Supported Liquid Membrane Technique for Time-Integrating Field Sampling of Acidic Herbicides at Sub Parts per Billion Level in Natural Waters

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A method for continuous sampling of acidic herbicides in natural waters based on supported liquid membrane extractions has been developed. A porous PTFE membrane was impregnated with an organic solvent, ensuring only uncharged molecules passed through the membrane. Selecting the pH in the donor and acceptor phases selectively enriched acidic substances on the acceptor side. The herbicides (bentazon, 2,4-D, dicamba, dichlorprop, MCPA, and mecoprop) were continuously sampled during 24 h. After collection, the samples were taken to the laboratory for quantification using liquid chromatography with UV detection. The extraction efficiences for the herbicides were ca. 0.70, resulting in detection limits of ca. 40 ng/L, sample volumes of 1 L (24-h sampling), in clean aqueous samples. The detection limits in natural waters are somewhat higher and are estimated to ca. 0.1 μg/L. Changes in both air and water temperatures had no significant effect on the extraction efficiencies.

INTRODUCTION

The use of herbicides is widely spread all around the world. Because of their extensive use, they may find their way into natural waters in areas of agricultural activity (Richards et al., 1980). The concentrations in these waters are often below 1 μg/L (1 ppb), which generally necessitates good separation and sensitive detection for their determination. Phenoxyalkanoic acids are often derivatized with a halogen-containing reagent, thus making capillary gas chromatography with electron capture detection suitable for the determination (Lee et al., 1986; Gurka et al., 1987). Liquid chromatography (LC) is advantageous because no derivatization is needed for good chromatographic performance. If UV absorption is used for detection, the relatively low sensitivity and selectivity make preconcentration and cleanup steps necessary. Accordingly, the final analysis with LC–UV has generally been combined with a preconcentration step as solid-phase extraction on cartridges or precolumns, utilizing packings of C_{18} bonded phase on silica (Hoke et al., 1986) or porous polymers (Geerdink et al., 1989; Betti et al., 1990).

An alternative method for sample preparation, based on the use of supported liquid membranes, has been developed at our laboratory (Audunsson, 1986, 1988a). In brief, ionizable analytes are extracted in a flow system from aqueous solutions to a hydrophobic liquid in the membrane. The conditions are chosen so that the analytes in aqueous solutions enter the donor channel in the membrane unit as neutral species, diffuse across the hydrophobic membrane, and are then irreversibly trapped by ionization in a stagnant aqueous acceptor phase at a proper pH value. The methodology has been used, in combination with on-line GC, for selective enrichment of amines from urine (Audunsson, 1988b) and plasma (Lindegård et al., 1992). Carboxylic acids in manure were determined by GC after off-line enrichment and derivatization (Mathiasson et al., 1991a). In combination with LC, the technique has been applied for determinations of phenoxyacetic acids (Nilvé et al., 1989) and sulfonylurea herbicides (Nilvé and Stebbins, 1991). Preliminary experiments concerning metal ions (Cu and Co) have been successful. The methodology has recently been reviewed (Jönsson and Mathiasson, 1992).

For quantification of herbicides in natural waters, grab sampling is the most common technique. Sample workup and quantification is made in the laboratory. In addition to problems like degradation of the analytes during transport or storing and handling of large water volumes, a large number of samples are needed to reliably estimate the leakage of herbicides into the recipient water since the concentration may vary considerably with time (Sirons et al., 1982).

The membrane methodology makes it possible to combine sampling of recipient water and sample workup, avoiding the disadvantages mentioned above and resulting in time-average concentration values. Instead of workup of the water in the laboratory, it is processed at the field sampling point. The enriched sample is brought to the laboratory for separation and quantification.

