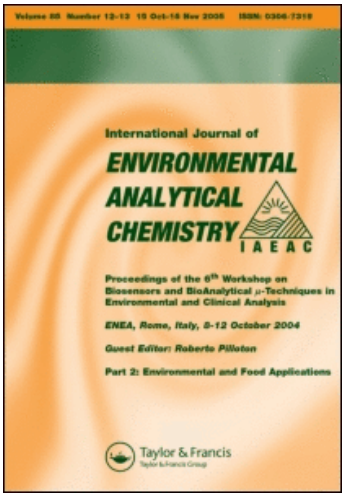

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Use of SPME extraction to determine organophosphorus pesticides adsorption phenomena in water and soil matrices

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Solid-phase micro extraction (SPME) coupled with GC enables rapid and simple analysis of organophosphorus pesticides in a range of complex matrices. Investigations were made into the extraction efficiencies from water of six organophosphorus insecticides (methamidophos, omethoate, dimethoate, parathion methyl, malathion, and parathion ethyl) showing a wide range of polarities. Three SPME fibres coated with different stationary phases, polydimethylsiloxane, polyacrylate, and carbowax-divinylbenzene (CW-DVB), were investigated. Water was spiked with the pesticides at concentrations from 1 to 0.01 $\mu g\,mL^{-1}$, and the solutions used for optimization of the procedure. The CW-DVB fibre, with a 65 μm coating, gave the best performance. The optimized experimental conditions were sample volume 10 mL at 20°C, equilibration time 16 min, pH 5, and presence of 10% w/v NaCl. SPME analyses were performed on solutions obtained by equilibrating aqueous pesticide solutions with six certified soils with various physico-chemical characteristics. SPME data were also assessed by comparison with analyses performed by using conventional solid-phase extraction. Results indicate the suitability of SPME for analysis of pesticides in environmental water samples.

Keywords: SPME; Organophosphorus insecticides; Water; Soil

1. Introduction

A number of studies in the 1980s and 1990s showed that crop-protection products, applied to drained fields, could move downwards through the soil profile to the groundwater. A knowledge of physico-chemical properties, i.e. v.p. (vapour pressure), b.p. (boiling point at stated pressure), Henry constant, K_{ow} (octanol/water partition coefficient), and solubility in water allows the fate and behaviour of such chemicals in the environment to be predicted [1].

Organophosphorus insecticides (OPs) are used all over the word for crop protection, for other agriculture practices such as sheep dipping, and in aquaculture for the control of sea lice. They have superseded many of the second-generation organochlorine

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insecticides (OCs) intensively used in many countries until the late 1980s and now prohibited because of their persistence in the environment, biomagnification along the food chain, and toxicity to non-target organisms [2, 3]. In general, OPs are more rapidly transformed in the environment to less toxic species than are OCs. Despite this, a number of studies have shown that OPs can persist in the environment for extended periods [4]. OPs show a characteristic toxicity and have also been linked to various modern diseases, including Creutzfeldt–Jakob (CJD) and the Gulf War syndrome [5]. Although OPs are less persistent than OCs, they are not without environmental risks, and this has led to an increase in social concern about their levels in soils, surface waters, and ground waters.

The presence of OPs has been recently detected at variable concentrations in groundwaters, surface waters, lagoons, and even in drinking water [6]. Consequently, more stringent regulations have been issued in several countries, and there is a requirement for appropriate, preferably fast, methods, to enforce these regulations.

Analysis of pesticide residues in environmental matrices is usually based on chromatographic separation/determination combined with preliminary extraction and clean-up procedures such as liquid–liquid extraction (LLE) with organic solvents and solid-phase extraction (SPE) using various adsorbent cartridges and solvents [7]. These procedures isolate the analytes from co-extracted materials on the basis of their physico-chemical characteristics. However, there are disadvantages with these procedures, particularly related to the time required for the analyses.

Solid-phase microextraction (SPME) is a relatively new technique, devised by Pawliszyn and coworkers [8] which, by combining both extraction and concentration in a single step, provides for procedures which are fast, simple to use, easy to couple with chromatographic analysis, and can achieve good sensitivity. Isolation of the analytes is achieved using a fused silica fibre coated with an appropriate material. Immersion of the fibre in water will result in the distribution of analytes between sample and fibre. The fibre is then transferred to the inlet of a gas-chromatograph for desorption and analysis of the trapped substances. SPME appears to offer real analytical advantages in environmental analysis and has been recently applied to studies of various organic substances, including petroleum derivates and pesticides, in water and other more complex environmental matrices [9, 10].

The aim of this study was to investigate the possible use of SPME for the simultaneous analysis of a number of OPs in aqueous samples that had been in contact with soils. Such solutions would comprise a water phase which also contains organic substances derived from the soils. These water/soil systems were intended to be representative of real environmental samples, and their study should also allow for some information about soil/pesticide interactions to be obtained.

A liquid extraction method has been developed and used for evaluation of pesticides in soils. The SPME method has been fully optimised taking into consideration the most relevant experimental conditions. To check whether organics from the soil have an effect on the extraction procedure, the SPME method above mentioned has been also considered with water that has been equilibrated with soils. Furthermore these data has been compared with those obtained with SPE solvent extractions.

