Passive extraction and clean-up of phenoxy acid herbicides in samples from a groundwater plume using hollow fiber supported liquid membranes

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Abstract

Hollow fiber supported liquid membranes were applied for the passive extraction of phenoxy acid herbicides from water samples. Polypropylene hollow fiber membranes (240 μm i.d., 30 μm wall thickness, 0.05 μm pore size, 30 cm length) were impregnated with 2.0% tri-*n*-octylphosphine oxide (TOPO) in di-*n*-hexyl ether in the pores of the fiber wall to form a liquid membrane. They were then filled with basic solution in the lumen as acceptor and finally placed into the sample (donor). Complete extraction of phenoxy acid herbicides including 2,4-D, MCPA, dichlorprop, and mecoprop from an acidified sample (4 mL, adjusted to pH 1.5 with HCl) into basic acceptor (10 μL of 0.2 M NaOH) was achieved after 4 h of shaking (100 rpm) resulting in an enrichment factor of 400 times. The acceptor was then neutralized by addition of HCl and injected into a HPLC system for the determination of the phenoxy acid herbicides. Environmentally relevant salinity (0–3.5% NaCl) and dissolved organic matter (0–25 mg/L of dissolved organic carbon) had no significant effect on the extraction. The method provided extraction efficiencies of more than 91%, detection limits of 0.3–0.6 $\mu\text{g/L}$, and combined extraction and clean up in one single step. This procedure was applied to determine aqueous concentrations of phenoxy acid herbicides in groundwater samples collected from an old dumping site (Cheminova, Denmark) with detected concentrations up to 5800 $\mu\text{g/L}$. Although the samples were very dirty with large amounts of suspended particles, non-aqueous phase liquids (NAPLs) and dissolved organic matters, good spike recoveries (80–126%) were obtained for 10 of the 11 samples.

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1. Introduction

Phenoxy acid herbicides have been extensively used for the control of weeds in agriculture. A majority of the herbicides used in Europe are acidic herbicides [1], and phenoxy acid herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), dichlorprop (DCPP), and mecoprop (MCPP) are among the 10 most important pesticides in Europe [2]. Due to their high solubility in water, phenoxy

acid herbicides easily enter surface or ground waters through natural drainage or infiltration, and have been widely detected in groundwater [3–5].

Because of the toxicity of phenoxy acid herbicides and their metabolic products, monitoring their concentration in water and groundwater is of importance. Due to the matrix complexity and the low concentration of these compounds in environmental water samples, the most commonly applied methods for the determination of these compounds are gas chromatography (GC) after derivatization or liquid chromatography (LC), where a preconcentration step is usually needed [1].

Various procedures have been developed for the extraction and preconcentration of phenoxy acid herbicides from water samples. Conventional methods are liquid–liquid extraction (LLE) with organic solvents such as dichloromethane from

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acidified samples. Solid-phase extraction (SPE) has widely been adopted as an alternative to LLE [6], and ion exchangers [7,8], C_{18} bonded silica [9,10], polymers [11–13], and graphitized carbon black (GCB) [14,15], or tandem adsorbents [16] have been reported as adsorbent materials. SPE of phenoxy acid herbicides has the advantages of high extraction efficiency and thus high method sensitivity, but often suffered from the plugging of cartridge and overlapping of analyte chromatographic peaks by dissolved organic matter (DOM) in water samples, especially when C_{18} bonded silica is used as adsorbent [17]. Dynamic ion-exchange solid-phase extraction (DIE-SPE), based on the ionic functional group of the surfactant adsorbed on the surface of C_{18} bonded silica to act as ion-exchange sites to attract ionized phenoxy acid herbicides, was also established to eliminate the interference of humic acids [17]. Phenoxy acid herbicides in water were also extracted with solid-phase microextraction (SPME) after derivatization with benzyl bromide [18], alkylchloroformate [19] or *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide [20]. While the former two derivatization/SPME methods [18,19], with low sensitivity and poor repeatability, can only be used as screening technique; the later one [20] possesses sufficient sensitivity and good repeatability for determining phenoxy acid herbicides in real wastewater and groundwater samples. Supported liquid membrane (SLM) extraction, both flat membrane based [21] and hollow fiber membrane based [22,23], were also used as an alternative sample preparation technique for the determination of phenoxy acid herbicides. These methods have the merits of high selectivity, low cost, negligible consumption of organic solvent, and are readily coupled with LC.

