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Simultaneous Filtration and Liquid Chromatographic Microextraction with Subsequent GC-MS Analysis To Study Adsorption Equilibria of Pesticides in Soil

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Understanding the sorption equilibria of microcontaminants in soils requires the determination of the adsorbed analytes as well as those remaining in solution. On-line filtration-plus-LC-type microextraction offers an efficient alternative to the time-consuming classical procedures. The feasibility of a new simultaneous filtration-plus-liquid-chromatographic microextraction system with subsequent GC-MS to study the partition equilibrium of pesticides in the interface soil−water was investigated. The method allows the determination of the amount of pesticide adsorbed in the soil and that remaining in solution by a single injection of the total slurry. As an example, the adsorption equilibria of selected pesticides, ranging from relatively polar triazines to nonpolar compounds such as hexachlorobenzene or bromophos-ethyl, in an organic soil were studied. Once separated and preconcentrated, the filter and the solid-phase cartridge fractions were independently dried by a stream of nitrogen, extracted with methyl acetate, and analyzed by GC-MS. The standard deviations for the total procedure were lower than 6.2% (soil) and 10% (solution). The soil−water partition coefficients calculated for the selected compounds showed a good correlation with published octanol−water partition coefficients ($r^2 = 0.973$). This demonstrates clearly the practicality of the proposed methodology for adsorption equilibrium studies.

Introduction

Risk assessment for pesticides and toxic chemicals must include their mobility in the environment. In soils, that mobility depends on their sorption/desorption mechanism and kinetics. Both play a role in determining their bioavailability and the possibility to be transferred to another environmental compartment, directly or by dissolution in the surrounding water medium. Hence, understanding this kind of mechanism is essential in remediation or transport modeling.

The partition equilibrium of pesticides between the insoluble and dissolved phases in soil solutions has been widely studied (*1*−*6*). Two different experimental techniques are commonly employed to study the sorption of nonvolatile pesticides in soils, miscible displacement and batch sorption. With the former method, the solute of interest is leached through a saturated column of soil. This technique has mainly been used to describe pesticide transport in soil profiles under nonequilibrium conditions (*7, 8*). However, it is not suitable for the investigation of the sorption kinetics of pesticides (*8*). This kind of study has traditionally been conducted by batch sorption techniques (*1, 2, 5, 9*). Batch sorption methods require the separation of the solids from the supernatant liquid, usually by means of filtration (*5, 10*) and/or centrifugation (*1, 9, 11*). The separated phases are then analyzed after extraction by either liquid (*1, 5, 10*) or gas (*9, 12*) chromatography or, occasionally, direct spectrophotometric methods (*13*). In some studies, only the liquid phase is analyzed, and the difference between the pesticide fraction so determined and the total amount spiked is assumed as having been sorbed by the soil (*1, 5, 10*).

The above analytical approaches are all time-consuming and laborious and require a large amount of sample and much organic solvent. On-line procedures can become an interesting alternative and solve some of the shortcomings. Despite their obvious advantages, it was not until recently that Gamble and Khan (*14, 15*) and Sojo et al. (*16*) used on-line liquid chromatographic (LC) microextraction methods to study pesticide sorption in soils and tissue slurries. The most important limitations of these methods were the limits of detection that were rather high since UV−vis detection was used. Additional problems were that rather small amounts of particles were extracted, i.e., 20−50 μg, and that those systems did not allow either sample concentration or cleanup because the extracted analytes went on-line transported to the analytical column. The relatively limited resolution of the C_{18}-bonded silica columns used throughout and the lack of mass spectrometric (MS) confirmation capabilities were other disadvantages. Finally, two separate injections, whole slurry and off-line filtered slurry, were necessary to determine the concentration of the solutes adsorbed in the particles and those remaining in solution.