Six commercial certified soils and the six organophosphorus insecticides, methamidophos (*O*,*S*-dimethyl phosphoramidothioate), omethoate (*O*,*O*-dimethyl *S*-methylcarbamoylmethyl phosphorothioate), dimethoate (*O*,*O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate), parathion methyl (*O*,*O*-dimethyl *O*-4-nitrophenyl

phosphorothioate), malathion (*S*-1,2-bis ethyl *O*,*O*-dimethyl phosphorodithioate), and parathion ethyl (*O*,*O*-diethyl *O*-4-nitrophenyl phosphorothioate), showing a wide range of polarities, as indicated by their K_{ow} (from –0.8 to 3.83), have been investigated in this study [11, 12].

Methamidophos, omethoate, and dimethoate have been detected in enviromental waters [13], confirming the potential for pesticides with a higher polarity (low K_{ow}) to move through the soil toward groundwater.

2. Experimental

2.1 *Chemicals and reagents*

Methamidophos was obtained from Riedal-de Haen (UK), omethoate and dimethoate from QM_x Laboratories (UK), parathion methyl from Promochem Ltd (UK), and malathion and parathion ethyl from Sigma. A stock standard mix solution (1000 μg mL^{-1}) was prepared by dissolving the OP pesticides in ethyl acetate and stored at –20°C. Working solutions containing 100 μg mL^{-1} in 60 : 40 ethyl acetate/acetone or acetone alone were prepared from the stock solution and used for all the experiments. Water, ethyl acetate, methanol, acetonitrile, and acetone (all HPLC or fluorescence grade) were obtained from Fisher Scientific (UK). Anhydrous sodium sulphate (99.5% purity), sodium chloride (99.9% purity), and sodium hydrogen carbonate (99.99% purity) were obtained from Fisher Scientific; calcium chloride (90% purity) was obtained from BDH Chemicals Ltd. (UK). The SPE cartridges, OASIS HLB 60 mg, were from Waters Corporation (UK).

The standard soils were obtained from Landwirtschaftiche Untersuchungs und Forschhungsanstalt (LUFA) Speyer (Germany). They represent a range of soils characterized by different pH, cation exchange capacity, buffer effect, nutrient availability, amount of clay minerals, and organic matter. Their physicochemical characteristics are listed in table 1. The soils were sterilized and stored at 4°C in order to prevent microbial activity.

The PDMS (100 μm polydimethylsiloxane), PA (85 μm polyacrylate), and CW-DVB (65 μm carbowax-divinylbenzene) fibres, all equipped with holders for manual injection,

Table 1. Physico-chemical characteristics of standard soils.

Properties/soil code	2.1	2.2	2.3	3A	5M	6S
Org C (%)	1.23 ± 0.30	2.26 ± 0.12	1.02 ± 0.17	2.2 ± 0.1	1.4 ± 0.1	1.9 ± 0.3
pH value (0.01 M $CaCl_2$)	6.2 ± 0.7	5.8 ± 0.3	6.3 ± 0.4	7.1 ± 0	7.0 ± 01	6.7 ± 0.6
Cation exchange Capacity (meg/100 g)	8 ± 1	11 ± 2	10 ± 2	17 ± 4	12 ± 1	17 ± 3
Particle sizes according to USDA (%)						
< 0.002 mm	3.6 ± 1.2	8.0 ± 1.1	8.5 ± 1.4	16.9 ± 0.1	11.0 ± 2.5	41.5 ± 1.4
0.002–0.05 mm	9.5 ± 2.2	14.9 ± 2.6	29.2 ± 3.2	34.6 ± 2.7	30.4 ± 3.6	36.4 ± 3.1
0.05–2.0 mm	86.8 ± 1.9	77.1 ± 3.1	92.3 ± 4.10	48.5 ± 2.6	58.9 ± 5.0	22.1 ± 2.2
Soil type	Sand	Loamy sand	Sandy loam	Loam	Sandy loam	Sandy clay
Water-holding capacity (g/100 g)	34.8 ± 5.3	48.6 ± 4.1	35.2 ± 3.4	51.2 ± 6.2	42.3 ± 5	41.4 ± 3.2
Weight per volume (g/1000 mL)	1390 ± 40	1148 ± 40	1335 ± 85	1140 ± 100	1170 ± 35	1265 ± 60

were from Supelco (UK). Prior to use, the PDMS fibres were conditioned at 250°C for 30 min, the PA fibres at 300°C for 2 h, and the CW-DVB fibres at 220°C for 30 min, each in a GC injector port.

An Ultra Turrax homogenizer model T25, Turbo Vap II concentration workstation, and a DB3 sample concentrator were supplied by IKA Labortechnik, Zymark, and Techne, respectively.