Recently we reported for the first time the use of supported liquid membrane technology for time-integrating field sampling, with MCPA [(4-chloro-2-methylphenoxy)acetic acid] as a model substance (Mathiasson et al., 1991b). The concentration values, over a period of 26 days, were estimated using 24-h sampling periods. In this paper we present a further development aiming at a simultaneous determination of most of the phenoxy acids and related substances (see Table I) which are expected to occur in rural areas in Sweden.

EXPERIMENTAL PROCEDURES

Chemicals. The organic solvents used were di-*n*-hexyl ether (Sigma Chemical Co., St. Louis, MO), *n*-undecane (Merck, Darmstadt, Germany) (p.a.), methanol (FSA Laboratory Supplies, Loughborough, U.K.) (HPLC grade), and acetic acid (Riedel-de Haën AG, Seelze, Germany) (minimum 99.8%). The herbicides were 2,4-D, dicamba, dichlorprop, MCPA, mecoprop (all from Serva Feinbiochemica GmbH and Co., Heidelberg, Germany) (analytical grade) and bentazon (BASF AG, Ludwigshafen, Germany) (99.5%). Sulfuric acid (May and Baker Ltd., Dagenham, U.K.) (analytical reagent grade) and sodium dihydrogen phosphate monohydrate (Merck) (p.a.) were also used. Water was purified with a Milli-Q/RO4 unit (Millipore, Bedford, MA).

Equipment. *Field Sampling Equipment.* The field sampling configuration is shown in Figure 1. The sampler (A), which was placed 10 cm under the water surface, consisted of a tube (i.d. 53 mm, L = 100 mm) with 100-μm mesh nylon net in both ends, to avoid larger particles and small animals from entering the sampler. From inside the sampler, water was pumped in a PTFE tube (i.d. 0.5 mm) with a peristaltic pump (B) (Minipuls 3, Gilson

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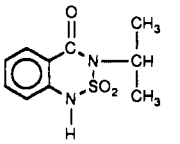
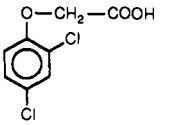
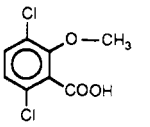
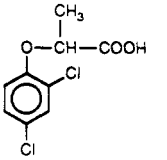
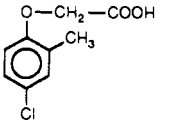
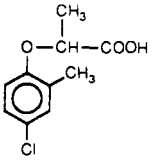
Table I. Herbicides Used in This Study and Their Dissociation Constants

systematic name	common name [CAS number]	structure	pK_a
3-(1-methylethyl)-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide	bentazon [25057-89-0]		3.45[a]
(2,4-dichlorophenoxy)acetic acid	2,4-D [94-75-7]		2.87[b]
3,6-dichloro-2-methoxybenzoic acid	dicamba [1918-00-9]		1.90[b]
2-(2,4-dichlorophenoxy)propanoic acid	dichloroprop [120-36-5]		2.86[b]
(4-chloro-2-methylphenoxy)acetic acid	MCPA [94-74-6]		3.13[b]
2-(4-chloro-2-methylphenoxy)propanoic acid	mecoprop [7085-19-0]		3.11[b]

[a] Sterling et al. (1990). [b] Cessna and Grover (1978).

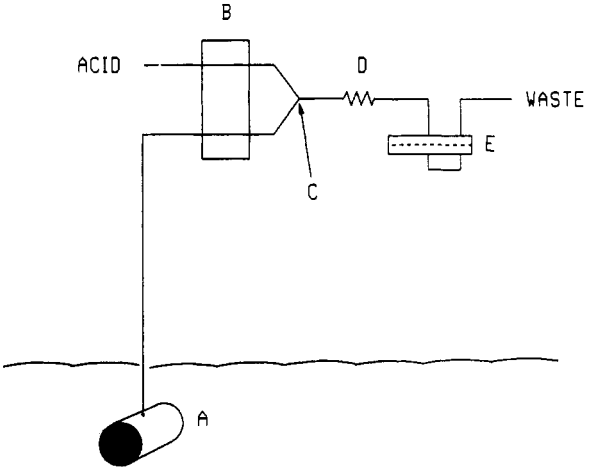


Figure 1. Field sampling setup for membrane enrichment of acidic herbicides in natural waters: (A) sampling point; (B) peristaltic pump; (C) confluence point of sample stream (0.8 mL/min) and a stream of 0.4 M H_2SO_4 (0.15 mL/min); (D) mixing coil; (E) membrane separator, with stopped flow in the acceptor channel.