Up to now, most SLM based sample preparation procedures were conducted in the regime of incomplete extraction, i.e., only a small part of the target analytes were extracted from a large amount of sample (donor) into a small amount of trapping solution (acceptor) to obtain a high enrichment factor in short extraction time [24]. This extraction mode usually results in sample matrix dependent extraction efficiency and thus calibration difficulty when real samples are analyzed [25,26]. Recently, it was found that this matrix effect can be reduced by performing SLM in complete extraction mode; where the analytes are completely extracted from relatively small amount of sample, e.g. a few milliliter into a few microliter volume of acceptor [27].

The aim of this study was to investigate the potential of using hollow fiber membrane based SLM for the extraction of phenoxy acid herbicides from water samples. This proposed procedure was applied to determine aqueous concentrations of phenoxy acid herbicides in polluted groundwater samples.

2. Experimental

2.1. Reagents and materials

Phenoxy acid herbicides including 2,4-D (98.0%), MCPA (97.5%), DCPP (99.0%) and MCPP (97.0%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Tri-*n*-octylphosphine oxide (TOPO) and undecane were obtained from

Sigma–Aldrich (Steinheim, Germany). Dihexyl ether (DHE) was purchased from Fluka (Buchs, Switzerland). Terrestrial origin humic acid sodium salt (tech., lot. S15539-384, Sigma–Aldrich) with 35.1% of dissolved organic carbon (DOC) was used as obtained. HPLC-grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). All other chemicals were of analytical grade or above and ultrapure water purified by a Milli-Q Gradient system (Millipore, Bedford, MA, USA) was used throughout.

Individual standard stock solutions of phenoxy acid herbicides (1000 mg/L) were prepared by dissolving 10 mg of standards in 10 mL of HPLC-grade methanol. Working solutions were prepared by appropriate dilution of the stock solutions with water. The standard stock solutions and working solution were stored at 4 °C.

X30-240 Celgard polypropylene microporous hollow fiber membrane (30 μ m wall thickness, 240 μ m inner diameter, 0.04 μ m pore size, 40% porosity), and 50/280 Accurel PP polypropylene hollow fiber tubing (50 μ m wall thickness, 280 μ m inner diameter, 0.1 μ m pore size) were obtained from Membrana (Wuppertal, Germany). BD Micro-Fine Syringe (with a needle of 0.30 mm outer diameter and 8 mm length, 0.5 mL, prepared for U-100 insulin injection), obtained from BD Consumer Healthcare (Franklin Lakes, NJ, USA) was used to fill the acceptor into the lumen of the hollow fiber for extraction and to flush out the acceptor. The needle of the syringe was ground to $\sim$ 0.25 mm outer diameter for easy insertion into the lumen of the hollow fiber.

2.2. Extraction procedure

The extraction was carried out as described in our previous study [28] with some modifications. Briefly, the lumen of a piece of hollow fiber ($\sim$ 30 cm length) was flushed and filled with acceptor solution by using a BD Micro-Fine Syringe. Then the fiber was dipped into the membrane liquid (2.0% TOPO in DHE) for a few seconds to impregnate the pores of the hollow fiber wall, thus forming the organic liquid membrane. After that, the lumen of the fiber was slowly flushed and completely filled with the acceptor without any air bubble. Then, the two ends of the fiber were folded and enveloped with a piece of aluminum foil, and the surplus membrane liquid on the fiber surface of the obtained extraction device was washed away with water. This prepared extraction device was inserted in a 4-mL capped vial and it was made sure that the whole fiber was fully immersed in the sample solution. The vial was capped and shaken on a HT orbital shaker from Infors (Bottmingen, Switzerland) for 4 h at 100 rpm to perform the extraction and enrichment. After extraction, the hollow fiber extraction device was harvested and one of the sealed ends was cut and the fiber was connected to the needle of a BD Micro-Fine Syringe filled with air, then the other sealed end was cut and the acceptor containing the extracted analytes was flushed from the fiber lumen into a clean and dry glass vial (50 μ L, Alltech, Deerfield, IL, USA). The whole acceptor ($\sim$ 10 μ L) was manually aspirated into a 20 μ L HPLC microsyringe filled with $\sim$ 3 μ L of 0.5 M HCl and injected into the HPLC system for analysis.

Optimization of the extraction parameters was performed with standard solutions containing 50 µg/L of phenoxy acid herbicides unless otherwise stated.

