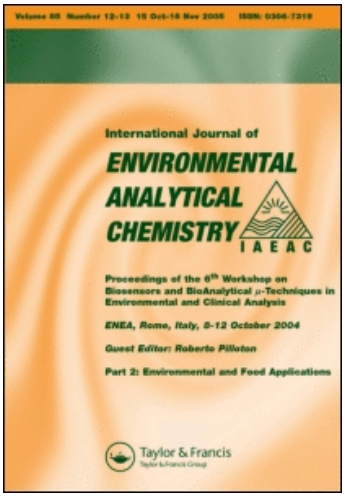

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HPLC METHOD WITH ON-LINE SPE PRECONCENTRATION FOR QUANTIFICATION OF PERMETHRIC ACID SORPTION TO GOETHITE

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Pesticide metabolites are often found to be more mobile in soil than their parent compounds. Pyrethroids are bound strongly to soil and therefore sorption of the pyrethroid metabolite permethric acid (PA) to a typical soil sorbent, goethite, was investigated. An on-line solid-phase extraction (SPE)-HPLC-UV procedure was developed for quantification of *trans*- and *cis*-permethric acid in aqueous samples. Limits of detection (LOD) were 500 times lower than those obtained with conventional HPLC-UV, resulting in LODs of 1.4 and 0.3 nM for the *trans*- and *cis*-isomers, respectively. Sorption of nanomolar concentrations of PA to goethite was found to be specific up to less than 1% surface coverage. In this range the data was described by a Langmuir equation with $K_{ads} = 7.1 \times 10^{-9}$ L/mol and $\Gamma_{max} = 7.1 \times 10^{-9}$ mol/m^2 for total PA (trans + cis) cis) at pH = 3. $K_{ads,cis}$ (1.4×10^6 L/mol) was approximately twice $K_{ads,trans}$ (7.9×10^5 L/mol). At higher PA concentrations the slope of the sorption isotherm increased, which is ascribed to hydrophobic interactions between adsorbed and dissolved PA molecules. Based on comparison with reported K_{om} values, metal oxides are expected to have a relatively greater significance to the retention of PA than soil organic matter.

Keywords: Permethric acid; Online-SPE; HPLC; Goethite; Isotherm; Sorption

INTRODUCTION

The degradation of pesticides often produces metabolites that are more soluble in water and hence more mobile in soil than the parent compounds [1]. Several pesticide metabolites can be found in the groundwater [1], and some of them are also more toxic to non-target organisms than their parent compounds [2].

Permethric acid (PA) is one of two primary metabolites of several pyrethroids, e.g., cypermethrin and permethrin (Fig. 1, Table I). Pyrethroids are widely used, potent non-specific insecticides. Pyrethroids are known to have a very low mammalian toxicity and to be toxic to only a few beneficial terrestrial organisms such as honey bees [7,8]. They

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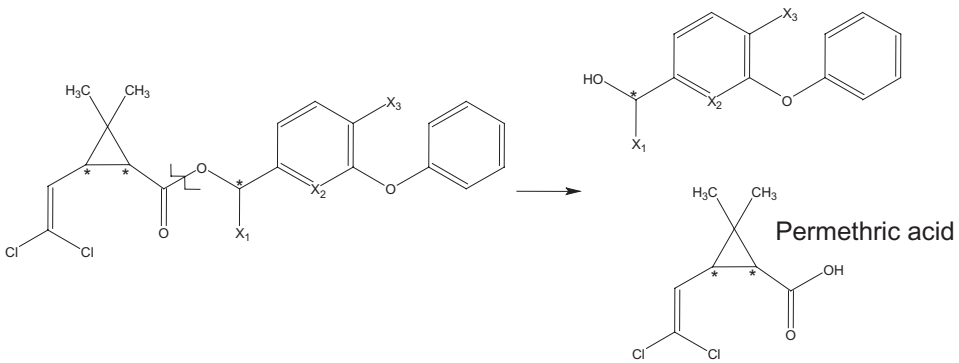

FIGURE 1 General representation of the chemical structure of PA-based pyrethroids and their two primary metabolites. ⋆ denotes a chiral carbon. Cypermethrin: $X_1 = CN$, $X_2 = C$, $X_3 = H$; permethrin: $X_1 = X_3 = H$, $X_2 = C$; fenpyrithrin: $X_1 = CN$, $X_2 = N$, $X_3 = H$; cyfluthrin: $X_1 = CN$, $X_2 = C$, $X_3 = F$.