2.2 *Instrumentation and experimental conditions*

Gas chromatographic (GC) analyses were performed using an Agilent 6890 system, equipped with a 7683 autosampler and flame photometric detector (FPD). All compounds were resolved on a DB-1701 30 m fused-silica capillary column (0.25 mm ID, 0.25 μm film thickness) supplied by J&W Scientific. Liners, 4 mm ID with glass wool, were used for conventional splitless analysis, while 0.75 mm ID was more appropriate for SPME analysis. The GC oven programme was started at 70°C (30 s), increased at 15°C min^{-1} to 175°C, and then increased to 260°C at 5°C min^{-1}. Helium was used as a carrier gas with a column head pressure of 20 psi (138 kPa) and a flow rate of 1.8 mL min^{-1} (linear velocity of 40 cm s^{-1}). The detector temperature was set at 250°C with a hydrogen flow of 110 mL min^{-1}, air flow of 90 mL min^{-1}, and nitrogen make-up flow of 60 mL min^{-1}. Conventional splitless analyses were performed using an inlet temperature of 180°C, while SPME analyses were performed using inlet temperatures of 240°C for the CW-DVB fibre, 260°C for the PA fibre, and 280°C for the PDMS fibre. The desorption time was 3 min in all cases.

3. Experimental-procedure optimization

3.1 *Water systems*

Ten millilitres of the working mix solution of pesticides was evaporated under a gentle nitrogen stream to 1 mL and then redissolved in HPLC-grade water to give a final concentration of 1 μg mL^{-1}. This reduced the amount of solvent present to less than 0.1% (v/v) in spiked samples. Since losses of analytes during the evaporation process were possible, standard working mix ethyl acetate solutions at concentrations from 1 μg mL^{-1} down to 0.01 μg mL^{-1} were evaporated under a gentle nitrogen stream to dryness and redissolved in ethyl acetate. The process resulted in losses of less than 5% for all compounds.

All the experiments were carried out by immersing the selected fibre in the above-described water solution, which was magnetically stirred. Since the extraction efficiency of the fibres for some pesticides was likely to be low, a sample volume of 10 mL was used throughout. Immediately after adsorption, the fibre was transferred to the GC for analysis. All the data given below are mean values obtained from triplicate determinations of fortified samples and single values from blank samples.

To carry out quantitative analyses, there must be a linear relationship between the amount of analyte adsorbed by the SPME polymer film and the initial concentration of the analyte in the sample matrix. During an SPME sampling process, the analyte is partitioned between the polymer phase and the sample matrix phase. If the sampling time is long enough, an equilibrium is attained, and the above-mentioned relationship

between the absorbed amount and its initial concentration in the sample matrix is satisfied [14]. The time needed to reach equilibrium during the SPME sampling is dependent on the properties of both the analyte and the matrix [15, 16]. Once the adsorption equilibrium is reached, the maximum sensitivity for an analyte is also attained. To understand the relationship between adsorbed amount and initial concentration in non-equilibrium situations, the dynamic process of the SPME needs to be studied. The theoretical treatment of this has been described by Pawliszyn and coworkers [17, 18]. Literature reports indicate that pesticides with different chemical characteristics show different behaviour when subjected to SPME. For some of the pesticides considered here, fairly long times are required for equilibrium [19]. It has been considered that working under non-equilibrium conditions is feasible when experimental conditions are kept constant. In this way, mass diffusion was considered as the rate-determining step in the process of reaching an adsorption equilibrium [20, 21]. On the above basis, preliminary investigations were carried out (data not shown) into the linear response of the fibres at shorter selected times in non-equilibrium conditions. As a result, it was decided that all the experiments would be performed with a 16 min contact time at room temperature, $20 \pm 1^{\circ}C$. Optimization of pH and salt addition was also considered in order to obtain the maximum fibre extraction ability.

In certain instances, enhancements in the selectivity can be accomplished with careful optimization of sample pH [22]. The fibre-sample distribution constant (K_{fs}) is greatly affected by the pH value, resulting in a change in extraction selectivity [23]. Solutions with pH values between 3 and 6 were studied with the pH adjusted using HCl/NaOH and monitored before and after the extraction. The results are listed in table 2. The highest extraction rates were obtained with a pH between 4 and 5. By considering the relative standard deviation, RSD%, and the confidence interval of the chromatographic responses, it appears that the best sampling conditions occur at pH 5.

The effect of ionic strength has been studied at pH 4 and pH 5 in samples containing 10, 20, and 30% w/v NaCl respectively. Data are listed in table 3. It is notable that, as the pH value is raised to 5, the CW-DVB fibre appears suitable for measurements only at the lowest NaCl concentration.

The results suggest that the highest sensitivity for SPME analysis of the compounds of interest is attained by using the CW-DVB fibre directly immersed in the aqueous solution at pH 5 with addition of NaCl, 10% w/v, and these conditions were used in all further work during the SPME analysis.

Experiments in which NaCl was substituted by Na_2SO_4 were also performed, although non-systematically, by changing fibres, pH, and salt addition but, no definite advantages were observed in using the sulphate salt instead of the chloride. Figure 1 shows a typical chromatogram obtained under the above-stated experimental conditions (figure 1). The limit of detection (LOD) of the method is defined as a signal-to-noise ratio equal to 3. The LOD for the analytical procedure has been determined by an empirical approach, consisting of measuring progressively more dilute concentrations of analytes in the above-described experimental conditions [24].

LOD values were obtained from spiked distilled water, having established that water extracted from blank soil and then spiked with pesticides gives the same responses to those from standard water spiked solutions of OPs.

Recovery studies were conduced on water solutions previously contacted with soils of a different origin and therefore a different salinity, pH, and organic matter. Because SPME is a non-exhaustive extraction procedure, the recovery of the pesticides from

Table 2. Chromatographic area and statistical data for the SPME fibres at different pH[a].