In this study the feasibility of using an on-line filtration plus LC-type microextraction and final analysis by GC-MS was studied as another approach to determine soil−water partition equilibria of pesticides in soil slurries. A modification of systems currently used for on-line water analysis (*17, 18*) was carried out to include a microfilter placed before the solid-phase extraction cartridge. A stainless steel microfilter was used as alternative to organic polymeric membranes to prevent possible adsorption of the target compounds. A single sample injection now provided information on the analyte concentrations in the particulate and the dissolved phase. Limits of detection were substantially improved by incorporating an on-line cleanup step and using MS detection.

Experimental Section

Chemicals. All pesticides, desethylatrazine, atrazine, diazinon, terbutryn, trifluralin, fenchlorphos, chlorpyrifos, hexachlorobenzene (HCB), and bromophos-ethyl, were purchased from Riedel de Haen (Seelze, Germany). Two working stock solutions were prepared and used for further dilution and spiking of the samples. One contained 111 μg mL^{-1} of six of the selected pesticides, desethylatrazine, atrazine, diazinon, terbutryn, HCB, and bromophos-ethyl, in methyl acetate and was used in the preliminary studies. The other contained

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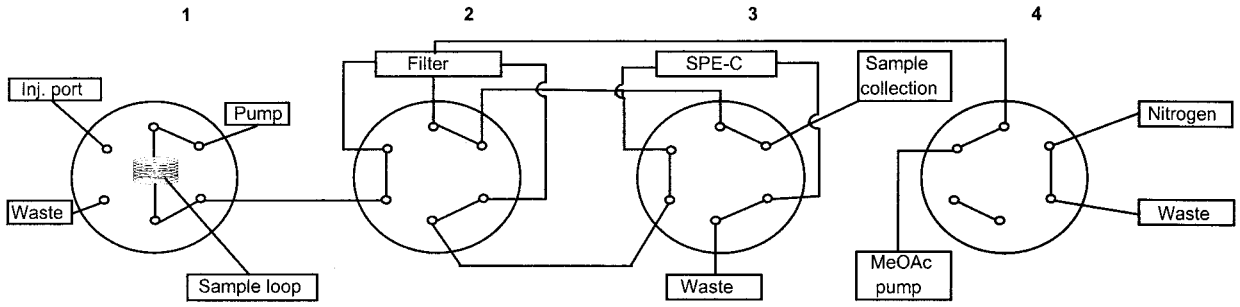

FIGURE 1. Schematic diagram of the setup for simultaneous filtration and LC microextraction. In the figure the injection (i.e. on-line filtration and SPE) step is shown.

TABLE 1. Molecular Weight and Octanol/Water Partition Coefficients of the Selected Pesticides

pesticides	MW[a]	*m/z*[b]	log K_{ow}[c]
desethylatrazine	187.1	187/172	1.51−1.53
atrazine	215.0	215/200	2.21−2.75
diazinon	304.1	179/137	3.11−3.81
terbutryn	241.2	226/185	3.43−3.74
trifluralin	335.3	306/264	3.97
fenchlorfos	321.6	285/125	4.81−5.07
chlorpyrifos	350.6	197/97	4.96−5.27
hexachlorobenzene	283.9	284/249	5.44−6.18
bromophos-ethyl	330.9	303/97	5.68−6.15

[a] Molecular weight, MW. [b] Values of two most abundant ions, *m/z*. [c] Log octanol/water partition coefficient (*19*), log K_{ow}.

111 μg mL^{-1} of the nine pesticides quoted in Table 1 and was used in adsorption studies once the methodology had been optimized. Pesticide-residue-grade methanol and methyl acetate were obtained from J. T. Baker (Deventer, The Netherlands). Methyl acetate was glass distilled. Quartz-distilled water was used in all experiments.

An organic soil from Amsterdam (The Netherlands) was used throughout the study. The soil sample was air-dried and sieved to 53 μm before being used.

Batch Methodology. Preliminary experiments were conducted in order to optimize the on-line LC microextraction methodology. In these studies spiked quartz-distilled water samples and synthetic slurry (7.7 mg mL^{-1} of 50−70 μm, 100 Å PLRP-S, a polystyrene-divinylbenzene copolymer, Polymer Laboratories, Church Stretton, U.K.) samples were used. The typical spiking was 0.71 μg of each pesticide per milliliter of solution. Slurries were equilibrated and magnetically stirred during 30 min before spiking.