Medical Electronics, Villiers-le-Bel, France) using standard PVC pump tubing or "acid-resistant" pump tubing (Elkay Products, Shrewsbury, MA). The different parts of the sampling equipment were connected with 0.5 mm i.d. PTFE tubing and Altex screw fittings. The confluence connector (C) where the channels meet at an angle of 60° was made of PTFE. The mixing coil (D) consisted of ca. 1 m of 0.5 mm i.d. PTFE tubing coiled with a diameter of ca. 25 mm.

The membrane separator (E) (Figure 2) was made of two circular PTFE blocks (diameter 120 mm and thickness 8 mm) with machined grooves like Archimedes' spirals (depth 0.25 mm,

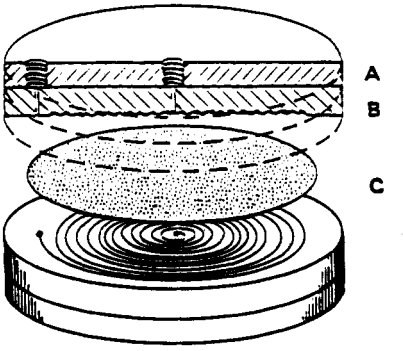


Figure 2. Membrane separator: (A) aluminum backup; (B) PTFE block with grooves like Archimedes' spiral; (C) porous PTFE membrane with polyethylene backing.

width 1.5 mm, length 250 cm; total volume of ca. 0.95 mL). Aluminum blocks with 6-mm thickness were used to stabilize the construction. A porous PTFE membrane with polyethylene backing, Fluoropore FG (pore size 0.2 μm, total thickness 175 μm, of which 115 μm is polyethylene backing, porosity 0.70; Millipore), was impregnated by soaking for 15 min in a mixture of *n*-undecane and di-*n*-hexyl ether (1:1). The membrane was placed between the two PTFE blocks, and the whole unit was clamped together with eight screws. Thereby, two channels (donor and acceptor) separated by the membrane are formed, provided with connectors for tube fittings.

Separation Equipment. Separation and quantification was made by LC–UV (Figure 3). A high-pressure pump (Consta Metric III, Laboratory Data Control, Riviera Beach, FL) and a variable-wavelength UV detector (Model 770, Schoeffel Instrument Corp., Westwood, NJ) were used. Injections were made with a Valco injector in which the sample loop was replaced by a precolumn (i.d. 1 mm, length 20 mm, Upchurch Scientific Inc., Oak Harbor, WA) packed with Hamilton PRP-1 (12–20 μm,