TABLE I Physicochemical parameters for permethric acid and parent compounds

Compound	*Systematic name*	*pKa*	*log* K_{ow}[a] (L/L)	*log* K_{om}[b] (L/kg)
Permethric acid (PA)	3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid	5.02[c]	pH $\leq 4 : 2.5$[d] pH $\geq 7 : \leq 0.5$[d]	pH $\leq 4 : 3$ pH $\geq 7 : \leq 0.7$
Cypermethrin	α-cyano-3-phenoxybenzyl (2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate	–	6.6[e]	5.4
Permethrin	3-phenoxybenzyl (2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate	–	6.1[e]	5

[a]Partition coefficient between octanol and water.
[b]Partition coefficient between organic matter and water; estimated values based on linear free energy relationships (LFER) [3].
[c]Data from ref. [4].
[d]Data from ref. [5].
[e]Data from ref. [6].

are also rather toxic to fish but sorb strongly to soil and are generally not expected to be introduced into water bodies by leaching from soil [7,9]. PA is the primary product of hydrolytic, photolytic and enzymatic degradation of the parent compounds; further mineralization of the acid in soil can be relatively slow, particularly at low temperatures or under anaerobic conditions [10–12]. PA is also far more stable in solution and when exposed to light than the parent compounds [13,14]. In addition, the higher polarity of PA compared with the parent compounds is expected to make this compound more mobile in soil and more susceptible to leaching [9]. Investigations of metabolite toxicity are scarce but in three out of six investigations PA had a greater effect than permethrin or cypermethrin on non-target organisms or receptors. These were human androgen receptors in yeasts [15], mice [16] and soil fungi [17], whereas the effect on algae [18], fish [7] and *Daphnia magna* [7] were the same or less than those of the parent compounds. Hence, the formation of PA may affect soil organisms.

The increased polarity of PA compared to the parent compounds renders it likely that PA may sorb to soil minerals, e.g. phyllosilicates and in particular metal oxides, by surface complexation. Goethite (α-FeOOH) is an iron oxide abundant in most soil types and has a large reactive surface area, which makes it widely applied as a

model substance in investigations of the sorption of polar and ionic substances [19]. Since the sorption of the pyrethroids to metal oxides is dependent on the *trans*-/*cis*-configuration of the cyclopropane moiety [20], this may also be the case for PA sorption to goethite.

In most recent studies PA has been quantified using either GC methods, which separate the diastereomers, with MS or electron capture detection (ECD), giving detection limits of 0.1–2.5 nM [21,22] and approximately 10 nM [23], respectively. Reversed-phase HPLC has been used for ready separation of the diastereomers [24] or enantiomers [4] on various columns, but detection limits obtainable with UV detection are 100–1000 times higher than with MS or ECD detectors [24]. However, PA isomers are not volatile and derivatization is needed for GC analysis whereas no derivatization is required for HPLC analysis. Improvement of the HPLC-UV detection limit can for instance be obtained by preconcentrating the samples using a solid-phase extraction (SPE) system connected directly (on-line) to the HPLC-system. SPE-HPLC procedures have been successfully applied to the quantification of organic compounds in trace amounts, in several cases using C_{18} or C_8 column material for the SPE preconcentration [25–27].

The scope of this study was to test and optimize a simple SPE-HPLC-UV procedure for the quantification of low concentrations of *trans*- and *cis*-PA. Furthermore it was the aim to apply this method in quantification of PA sorption to goethite at PA concentrations in the nanomolar range in order to evaluate the significance of iron oxides for PA retention in soils.

