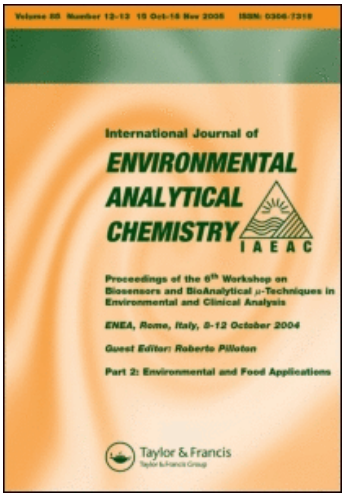

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Liquid Membrane Enrichment Technique for Integrating Field Sampling in Water Applied to MCPA

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To cite this Article Mathiasson, L. , Nilvé, G. and Ulén, B.(1991) 'A Liquid Membrane Enrichment Technique for Integrating Field Sampling in Water Applied to MCPA', International Journal of Environmental Analytical Chemistry, 45: 2, 117 — 125
To link to this Article: DOI: 10.1080/03067319108026981
URL: http://dx.doi.org/10.1080/03067319108026981

Intern. J. Environ. Anal. Chem., Vol. 45, pp. 117–125
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A LIQUID MEMBRANE ENRICHMENT TECHNIQUE FOR INTEGRATING FIELD SAMPLING IN WATER APPLIED TO MCPA

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(Received 28 February 1991; in final form 20 April 1991)

An integrating field sampling method for MCPA has been developed. Continuous sampling from a water stream for a desired period of time is achieved using a peristaltic pump and a liquid membrane device. The substance of interest is transferred as an uncharged species from a donor phase to a stagnant acceptor phase, where it is trapped in a buffer, permitting a high degree of enrichment. The final determination is made by reversed-phase liquid chromatography utilizing a pre-column instead of a sample loop in the injector. The method has been found to give values in good agreement with a technique based on batch extraction and gas chromatography. The precision at a recipient concentration of 1 ppb of MCPA is ca. 9% and the detection limit using a 24 h sampling period ca. 0.03 ppb.

KEY WORDS: 2-methyl-4-chlorophenoxyacetic acid (MCPA), integrating field sampling, recipient water, liquid membrane technique

INTRODUCTION

Field sampling of water from soil profiles or recipients are usually performed using a grab sampling technique, i.e. aqueous samples are collected in flasks at certain time intervals. To make a correct estimation of the total amount of herbicide reaching the recipient water a large number of grab samples should be collected, which is both time-consuming and expensive. In addition, storing of these grab samples may also lead to errors, since the matrix may contain material which reacts with the substances of interest. A sampling procedure which minimizes both these types of errors, is desirable.

Here we present a method for integrated sampling, utilizing a liquid membrane separation unit connected to a multichannel peristaltic pump. The method has been evaluated using the phenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid (MCPA) as model substance. MCPA is one of the most commonly used herbicides in Sweden. The fundamental principles of the use of a liquid membrane unit for sample preparation and its applications to different basic and acidic substances have

been discussed in recent papers from our laboratories[1–4]. With this device the substances of interest are continuously removed from the sample matrix and integrated values can be obtained for a desired time period. Furthermore the total sample volume is greatly reduced facilitating transportation and storing.

EXPERIMENTAL

Equipment for sampling

The sampling set-up is schematically shown in Figure 1. From the sampling point (A) about 10 cm below the aqueous surface, the water was pumped by an 8-channel peristaltic pump (B) (Minipuls 3; Gilson Medical Electronics, Villiers-le-Bel, France), with standard PVC manifold pump tubing (Elkay Products, Shrewsbury, MA, U.S.A.) to the confluence point (C), made of Teflon, where the channels met at an angle of 60°. The sampling compartment (A) consisted of the sampling tube immersed in a draining tube (I.D. 5 cm, length 15 cm) surrounded by a net with 100 μm mesh size. This turned out to be necessary to avoid clogging of the tubes and of the membrane