	Carbowax-divinylbenzene			Polyacrylate			Polydimethylsiloxane		
	Area counts	RSD%	Confidence	Area counts	RSD%	Confidence	Area counts	RSD%	Confidence
pH 3									
Methamidophos	1522.14	5.80	4.44	268.47	13.49	4.34	61.54	40.70	6.29
Omethoate	88.35	23.58	4.35	31.96	15.67	1.76	13.84	78.92	5.94
Dimethoate	3099.99	4.29	4.69	982.87	8.18	5.03	172.43	20.98	5.41
Parathion methyl	91 330.24	6.12	36.22	57 768.64	15.46	72.84	96 260.45	16.97	103.19
Malathion	100 901.22	3.73	23.20	72 773.61	13.88	73.41	89 655.31	13.52	79.33
Parathion ethyl	290 293.59	5.95	62.88	176 013.33	12.17	100.11	16 8606.67	16.88	135.82
pH 4									
Methamidophos	1171.99	4.34	2.91	447.70	21.00	8.71	115.63	51.32	10.85
Omethoate	181.34	25.92	6.85	82.42	16.80	3.00	51.50	63.60	8.99
Dimethoate	4343.15	14.56	18.80	1923.79	0.89	0.77	284.39	33.86	11.20
Parathion methyl	96 796.27	6.50	39.62	90 560.09	7.41	43.68	18 3111.80	12.19	102.24
Malathion	102 977.76	9.44	59.35	95 951.10	6.94	42.16	167 526.74	10.59	84.92
Parathion ethyl	202 843.99	17.46	154.13	135 132.27	6.13	44.20	268 409.76	10.58	107.47
pH 5									
Methamidophos	878.76	8.48	4.93	447.90	27.14	11.27	41.83	44.41	5.69
Omethoate	127.74	2.67	0.59	78.13	19.59	3.40	8.58	71.52	4.25
Dimethoate	3122.63	2.46	2.70	1835.16	2.77	2.32	190.37	9.21	2.49
Parathion methyl	105 256.63	3.60	22.89	118 712.47	4.03	27.23	178 843.33	12.24	101.45
Malathion	113 288.25	2.61	17.20	114 609.63	3.54	23.47	154 886.67	12.92	99.68
Parathion ethyl	267 689.00	1.41	14.31	202 318.87	11.95	105.37	229 079.80	15.96	149.76
pH 6									
Methamidophos	904.39	14.31	8.44	277.62	7.45	2.44	64.46	51.10	8.07
Omethoate	50.17	34.06	4.74	55.73	6.23	0.92	21.76	70.97	6.60
Dimethoate	2112.66	10.00	9.01	1119.60	5.81	3.81	181.15	23.27	6.14
Parathion methyl	46 396.15	16.39	69.20	61 875.71	1.89	9.20	96 507.86	24.54	149.43
Malathion	61 651.09	11.76	57.23	68 200.47	1.72	8.83	94 878.17	20.25	122.24
Parathion ethyl	212 283.33	9.12	82.35	156 844.72	18.26	141.74	19 3757.20	28.86	248.97

[a]Confidence values are at the 95% confidence level.

Table 3. Chromatographic areas and statistical data for the SPME fibres at different pH and NaCl concentrations[a].

	Carbowax-divinylbenzene			Polyacrylate			Polydimethylsiloxane		
	Area counts	RSD%	Confidence	Area counts	RSD%	Confidence	Area counts	RSD%	Confidence
pH 4									
NaCl 10%									
Methamidophos	1171.99	4.34	2.91	447.70	21.00	8.71	115.63	51.32	10.85
Omethoate	181.34	25.92	6.85	82.42	16.80	3.00	51.50	63.60	8.99
Dimethoate	4343.15	14.56	18.80	1923.79	0.89	0.77	284.39	33.86	11.20
Parathion methyl	96 796.27	6.50	39.62	90 560.09	7.41	43.68	18 3111.80	12.19	102.24
Malathion	10 2977.76	9.44	59.35	95 951.10	6.94	42.16	16 7526.74	10.59	84.92
Parathion ethyl	20 2843.99	17.46	154.13	13 5132.27	6.13	44.20	26 8409.76	10.58	107.47
NaCl 20%									
Methamidophos	553.16	8.84	4.07	324.80	19.45	6.88	102.64	8.71	1.73
Omethoate	50.72	26.10	3.67	24.54	9.74	0.96	17.92	91.89	7.83
Dimethoate	6224.31	6.31	9.76	2499.12	8.75	8.58	372.15	3.14	1.19
Parathion methyl	12 6576.67	15.30	106.66	70 070.54	10.22	53.03	17 7740.00	13.89	114.80
Malathion	13 3919.72	18.95	135.93	90 547.91	8.56	50.48	14 9520.00	13.55	102.68
Parathion ethyl	25 4060.48	20.30	200.58	25 2734.31	3.49	34.43	27 3170.01	1.53	15.66
NaCl 30%									
Methamidophos	1143.12	18.74	12.42	548.22	34.54	15.86	145.8	52.70	12.51
Omethoate	91.20	4.86	0.91	80.62	79.34	14.02	13.51	71.23	5.23
Dimethoate	12 386.76	23.54	51.35	4824.87	36.00	49.02	494.70	11.55	5.04
Parathion methyl	13 1200.18	26.02	184.71	73 903.51	32.60	173.73	13 3939.32	25.43	182.45
Malathion	11 8216.35	24.30	163.74	87 893.93	29.41	170.87	14 7486.67	23.04	173.44
Parathion ethyl	16 4904.99	9.44	75.11	15 6134.26	26.98	208.98	13 9861.32	22.02	161.44
pH 5									
NaCl 10%									
Methamidophos	878.76	8.48	4.93	447.90	27.14	11.27	41.83	44.41	5.69
Omethoate	127.74	2.67	0.59	78.13	19.59	3.40	8.58	71.52	4.25
Dimethoate	3122.63	2.46	2.70	1835.16	2.77	2.32	190.37	9.21	2.49
Parathion methyl	10 5256.63	3.60	22.89	11 8712.47	4.03	27.23	17 8843.33	12.24	101.45
Malathion	11 3288.25	2.61	17.20	11 4609.63	3.54	23.47	15 4886.67	12.92	99.68
Parathion ethyl	26 7689.00	1.41	14.31	20 2318.87	11.95	105.37	22 9079.80	15.96	149.76