After optimization, 0.34 g of soil sample was used for each series of adsorption measurements. The soil sample was presoaked with 50 mL (i.e., 1:147, w/v) of the selected solution (batch solvent) and homogenized by magnetic stirring during 30 min to release organic colloids from the soil and to break down any soil aggregates before spiking (*6*). Four different initial levels of concentration in solution were used: 0.089, 0.20, 0.35, and 0.71 μg mL^{-1} of each pesticide. The first slurry subsample was taken 5 min after spiking and then every 90 min. Measurements were extended for a minimum of 24 h. During this time, the soil slurry was magnetically stirred to achieve equilibrium and kept at room temperature (25 °C). The temperature was monitored throughout the experiment. All experiments were carried out in duplicate.

Blank soils were analyzed to check any contamination throughout the analytical procedure. Blanks were prepared following the same procedure as batch soil experiments but without spiking. No background interference was found to be introduced by the proposed methodology.

In all cases, brown glass containers were used as vessels. These were kept closed during the whole experiment to prevent losses by volatilization.

Simultaneous Filtration Plus LC Microextraction System. The simultaneous filtration and LC microextraction system used in this study is shown in Figure 1. It consisted of four Valco six-port valves (all ports and rotor capillaries were manufactured in house to a bore size of 0.5 mm for valves V1 and V2 and 0.3 mm for valves V3 and V4), a 100-μL sample loop (1 mm i.d.), a 10 mm × 3.0 mm i.d. stainless steel hollow holder, and a 10 mm × 2.0 mm i.d. solid-phase extraction (SPE) cartridge packed with 15−25 μm PLRP-S. In every experiment, the whole slurry (particles plus dissolved phase) was injected into the sample loop. Then, the slurry was pushed through the hollow filter by the selected mobile phase stream (transport solvent). Particles were retained on the filter and, thus, separated from the dissolved phase. Pesticides remaining in solution were preconcentrated on the SPE cartridge. A 5 μm stainless steel screen was used as microfilter, which was replaced by a 0.5 μm frit (Sigma, Zwijndrecht, The Netherlands) in the final stage of the study. All tubing was of stainless steel. Tubing leading from the injection port to the microfilter was of 1 mm i.d. All other tubing was of 0.1 mm i.d. A Gilson (Villiers-le-Bel, France) Model 302 pump was used to transport the sample into the microfilter and the SPE cartridge. A manometer was installed between this pump and the first valve to monitor the pressure on the LC microextraction device during different experiments. A Phoenix 20 CU syringe pump (Carlo Erba Strumentazione, Milan, Italy) was used to deliver the desorbing solvent.

Prior to use, the SPE cartridge was conditioned with 5 mL of methanol and 5 mL of quartz-distilled water. Spiked samples were magnetically stirred during the time of the analysis to ensure sample homogeneity. A 500-μL sample was injected to rinse and fill the 100-μL loop. The sample was pumped for 5 min at a flow rate of 2 mL min^{-1}. Particles retained in the filter were dried by 30 min of nitrogen gas purging at 3 bar and subsequently extracted with 100 μL of methyl acetate at a flow rate of 125 μL min^{-1}; the organic solvent was collected in microvials. Then, the stainless steel screen (or frit) used as a filter to retain the injected particles was replaced by a clean one. Simultaneously, the SPE cartridge was dried by 30-min nitrogen gas purging at 3 bar. Desorption of the pesticides preconcentrated on the polymeric sorbent was carried out with 100 μL of methyl acetate at a flow rate of 125 μL min^{-1}. The desorption solvent was collected in microvials. Next, the system was reconditioned by pumping 10 mL of quartz-distilled water.

