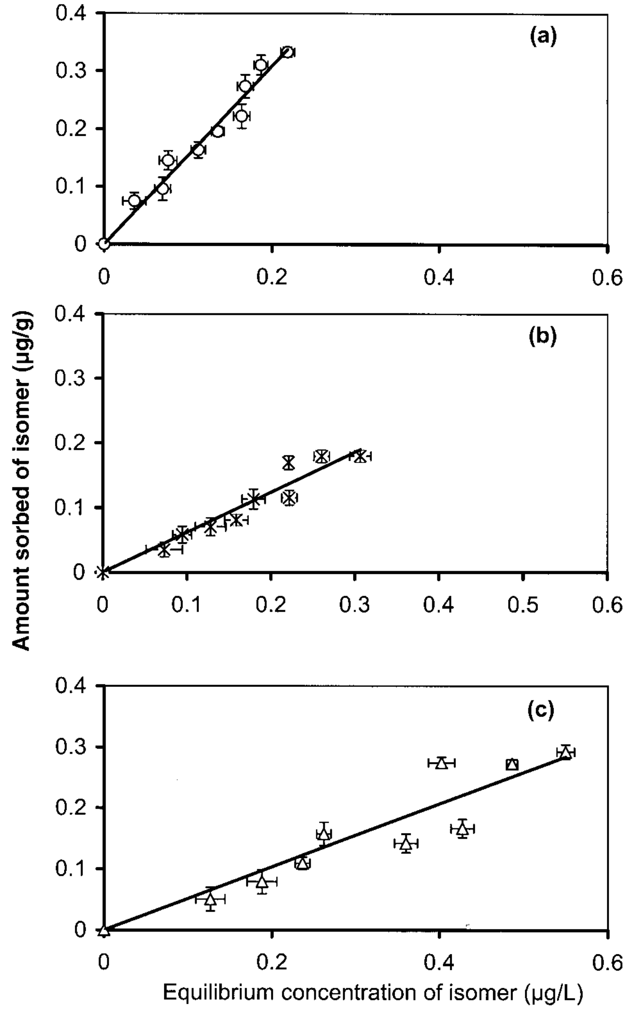

FIGURE 5 Isotherms for sorption of the diastereoisomeric fractions: (a) *Cis* A, (b) *Trans* C, and (c) *Cis* B + *Trans* D to goethite. Error bars represent standard deviations.

Stereospecific Sorption

Differences with respect to sorption of the diastereoisomeric fractions appear from Figs. 5–7 and the Freundlich constants listed in Tables II and III. Figure 7 shows the sorption capacity per unit surface area of the different minerals for the three-diastereoisomer fractions at a fixed equilibrium concentration of 0.2 μg/L. The minerals quartz, corundum, goethite and montmorillonite show a significantly stronger sorption of *Cis* A than the two other fractions. Meanwhile, kaolinite shows stronger sorption of *Trans* C than the two other fractions. The only sorbent which shows stronger sorption of *Cis* B + *Trans* D fraction than the *Trans* C fraction is corundum. The selectivity pattern shown in Fig. 7 also appears from the K_F^S values which varied in the order *Cis* A > *Cis* B + *Trans* D > *Trans* C for all minerals except kaolinite.