EXPERIMENTAL

Chemicals

Permethric acid was kindly supplied by Cheminova Agro A/S as a 68/31 mix of the *trans*- and *cis*-isomers. PA stock solutions of 5 and 50 mM were prepared in methanol and stored at 4°C in glass containers with tight screw caps. Standard solutions in the range 2–200 nM were prepared every day by dilution of minimal amounts of stock solutions (‰) in Milli-Q (mQ) water containing 0.1 M $NaNO_3$ and 1 mM HNO_3. Adjustment of pH in samples was achieved by adding 0.1 M NaOH or HNO_3. The mQ water was from a Millipore milli-Q Element System (triply deionized, UV radiated and filtered through a 1-μm membrane filter) and all other chemicals were of analytical grade.

Goethite

Synthesis was carried out following the method of Schwertmann and Cornell [28]. 300 mL solution of 1 M $Fe(NO_3)_3$ was mixed with 540 mL solution of 5 M KOH in a polyethylene beaker. The precipitate was left to react in an oven at 70°C for 60 h during which it was stirred three times daily. The product was cleaned by repeated centrifugation, decantation and shaking with fresh portions of mQ water until the conductivity of the supernatant was near that of deionized water and did not change with further washing. The yield was approximately 25 g.

The identity and purity of the product were verified by comparing X-ray diffractograms and infrared (IR) spectra to those of goethite reference materials. X-ray diffraction was carried out on a Siemens X-ray Diffractometer D5000 (40 kV; 40 mA) and the unoriented samples were scanned from 5 to 80° 2θ at 0.005° 2θ per s. Diffractograms showed no shift of peaks compared to reference materials or new peaks related to impurities. For IR analysis, samples were prepared as KBr pellets containing 1 mg/cm^2 of goethite. Samples were scanned before and after drying at 110°C. Transmission IR spectra were recorded as the average of 25 scans using a Perkin Elmer System 2000 FT-IR-spectrometer. There were no bands present due to water, nitrate or organic impurities. The specific surface area (SSA) of goethite was determined by five-point BET-analysis using Micromeritics Gemini III 2375 and N_2 as the sorbing gas. Prior to SSA determination the sample was degassed for 19 h at room temperature. The SSA was 31.5 m^2/g.

Sorption

Sorption experiments were carried out in 50-mL Pyrex glass centrifuge tubes closed with screw caps containing Teflon-coated silicone gaskets. 50–400 µL methanolic stock solution of 68/31 *trans*-/*cis*-permethric acid was added to the tubes and the solvent was removed by evaporation under a stream of Ar. Goethite and background electrolyte solution were then added to a final goethite concentration of 2.9 g/L and PA concentrations in the range 0–957 nM. The pH in the samples was adjusted by adding NaOH or HNO_3 to the background electrolyte solutions according to a titration curve obtained for the goethite/background electrolyte system. The test tubes were placed on an end-over-end shaker at 5.5 rpm for 60 h, at which time sorption equilibrium was established according to preliminary experiments. After shaking, the tubes were centrifuged at 1000 *g* for 20 min and the supernatants filtered through 0.45-µm regenerated cellulose membrane filters. To avoid errors due to PA sorption to the filters, the first 5 mL of filtrate were discarded. Filtrates with pH $\neq 3$ were transferred to volumetric flasks for pH adjustment with minimal amounts of NaOH or HNO_3 solutions prior to analysis.

Instrumental

The SPE-HPLC-UV system is illustrated in Fig. 2. All columns used were of i.d. = 4.6 mm containing silica RP C_{18} material with a particle size of 5 µm. The chromatographic analysis was carried out using an HPLC system including an HPLC pump (LKB 2249), a UV-detector (LKB 2151) and an automatic integrator (LKB 2221) equipped with a six-way injection valve from Rheodyne (7125i), a 10-mL loop from Upchurch Scientific and an analytical column from Supelco (Discovery 504971, 25 cm), thermostated at a temperature of approx. 50°C. For preconcentration by SPE the system was further equipped with an extra injection valve holding a guard column kit from Supelco (Discovery 505129, 1 cm) in place of a sample loop, an additional HPLC pump from Shimadzu (LC-6A) and a peristaltic pump from Alitea (C4-V). The analytical column was also equipped with a guard column kit from Supelco. The carrier fluid for loading of sample onto the SPE column was mQ water, and between loadings the loop was rinsed with 50/50 (v/v) methanol/mQ