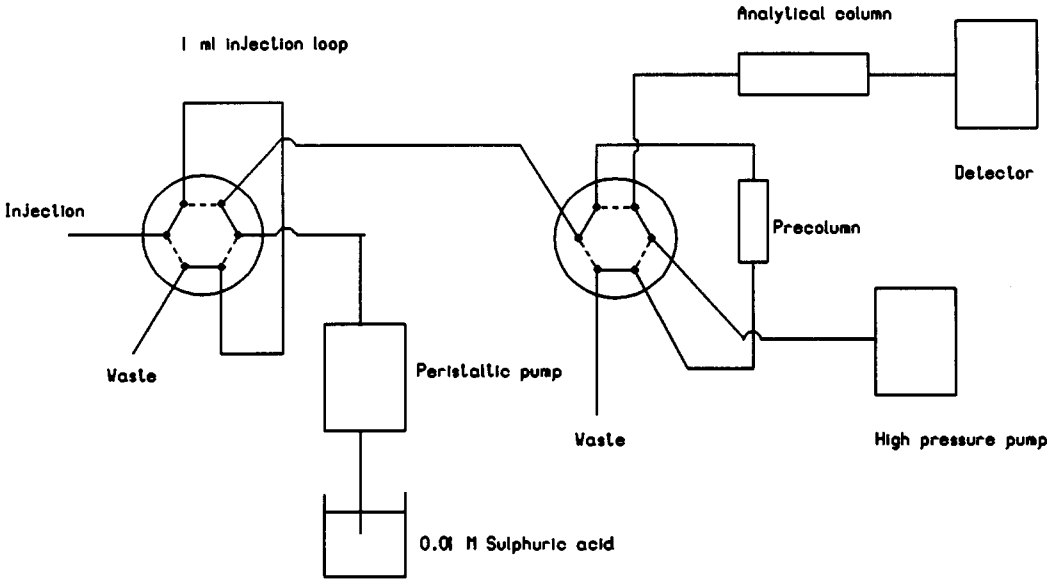


Figure 3. Experimental setup for the final analytical step.

Alltech Associates, Inc., Deerfield, IL). The analytical column was a C_{18} column Spherisorb S5 ODS-5 (i.d. 4.6 mm, length 150 mm, particle size 5 μm; Hichrom Ltd., Berkshire, U.K.). The chromatographic data were collected and evaluated with a PE Nelson 1020 S chromatographic data system (Perkin-Elmer, Norwalk, CT).

Procedure. *Field Sampling.* From a point ca. 10 cm under the water surface, water was pumped with a flow rate of ca. 0.8 mL/min and mixed with 0.4 M H_2SO_4 (ca. 0.15 mL/min) before it was introduced to the membrane separator. The acidified water sample passed the donor channel, and after diffusing through the liquid membrane, the analytes were collected in 0.1 M phosphate buffer at pH 7 in the acceptor channel. The enrichment time for each sample was ca. 24 h, and ca. 1 L of water was processed. After completed sampling, the enriched plug was pressed out of the acceptor channel with 0.1 M phosphate buffer using a syringe, and a 1.7-mL sample was collected in a capped tube and brought to the laboratory. Before a new sampling cycle was started, the acceptor channel was filled with water and the membrane was tested by pumping H_2SO_4 and water on the donor side and subsequently checking the pH in the acceptor phase to make sure that the membrane was intact. The nylon net was inspected daily and exchanged every second or third day.

Analysis of the Field Samples. The enriched sample was transferred to a 2.0-mL volumetric flask and diluted to the mark with 0.4 M H_2SO_4. The pH was checked to be below 2 with pH indicator paper. The sample was injected into a 1-mL loop through a six-channel valve and pumped with a peristaltic pump onto the precolumn, followed by 1 mL of 0.01 M H_2SO_4. By switching the LC injector valve, the sample from the precolumn was injected into the analytical column in the back-flush mode. The phenoxy acids have UV absorption maxima near 205, 230, and 285 nm (Pribyl and Herzel, 1978). Dicamba has an absorption maximum at 277 nm, while bentazon has two maxima at 219 and 316 nm, respectively (Liska et al., 1992). At 205 and 230 nm interfering substances will have large absorbances, while at 285 nm the selectivity is much larger. Therefore, UV detection at 285 nm was chosen in this study. The mobile phase was methanol and 1% aqueous acetic acid (58:42).

Partition Coefficients. The partition coefficients for the herbicides between the aqueous donor phase and the organic solvent used in the membrane were determined as follows: Standard aqueous solutions of the herbicides in the range 10–250 mg/L (five solutions) were batch extracted, with an organic phase consisting of *n*-undecane and di-*n*-hexyl ether (1:1). One milliliter of the standard solution (0.07 M H_2SO_4) and 1 mL of the organic solvent were mixed and shaken for 15 min. The concentrations in the aqueous phase were measured before and after the extraction using the same LC system as described above; the partition coefficients were calculated from the concentrations before and after the extraction.