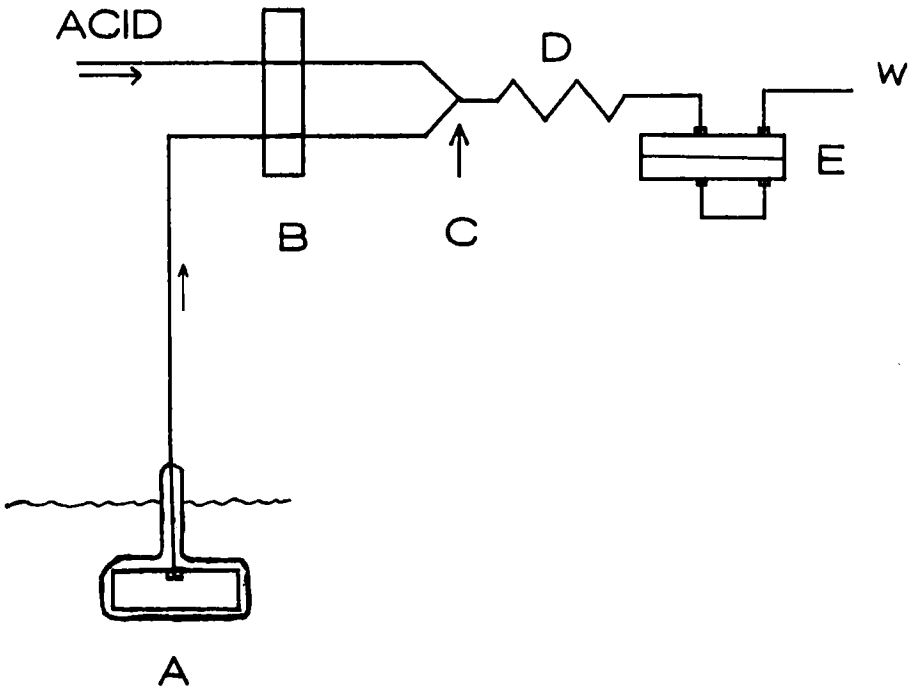

Figure 1 Set-up for integrating field sampling. A, Sampling compartment (A draining tube surrounded by a net with 100 μm mesh size). B, Peristaltic pump. C, Confluence point of sample stream (0.8 ml/min) and a stream of 0.4 M H_2SO_4 (0.15 ml/min). D, Mixing coil. E, Membrane separator, with stopped flow in the acceptor channel. W, Waste.

separator by particulate matter and small animals. The draining tube was fixed parallel to the stream of the brook and kept at a constant depth.

In the mixing coil (D) the aqueous sample was mixed with the acid and was transported through the membrane separator (E). The membrane separator consisted of two circular Teflon blocks (diameter 12 cm and thickness 0.8 cm) backed up with aluminum blocks (thickness 0.6 cm) to make the construction more rigid. In each block channels (0.25 mm deep, 1.5 mm wide, 250 cm long, total volume ca. 0.95 ml) were machined. The channels were arranged like an Archimedes spiral with the inlet situated in the center and the outlet in the periphery. A porous Teflon membrane (Fluoropore FG, Millipore, Bedford, MA, U.S.A., average pore size 0.2 μm, thickness 175 μm including 115 μm polyethylene backing, porosity 0.70) was impregnated by immersing it for 15 min in an organic liquid consisting of 50% v/v of n-undecane and di-n-hexylether which has been shown previously to be suitable for enrichment of phenoxyacetic acids[4]. The membrane was clamped tightly and evenly between the faces of the two Teflon blocks with the channels on each side of the membrane. Eight screws were used to hold the different parts together.

After installation in the separator excess organic liquid on the membrane surfaces was removed by pressing water through both channels. The volume of water needed to fill the channel was checked before each sampling period to be certain that no air was present in the acceptor channel, resulting in too small acceptor volume. During transportation of the membrane device both channels were filled with water and sealed to prevent evaporation of the organic liquid in the membrane.

The various parts of the flow manifold were connected with 0.5 mm I.D. Teflon tubing and Altex screw fittings.