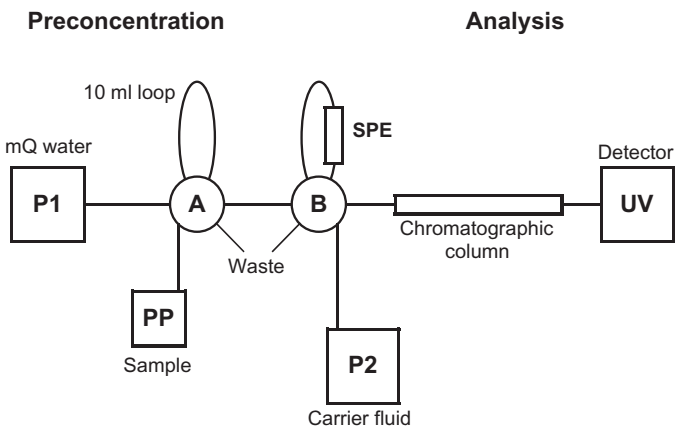

FIGURE 2 Schematic representation of the on-line-SPE-HPLC analytical system. P1, P2 = HPLC pump, PP = peristaltic pump, A, B = six-way injection valve, SPE = solid-phase extraction column, UV = ultraviolet detector.

water. The chromatographic carrier liquid was 65/35 (v/v) methanol and 0.02 M phosphate buffer in mQ water (pH = 3).

The sample was introduced into the 10-mL loop on injection valve A by means of the peristaltic pump and then transferred to the SPE column on injection valve B by P1 with mQ water as carrier liquid. After preconcentration the sample was eluted from the SPE column by way of P2, carrying the chromatographic carrier fluid in the same direction as the sample fluid. The analytes and impurities were separated on the thermostated analytical column and then reached the UV detector. Peak heights and integrals were calculated by an automatic integrator connected to the detector. 20 mL of sample was used to fill the loop at approximately 5 mL/min and flushing and preconcentration were achieved by pumping 25 mL of mQ water through loop and SPE at 2.5 mL/min. Testing showed that these were the optimum volumes of sample and carrier fluid for preconcentration.

Statistics and Regression

All confidence intervals were calculated using Student's *t*-distribution and a significance level of $p = 0.05$. Langmuir fits of sorption isotherm data were performed by non-linear regression using TableCurve 2D software, version v2.03 for Windows [29].

RESULTS AND DISCUSSION

Analytical Procedure

Representative chromatograms from analysis of sample and standard solutions are shown in Fig. 3; peaks eluted before and after the analyte peaks are system peaks and impurities; these were also found to be present in pure mQ water. The *trans*-isomers are eluted first ($t_R = 6.68$) and the *cis*-isomers last ($t_R = 7.73$). The combination of the parameters temperature, flow and carrier solution were optimized to separate the PA