2.3. HPLC instrument and separation

The HPLC equipment used included two Waters 515 HPLC pumps (Waters, Milford, MA, USA), a Waters 996 photodiode array detector set at 280 nm wavelength, and a personal computer equipped with a Millennium³² Chromatography Manager (Waters) for controlling the system and processing chromatographic data. A LiChrospher 100 RP-C₁₈ endcapped column (250 mm × 4.0 mm, particle size 5 µm) was used as the analytical column.

HPLC separation of phenoxy acid herbicides was conducted by using a mixture of acetonitrile and 2.0% acetic acid (adjusted pH 3.8 with NaOH) as mobile phase at a flow rate of 1.0 mL/min. The gradient profile was: 20% acetonitrile in 0–1 min, linear increase to 50% acetonitrile in 1–8 min and then linear increase to 80% acetonitrile in 8–11 min, there after restored to 20% in 3 min followed by a 2 min equilibration time. The four phenoxy acid herbicides were baseline separated, and the peak area difference between chlorophenols prepared in water and prepared in 0.1 M NaOH was less than 10%.

2.4. Sample collection

Groundwater samples were collected from the wells of an old dumping site at the groin 42-deposit (Cheminova, Denmark) on 17 November 2005. Samples labeled with A were collected from deep wells (about 9–10 m below surface), those labeled with B were from shallow wells (about 5–7 m below surface). The shallow and the deep wells were naturally separated by a thin clay layer located approximately 8 m below the surface. All wells were pumped for 5 min using a MP1 pump before samples were collected in 1 L glass bottles. The samples were spiked with 100 mg/L of HgCl₂ immediately after collection in order to avoid biodegradation, and were kept at room temperature. These samples were extracted with the proposed procedure without any further pretreatment, except that a few samples were diluted with water due to the very high concentration of some analytes.

2.5. Calibration and data processing

All experiments were conducted at least twice and the mean values are reported. The extraction was evaluated by extraction efficiency (*E*), which is defined as the percentage of analyte extracted from the donor solution to the acceptor solution and was calculated from equation:

$$E = \frac{C_A \cdot V_A}{C_D \cdot V_D} = \frac{n_A}{n_D}$$

where *C_A* and *V_A* are the analyte concentration and volume of the acceptor after extraction, *C_D* and *V_D* the analyte concentration and volume of the sample before extraction; *n_A* the analyte amount in the acceptor after extraction, and *n_D* the initial analyte amount in the donor. Calibration of *n_A* was carried out based on

Fig. 1. The profiles of extraction efficiency against time with different hollow fiber membranes. Donor, 50 µg/L of 2,4-D and MCPA spiked in 4 mL of 0.1 M HCl; acceptor, 10 µL of 0.1 M NaOH; liquid membrane, 2.0% TOPO in DHE; shaking rate, 100 rpm. (x) 2,4-D with X30-240 Celgard fiber; (□) 2,4-D with 50/280 Accurel PP fiber; (●) MCPA with X30-240 Celgard fiber; (◇) MCPA with 50/280 Accurel PP fiber.

HPLC peak areas of a analyte, and a calibration curve of peak area against analyte mass. The calibration curve was obtained by injection 10 µL of various concentrations of standard into the HPLC system, and plotting the obtained peak areas against the analyte mass.

Real sample analysis was calibrated with external standard calibration by conducting the same extraction procedure for both the standard solutions and the real groundwater samples.

3. Results and discussion

3.1. Evaluation of the supported liquid membrane extraction conditions

3.1.1. Selection of hollow fiber

Two kinds of membranes, X30-240 Celgard and 50/280 Accurel PP polypropylene hollow fiber tubing, were tested as liquid membrane support. Fig. 1 shows the profiles of extraction efficiency against extraction time for MCPA and MCPA as examples. When X30-240 Celgard membranes were employed, the extraction efficiency rapidly reached the highest and then kept constant over a long extraction time. When 50/280 Accurel PP was used, however, the extraction efficiency reached the maximum value and then reduced gradually with the prolonging of the extraction. The cause for the reduction in extraction efficiency is not clear yet. Probably membrane leakage happened with the prolonging of the extraction time. Though the maximum extraction efficiency with X30-240 Celgard hollow fiber was relatively lower than that with 50/280 Accurel PP hollow fiber, the former was adopted in the following studied as the extraction efficiency was constant over long extraction time.