Field sampling procedure

Water from the brook was pumped with a typical flow rate of 0.8 ml/min, and mixed with a stream of 0.2 M sulphuric acid pumped with a flow rate of 0.15 ml/min. After traversing the membrane, acidic species (including MCPA) were trapped in the stagnant acceptor phase (0.1 M phosphate buffer, pH = 7) by dissociation, resulting in an enrichment. A typical sampling period was 24 h which resulted in the processing of ca. 1 l of water. The flow rates were checked at least three times during each sampling period.

After completion of the sampling, the acceptor phase was transferred to a 4 ml test tube with a Teflon-faced screw cap. This was done by disconnecting one end of the tube connecting the inlet and the outlet of the acceptor channel, putting this end into the test tube, connecting a syringe to the free end of the acceptor channel and displacing the acceptor phase by pressing 1.5 ml of fresh acceptor solution through the channel. The test tube was sent to the laboratory for analysis, which normally could be performed within three days.

Before connecting the acceptor channel tubing for a new sampling, the membrane was checked for leakage by injecting water into the acceptor channel while pumping the acidic donor phase and then controlling the pH of the water at the outlet of the acceptor channel.

The 8-channel pump permits up to four parallel samplers to be operated simultaneously. This was utilized here to obtain duplicate and in some cases triplicate measurements at the same sampling point. By arranging the inlet tubes in other ways, sampling can be made, e.g., at different depths.

One or two grab samples (in 1-l bottles) were taken each day for comparison. These were kept in a freezer before transportation to the laboratory. At the delivery ice was still remaining in the bottles. After thawing, large particles were removed by decantation. These grab samples were processed at the laboratory using a similar set-up as in Figure 1 (except that the sampling compartment in this case was exchanged for the bottle containing the grab sample). A typical processing time for a grab sample was 12 h.

Equipment for analysis

The final determinations were made by liquid chromatography (LC) with a system consisting of a Consta Metric III high-pressure pump, a Spectro Monitor III variable wavelength UV detector (Laboratory Data Control, Riviera Beach, FL, U.S.A.) with a Valco loop injector, where the loop was substituted with a pre-column (I.D. 1 mm, length 20 mm, Upchurch Scientific, Oak Harbor, WA, U.S.A.) packed with Hamilton PRP-1 resin (Alltech Assoc., Applied Science Labs, Deerfield, IL, U.S.A.). The analytical column was a reversed-phase C_{18} column, Spherisorb S5 ODS-2, I.D. 4.6 mm, length 15 cm (Hichrom, Berkshire, U.K.). The mobile phase was a mixture of methanol and 1% v/v aqueous acetic acid (58:42, v/v) delivered at a flow rate of 1 ml/min.

Analytical procedure

The enriched sample was diluted to 2 ml with 0.4 M H_2SO_4 in a 2-ml volumetric flask and a 1-ml aliquot was injected with a syringe into the precolumn. With the valve still in the 'load' position, the precolumn was washed with 1 ml of 0.01 M H_2SO_4. The sample was then injected on the analytical column in the back-flush mode. The peaks were monitored at 285 nm.

Chemicals

Chemicals used were n-undecane (pro analysi, Merck), di-n-hexylether (Sigma), MCPA (purum, Fluka). Other chemicals were purchased from Merck and were of analytical-reagent grade. Water was purified using a Milli-Q/RO-4 unit (Millipore).

RESULTS AND DISCUSSION

Before application of the membrane sampling method to actual field sampling, a more fundamental study of the method was performed concerning efficiency, long-time stability, precision and accuracy.

Extraction efficiency

Extraction efficiency, i.e. the portion of the analyte extracted from the donor phase to the acceptor phase, was investigated using three different membrane devices (with membranes from the same batch of 25 membranes), a sampling time of 4 h, a flow rate of 1 ml/min and two different concentrations of MCPA, 5 and 50 ppb (μg/l) in aqueous solution. Duplicate samples were run on each membrane. No significant variation in the extraction efficiency was found either with respect to the membrane device used or with respect to the concentration of MCPA. The extraction efficiency in this experiment was 0.30. The precision decreases at lower concentrations. The relative standard deviation was 4.9% at a sample concentration of 50 ppb and 8% at a concentration of 5 ppb. In another experiment performed at a sample concentration of 10 ppb the extraction efficiency was 0.34 with a relative standard deviation of 7.0% using 8 repetitive measurements with the same membrane device. These results indicate that once the extraction efficiency for a compound is determined on a membrane in a batch, one has good reason to believe that this value can be used for all the membranes in the same batch (with otherwise unchanged experimental conditions).