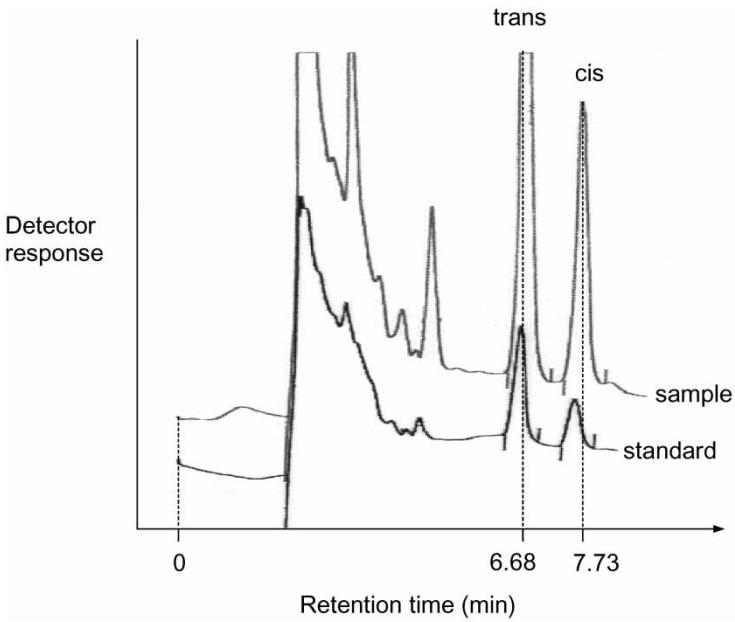

FIGURE 3 Representative chromatograms of sample and standard solution of PA. Standard: $[PA]_{tot} = 19$ nM, sample: filtrate from sorption experiment, $[PA]_{tot} \approx 81$ nM. Vertical bars mark the onset and termination of the integration. Temperature = 50°C, carrier liquid composition = 65/35 MeOH/buffer, pH = 4.5 and column flow = 1.5 mL/min. Non-assigned peaks are due to impurities.

TABLE II Limits of detection and repeatability

	trans	*cis*
LOD (nM)	1.4	0.31
RSD[a] (%)	5.8	7.2
Slope[b] (nM/min)	-0.0007 ± 0.0013	-0.0013 ± 0.0003

[a]Relative standard deviation.
[b]Slope from linear regression of repeated analyses plotted *vs* time.

peaks from those impurity peaks that could not be removed by cleansing of glassware with oxidants [HNO_3, $(NH_4)_2S_2O_8$], base, organic solvents and/or combustion at 500°C.

Limits of detection, (LODs, Table II), were determined as the concentration where the chromatographic signal is equal to $y_B + 3 \times s_B$ [30]. Here, y_B is the peak height of an average blank sample and s_B is the standard deviation of the peak height of blank samples.

Since a blank sample did not give rise to a peak, and therefore s_B could not be determined, an approximate s_B was calculated as the standard deviation of 15 repeated analyses of a standard solution of $[PA]_{tot} = 9.6$ nM, the analyses being carried out over a whole day. LODs were quantified using 2–200 nM standard solutions analyzed on the same day, and the intercept of the regression line with the ordinate axis considered an estimate of y_B.

To evaluate the repeatability the repeated analyses were plotted against time, and fitted by linear regression. The slope of the regression line for the *trans*-isomer was

TABLE III Parameters from linear regression of standard curves analyzed on three different days

Standard curve	*Day 1*		*Day 2*		*Day 3*	
	trans	*cis*	*trans*	*cis*	*trans*	*cis*
Correlation (r^2)	0.9992	0.9998	0.9976	0.9976	0.9994	0.9991
Slope (height/nM)	808 ± 19	544 ± 6.9	963 ± 23	604 ± 18	871 ± 42	572 ± 28
Intercept (height)	901 ± 1053	82 ± 270	812 ± 1161	481 ± 652	498 ± 2125	-74 ± 985

found to be equal to zero at $p = 0.05$ (Table II), and thus there was no significant dependence of quantification upon time of day, including drift of the instrument. On the contrary the slope of the regression line for the *cis*-isomer was found to be less than zero at $p = 0.05$ (Table II). However, this was not taken into consideration in the following quantification of samples, because the difference from zero was very small compared to the LOD.

Calibration curves for quantification were carried out using 10 standard solutions with total (trans + cis) concentrations in the range 2–200 nM. Linearity was confirmed and correlations were good (Table III). The between-days precision was investigated by comparison of calibration curves analyzed on three different days. This showed that the slopes of the curves from different days could not be considered the same at $p = 0.05$ (Table III). Therefore, quantification of each test batch was carried out using a calibration curve of four freshly prepared standard solutions randomly analyzed on the same day as the samples.

Rough estimates of the LODs obtainable when injecting 20 μL of sample without preconcentration are approximately 500 times larger than those obtained in this study. Since the sample volume in this study was 500 times larger than 20 μL, the recovery is nearly 100% and thus preconcentration of PA on C_{18} material is very efficient. Furthermore, the LODs of the SPE-HPLC-system are comparable with those obtained using GC-ECD and GC-MS, but the sample preparation before analysis by the SPE-HPLC method involves far less work and risk of losing analyte, since no derivatization is involved. Loss of analyte is also minimized compared to conventional offline preconcentration procedures involving extra steps of transfer between containers and dilution. Furthermore, the procedure involves no use of toxic chemicals for derivation, extraction and/or solvation. The procedure can be automated by use of commercial equipment with autosampler and automatic switch between preconcentration and elution [25,27].

