Solid phase microextraction coupled to gas chromatography-mass spectrometry for the determination of the adsorption coefficients of triazines in soil

The Analyst

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Solid phase microextraction coupled to gas chromatography-mass spectrometry (SPME-GC-MS) was used to determine the adsorption coefficients (K_{oc}) for six target triazines in soil and sediment samples with different organic matter contents and textures. SPME-GC-MS was used in conjunction with a conventional batch equilibrium method. The recoveries of the selected triazines from soils and sediments having organic carbon contents in the range 0.2–2.4% were satisfactory. Drawbacks of conventional analytical techniques are avoided; owing to the selectivity of SPME-GC-MS, no sample pre-treatment or solvent enrichment steps were required so that K_{oc} values could be easily determined. Moreover, the sensitivity of the technique makes it possible to work at low triazine concentrations (50–500 ng g^{-1}) where the Freundlich adsorption isotherm can be considered linear.

Introduction

Triazines are among the most widely used soil-applied herbicides in Europe[1] for the selective control of weeds in cultures such as corn, sorghum, sugar cane, pineapple and many others.[2] The interaction of triazines with the environment depends on the physical, chemical and biological characteristics of both the pesticides and soil. Bioavailability is, for instance, influenced by the presence of soil organic matter (SOM), capable of binding pesticides.[3,4] In fact, a positive correlation is normally found between the adsorption of triazines and SOM content.[5] Cation exchange,[6] charge transfer interactions[7] and hydrogen bonding[8] have been proposed for the binding of triazines to humic and/or fulvic acids, which represent the main organic constituents of soils and sediments.

Describing and modelling the behaviour of pesticides in soils and their eventual leaching to ground water require the knowledge of the soil adsorption coefficient, K_{oc}, defined as

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (1)$$

where K_d is the distribution coefficient and f_{oc} is the organic carbon fraction of the soil. The distribution coefficient K_d is given by

$$K_d = \frac{C_{soil}}{C_{water}{}^{n}} \quad (2)$$

where C_{soil} is the concentration (μg kg^{-1}) of the adsorbed chemical, C_{water} is the concentration (μg^n l^{-n}) in the soil solution and n is a dimensionless exponent depending on the nature of the adsorbed chemical and the characteristics of the soil substrate. Typical values[9] of n for triazines in different soils are 1.00 ± 0.14 but at low pesticide concentrations the Freundlich adsorption isotherm described by eqn. (2) can be considered linear ($n = 1$) and the K_{oc}, calculated with eqn. (1) can be conveniently expressed in l kg^{-1} units.

The most commonly used method for K_{oc} evaluation is the so-called batch equilibrium method, in which a given amount of soil sample is equilibrated with a known volume of an aqueous solution containing a known amount of the investigated chemical(s). After adsorption equilibrium has been reached, C_{water} is measured by an appropriate analytical method and C_{soil} is calculated as the difference between the initial concentration and C_{water}. The method is, however, intrinsically laborious and time consuming. In order to circumvent these drawbacks, many attempts have been made to estimate K_{oc} values from, *e.g.*, solubility and octanol–water partition coefficients,[10] quantum mechanical descriptors,[11] the solvatation parameter model[12] and the first order molecular connectivity index.[13] Alternatively, experimental estimates of K_{oc} values can be obtained by liquid chromatography (LC) using stationary phases such as immobilised humic acids[14] and trimethylammoniumpropyl or cyanopropyl[15] functionalised silica. More recently, K_{oc} values relevant to a number of triazines and triazine metabolites have been determined on octadecyl-based stationary phases by HPLC[16] and gradient elution HPLC methods.[17]

Solid phase microextraction (SPME), an extraction technique introduced by Pawliszyn and co-workers[18,19] for the determination of organic compounds, has been shown to be an excellent sampling method for polar and non-polar, volatile and semi-volatile organic compounds.[20–23] SPME allows the simultaneous extraction and preconcentration of analytes from the sample matrix. Furthermore, SPME eliminates some disadvantages of conventional extraction techniques such as solid phase extraction (*e.g.*, plugging of cartridges) and liquid–liquid extraction (*e.g.*, use of toxic solvents).

Existing SPME applications in the field of triazine pesticides[24–26] have essentially aimed at the determination of these chemicals in aqueous samples. As far as we know, applications of the SPME technique to the study of pesticide–soil interactions are essentially lacking, the only exception being one paper[5] concerning the prediction of the leachability of several pesticides from soils using near infrared reflectance spectroscopy.