(*continued*)

Table 3. Continued.

	Carbowax-divinylbenzene			Polyacrylate			Polydimethylsiloxane		
	Area	RSD%	Confidence	Area	RSD%	Confidence	Area	RSD%	Confidence
NaCl 20%									
Methamidophos	ns[b]	ns[b]	ns[b]	375.71	21.95	8.35	43.57	43.62	5.68
Omethoate	ns[b]	ns[b]	ns[b]	39.93	47.36	5.93	8.71	71.79	4.33
Dimethoate	ns[b]	ns[b]	ns[b]	2735.15	4.02	4.12	265.36	10.01	3.20
Parathion methyl	ns[b]	ns[b]	ns[b]	61 145.20	8.36	40.53	11 8161.54	21.00	141.48
Malathion	ns[b]	ns[b]	ns[b]	83 367.45	11.13	63.01	10 3373.14	22.27	140.31
Parathion ethyl	ns[b]	ns[b]	ns[b]	18 1710.80	2.17	18.17	18 5735.74	18.91	159.76
NaCl 30%	ns[b]	ns[b]	ns[b]						
Methamidophos	ns[b]	ns[b]	ns[b]	534.33	37.80	17.13	71.13	45.57	7.54
Omethoate	ns[b]	ns[b]	ns[b]	86.09	70.71	12.87	14.46	70.71	5.35
Dimethoate	ns[b]	ns[b]	ns[b]	3937.53	31.22	38.40	617.61	13.31	6.49
Parathion methyl	ns[b]	ns[b]	ns[b]	55 109.20	7.56	34.81	16 5021.81	19.20	152.86
Malathion	ns[b]	ns[b]	ns[b]	57 404.79	12.56	58.97	17 0740.72	19.65	159.15
Parathion ethyl	ns[b]	ns[b]	ns[b]	12 1211.48	2.72	18.56	16 4502.49	5.60	44.48

[a]Confidence values are at the 95% confidence level. [b]Not suitable.

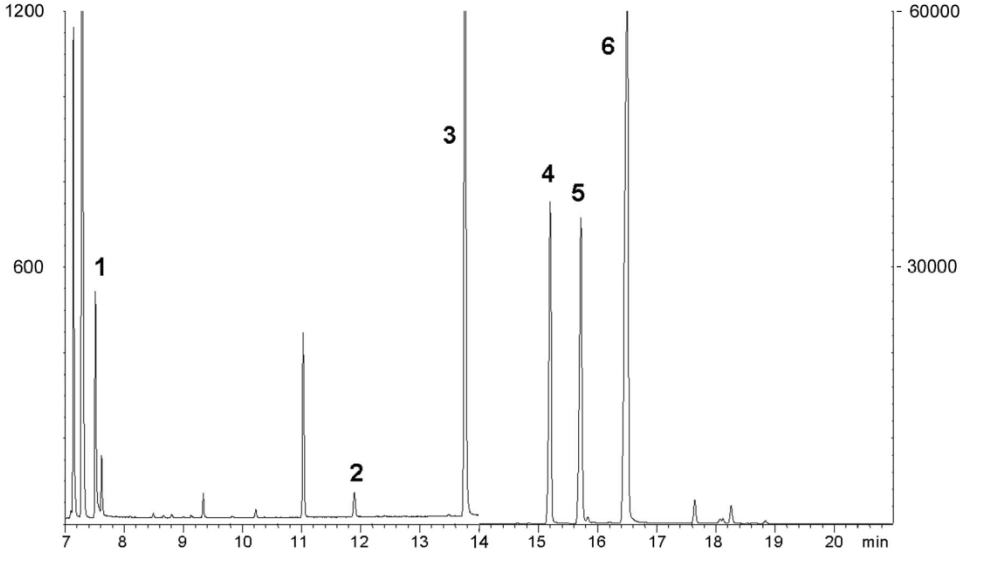

Figure 1. Sample chromatogram. Peaks: (1) methamidophos, (2) omethoate, (3) dimethoate, (4) parathion methyl, (5) malathion, and (6) parathion ethyl.

Table 4. Mean SPME relative recovery (%) values of OPs in water after 18 h in contact with standard soils.