3.1.2. Effect of donor acidity and acceptor

The studied 2,4-D, MCPA, DCPA, and MCPA are weak acids with *pK_a* value of 2.73, 3.07, 3.00 and 3.78, respectively [29]. Based on the principle of SLM, a donor pH of about 1.0 and acceptor pH of over 7.0 should be adopted in order to trap these

compounds efficiently. Preliminary experiments show that when samples were prepared in 0.1 M HCl as donor, the obtained extraction efficiency by using 0.5 M NaOH were close to that with 0.5 M phosphate buffer (pH 12) as acceptor. However, the repeatability was much better by using NaOH as acceptor. The HCl concentration in donor and NaOH concentration in acceptor were optimized to obtain higher extraction efficiency. As can be seen in Table 1, when 0.1 M NaOH was adopted as acceptor, the extraction efficiencies did not change significantly by acidifying the donor with 0.005–0.02 M HCl. However, the extraction efficiencies decreased slightly with the increasing of HCl concentration in the range of 0.02–0.5 M. The NaOH acceptor concentration was further optimized in the range of 0.1–1.0 M by acidifying the donor with 0.02, 0.05, and 0.1 M HCl, respectively. Results shown in Table 1 suggest that the most efficient extraction was achieved by using 0.2 M NaOH as acceptor and acidify the sample with 0.02–0.05 M HCl, which corresponds to pH about 1.5. In the following studies, 0.2 M NaOH was adopted as acceptor, while standard sample solutions were prepared in 0.05 M HCl and real samples were acidified to pH 1.5 with HCl.

3.1.3. Selection of membrane liquid

Undecane and DHE were tested as membrane liquid, and it was found that DHE has much higher extraction efficiency than undecane. TOPO is usually added into the membrane liquid to enhance the extraction efficiency of weak organic acids with low pK_a and K_{ow} [30–32]. The addition of TOPO can significantly change the behavior of the membrane liquid due to the hydrogen bonding between TOPO and the analytes. Usually the higher the concentration of TOPO in the membrane liquid the higher NaOH concentration in the acceptor is required to back extract the analytes from the membrane liquid into the acceptor. The optimum TOPO concentration in the membrane liquid is analyte dependent [30–32]. In one of our studies (not published), the highest extraction efficiency of MCPA was obtained with 2.0–5.0% TOPO. The respective profiles of extraction efficiency against time by using DHE and 2.0% TOPO in DHE as membrane liquid are shown in Fig. 2, which clearly shows that 2.0% TOPO in DHE remarkably reduced the extraction time. Fig. 2 also indicates that essentially the same extraction efficiency was obtained for both membrane liquids when the extraction time is over 6 h. It is noticeable that 2.0% TOPO in DHE can effectively eliminate the influence of sample salinity (see details in matrix effect discussed later).

3.1.4. Volume ratio of donor to acceptor

Keeping a constant acceptor volume of 10 μ L and extraction time of 3 h, the influence of sample volume was studied and results are shown in Fig. 3. With increasing sample (donor) volume, the extraction efficiency decreased but the chromatographic peak area increased for all the studied analytes as expected. Therefore, low sample volume is preferred to be used for reducing the extraction time, while large sample volume is helpful for obtaining lower detection limit at the expense of longer extraction time. In the following studies, 10 μ L acceptor and 4 mL sample were adopted as a compromise. Under this

Table 1
Influence of HCl concentration in donor and NaOH concentration in acceptor on the extraction efficiency (%)