Extraction Efficiency. The extraction efficiencies in the membrane system for the herbicides were determined after a 24-h enrichment of standard aqueous solutions, containing 0.5 or 5 μg/L of each herbicide, and brook water spiked at the 0.5 μg/L level.

Temperature Effect. Both the water temperature and the air temperature may vary considerably during a sampling period of 24 h. The effect on the extraction efficiences due to these temperature changes was investigated. The extraction efficiency was determined by enriching a 100 μg/L standard solution for 1 h at temperatures between 5 and 20 °C in the sample solutions. Finally, the entire apparatus was kept at 5 °C in a refrigerated room, and the extraction efficiencies were compared with the efficiencies at 20 °C.

Application. Field sampling was made in a brook (Vemmenhögsån) during 30 days in May and June 1990. The agricultural activity in the area in southern Sweden is intensive, and the use of herbicides is great. The time between spreading of the herbicides in the fields and the appearance of herbicides in water depends mainly on the mobility of the compounds, composition of the soil, and precipitation.

The flow rate of water and acid was checked daily during the sampling period by measuring the flow rate during a short period (ca. 15 min) and by measuring the total amount of water and acid that was processed during each 24-h sampling period.

RESULTS AND DISCUSSION

Extraction Efficiency. The extraction efficiency (E) is the portion of the analyte extracted in the membrane process and is calculated as

$$E = C_a V_a / C_d V_d$$

where C_a is the concentraction of analyte in the acceptor phase, V_a is the volume of the acceptor phase, C_d is the concentraction in the aqueous sample, and V_d is the sampling volume.

In Table II the extraction efficiencies for the herbicides are given. The standard deviations in the extraction efficiencies for the six herbicides are ca. 10% and include variations due to changes in flow rates as well as the variation in the chromatographic determination. As seen in Table II, the differences in extraction efficiences are small and are neither dependent on the concentrations in the range used nor dependent on the sample matrix when natural waters or standard solutions are used. Some of the parameters governing the extraction efficiencies have been discussed in an earlier paper (Nilvé and Stebbins, 1991). The partition coefficients for dicamba, 2,4-D, and MCPA were determined to be 32, 25, and 43, respectively.

Table II. Extraction Efficiencies for the Six Herbicides, Determined after a 24-h Enrichment of 0.5 (n = 6) and 5 μg/L (n = 6) Standard Solutions and Brook Water Spiked with 0.5 μg/L (n = 3)[a]

substance	0.5 μg/L standard solution	5 μg/L standard solution	0.5 μg/L spiked brook water
bentazon	0.71 ± 0.10	0.64 ± 0.05	0.65 ± 0.01
2,4-D	0.68 ± 0.07	0.64 ± 0.05	0.65 ± 0.08
dicamba	0.77 ± 0.10	0.74 ± 0.09	0.82 ± 0.07
dichlorprop	0.74 ± 0.06	0.69 ± 0.05	0.72 ± 0.08
MCPA	0.68 ± 0.07	0.64 ± 0.05	0.64 ± 0.02
mecoprop	0.69 ± 0.08	0.66 ± 0.05	0.67 ± 0.01

[a] Values are given as mean ± standard deviation.