Sorption

The on-line-SPE-HPLC-UV procedure was applied to the investigation of PA sorption to goethite. First it was tested whether the procedure of evaporating PA stock solution methanol and subsequently redissolving the analyte in background electrolyte solution affected the PA concentrations in solution. Analyses of seven replicate sample solutions prepared by this procedure were compared with analyses of seven replicate standard solutions. There was a slight decrease in the average PA concentration in samples compared to standards but this was not significant ($p = 0.07$) and the sample preparation procedure was approved.

The sorption experiments were carried out with PA in a 68/31 trans/cis-ratio and the resulting data are shown in Fig. 4. The data were fitted with the Langmuir equation:

$$\Gamma_A = \Gamma_{\max} \frac{K_{\text{ads}}[A]}{1 + K_{\text{ads}}[A]} \tag{1}$$

where $[A]$ (M) is the dissolved concentration of adsorbate, Γ_A (mol/m^2) the surface density of bound adsorbate, $\Gamma_{\max}$ (mol/m^2) the maximum sorption density and K_{ads} (m^2/mol) the affinity constant of the sorption reaction. The curve is a hyperbola approaching $\Gamma_{\max}$ asymptotically and describes the situation where a finite number of surface sorption sites with similar sorption affinity is available. This will be the case if the sorption is due to surface complexation, involving specific chemical bonding between surface sites and adsorbate. Sorption isotherms with an infinite number of sorption sites can be described by the Freundlich equation: $\Gamma_A = m[A]^n$ in which m and n are constants. When $n < 1$ the resulting curve is somewhat similar in shape to that of a Langmuir equation. However, the Freundlich equation gives rise to a straight line when displayed in a double logarithmic plot. Such a plot is presented in Fig. 5 and

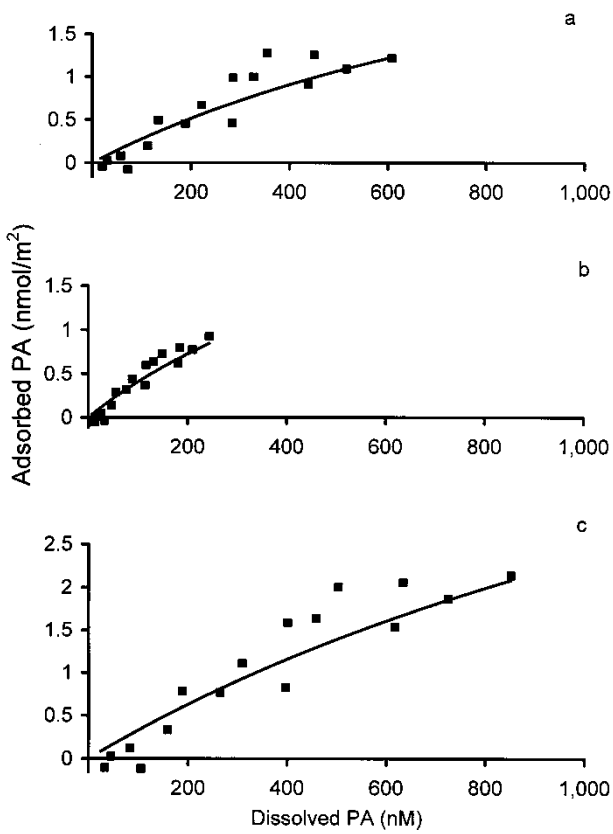

FIGURE 4 Sorption isotherms for binding of PA to goethite: (a) *trans*-PA, (b) *cis*-PA, (c) total PA. Data points are averages of 1–4 analyses of samples with equal initial concentrations. Curves are Langmuir regression fits including all individual data points. pH = 3, [$NaNO_3$] = 0.1 M, [goethite] = 2.9 g/L.