The extraction efficiency in this type of measurements depends on the kinetics of the mass transfer process and not on the equilibrium constant. The conditions can easily be kept sufficiently constant to provide a constant extraction efficiency. Thus, good quantitative accuracy and precision can be obtained. The extraction coefficient can be increased by decreasing the sample flow rate. At sufficiently low flow rates, it approaches unity. However, as was detailed by Audunsson[1], a larger amount of analyte is collected per unit time at higher flow rates, provided that the available volume of sample is sufficient, which obviously is the case here.

Long-term stability

Natural water containing MCPA was processed for periods of ca. 16 h. The performance of the membrane after each 16-h run was checked by processing a standard solution of 10 ppb of MCPA in pure water for 4 h giving a measure of the extraction efficiency. Duplicate samples were processed each time of these standard solutions. The two steps were repeated on two different membranes until natural water with MCPA had been processed for totally 72 h. No significant change nor any trend in the extraction efficiency with time could be observed for either membrane. This is not surprising, since aqueous standard solutions of phenoxyacetic acids spiked with 350 ppm humic acid have previously been investigated by Nilvé *et al.*[4] with similar results. These type of membranes have also been used by Audunsson[2] who found that more than 600 urine samples spiked with amines could be processed with no alteration in the performance of the liquid membrane. Apparently, these type of membranes are to a very little extent affected by relatively large amounts of organic material passing the membrane.

Quantification

Typical concentrations of phenoxyacetic acids in recipient water in rural areas during herbicide treatment are in the order of 1 ppb. With a sampling volume of 1 l, an acceptor volume in the membrane separator of 1 ml and an extraction efficiency of 0.34, this corresponds in our measurements to a concentration of 340 ppb in the acceptor phase.

A calibration curve was made for MCPA between 10 and 1000 ppb, based on 6 concentrations. Duplicate injections of 1 ml were made into the pre-column as described above. The linear correlation coefficient was 0.9998 and the intercept was very close to the origin. The detection limit for MCPA in the chromatographic system was ca. 10 ppb (2 times the noise), corresponding to a concentration in natural waters of 0.03 ppb prior to membrane processing.

The relative standard deviation in the chromatographic measurements was ca. 2% at an MCPA concentration of ca. 1 ppm. The relative standard deviation for the extraction efficiency was, as shown above ca. 8%, when transferring an amount of MCPA corresponding to the 1 ppm solution above across the membrane (24 h sampling of a 5-ppb standard solution). Assuming that the errors are independent, the total precision in the determination of MCPA is then ca. 8% at the 5-ppb level in natural water.

The accuracy was tested by comparison with an independent method. In this method[5] used by the National Laboratory for Agricultural Chemistry (SLL), the first step is extraction with an organic solvent, followed by derivatization and GC-MS analysis. Nine parallel grab samples of natural waters (in 1-l bottles) containing MCPA in the concentration range 0.5–3 ppb, were compared. It was found that in four samples our method gave higher values for the MCPA concentration while the opposite was found for the remaining five samples. A paired t-test showed no significant difference between the methods at 95% confidence level.

Not very much of the total amount of MCPA is supposed to be bound to particles[6]. This is supported by the observation that no differences could be detected in spite of the fact that in our method these particles are removed. The extraction method used by SLL is expected to also measure particle-bound MCPA[5]. Here, during sampling, water as well as suspended particles are collected. After a hydrolysis step in an alkaline solution the phenoxy acids are extracted from an acidic solution into methylene chloride. Since the phenoxy acids are relatively loosely bound to soil, reflected by an octanol/water partition coefficient below 100, an extraction with methylene chloride is expected to be efficient also for acids bound to suspended particles.