Pesticides/soil code	2.1	2.2	2.3	3A	5M	6S
Methamidophos	99	96	93	94	98	91
Omethoate	96	92	94	92	96	94
Dimethoate	99	88	99	90	93	97
Parathion methyl	100	97	104	93	95	92
Malathion	104	94	98	96	101	98
Parathion ethyl	97	90	94	98	99	91

[a]Spiking levels of 1, 0.5, 0.1, 0.05, and 0.01 μg/mL; mean of three replicate experiments, RSD values 4–9%.

water that had been in contact with soil was determined with reference to ultra-pure water spiked with the analyte at the same starting concentration (1, 0.5, 0.1, 0.05, and 0.01 $\mu g\,mL^{-1}$). The data are reported in table 4.

3.2 *Soil systems*

Soil samples were dried at 40°C for 24 h, spiked with different amounts of an acetone solution of the standard mix, and shaken for 2 h. The solvent was then evaporated under a gentle nitrogen stream at 20°C. The spiked soil samples, 10 mL, were combined with water, 9.5 mL, and the mixture blended using a homogenizer at 20 500 rpm for 1 min. Then, ethyl acetate, 200 mL, was added and shaken for 30 min; 23 g of Na_2SO_4 and 3 g of $NaHCO_3$ were added to improve the soil flocculation process and extraction of the analytes.

An aliquot of the organic phase (100 mL) was concentrated under a gentle nitrogen stream, using a Turbo Vap II Concentration Workstation to about 100 μL, filtered

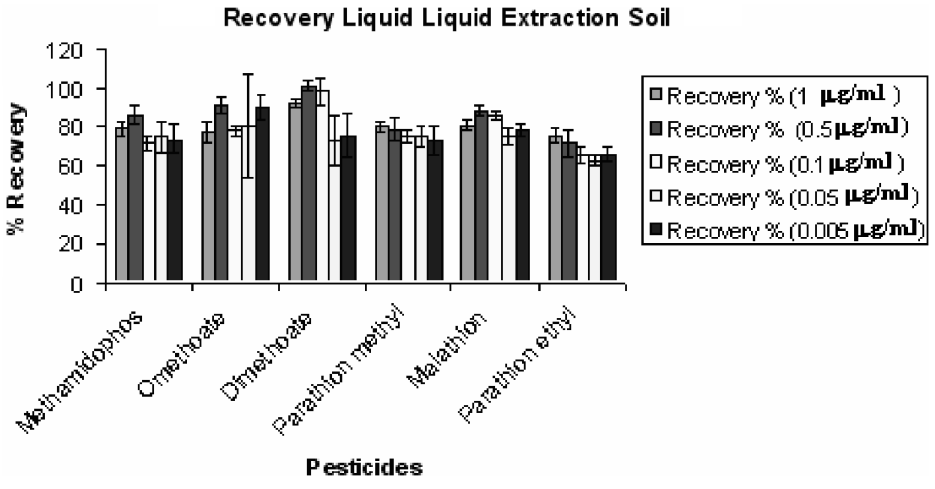

Figure 2. Recovery of OPs from spiked soils (spiking concentrations in parentheses).

through a 0.2 µm PTFE syringe filter (Ø 13 mm), and quantitatively redissolved in ethyl acetate for GC analysis. The recovery data (mean values over the six soils) are reported in figure 2.

The analyses were fortified at a range of level between 1 and 0.005 µg mL^{-1}. For the fortification level, a control sample was analysed, and the levels of each compounds in the controls were less than 30% of limit of quantification (LOQ).

3.3 *Soil/water systems*

There are two basic ways in which pesticides may reach surface and ground waters: runoff and leaching. Runoff is the physical transport of pollutants over the ground surface by rainwater which does not penetrate the soil; leaching is a process whereby pollutants are flushed through the soil by rain or irrigation water as it moves downward. This latter phenomenon is directly correlated with soil physico-chemical properties. Sorption is probably the single most important property influencing a pesticide's movement in soil. Soil is a complex mixture of solids, liquids, and gases. A pesticide in a soil is partly adsorbed and partly dissolved in 'soil water'. In natural environments, soil adsorption reduces the concentration of chemicals in aqueous solution.

Therefore, in looking for a possible environmental application of the SPME method, we performed adsorption tests to evaluate the migratory tendency of chemicals. The intention of these experiments was to simulate natural water environmental samples and to examine the pollution potential of the compounds studied. Ten millilitres of the working mix solution were evaporated under a gentle nitrogen stream to 1 mL and then redissolved in a 0.01 M aqueous $CaCl_2$ solution to attain a final pesticide concentration of 1 µg mL^{-1}. Addition of $CaCl_2$ was considered necessary to minimize cation exchange and improve sedimentation in centrifugation processes. All experiments were performed by contacting the soil, 6 mL, and the aqueous solution, 30 mL, in 50 mL centrifuge tubes. Preliminary studies showed that in all cases, adsorption equilibration could be reached within 18 h. The above mentioned centrifuge tubes were agitated in a Luckham Multimix roller for 18 h and then centrifuged using a Mistral 2000 centrifuge