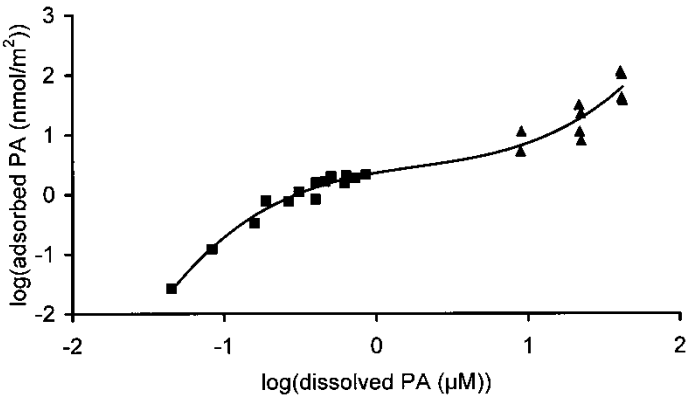

FIGURE 5 Sorption isotherms of PA adsorbed to goethite at different pH and initial concentration. ■: pH = 3, [$NaNO_3$] = 0.1 M, [goethite] = 2.9 g/L, ▲: pH = 6.5, [$NaNO_3$] = 0 mM, [goethite] = 2–5 g/L. Solid trendline added as a guide to the eye.

TABLE IV Parameters of the Langmuir regression analyses applied to PA sorption isotherm data in Fig. 4

	Γ_{max} (mol/m^2)	K_{ads} (L/mol)	r^2
Total PA	7.1×10^{-9}	4.8×10^5	0.68
cis-PA	3.4×10^{-9}	1.4×10^6	0.71
trans-PA	3.8×10^{-9}	7.9×10^5	0.64

it is obvious that the sorption data displays a curve in which the slope decreases as the concentration of PA in solution increases. The curve seems to be approaching an asymptote, as is the case for a Langmuir isotherm displayed in a double logarithmic plot. The parameters from the regression fits of the PA data to the Langmuir equation are displayed in Table IV. The low r^2 values and large variation in the parameters are mainly attributed to the variation in the sorption data (adressed below).

Figure 5 compares the sorption data with PA concentrations in the nanomolar range to results of preliminary experiments with PA concentrations in the micromolar range. Sorption isotherms of the S-shape implied in Fig. 5 are typically seen for the sorption of surfactants, and this is attributed to hydrophobic interactions at the solid–liquid interface. Surfactants exhibit a marked rise in sorption affinity at a certain point of surface coverage due to the formation of hemimicelles [31,32]. It is characteristic that the increase in sorption is initiated at sorption densities below 1/10 of monolayer coverage and that the affinity of the initial sorption is low. Sorption isotherms with the same shapes and characteristics have been observed for sorption to goethite and other iron oxides of the herbicide 2,4-D (2,4-dichlorophenoxy acetate) [33,34], which is structurally related to PA. In our case the Γ_{max} of the total PA sorption is found to be 7.1 nmol/m^2 (Table IV). This is, of course, a rough estimate based on extrapolation, but it seems reasonable when compared to the sorption plateau seen in Fig. 5 at sorption of approximately 10 nmol/m^2. Assuming that one molecule of PA occupies $(3–9) \times 10^{-18}$ m^2/molecule [35], monolayer sorption corresponds to $(1.8–5.5) \times 10^{-7}$ mol/m^2, which makes $\Gamma_{max} \leq 1\%$ of monolayer coverage. The pH in the preliminary PA sorption experiments was 6.5 while the experiments in the lower nanomolar

concentration range were carried out at pH = 3. It is unlikely that PA sorption directly to the goethite surface should be highest at pH = 6.5 since the goethite surface as well as the sorbent molecules will be mainly negatively charged at this pH. Hence, hydrophobic interactions are the most likely cause for the increased sorption seen in the micromolar concentration range (Fig. 5).

The sorption in the lower nanomolar range is thought to be due to surface complexation. This is based partly on the shape of the sorption isotherm, which indicates that there is a finite number of sorption sites, and partly on the fact that other low molecular organic acids have been shown to adsorb specifically to goethite [36,37].