GC-MS. The determination of the pesticides in the collected extracts was performed by capillary gas chromatography (HP 6890 Series, Hewlett-Packard, Palo Alto, CA) with MS (HP 6890 Series) detection (GC-MS) in the selected ion monitoring (SIM) mode. Samples were injected in the splitless mode (splitless time, 1.0 min) in a capillary Restek XTI-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The column temperature was programmed from 69 °C (3.5 min) to 280 °C at a rate of 15 °C min^{-1}. The final temperature

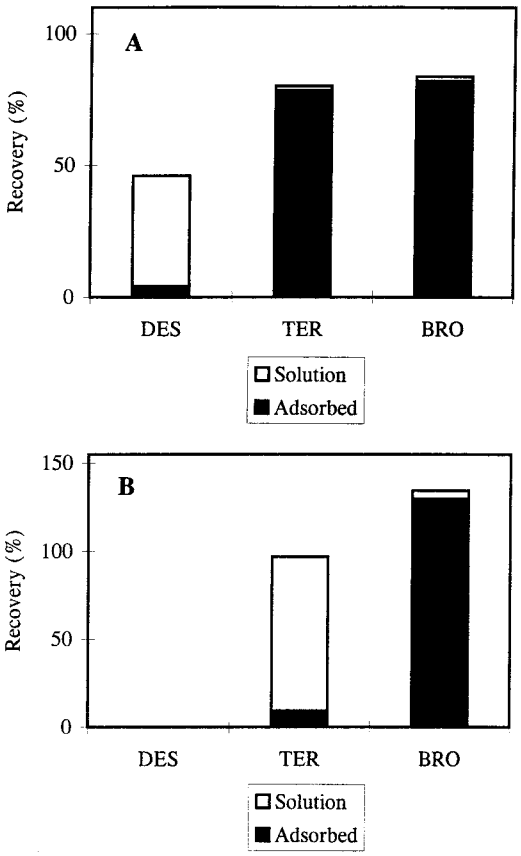

FIGURE 2. Effect of the transport solvent polarity on the partition of selected pesticides in spiked synthetic slurries containing 30 vol % of methanol: (A) 100% water and (B) water containing 30 vol % of acetone. Slurry particles, 7.7 mg mL^{-1}. Weight of particles extracted, 0.77 mg using a 100-μL loop. Spiking level, 0.71 μg mL^{-1} level. DES, desethylatrazine; TER, terbutryn; BRO, bromophos-ethyl.

was held for 1 min. Helium was used as the carrier gas at a column head pressure of 97 KPa. For each compound, the two most abundant ions produced by electron impact (EI) at 70 eV were monitored (Table 1).

Results and Discussion

Selection of the Batch Solvent and the Transport Solvent. As one typical example from among many sets of experimental conditions studied, Figure 2 shows some of the results found when a synthetic slurry sample presoaked for 30 min in water containing 30 vol % of methanol, spiked at the 0.71 μg mL^{-1} level, and equilibrated for 26 h was analyzed by the simultaneous filtration and LC microextraction procedure using either pure water or water containing 30 vol % of acetone as transport solvent. Except for desethylatrazine, all pesticides were found to be adsorbed almost quantitatively on the PLRP-S particles when quartz-distilled water was used as the transport solvent (Figure 2A). However, addition of 30 vol % of acetone to the transport solvent resulted in a complete distortion of the original partition equilibria of the pesticides (Figure 2B). Not unexpectedly, the presence of such a large percentage of acetone in the mobile phase helped to extract the pesticides with high and medium polarity initially sorbed in the particles. Under these conditions, sorption was predominant only for bromophos-ethyl. In addition, and in accordance with general experience from SPE-LC studies, the most polar analytes such as desethylatrazine and trebutryn showed breakthrough on the SPE cartridge. Obviously, a less polar transport solvent should be selected. Even though some pesticides were partly lost due to sorption onto the walls of the equilibration vessel and/or

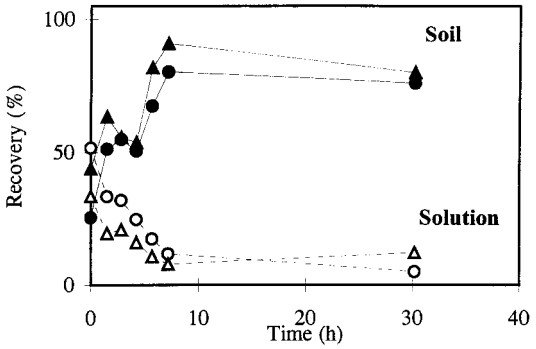

FIGURE 3. Adsorption-time profile found for HCB (circles) and bromophos-ethyl (triangles) in organic soil slurries presoaked with water containing 30 vol % of methanol. See text for conditions.