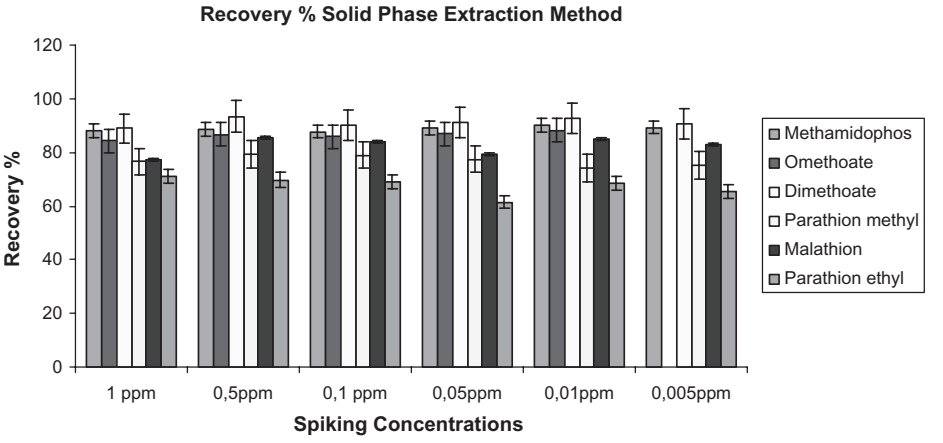

Figure 3. SPE percentage recovery of OPs from spiked water that had been in contact with soils.

at 3632G for 30 min. Water and soil samples were collected and analysed separately. Experiments were carried out in triplicate with a blank and a control test solution.

Results obtained from the water phase using the SPME technique were compared with results obtained on the same samples using a methodology based on the SPE method, and several control analyses were performed on soil matrices using the above-described method in order to control possible losses of pesticides during the experiment procedures.

Before use, the SPE cartridges were conditioned with 6 mL of methanol, followed by 6 mL of water and 3 mL of H_2O saturated with NaCl at 20°C. Water samples to be analysed were mixed with an equal volume of NaCl saturated water, and 2 mL of this solution was passed through the cartridges at a flow rate of 6 mL min^{-1} under vacuum. The cartridges were then dried with a nitrogen stream and two different elution fractions collected using 3 mL of methanol and 3 mL of acetonitrile/ethyl acetate (50/50). Both fractions were dried over Na_2SO_4 and the solvent evaporated using a gentle nitrogen stream at 20°C in a DB3 sample concentrator. The residue was redissolved in 2 mL of ethyl acetate and transferred to the GC instrument for analysis. Recovery data are reported in figure 3. The analyses were fortified at a range level from 1 to 0.01 μg mL^{-1}. For the fortification level, a control sample was analysed, and the levels of each compound in the controls were less than 30% of LOQ.

Data obtained from waters and soils after adsorption experiments, by comparative use of SPME and SPE analyses and the LLE method for soil matrices, are given in table 5.

4. Results and discussion

Linear six-point calibration curves were generated from conventional GC injections for all the OPs, with regression coefficients (R^2) between 0.9986 and 0.9991, in the concentration range 1–1000 ng mL^{-1} for all compounds, except for omethoate (5–1000 ng mL^{-1}).

Recoveries from soils were between 101.5% (dimethoate) and 63.05% (parathion ethyl) with an LOD of 5 ng mL^{-1} and RSD% between 1.95 and 12.2.

Table 5. Concentrations of pesticides in water/soil systems after adsorption experiment: comparison of SPME and SPE data.

	SPME conc. ($\mu g\,mL^{-1}$)	SPE conc. ($\mu g\,mL^{-1}$)	SPME RSD% area	SPE RSD% area	SPME confidence interval area	SPE confidence interval area	LLE soil concentration ($\mu g\,mL^{-1}$)
Soil 2.1							
Methamidophos	0.91	0.90	1.55	2.26	0.76	1.96	0.48
Omethoate	0.26	0.37	4.98	13.82	0.75	4.45	3.43
Dimethoate	0.89	0.90	3.91	2.95	3.67	2.06	0.53
Parathion methyl	0.17	0.21	2.02	19.53	5.86	5.44	4.05
Malathion	0.12	0.15	3.03	13.61	9.02	3.22	4.33
Parathion ethyl	0.09	0.09	2.93	41.92	8.68	7.48	4.55
Soil 2.2							
Methamidophos	0.93	0.90	3.83	1.77	1.90	1.53	0.43
Omethoate	0.43	0.37	4.42	49.88	0.84	19.81	3.00
Dimethoate	0.90	0.93	4.57	4.34	4.31	3.09	0.43
Parathion methyl	0.08	0.09	5.69	3.58	11.00	0.65	4.58
Malathion	0.05	0.08	0.46	4.74	0.88	1.92	4.68
Parathion ethyl	0.02	0.02	3.28	2.16	4.76	0.19	4.90
Soil 2.3							
Methamidophos	0.96	0.92	4.89	10.46	2.46	9.16	0.30
Omethoate	0.48	0.54	9.91	52.25	2.00	20.32	2.45
Dimethoate	0.88	0.90	3.83	6.59	3.57	4.61	0.55
Parathion methyl	0.14	0.16	2.68	8.82	7.03	2.17	4.25
Malathion	0.09	0.17	0.43	7.54	1.12	0.80	4.35
Parathion ethyl	0.02	0.07	3.28	11.10	4.76	1.76	4.78