HCl (M)	0.1 M NaOH				0.2 M NaOH				0.5 M NaOH				1.0 M NaOH			
	2,4-D		MCPA		2,4-D		MCPA		2,4-D		MCPA		2,4-D		MCPA	
	DCPP	MCPP	DCPP	MCPP	DCPP	MCPP	DCPP	MCPP	DCPP	MCPP	DCPP	MCPP	DCPP	MCPP	DCPP	MCPP
0.005	85 $\pm$ 5	82 $\pm$ 3	83 $\pm$ 4	83 $\pm$ 4	83 $\pm$ 4	83 $\pm$ 4	83 $\pm$ 4	83 $\pm$ 4	83 $\pm$ 5	83 $\pm$ 5	76 $\pm$ 4	79 $\pm$ 1	78 $\pm$ 3	78 $\pm$ 6	70 $\pm$ 7	73 $\pm$ 7
0.01	83 $\pm$ 1	80 $\pm$ 1	78 $\pm$ 4	80 $\pm$ 2	90 $\pm$ 13	84 $\pm$ 12	85 $\pm$ 12	92 $\pm$ 0	100 $\pm$ 6	82 $\pm$ 3	90 $\pm$ 1	93 $\pm$ 3	84 $\pm$ 1	84 $\pm$ 3	65 $\pm$ 7	48 $\pm$ 5
0.02	89 $\pm$ 4	86 $\pm$ 7	86 $\pm$ 4	86 $\pm$ 7	102 $\pm$ 3	92 $\pm$ 4	95 $\pm$ 3	92 $\pm$ 2	82 $\pm$ 3	82 $\pm$ 3	52 $\pm$ 8	75 $\pm$ 6	57 $\pm$ 9	68 $\pm$ 7	58 $\pm$ 6	50 $\pm$ 9
0.05	86 $\pm$ 3	75 $\pm$ 3	82 $\pm$ 6	77 $\pm$ 8	79 $\pm$ 1	66 $\pm$ 1	72 $\pm$ 2	65 $\pm$ 1								
0.1	82 $\pm$ 4	56 $\pm$ 5	78 $\pm$ 5	57 $\pm$ 10												
0.2	80 $\pm$ 2	53 $\pm$ 10	77 $\pm$ 5	56 $\pm$ 11												
0.3	77 $\pm$ 6	49 $\pm$ 1	76 $\pm$ 7	52 $\pm$ 1												
0.5	79 $\pm$ 4	57 $\pm$ 2	76 $\pm$ 1	58 $\pm$ 1												

Samples (50 μ g/L standard solutions) were extracted with 10 μ L of acceptor by using 2.0% TOPO in DHE as membrane liquid. Uncertainties are given as standard deviations.

Fig. 2. The profiles of extraction efficiency against time with different membrane liquids. Donor, 50 $\mu\text{g/L}$ of 2,4-D, MCPA, DCP and MCP spiked in 4 mL of 0.05 M HCl; acceptor, 10 μL of 0.2 M NaOH; hollow fiber, X30-240 Celgard fiber; shaking rate, 100 rpm. The lines represent the fit of a first-order one-compartment uptake model to the data. (□) pure DHE as membrane liquid; (■) 2.0% TOPO dissolved in DHE as membrane liquid.

Fig. 3. Effect of sample (donor) volume on the extraction efficiency. Donor, 50 $\mu\text{g/L}$ of 2,4-D, MCPA, DCP and MCP spiked in 0.05 M HCl; acceptor, 10 μL of 0.2 M NaOH; liquid membrane, 2.0% TOPO in DHE supported X30-240 Celgard hollow fiber; shaking rate, 100 rpm.

volume ratio of donor to acceptor, an enrichment factor of 400 can be obtained with a complete extraction.

3.1.5. Effect of agitation

Fig. 4 shows the profiles of extraction efficiency against extraction time under static and 100 rpm shaking rate, respectively. For static extraction about 8 h is needed to reach 90% extraction efficiency. When extraction was carried out at 100 rpm shaking rate, however, the extraction efficiency reached at least 91% in 4 h, suggesting that 4 h was needed to reach essentially complete extraction for all the studied compounds. Higher shaking rate did not reduce the extraction time probably because the headspace of the sample vial is limited and the increase

of shaking rate did not improve the agitation efficiency significantly. Consequently, extraction was performed at 100 rpm for 4 h as optimum. Results shown in Fig. 4 indicate that the static equilibrium extraction efficiencies obtained from the fit of a first-order one-compartment uptake model to the data were slightly lower than that with 100 rpm shaking, but the 8 h extraction efficiencies results at static extraction were very close to the results at 100 rpm shaking rate. The cause was not clear; probably the first-order one-compartment uptake model was not very suitable for depicting the extraction when TOPO was used as a carrier.

3.2. Matrix effect

The matrix in real groundwater samples might influence the extraction efficiency. To study the matrix effect, individual sample solutions with environmentally relevant salinity (0–3.5% NaCl) and humic acid concentration (0–25 mg/L DOC) were extracted under the above optimized conditions. The extraction efficiencies were in the range of 98–112% for all the studied compounds with no significant change over the studied concentration range of humic acids. Although some precipitation occurred when acidifying the sample to pH 1.5 at DOC values >10 mg/L, the constant extraction efficiencies indicate that neither the dissolved nor the precipitated humic acids had significant influence on the extraction efficiency.