the tubing of the on-line system (*20, 21*) when pure water was used as transport solvent (total recovery maximal 80% in Figure 2A), this did not adversely affect the partitioning data, i.e., the final ratio (sorbed/dissolved) found. As this was the main goal of the present study, quartz-distilled water was provisionally chosen as transport solvent for subsequent experiments with soil slurries. Under these experimental conditions the effect of the batch solvent polarity on the partitioning of the pesticides was studied.

Adsorption vs time profiles of pesticides at 0.36 μg mL^{-1} level in organic soil slurries presoaked for 30 min with either water containing 30 vol % of methanol or with pure water were compared. Slurry profiles of the test solutes obtained in the presence of 30 vol % of methanol showed that the sorption of the polar pesticides, desethylatrazine, atrazine, diazinon and terbutryn, in the soil particles was seriously reduced due to the competition of methanol. After 30 h of equilibration, the percentages adsorbed were, in all four cases, lower than 20%. The adsorption of the most hydrophobic pesticides, HCB and bromophos-ethyl, in soil was also still very high (Figure 3) but lower than those previously reported for topsoil (*5*). It also took a fairly long time for equilibrium to be established, viz. some 8 h. For comparison, the adsorption vs time profiles obtained for three model pesticides with high (desethylatrazine), medium (terbutryn). and low (bromophos-ethyl) polarity, with water as batch solvent as well as transport solvent, showed that the adsorption of the test pesticides in the soil particles reached an apparent equilibrium more rapidly, i.e., within the first 4 h (Figure 4). The combined result presented above shows that, to obtain realistic information on the partition equilibrium kinetics of the pesticides in soil, the soil slurries have to be prepared in water, even if this will cause the total recoveries of the pesticides to decrease. This will be especially true for the highly hydrophobic compounds. However, the well-known remedy—addition of an organic modifier to the transport solvent—(*20, 21*) cannot be used if analytes covering a wide polarity range are studied, as in this paper, because the polar solutes such as desethylatrazine and atrazine will then show breakthrough in the SPE cartridge.

In an attempt to further evaluate this problem in our particular case, an experiment with a soil slurry presoaked in water, spiked at the 0.36 μg mL^{-1} level and equilibrated for 48 h was conducted. Water containing up to only 10 vol % of methanol was tested as transport solvent. The data of Table 2 show that the presence of such low percentages of modifier in the transport solvent did not really change the partition equilibria nor—and this was somewhat unexpected—the total recoveries of most analytes. The proportion between the pesticides percentages found adsorbed and remaining in solution were constant in all cases, except for atrazine and diazinon when using water 5 vol % methanol as transport solvent and for HCB when using 10 vol % methanol. In these