The present work shows that SPME coupled to gas chromatography-mass spectrometry (SPME-GC-MS) can be conveniently used to determine K_{oc} values for some triazines in soil and sediment samples with different organic matter content.

Experimental

Chemicals

A triazine mixture containing propazine, terbuthylazine, sebuthylazine, ametryn, prometryn and terbutryn in acetonitrile (Triazines mix XXXXIII) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Methylene chloride was obtained from Labscan (Dublin, Ireland). Stock standard solutions were stored in the dark at 4 °C. All working standard solutions were prepared with triply distilled water. Other chemicals were analytical-reagent grade reagents.

Apparatus

GC-MS analysis was performed with an HP 5890 Series II gas chromatograph equipped with a HP 5890 GC split–splitless injector (Hewlett-Packard, Palo Alto, CA, USA) and interfaced, by a GC transfer line, to a VG Trio-2000 quadrupole mass spectrometer (VG Biotech, Altrincham, UK). The carrier gas was helium; contaminants were removed by using a drying tube, a Supelpure-HC trap and an OMI-1 indicating purifier (all from Supelco, Bellefonte, PA, USA) in series.

The GC column consisted of a Supelco fused silica SPB-5 capillary column (30 m × 0.20 mm id, 0.25 μm film thickness) connected to the split–splitless injector.

Chromatographic and detection conditions

Initial experiments to optimise the chromatographic and detection conditions were carried out by direct injection of 1 μl of the standard mixture in acetonitrile. The oven temperature programme was: initial temperature 90 °C (held for 4 min), increased to 220 °C at 5 °C min^{-1} and then from 220 to 280 °C at 20 °C min^{-1} (final temperature held for 10 min). A column head pressure of 15 lb in^{-2} and an injector temperature of 250 °C were used. The GC transfer line was maintained at 250 °C. The mass spectrometer was operated in the positive electron ionization (EI^+) mode with a source temperature of 200 °C. The electron energy was 70 eV and the filament current 200 μA.

Mass spectra were acquired in the mass range from *m/z* 50 to 500 using a scan time of 0.9 s and an inter-scan time of 0.1 s. Detection of analytes was also accomplished in the selected ion monitoring (SIM) mode, using the following fragment ions: *m/z* 229, 172 (propazine); 214, 173 (terbuthylazine); 229, 200 (sebuthylazine); 227, 212 (ametryn); 241, 184 (prometryn); and 226, 185 (terbutryn). The dwell time and the mass span were 0.04 s and 0.3 u, respectively, for each fragment.

Soil samples

Two sediments and three soils differing in organic matter content and texture (see Table 1) were used. Samples were air-dried at 35 °C and sieved through a 1 mm sieve. The organic carbon fraction of the soil (f_{oc}) was measured according to the method of Walkey and Black.[27]

Table 1 Some physico-chemical characteristics of soil and sediment samples used in this study

	Soil		Sediment		
	Soil 1	Soil 2	Peat	Sediment 1	Sediment 2
Sand (%)	93	83.4			
Silt (%)	2.17	11			
Clay (%)	4.83	5.6			
pH	5.2	6.1	5.3		
Organic carbon (%)	0.19	2.44	19.2	0.42	0.23

Sample preparation

Soil and sediment samples (3.0 g) were pre-mixed with water (5 ml) in order to hydrate the active sites, thus allowing the analytes to distribute evenly over the soil and to interact with active sites. Then, 50 μl of the triazine standard mixture in acetonitrile were added and the resulting mixture was stirred for 0.5 h and left at room temperature overnight. The samples were then centrifuged (6000 rpm, 5 min) and the supernatant was subjected to SPME.

Solid-phase microextraction

Two kinds of silica fibres, coated with a 100 μm thick polydimethylsiloxane (PDMS) film or an 85 μm thick polyacrylate (PA) film, were employed for comparative studies. A manual SPME device (Supelco) was used to hold the fibres. The SPME device and procedure have been extensively described elsewhere.[18–26] Standard solutions were prepared by spiking 5 ml of triply distilled water into 7 ml clear vials (Supelco). The vials were sealed with hole caps and Teflon-faced silicone rubber septa (Supelco). Adsorption was carried out at room temperature for 30 min with magnetic stirring in order to improve the mass transfer from the aqueous sample into the fibre coating. Thermal desorption (5 min desorption time) was performed directly into the GC injection port maintained at 250 °C.