Fig. 5 shows the effect of salinity on extraction efficiency. When 2.0% TOPO was presented in the membrane liquid, the

Fig. 4. Profiles of extraction efficiency against extraction time under static and 100 rpm shaking rate. Donor, 50 $\mu\text{g/L}$ of 2,4-D, MCPA, DCPP and MCPP spiked in 4 mL of 0.05 M HCl; acceptor, 10 μL of 0.2 M NaOH; liquid membrane, 2.0% TOPO in DHE supported X30-240 Celgard hollow fiber. The lines represent the fit of a first-order one-compartment uptake model to the data. ($\square$) static; ($\blacksquare$) shaking at 100 rpm.

Fig. 5. Effect of salinity (NaCl) on the extraction efficiency. Donor, 50 $\mu\text{g/L}$ of 2,4-D, MCPA, DCPP and MCPP spiked in 4 mL of 0.05 M HCl with various concentrations of NaCl; acceptor, 10 μL of 0.2 M NaOH; extraction time, 4 h. (a) 2.0% TOPO in DHE as liquid membrane; (b) pure DHE as liquid membrane.

sample salinity of fresh water and sea water ($\leq 3.5\%$) had no effect on the extraction efficiency. Without TOPO, however, the extraction efficiency of MCPA and DCPP decreased with the increasing of salinity over the range studied. Further experiments showed that the extraction efficiencies of MCPA and DCPP in a 3.5% NaCl solution were not improved with the prolonging of extraction time up to 12 h. This result suggests it was due to some thermodynamic rather than kinetic reasons that the extraction efficiencies of MCPA and DCPP decreased with the increasing of donor salinity. Probably higher partition coefficients between the membrane phase and donor were obtained with the addition of TOPO in the membrane.

3.3. Analytical performance data

Under the optimized conditions, the extraction efficiency of the proposed procedure was determined using a mixed standard solution. As shown in Table 2, essentially the same extraction efficiencies were obtained when 5 and 50 $\mu\text{g/L}$ of the phenoxy acids herbicides standard solutions were extracted; thus the extraction efficiency is independent of the sample concentration in this range. The method linearity was assessed by extraction of standard solutions with five concentration levels in the range of 1–125 $\mu\text{g/L}$, and results shown in Table 2 indicate the good linearity with regression coefficients in the range of 0.9987–0.9995. The precisions presented as relative standard deviation at 5 $\mu\text{g/L}$ level was 1–12% ($n = 3$).

Table 2
Analytical performance data of the proposed extraction procedure

Compounds	Extraction efficiency (%)		Linear range ($\mu\text{g/L}$)	Correlation equation	Correlation coefficient	Detection limit ($\mu\text{g/L}$)
	5 $\mu\text{g/L}$	50 $\mu\text{g/L}$				
2,4-D	118 $\pm$ 5	107 $\pm$ 4	1–125	$Y = 1427x + 532.5$	0.9995	0.3
MCPA	91 $\pm$ 6	100 $\pm$ 3	1–125	$Y = 1322x + 1636$	0.9987	0.4
DCPP	91 $\pm$ 12	106 $\pm$ 2	1–125	$Y = 1194x + 1196$	0.9977	0.6
MCPP	116 $\pm$ 1	98 $\pm$ 2	1–125	$Y = 1238x - 523.5$	0.9995	0.6

Samples (standard solutions prepared in 0.05 M HCl) were extracted for 4 h with 10 μL of acceptor (0.2 M NaOH) by using 2.0% TOPO in DHE as membrane liquid. Uncertainties are given as standard deviations.

The calculated detection limits of these compounds were 0.3–0.6 $\mu\text{g/L}$ ($S/N = 3$), which mainly are the result of enrichment factor, injection volume and detector sensitivity. The enrichment factor of the present method was about 400, which is similar or exceeds concentration factors of typical solid phase extraction procedures. The injection volume was rather low, and higher injection volumes will lead to lower detection limits. Higher injection volumes can easily be obtained by using longer pieces of hollow fiber in larger samples. The applied diode array detector is very robust, versatile and widely available, whereas its sensitivity and selectivity often is insufficient for environmental analysis. The coupling of passive enrichment and mass sensitive detectors will lead to substantially lower detection limits in the pg/L range.