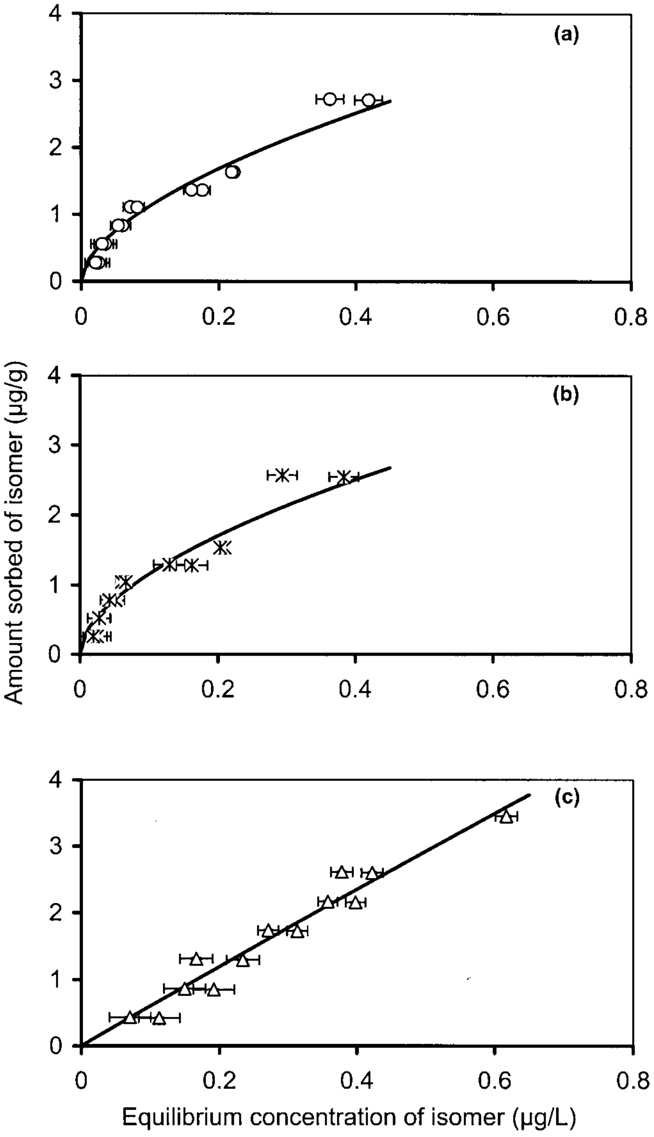

FIGURE 6 Isotherms for sorption of the diastereoisomeric fractions: (a) *Cis* A, (b) *Trans* C, and (c) *Cis* B + *Trans* D to kaolinite. Error bars represent standard deviations.

As mentioned previously the sorption of the different diastereoisomers to quartz, corundum and kaolinite is linear ($n \approx 1$). However, for montmorillonite and kaolinite the sorption isotherms for *Cis* A and for *Trans* C are both curved ($0.56 < n < 0.70$) (Table III). For both *Cis* A and *Trans* C the sorption affinity at low concentrations is considerably higher than for *Cis* B + *Trans* D, whereas at higher concentrations the sorption affinities are almost equal. This indicates the possible presence of a limited number of high affinity sites for *Cis* A and *Trans* C isomers.

TABLE II Parameters for Freundlich isotherms fitted to sorption of cypermethrin on quartz, corundum and goethite

Cypermethrin diastereoisomers	*Quartz*				*Corundum*				*Goethite*			
	$^{a}K_F^m$	$^{b}K_F^s$	^{c}n	$^{d}R^2$	$^{a}K_F^m$	$^{b}K_F^s$	^{c}n	$^{d}R^2$	$^{a}K_F^m$	$^{b}K_F^s$	^{c}n	$^{d}R^2$
Cis A^{e}	0.16^1	1.68^1	0.91^1	0.98	0.63^1	3.73^1	1.1	0.95	1.51^1	0.05^1	0.97	0.97
Trans C^{e}	0.12	1.18	1	0.93	0.34^2	2.01^2	1.06	0.96	0.59^2	0.02	1.04	0.96
Cis B + *Trans* D^{e}	0.12	1.20	1.03	0.91	0.55	3.25	1.1	0.95	0.48	0.02	1	0.97

$^{a}K_F^m$: Freundlich constant per unit mass with solution concentration and sorbed amount in units of µg/L and µg/g, respectively.

$^{b}K_F^s$: Freundlich constants normalised to specific surface area with solution concentration and sorbed amount in units of µg/L and µg/m^2, respectively.

^{c}n: Exponent in Freundlich equation.

$^{d}R^2$: Correlation coefficient corresponding to regression analysis of Freundlich equation using the logarithmic function when calculating the constants K_F and n values.

^{e}For each mineral diasteromeric sorption parameters are significantly different ($p < 0.05$) when parameter values are marked with different arabic numerals in superscript.

TABLE III Parameters for Freundlich fitted to sorption of cypermethrin on kaolinite and montmorillonite

Cypermethrin diastereoisomers	*Montmorillonite*				*Kaolinite*			
	$^{a}K_F^m$	$^{b}K_F^s$	^{c}n	$^{d}R^2$	$^{a}K_F^m$	$^{b}K_F^s$	^{c}n	$^{d}R^2$
Cis A^{e}	2.54^1	0.08^1	0.7	0.92	4.28	0.18	0.58	0.96
Trans C^{e}	2.26	0.07	0.69	0.94	4.17	0.18	0.56	0.95
Cis B + *Trans* D^{e}	2.29	0.07	1.02^1	0.97	5.75^1	0.24^1	0.98^1	0.95

Footnotes: See Table II.