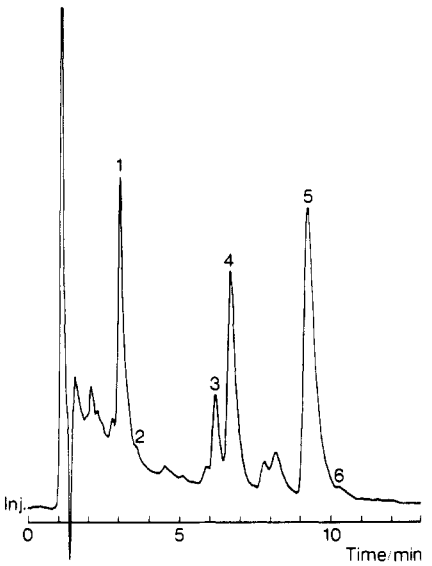


Figure 4. Typical chromatogram for a determination of six herbicides after a 24-h time-integrating field sampling in a Swedish brook (Vemmenhögsån): (1) dicamba (5.5 μg/L); (2) corresponds to the retention time of bentazon; (3) 2,4-D (1.3 μg/L); (4) MCPA (4.3 μg/L); (5) dichlorprop (6.9 μg/L); (6) corresponds to the retention time of mecoprop.

For analytes with large partition coefficients (>20) the extraction efficiency mainly depends on the mass transfer of the analyte to the membrane in the donor channel and is relatively insensitive to changes in the partition coefficients.

Temperature Effect. The temperature of a standard solution of the herbicides was varied between 5 and 20 °C. Within this temperature span no significant changes in the extraction efficiencies could be observed. To investigate the effects of changes in air temperature, the entire apparatus was kept at 5 or 20 °C. No significant difference in the extraction efficiencies at the two temperatures could be seen. It can thus be concluded that for the changes in both water and air temperatures likely to occur during a field sampling period of 24 h, there is no significant effect on the extraction efficiencies for the herbicides.

Optimization of the Analytical Step. Injecting the analytes onto a precolumn instead of into a loop allows larger sample volumes to be handled by the chromatographic system. The analytes are focused on the precolumn, resulting in a second enrichment step. The capacity of the precolumn was checked by injection of 1 mL of 1–40 mg/L (1–40 ppm) standard solutions, followed by 1 mL of 0.01 M H_2SO_4. For concentrations up to 40 mg/L, which corresponds to concentrations of ca. 100 μg/L in natural waters, no breakthrough occurs. This means that the risk for overloading the precolumn is small.

The effect of the washing step of the precolumn was determined by injection of a 2.0 mg/L standard solution