Results and discussion

Preliminary experiments were performed in order to compare the extraction efficiencies of PDMS and PA coated fibres. Table 2 shows relative extraction efficiencies of the two fibres calculated as peak area ratios on the relevant GC-MS traces. As can be seen, the PA coating was clearly capable of the most efficient extraction of all the target triazines and was therefore chosen for further experiments.

Adsorption times ranging from 5 to 180 min were investigated in order to establish the equilibration time for partition of the analytes between the aqueous and the polymer phases. For all the analytes equilibrium conditions were reached after 120 min; however, as long as the extraction was performed under reproducible conditions, an adsorption time of 30 min represented a good compromise between sample throughput and peak response.

The extraction efficiency was not significantly affected either by the pH of the solutions in the range 4–7 (which covers the pH of the soil solution; see Table 1) or by the extraction temperature (from ambient to 80 °C).

After each adsorption step, the fibre was immediately transferred into the injector port where it was thermally

Table 2 Relative extraction efficiencies of PA and PDMS coated fibres. Data calculated as peak area ratio on the relevant GC-MS traces

Analyte	PA/PDMS
Propazine	6.08
Terbuthylazine	4.35
Sebuthylazine	5.78
Ametryn	4.54
Prometryn	3.06
Terbutryn	2.04

desorbed at 250 °C for 5 min. Quantitative desorption could be obtained under these conditions, as demonstrated by the absence of memory effects of the fibre.

Once the ideal extraction conditions had been established, the linear dynamic range of the SPME-GC-MS procedure was investigated. The MS response (SIM mode) was linear over at least two concentration decades (1–220 ng ml^{-1}) with a correlation coefficient better than 0.996 and an intercept not significantly different from zero at the 95% confidence level.

The developed procedure was used to investigate the behaviour of triazines in soil and sediment solutions by a batch equilibrium method. After equilibrium had been reached, the aqueous solution was analysed by SPME-GC-MS. Fig. 1(a) and (b) show typical chromatographic traces for the SPME-GC-MS analysis acquired in the total ion current (TIC) and SIM modes, respectively. As can be seen, the complexity of the matrix could be drastically reduced by working in the SIM mode, since a very clean chromatogram, showing no interference from matrix components, could be obtained in the time window where triazine herbicides eluted. This finding clearly indicates that batch equilibrium method coupled to SPME-GC-MS gave a very convenient way to determine C_{water} and then to calculate water recoveries from spiked soils and sediments (see Table 3) and also soil adsorption coefficients (see Table 4).

As can be seen from Table 3, none of the analytes investigated was recovered from peat, as expected for a soil having a very high content of organic matter.

As far as the K_{oc} values reported in Table 4 are concerned, it appears that the soil adsorption coefficients for sediments fit the literature data fairly well whereas they are lower than expected for soils, especially soil 1, having the lowest content of organic carbon. This could be understood by considering that for soils with a very low organic carbon content, sorption mechanisms not involving the organic matter could predominate. It is worth noting that K_{oc} is largely, but not always, independent of the properties of the soil or sediment. A large part, but not all, of the variation in K_d between different sorbents can be eliminated by using K_{oc}. The remaining variation may be the result of other properties such as clay content, cation exchange capacity, pH, surface area, mineralogical composition, variation in the organic matter present and differences in experimental procedures.

In the particular case here, the role of possible measurement artefacts caused by silt and clay fractions in soils cannot be excluded. A tentative explanation is that soil microparticles with adsorbed chemicals, not separated by the centrifugation step, remain in the aqueous phase, giving apparently higher C_{water} values and, consequently, lower K_{oc}. This is obviously a drawback intrinsic to the batch equilibrium method and not to the SPME-GC-MS technique.

In the light of the above consideration and the large variability in the existing data (see last column in Table 4), the apparent discrepancy in the K_{oc} values for the soils analysed in this work is not surprising. Note, anyway, that the same order of K_{oc} values is roughly observed for the selected triazines in all the investigated samples, with terbutryn having the highest value, as expected as it has the highest octanol–water partition constant of the compounds considered.