Whether a portion of MCPA may be bound to collodial particles is difficult to say. These particles pass the donor channel, which gives a possibility for adsorbed species to be extracted into the liquid membrane. From our previous measurements[4] it is known that the transfer coefficients across the membrane for phenoxyacetic acids such as MCPA are not changed even after addition of 350 mg/l of humic acid to the aqueous herbicide solutions. The explanation can be either that MCPA, present at the acidic donor side as uncharged species under the experimental conditions is

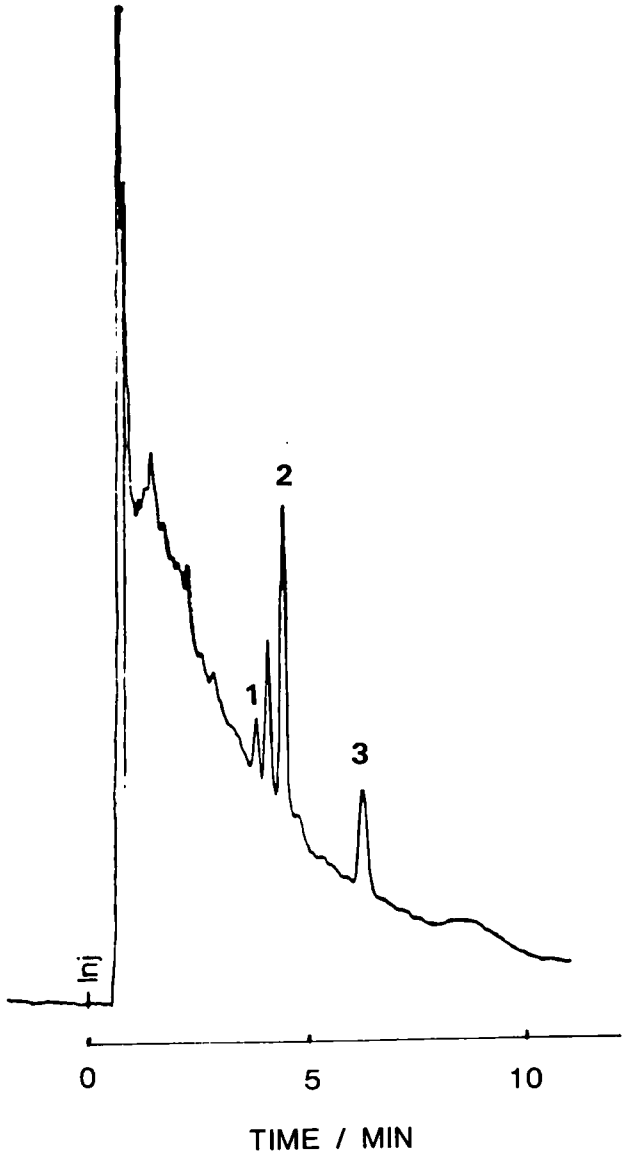

Figure 2 Chromatogram obtained from an integrating 24-h field sampling of MCPA in a Swedish brook, using membrane enrichment. Injection of 1 ml into a precolumn (Hamilton PRP-1 resin) followed by a washing step with 1 ml 0.01 H_2SO_4 before switching to the analytical C_{18} column (Spherisorb S5 ODS-2). Eluent, methanol-water 58:42, v/v, with 1% acetic acid added to aqueous phase. Flow rate, 1 ml/min; UV detection, 285 nm. Peaks: (1). 2,4-dichlorophenoxyacetic acid (2,4-D); (2). MCPA (concentration 290 ppb, corresponding to an average concentration of 1.4 ppb in the recipient water); (3). 2-(2,4-dichlorophenoxy)-propionic acid (dichloroprop).

to a large extent occurring as free acid or that the polarity of the liquid membrane is sufficiently high and the kinetics sufficiently fast to permit adsorbed phenoxyacetic acids to be desorbed and extracted into the liquid membrane during their passage of the membrane device which takes ca. 1 min.