3.4. Application in analysis of groundwater samples

The proposed procedure was applied to determine 2,4-D, MCPA, DCPP, and MCPP in groundwater plume samples collected from an old dumping site at the groin 42-deposit (Cheminova, Denmark) with results shown in Table 3. All the samples were first analyzed by the proposed method, and those samples with very high concentration of the analytes (V3A, V3B, V10A, V10B and V18A) were extracted and analyzed again after being diluted four times with reagent water. To

assess the spiked recovery, samples were extracted after spiking 50 $\mu\text{g/L}$ of these studied chemicals except for V3A, V3B, V10A, V10B and V18A, in which 100 $\mu\text{g/L}$ of analytes were spiked after the samples were diluted four times. As the MCPA concentrations in V3A and V18A are extremely high, the MCPA recovery for these two samples were determined on diluted samples. Results show that most of the studied samples contained 2,4-D, MCPA, DCPP, and MCPP with concentrations up to 5800 $\mu\text{g/L}$. Although the samples were very dirty with large amounts of suspended particles and DOM, good spike recoveries (80–126%) were obtained except for sample V3A. Relatively low recoveries (52–75%) were obtained for V3A due to the presence of large amounts of non-aqueous phase liquids (NAPLs).

3.5. Perspectives for environmental applications

The proposed passive extraction method can be applied to a wide range of analytes and samples. It will be a valuable supplement to current solid phase extraction techniques, particularly for very dirty samples, where the membrane barrier is crucial for the clean up. The proposed technique has very limited infra-structure requirements, which makes it highly suited for operation in the field. The volume and weight of the samples can thus be reduced on-site and the resulting extracts are easily

Table 3
Phenoxy acid herbicides concentration (C) and spike recovery (R) in samples collected from groundwater plume by the proposed method

Sample	2,4-D		MCPA		DCPP		MCPP	
	C ($\mu\text{g/L}$)	R (%)	C ($\mu\text{g/L}$)	R (%)	C ($\mu\text{g/L}$)	R (%)	C ($\mu\text{g/L}$)	R (%)
V3A ^a	290 $\pm$ 20	55	3380 $\pm$ 140	62 ^c	ND ^d	75	540 $\pm$ 70	52
V3B ^a	120 $\pm$ 20	90	800 $\pm$ 120	107	ND	83	300 $\pm$ 50	110
V8A ^b	16 $\pm$ 1	94	100 $\pm$ 10	100	ND	81	24 $\pm$ 1	88
V8B ^b	7 $\pm$ 1	86	27 $\pm$ 5	95	ND	92	ND	106
V10A ^a	58 $\pm$ 3	100	540 $\pm$ 20	116	ND	82	660 $\pm$ 30	126
V10B ^a	38 $\pm$ 2	100	600 $\pm$ 30	92	ND	95	360 $\pm$ 20	110
V11A ^b	7 $\pm$ 1	110	3 $\pm$ 2	126	ND	100	8 $\pm$ 1	104
V11B ^b	ND	102	ND	94	ND	102	ND	88
V12A ^b	12 $\pm$ 6	106	4 $\pm$ 2	80	12 $\pm$ 4	88	5 $\pm$ 2	88
V12B ^b	ND	108	ND	104	ND	104	ND	95
V18A ^a	140 $\pm$ 30	120	5800 $\pm$ 260	96 ^c	40 $\pm$ 5	89	200 $\pm$ 10	80
V79 ^b	20 $\pm$ 2	80	220 $\pm$ 60	100	27 $\pm$ 8	85	80 $\pm$ 22	84

^a C was determined by diluting the samples four times with reagent water before extraction. R was assessed by spiking 100 $\mu\text{g/L}$ of analytes in four-fold diluted samples.

^b C was determined without dilution, and R was determined by spiking 50 $\mu\text{g/L}$ of analytes.

^c Determined by spiking 100 $\mu\text{g/L}$ of MCPA in 20-fold diluted samples.

^d ND: not detected.

transported to the analytical laboratory. The proposed technique can also be combined with different detection principles, such as mass selective detector for highly sensitive analyses or it can be combined with spectrophotometry or fluorescence for simple on-site measurements [33]. Finally, the method has the potential to integrate extraction and cleanup with the transport and storage of samples. However, the latter requires further research in order to confirm the stability of supported membranes for extended periods of time.

4. Conclusions

A hollow fiber membrane based SLM procedure was developed for the complete extraction of phenoxy acid herbicides from very polluted water samples. Combining extraction and clean-up in one step, the proposed extraction procedure is simple with low cost and high efficiency. The membrane forms an efficient barrier, leading to very efficient matrix clean-up.

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