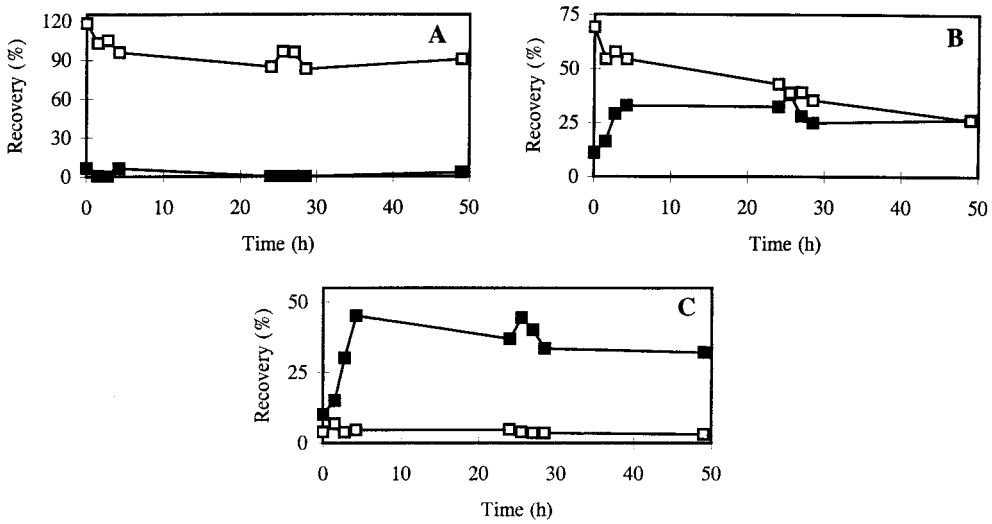

FIGURE 4. Adsorption vs time profile found for (A) desethylatrazine, (B) terbutryn, and (C) bromophos-ethyl in organic soil slurries presoaked with water. Full symbols represent soil phase, and open symbols, dissolved phase. See text for conditions.

TABLE 2. Dependence of Analyte Recoveries on Polarity of the Transport Solvent

	methanol in transport solvent								
	0%			5%			10%		
recovery (%)	adsor	solut	*total*	adsor	solut	*total*	adsor	solut	*total*
desethylatrazine	0	124	*124*	0	73	*73*	0	66	*66*
atrazine	0	99	*99*	3	81	*84*	5	92	*97*
diazinon	9	52	*61*	10	38	*48*	13	50	*63*
terbutryn	18	56	*74*	18	56	*74*	19	67	*86*
HCB	11	5	*16*	9	4	*13*	8	7	*15*
bromophosethyl	13	7	*20*	12	6	*18*	10	6	*16*

TABLE 3. Analytical Data Corresponding to the Calibration of the GC-MS and LOD in Real Soil Slurries

pesticide	regression coeff[a]	RSD (%)[b]	LOD (ng mL^{-1})[c]
desethylatrazine	0.972	5	15
atrazine	0.964	2	5
diazinon	0.996	4	2
trifluralin	0.999	6	3
terbutryn	0.995	7	2
fenchlorfos	0.999	5	2
chlorpyrifos	0.995	9	3
hexachlorobenzene	0.998	4	2
bromophos-ethyl	0.993	5	5

[a] Regression coefficient of response vs area plot in 0.004−0.36 μg mL^{-1} range. [b] At 0.089 μg mL^{-1} level $n = 3$. [c] Limit of detection as experimentally determined with signal-to-noise ratio, 3:1.

TABLE 4. Typical Sorption/Solution Data for Partition Studies of Selected Pesticides in an Organic Soil Slurry

	percent adsorbed		percent in solution		
pesticide	mean[a]	SD	mean[a]	SD	K_d[b]
desethylatrazine	–	–	97	10	–
atrazine	–	–	95	9.5	–
diazinon	14	3.3	62	6.5	33.2
terbutryn	14	4.0	52	5.3	39.6
trifluralin	29	1.2	32	0.1	133
fenchlorfos	18	2.3	24	2.6	110
chlorpyrifos	23	1.4	27	0.9	125
hexachlorobenzene	28	5.6	9	0.4	457
bromophos-ethyl	29	6.2	54	8.5	170

[a] Separate analyses of organic soil spiked at 0.36 μg mL^{-1} level, $n = 4$. [b] K_d (Lkg^{-1}); quotient between the calculated concentration adsorbed in the soil (μg kg^{-1}) and the concentration in the aqueous solution (μg L^{-1}).

experiments, unexpected higher percentages of the pesticides remained in solution. On the other hand, desethylatrazine still showed breakthrough with 5% of methanol. In addition, even with 5−10% of methanol, a practical problem arose. Soil particles retained on the filter started to break up when they came into contact with the methanol in the transport solvent. These smaller particles passed through the filter, clogging the tubing which connected valves V2 and V3 and the SPE cartridge. As a result, the SPE cartridge was irreversibly damaged, and precision of the procedure became very poor. Since adding a modifier to a purely aqueous transport solvent obviously did not bring any real advantages, water was finally selected as transport solvent for all subsequent experiments.