The estimated K_{om} for neutral PA (pH $\leq$ 4) is $10^{2.5}$ L/kg (Table I) and in this work the average K_d for total PA sorption to goethite at pH = 3 is approximately 10^2 L/kg in the nanomolar range. Cypermethrin sorption to goethite under similar experimental conditions has also been studied [20], but with no background electrolyte, owing to the very low solubility of the pyrethroid. Here, K_d for the various isomers were in the range $10^{2.5}$–$10^{3.5}$ L/kg, and according to Table I the estimated K_{om} for cypermethrin is $10^{5.4}$ L/kg. Hence, PA is expected to be more mobile in soil than the parent compounds, but metal oxides have a relatively greater significance for the retention of the metabolite than the organic matter as compared to the parent compounds.

The sorption affinity of *cis*-PA to goethite is larger than that of *trans*-PA. Before sorption the theoretical trans/cis ratio was 2.2 and the ratio between the peaks in analyses of standard solutions was 2.23 ± 0.03. At sorption equilibrium the ratio in solution was 2.35 ± 0.05. The difference is small but significant ($p = 1.58 \times 10^{-5}$), and this trend is confirmed by the estimated $K_{ads,cis}$ which is almost twice that of $K_{ads,trans}$ (Table IV). Analyses of blank samples from batch experiments without goethite, showed that no trans/cis isomerisation took place during shaking, and thus the change of the ratio in the sorption experiments must be due to increased sorption of the *cis*-isomer as compared to the *trans*-isomer. This difference is believed to be caused by differences in physico-chemical properties, since there is no obvious stereochemical hindrance to sorption of the *trans*-isomer as compared to the *cis*-isomer. The preferential sorption of *cis*-isomers over *trans*-isomers was also seen for sorption of cypermethrin to goethite [20].

Application of the Analytical Procedure

There were problems with reproducibility when the SPE-HPLC-UV procedure was applied to the quantification of sorption, which is indicated in Fig. 4 by the large and non-systematic variation in the sorption data. This inconsistency was not seen when no goethite was added to the samples, and since the X-ray diffraction and IR analysis of the goethite revealed no impurities, the problems were most likely associated with the sorption process. There are two possible reasons for this: (1) The dried goethite had formed aggregates that were not completely disintegrated when redispersed in the experiments, which may have led to variation in the surface area available to sorption. This seems unlikely since the freeze drying gave a finely grained homogeneous powder and there were no inhomogeneities to be seen. (2) Variable Γ_{max} and sorption affinity. This is quite likely since PA sorption is similar to surfactant sorption, which is characterized by an onset of hemimicelle formation and increase in sorption at low surface coverage. This means that the so called "critical hemimicelle concentration" can be dependent not only on the number of molecules adsorbed but also on how closely

they are adsorbed at the surface. This could lead to the large variation in distribution coefficients seen as the sorption approaches Γ_{max}. Problems with sorption data reproducibility with increasing surfactant concentration have also been observed for (*Z*)-9-octadiene acid sorption to Fe_2O_3 [38].

CONCLUSION

A successful on-line SPE-HPLC-UV procedure was developed for simultaneous quantification of *trans*- and *cis*-PA in aqueous samples. Limits of detection were 1.4 and 0.3 nM for the *trans*- and *cis*-isomers, respectively. This is of the same order as LODs obtained with GC-ECD and GC-MS, although involving much less sample preparation. The procedure was applied to the quantification of PA sorption to goethite.

Sorption of nanomolar concentrations of PA to goethite was found to be specific up to a point of less than 1% surface coverage and could be described by a Langmuir equation, the parameters of which are $K_{ads} = 7.1 \times 10^{-9}$ L/mol and $\Gamma_{max} = 7.1 \times 10^{-9}$ mol/m^2 for the sorption of total PA (trans + cis). K_d in this range is approximately the same as K_{om} of PA in acid soils, and so the mineral fraction is expected to play a significant role in retaining PA in soil. PA can also be expected to be more mobile in soil than cypermethrin and thus more susceptible to leaching than the intact pyrethroids. It was also found that K_{ads} for *cis*-PA (1.4×10^6 l/mol) is approximately twice K_{ads} for *trans*-PA (7.9×10^5 L/mol), demonstrating preferential sorption of the *cis*-isomer. At higher PA concentrations the sorption mechanism seemed to be similar to that of surfactants, that is, the affinity increases due to hydrophobic interactions between adsorbed PA molecules.

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