Application

The membrane method has been used for sampling in a small Swedish brook in Södermanland (Örbäcken), situated in an area of extensive agricultural activity. Samples were obtained during a period of 26 days with sampling periods of 24 h. Each day 1–2 grab samples were collected for comparison. A typical chromatogram of processed natural water is shown in Figure 2. Here two other phenoxyalkanoic acid herbicides have also been identified by comparing with retention times of standards using various compositions of the mobile phase. The same substances as in Figure 2 were identified by SLL (GC-MS method), in grab samples collected during the same time period.

Table I shows the MCPA concentrations obtained for a period of 10 days either using the integrating sampling method or the grab sampling method. The difference between the values reflects the uncertainty of using a single grab sample to estimate the total amount of substance of interest passing the measuring point during a day. After application of a herbicide there will, after a delay, be an increase of its concentration in the recipient water. The concentration profile, showing how the concentration changes with time, may be rather narrow, especially in combination with rain of short duration. Large differences between two grab samples obtained in the same day can be found. In three pairs of samples analyzed by SLL the values of MCPA (in ppb) were (3.8; 0.4), (3.0; 1.2) and (0.6; 1.3) with a time period between the two grab samples in a pair of 10–14 h.

If the total leakage of MCPA is to be estimated, the integrating sampling method is expected to give more reliable results if not a large number of grab samples are collected daily. In a report of the present investigation from an agricultural viewpoint[7], the following values of the transport of MCPA during a period of 10 days were presented. From integrating sampling, 0.36 mg/ha; from grab sampling and LC

Table I Determination of MCPA in a Swedish brook for a period of 10 days.*

Technique	*Concentration of MCPA (ppb)*									
	Day: 1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Integrating sampling	2.1	0.1	0.3	0.1	0.2	0.1	0.6	4.5	0.7	0.2
Grab sampling	0.2	0.3	0.1	0.1	0.1	0.1	1.5	1.2	1.2	0.1

* Values obtained either from integrating sampling using the membrane technique for a period of one day, or from grab samples taken each morning.

analysis (this work), 0.17 mg/ha; from grab sampling and GC analysis (SLL), 0.18 mg/ha. As was shown above, there was no significant difference between our method of final analysis based on LC, and the one used by SLL based on GC-MS. The difference obtained between time-integrating sampling and grab sampling then reflects a tendency to underestimate herbicide leakage using grab sampling strategy.

The difference between integrated sampling and grab sampling observed is not due to the membrane process as such, as also the grab samples are concentrated with that technique before LC analysis. Using grab sampling the risk of missing peaks of high concentration is obvious. This should result in an underestimation of the total leakage. Another explanation could be that the grab samples were stored for some time, possibly permitting biological degradation or other sample losses, while the compounds of interest are immediately isolated from the rest of the sample and stored in concentrated form using the membrane technique. However, in earlier investigations by SLL, the phenoxyacetic acids were found to be fairly stable in natural waters kept in darkness at the freezing point and using some methylene chloride as preserving agent. The main reason for losses during sample storing seems to be breakdown by microorganisms[6].

CONCLUSIONS

We have shown that a time-integrating sampling method based on liquid membrane enrichment can be used to estimate the leakage of a herbicide, MCPA, into a recipient water. In this paper we have used sampling periods of one day. The extension of the sampling period to weeks is interesting, as this greatly facilitates the problem of recipient control. It would then be possible to get adequate information from a relatively small number of samples. It seems most probable that the sampling method described here can be used for other acidic herbicides as well. The technique may also be extended to sampling of permanent ions using complexing or ion-pairing reagents.

Acknowledgments

We thank Mr. Jerker Forsell for valuable assistance with the field sampling and Miss Graszyna Szemiel for valuable technical assistance at our laboratories. Malin Åkerblom, National Laboratory for Agricultural Chemistry is acknowledged for fruitful discussions and gift of reference substances. The financial support from the Swedish Council for Forestry and Agricultural Research and from the Oscar and Lilly Lamm Foundation is gratefully acknowledged.

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