Under these conditions, the concentration of atrazine, diazinon, and terbutryn remaining in the aqueous solution slowly decreased with time (Figure 4), indicating losses from solution. Although this result was consistent with the long time reported for reaching a real equilibrium partition in soils (*2*, *11*, *13*, *22*), a measurement time of 24−48 h was considered adequate for subsequent experiments.

Analytical Data. Relevant analytical data concerning GC-MS are summarized in Table 3. The responses were linear over the whole range tested, 0.004−0.36 μg mL^{-1}. The regression values for desethylatrazine and atrazine were lower because these peaks showed some tailing. The repeatability, which was determined by analyzing a solution at the 0.089 μg mL^{-1} level, was satisfactory with relative standard deviations (RSD) of 2−9%. The experimentally calculated limits of detection in real soil slurries were in the range 2−15 ng mL^{-1}.

The repeatability of the whole procedure of simultaneous filtration and LC microextraction was evaluated by analyzing

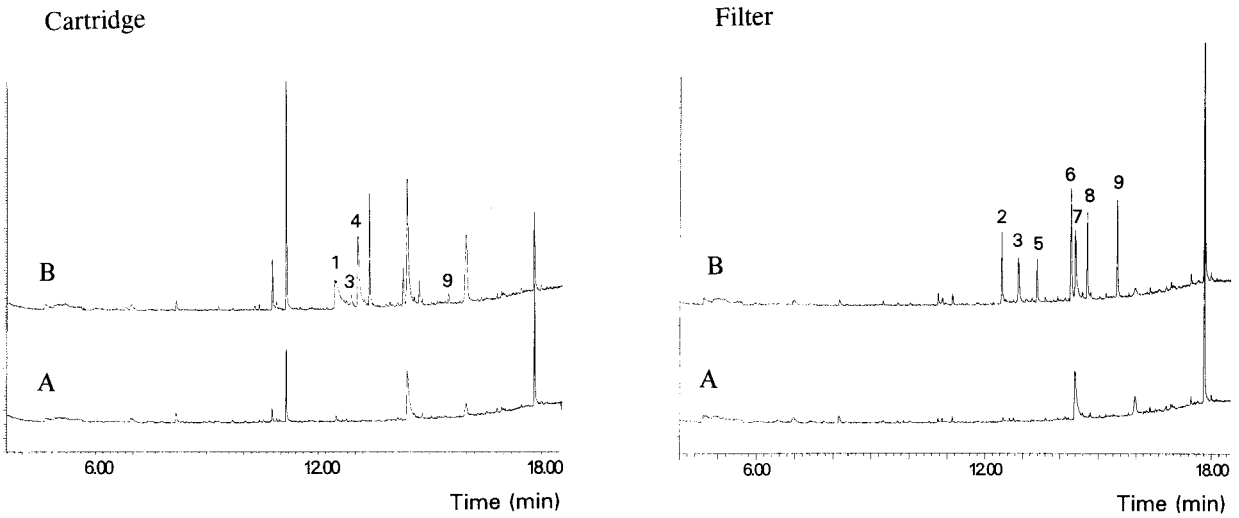

FIGURE 5. GC-MS chromatograms of soil and dissolved phases obtained after simultaneous filtration and on-line LC microextraction of an organic soil (A) without spiking and (B) after spiking at the 0.36 μg mL^{-1} level. Pesticides: 1. desethylatrazine, 2. trifluralin, 3. HCB, 4. atrazine, 5. diazinon, 6. fenchlorfos, 7. terbutryn, 8. chlorpyrifos, and 9. bromophos-ethyl.