Table 5. (*continued*)

Soil 3.A							
Methamidophos	0.97	0.92	3.89	4.04	1.97	3.54	0.28
Omethoate	0.39	0.42	3.80	35.70	0.69	12.30	2.98
Dimethoate	1.05	1.03	1.33	3.44	1.35	2.57	nd[a]
Parathion methyl	0.06	0.07	4.18	5.54	7.05	0.88	4.68
Malathion	0.02	nd[a]	4.53	nd[a]	7.68	nd[a]	4.95
Parathion ethyl	0.05	0.05	2.38	7.88	5.40	1.08	4.75
Soil 5.M							
Methamidophos	0.99	0.97	4.68	3.88	2.40	3.49	0.10
Omethoate	0.36	0.40	9.11	19.25	1.59	6.48	3.10
Dimethoate	1.00	1.00	0.63	3.96	0.63	2.92	nd[a]
Parathion methyl	0.17	0.21	2.15	8.64	6.33	2.41	4.05
Malathion	0.12	0.08	2.45	2.64	7.26	0.41	4.50
Parathion ethyl	0.10	0.09	1.73	16.46	5.47	3.08	4.53
Soil 6.S							
Methamidophos	0.98	0.98	3.32	4.69	1.69	4.26	0.10
Omethoate	0.25	0.21	7.87	19.52	1.16	4.73	3.85
Dimethoate	0.96	0.95	1.38	2.53	1.34	1.82	0.23
Parathion methyl	0.13	0.17	3.04	8.81	7.81	2.21	4.25
Malathion	0.10	0.08	1.38	12.57	3.66	2.15	4.55
Parathion ethyl	0.07	0.06	1.80	6.02	4.72	0.93	4.68

[a]Not detectable.

Recoveries, from water that had been in contact with soils using the SPE methodology were between 93.3% and 61.4%. The LOD was 5 ng mL^{-1} for all compounds, except for omethoate, 10 ng mL^{-1}. The RSD% values were between 0.52 and 5.34.

By using SPME, under the aforementioned experimental conditions, the RSD% obtained was better than 4% for all compounds except for methamidophos, 8.48%. This method allowed for six-point calibration curves in the range of 0.01–2.5 μg mL^{-1} to be generated for all compounds except for methamidophos (0.05–2.5 μg mL^{-1}) and omethoate (0.1–2.5 μg mL^{-1}). R^2 values were between 0.975 and 0.999.

The relative recoveries (%), the mean of three replicates, were between 88 and 104% with RSD values of 4–9%. For omethoate and methamidophos, recoveries were not feasible at concentration levels lower than 0.1 μg mL^{-1} and 0.05 μg mL^{-1}, respectively.

The results provide evidence that SPME can be successfully applied to pesticide residue determinations. Pesticides characterized by a wide range of polarity were investigated in single and multi-residue experiments. There are, however, limitations to the usefulness of SPME for environmental analyses of the more polar compounds.

One of the main problems is that the LOD value for omethoate is rather high, about 100 ng mL^{-1}. Other high-polarity OPs investigated gave lower LOD values: 50 ng mL^{-1} for methamidophos and 10 ng mL^{-1} for dimethoate. The less polar compounds, malathion, parathion methyl, and parathion ethyl, were investigated down to 0.5 ng mL^{-1}. A further limitation in the use of the CW-DVB fibre is its fast degradation [25]. During the experiments, with the relatively low NaCl concentration of 10% w/v, the fibre was usable for no more than 12–15 samples. At 20% w/v NaCl, only a few injections were possible.

Data obtained using both SPE and SPME are comparable, and the analytical procedure, developed using the CW-DVB fibre, is suitable for the quantitative evaluation of adsorption phenomena of the investigated OPs.

The possible usefulness of the optimized SPME procedure to real-world problems has been tested on laboratory samples obtained by contacting water and soils in the presence of six OPs. In particular, the SPME procedure allows the simultaneous screening of methamidophos, omethoate, dimethoate, malathion, parathion methyl, and parathion ethyl. Evidence has been obtained that a quantitative study of polar compounds is feasible, although further work is probably required to fully understand the behaviour of these compounds with regard to SPME. Moreover, SPME appears to be free from interferences and artefacts arising from the presence, in the water phase, of soluble organic species derived from the soil.

Adsorption and desorption phenomena are one of the main factors affecting pesticide fate in the environment. Soils are characterized by different and variable properties so that their interaction with chemical compounds, including OPs, in aqueous solutions cannot be simply defined. The different fates of polar and less polar OPs in the environment can depend upon their adsorption to soil. Adsorption of polar compounds, such as methamidophos, omethoate, and dimethoate, is more strongly correlated with the texture of soil than to the organic matter, whereas for less polar compounds, the adsorption is more strongly correlated with the organic matter content [26]. Organic matter content is the main factor correlated in the adsorption process. The data obtained from the adsorption experiments confirmed that soil shows a different affinity for these six pesticides.

The SPME methodology developed here appears therefore to be a useful tool in investigations concerning soil–pesticide interactions. Numerous experiments were

performed to investigate the possible effects of co-extracted materials from soils. One of the main parts of this work has been to show that SPME was not affected by co-extracted materials in 'environmental', i.e. dirty, water.

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