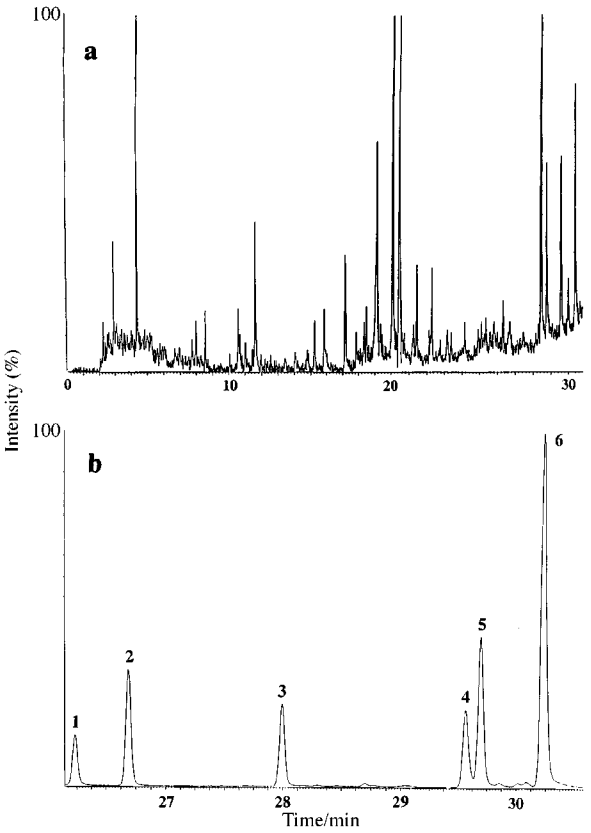

Fig. 1 a, SPME-GC-MS (TIC mode acquisition) of pesticide-free sediment 1 sample; b, SPME-GC-MS (SIM mode aquisition) of spiked sediment 1 sample (the time window where triazines eluted is shown). Peaks: 1 = propazine; 2 = terbuthylazine; 3 = sebuthylazine; 4 = ametryn; 5 = prometryn; 6 = terbutryn. Final concentration after spiking: 250 ng g^{-1} for each triazine.

Conclusions

An SPME-GC-MS method for the determination of K_{oc}, which is an important parameter for studying soil–triazine interactions, has been developed. The method is simple, highly

Table 3 Average recovery ± standard deviation of the target triazines from spiked soil and sediment samples. Values calculated on three replicate determinations performed at three different concentrations ranging from 50 to 500 ng g^{-1}.

	Soil			Sediment	
Analyte	Soil 1	Soil 2	Peat	Sediment 1	Sediment 2
Propazine	78 ± 6	70 ± 10	—	88 ± 15	81 ± 19
Terbuthylazine	60 ± 16	46 ± 11	—	92 ± 20	82 ± 4
Sebuthylazine	80 ± 10	68 ± 7	—	93 ± 5	85 ± 12
Ametryn	60 ± 18	52 ± 20	—	94 ± 6	90 ± 10
Prometryn	60 ± 4	44 ± 15	—	90 ± 20	87 ± 3
Terbutryn	20 ± 5	15 ± 10	—	60 ± 18	57 ± 4

Table 4 Log K_{oc} values of the target triazines determined by SPME-GC-MS compared with literature values

	Log K_{oc}				
	SPME-GC-MS				Literature[a]
Analyte	Soil 1	Soil 2	Sediment 1	Sediment 2	
Propazine	1.65	1.77	2.33	2.55	2.14 ± 0.21, (n = 81)
Terbuthylazine	1.77	1.95	2.29	2.55	2.51 ± 0.19, (n = 3)
Sebuthylazine	1.64	1.78	2.29	2.53	2.4[b]
Ametryn	1.77	1.90	2.27	2.51	2.50 ± 0.26, (n = 41)
Prometryn	1.77	1.97	2.31	2.52	2.66 ± 0.38, (n = 125)
Terbutryn	2.24	2.44	2.63	2.70	3.17 ± 0.48, (n = 18)

[a] Average log K_{oc} values ± standard deviation; n = number of available experimental data (see ref. 17 and references cited therein). [b] Estimated from gradient HPLC experiments (see ref. 17).

sensitive and solvent-free. Water recoveries of the investigated triazines, at least from soil and sediments with low organic carbon content, are satisfactory, suggesting that the quantitative SPME-GC-MS determination of these herbicides in such matrices could be feasible. Work in this direction is in progress.

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