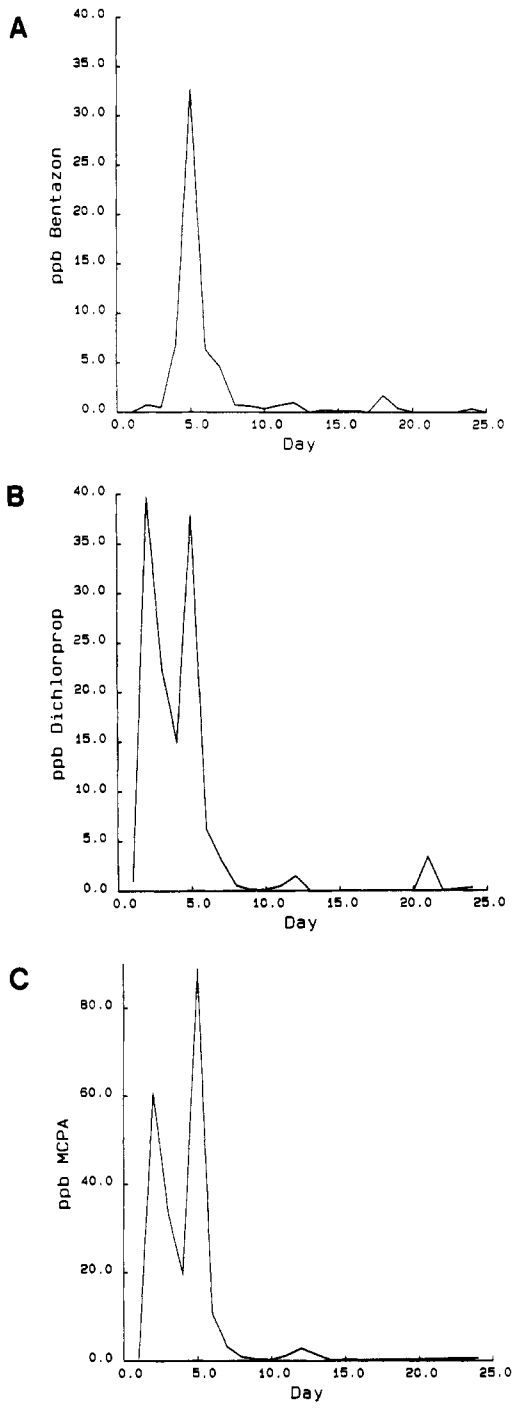


Figure 5. Concentration variation of bentazon (A), dichlorprop (B), and MCPA (C) in a Swedish brook (Vemmenhögsån) during a sampling period of 30 days, obtained using time-integrating sampling.

followed by different volumes of 0.01 M H_2SO_4 (range 0.25–10 mL). Varying the volume of 0.01 M H_2SO_4 used to wash the precolumn showed virtually no difference in the peak heights of the analytes. This means that if there are problems with early eluting compounds obscuring the analyte peaks in the chromatogram, it might be possible to decrease the interference by using a large wash volume. With longer enrichment times (e.g., 1 week) this may be necessary. For a 24-h enrichment a wash volume of 1 mL of H_2SO_4 was, however, sufficient. It is also possible to use a more efficient way of interference removal than washing with 0.01 M H_2SO_4 as described by Coquart and Hennion (1991) in a paper on solid-phase extraction.

Quantification. Calibration lines for the six herbicides were made in the range 50–5000 μg/L (five points) with

double injections of 1-mL sample on the precolumn. All herbicides gave a linear correlation coefficient of 0.9999 except dicamba (0.9990), and the intercepts did not significantly differ from zero.

The detection limits in the chromatographic step, calculated as 2 times the noise, were ca. 30 ng for the six herbicides. Since the extraction efficiencies are 0.70, it means that for sampling periods of 24 h when 1 L water is processed, the detection limits for the herbicides will be ca. 40 ng/L (40 ppt). For sampling of natural water the detection limit is higher, due to the increased background absorption, and is estimated to 0.1 μg/L.

The repeatability in the chromatographic step, based on five consecutive injections of a 2 mg/L standard solution, gave relative standard deviations between 2 and 4%.

Chromatography. A typical chromatogram after 24 h of sampling is shown in Figure 4. The chromatogram is fairly clean with only a few interfering peaks, reflecting the selectivity in the liquid membrane enrichment step.

Application. The field sampling in Vemmenhögsån showed unexpected high concentrations of all of the herbicides, and for MCPA values as high as ca. 85 μg/L (1-day average) were found, which is much higher than the values found in a previous study of another brook (Mathiasson et al., 1991b). In Figure 5 the amounts of bentazon, dichlorprop, and MCPA in the brook during the sampling period are shown (parts a, b, and c, respectively). The high concentrations of herbicides at the beginning of the sampling period are a result of spraying of the fields a few days before. In spite of the amount of precipitation being low during this period, the transportation of the herbicides through the soil is fast. The herbicide concentrations in the brook are rather high within a relatively short period of time. With the grab sampling technique, rapid concentration variations are incorrectly monitored, unless the sampling frequency is high. The time-integrating sampling technique gives a more reliable picture of the leakage of herbicides from the soil, since the sampling is continuous and gives the average herbicide concentrations.

Conclusions. We have shown that 24-h time-integrating field sampling can be used for simultaneous sampling of herbicides at sub parts per billion levels in natural waters. The combination of membrane enrichment, precolumn focusing technique, and a final HPLC separation gives high selectivity toward most interfering substances occurring in natural water. With time-integrating sampling, average values of herbicide concentrations are obtained, thereby facilitating calculations of total herbicide leakage into recipient water.

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