There is no simple explanation of the observed differences with respect to sorption of the different isomers. The fact that resolution of three-diastereoisomeric fractions is possible with GC using an ordinary non-chiral column (sequence of separation *Cis* A, *Trans* C, *Cis* B + *Trans* D) demonstrates that the diastereoisomeric fractions have different physical properties such as solubility and boiling points. Such differences in physical properties may also be the reason that the diastereoisomers are not sorbed to the same extent by the mineral surfaces. However, where the *Cis* A fraction is first eluted and hence most loosely sorbed to the GC column, the same fraction is generally the most strongly sorbed to mineral surfaces. A likely explanation is that *Cis* A is the diastereoisomeric fraction with the highest polarity; it sorbs most weakly to the nonpolar coatings of the GC column but most strongly to the polar surfaces of the minerals. This does not explain the more subtle differences observed between diastereoisomer sorptions, e.g. the relatively strong sorption of the *Cis* B + *Trans* D fraction to corundum or the relatively strong sorption of *Trans* C to kaolinite. As all minerals used may contain acentric surfaces [32–36] it is not possible to exclude that chiral interactions are taking place. E.g. the strong sorption of *Trans* C to kaolinite may be due to specific chiral sorption of the 1R-trans-αR or 1S-trans-αS or both to kaolinite surfaces. Use of chiral LC or GC columns which can separate all eight isomers is necessary for clarifying this point. The curved sorption isotherms observed for bonding of *Cis* A and *Trans* C to montmorillonite and kaolinite and in particular the high sorption affinities at low solution concentrations (Figs. 6a and b), also is an indication of specific steric interactions taking place at a limited number of sorption sites.

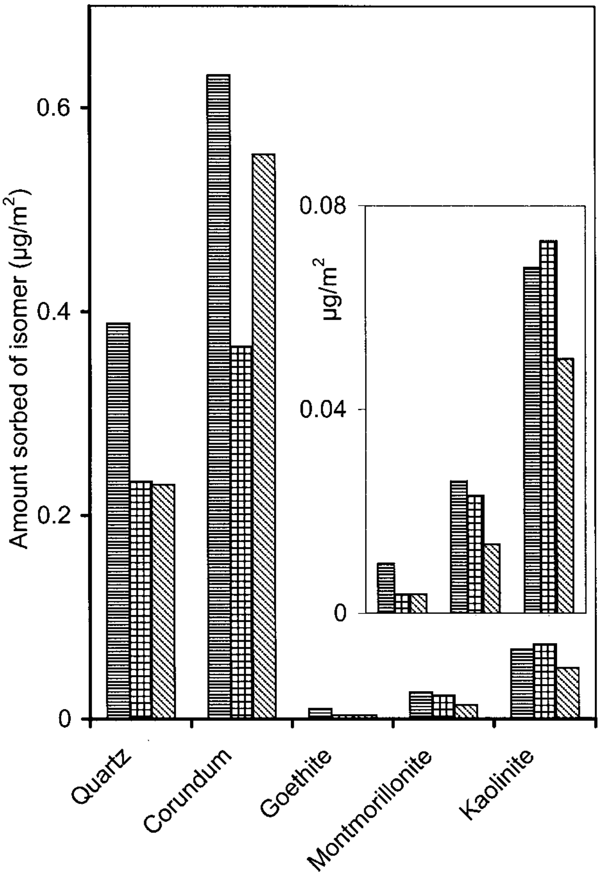

FIGURE 7 Sorption capacities of the 5 minerals for the three-diastereomeric fractions at a fixed equilibrium concentration of 0.2 µg/L calculated using the Freundlich constants in Tables II and III. ▤ *Cis* A, ⊞ *Trans* C, and ▧ *Cis* B + *Trans* D.

Implications

For corundum, quartz and goethite sorption isotherms are linear within the concentration range studied ($n \approx 1$). Such linear isotherms demonstrate that the adsorptive capacity of the minerals is not saturated; the linear adsorption isotherm is consistent with hydrophobic sorption as the sorption reaction taking place [40]. This behaviour is similar to that reported by Zhou *et al.* [40], in a study of pyrethroid sorption to clay minerals, in which all sorption isotherms of pyrethroids were also linear.

The high adsorption affinity of *Cis* A diastereoisomers in particular at low solution concentrations will reduce their concentration in solution in subsoils with high contents of fine textured quartz, goethite or montmorillonite. Consequently, this bonding may reduce the bioavailability of these isomers, which will reduce their rate of degradation. Hence, based on our data a relative accumulation of *Cis* A isomers in soils may be expected. On the contrary, the more weakly sorbed isomers such as the *Cis* B + *Trans* D fraction will sorb less and may be expected to dissipate more quickly if not constrained due to steric effects during biodegradation.

Sakata *et al.* [45], have reported in a study applied to two Japanese upland soils at 25°C with ^{14}C-labelled cypermethrin isomers, that the degradation rate of trans isomers is faster than the cis isomers. This might be attributed to a stronger adsorption of cis than trans isomers [46], in agreement with our findings. Our data for sorption affinities of the different diastereoisomers are not very different (Tables II and III; Fig. 7), which may point to only smaller differences in fate of the different isomers in soils. However, it is possible that more pronounced differences between cypermethrin stereoisomers had been discovered if we had quantified the sorption of all 8 isomers. It may happen that opposing effects (e.g. strong and weak sorption) of two stereoisomers in a diastereoisomeric fraction may blur the true differences in sorption behaviour between separate stereoisomers.

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