an organic soil spiked at the 0.36 μg mL^{-1} level. Mean percentages of the amount of each analyte in the soil and the dissolved phases were calculated after the system had reached an apparent equilibrium (24 h). The mean results of four separate analyses are summarized in Table 4. The standard deviations (SD) of these percentages were 1.2−6.2 for concentrations determined in the soil and 0.1−10 for concentrations in the aqueous phase. Similar results were obtained when the stainless steel screen used as filter were substituted for LC frits in order to improve the robustness of the device (data not shown). Table 4 also summarized the linear soil−water partition coefficients of the test solutes (K_d) calculated on the basis of these data. This model calculates the adsorption coefficient (K_d, l kg^{-1}) for a given compound in soil as the ratio of the concentration adsorbed in the soil (S, μg kg^{-1}) and that remaining in the aqueous solution (C, μg L^{-1})

$$K_d = S/C$$

Not unexpectedly, the calculated K_d values increased with the hydrophobicity of the analyte (Table 1).

Figure 5A,B shows the chromatograms obtained after the simultaneous filtration and LC microextraction of the organic soil slurry without and with spiking at the 0.36 μg mL^{-1} level and equilibrated for 24 h. None of the test solutes was found at detectable levels in the nonspiked organic soil.

Figure 6 shows, as an example, the typical adsorption vs time profiles obtained for diazinon when the soil slurry was spiked at the highest (0.71 μg mL^{-1}) and lowest (0.089 μg mL^{-1}) concentration levels studied. The mutual agreement is fully satisfactory. Similar agreement among profiles calculated at the different spiking levels was found for the other pesticides.

Application. To illustrate the potential of the proposed methodology for adsorption equilibrium studies of pesticides in soil slurries, the correlation between the log K_d calculated by applying the linear model to data from the analysis of the soil slurry spiked at the 0.36 μg mL^{-1} level and equilibrated for 24 h, and the log K_{ow} values of these pesticides reported in the literature (*19*) was studied. A satisfactory correlation (Figure 7; $r^2 = 0.973$) was found between the experimental partition coefficients and log K_{ow} values. The result also shows that, although the recoveries of some pesticides were lower than usual, the adsorption vs time profiles obtained by this on-line simultaneous filtration and LC microextraction system are similar to those obtained with conventional

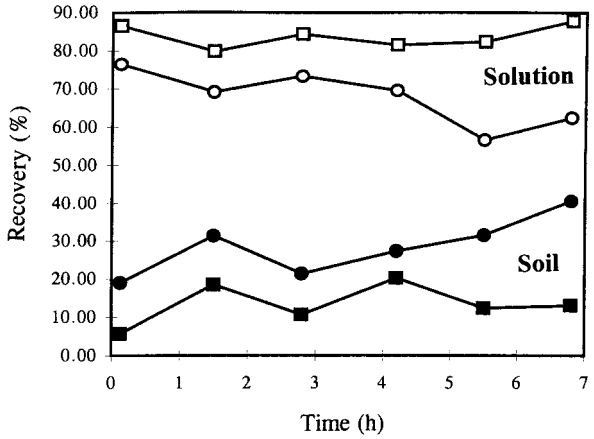

FIGURE 6. Adsorption vs time profiles obtained for diazinon in an organic soil spiked at 0.71 μg mL^{-1} (squares) and 0.089 μg mL^{-1} (circles) level.

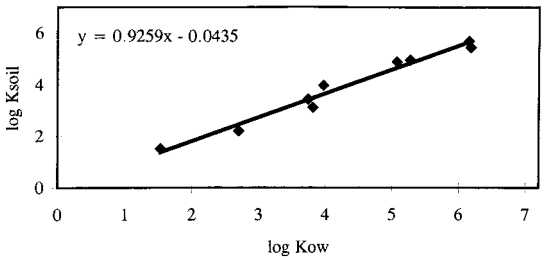

FIGURE 7. Correlation between the experimental soil−water partition coefficients, log K_{soil}, and reported log K_{ow} values for the nine test analytes.

methods. That is, the system provides real partition data for the adsorption equilibrium of the test compounds in the interface soil−water and, consequently, solves the most pressing problem of previously reported procedures. In a future paper, the methodology will be used to compare the behavior of soils and sediments with divergent physicochemical characteristics and to study the relative merits of different types of adsorption isotherms for data analysis.

Acknowledgments

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