ELSEVIER

Journal of Chromatography A, 930 (2001) 9–19

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of phenylurea herbicides in natural waters at concentrations below 1 ng l^{-1} using solid-phase extraction, derivatization, and solid-phase microextraction–gas chromatography–mass spectrometry

Andreas C. Gerecke, Céline Tixier, Thorsten Bartels, René P. Schwarzenbach, Stephan R. Müller*

Swiss Federal Institute for Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), Überlandstrasse 133, CH-8600 Dübendorf, Switzerland

Received 28 March 2001; received in revised form 31 July 2001; accepted 9 August 2001

Abstract

A procedure is presented which allows the ultratrace level determination of phenylurea herbicides (PUHs) in natural waters. Samples were enriched by solid-phase extraction (SPE) on Carbopack B and alkylated with iodoethane and sodium hydride to yield thermostable products. After derivatization, the aqueous samples were extracted and injected by SPME. The use of iodoethane instead of iodomethane allowed the differentiation between parent compounds and the N-demethylated metabolites. Limits of detection were between 0.3 and 1.0 ng/l for the parent compounds. Standard deviations below 10% were achieved for samples containing more than 4 ng/l in very different matrices including Nanopure water, lake water, and waste water treatment plant (WWTP) effluent. Moreover, the para-hydroxylated metabolite of diuron could be quantified with the same procedure. The presence of further metabolites was assessed qualitatively. Chromatography was stable over a large number of measurements even with dirty samples from WWTP effluent. The precision and sensitivity of the developed analytical method allowed the investigation of the fate of PUHs in lakes, their degradation during drinking water treatment and their transport within the North Sea.

Keywords: Water analysis; Derivatization, GC; Phenylureas; Diuron; Isoproturon; Chlorotoluron; Pesticides

1. Introduction

Phenylurea herbicides (PUHs) such as diuron, isoproturon and chlorotoluron are used in large quantities [1] for various purposes, for example: As herbicides in cereal crops (isoproturon and chlorotoluron), as total herbicides in agriculture or in settlements (diuron) [2], and as algicides in paintings and coatings (diuron) [3]. Since their degradation is rather slow in the environment [4], they are frequently detected at concentrations above 100 ng/l in surface waters [5]. That means above the European drinking water limit [6] often used as a quality standard of natural waters. In order to implement efficient measures to reduce the contents of these pesticides in natural waters, detailed studies about

*Corresponding author. Tel.: +41-1-823-5460; fax: +41-1-823-5471.

E-mail address: mueller@eawag.ch (S.R. Müller).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)01192-X

the sources, transport, and degradation are required. A prerequisite for such studies is a precise and sensitive analytical method.

Many trace analytical methods for PUHs have been published using various techniques (reviewed in Refs. [7–10]). PUHs are enriched with excellent recoveries by on- or off-line SPE with different SPE materials or by liquid–liquid extraction. SPE followed by HPLC–UV or HPLC–DAD is currently the most common method to quantify concentrations above 50 ng/l. For GC–MS methods, the limits of detection (LOD) are between 10 and 50 ng/l [11–15]. Recently, several LC–MS–(MS) methods have been published with LOD in the range of 0.3 to 10 ng/l [16–22]. The greatest advantages of GC–MS methods over LC–MS methods are the better separation on the GC column and the higher reproducibility of the ionization in the MS. Meanwhile, they require a derivatization step to prevent the degradation of the thermolabile PUHs in hot injectors and in GC columns. For this purpose, alkylation by iodomethane together with NaH as strong base and acetylation by heptafluorobutyric anhydride (HFBA) are often used. However, they have both two major drawbacks. First, time-consuming treatment is needed after the derivatization procedures to transfer the sample into a suitable GC solvent. Second, with normal GC injection techniques only a very small volume of 1 to 2 μl and, therefore, only a small fraction of the final extract can be analyzed (Fig. 1). A large fraction of the sample may only be transferred to the GC by the use of a large volume injector. However, Charrêteur et al. [23] encountered chromatographic problems when applying this technique with the acetylated derivatives.

In this paper, we describe a new approach that eliminates these two major drawbacks of the GC–MS procedures and compare the new approach with a normal liquid injection technique. By using solid-phase micro extraction (SPME) as an injection tool for enriched and derivatized samples, the time required for the whole sample workup is reduced. Furthermore, an increased amount of target molecules is transferred to the column compared with traditional injection techniques. The whole method consists of enrichment on Carbopack B adapted from di Corcia et al. [24] and Berg et al. [25], followed by an alkylation with iodoethane and sodium hydride

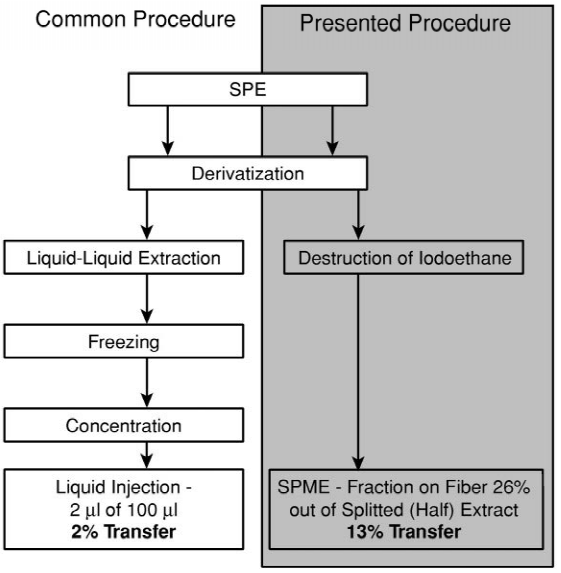

Fig. 1. Comparison of classical alkylation procedure for GC–MS detection of PUHs with the new procedure.

adapted and improved from three publications [11–13]. Then the aqueous solution from the derivatization was directly extracted by a polyacrylate SPME-fiber and desorbed into the GC.

2. Experimental section

2.1. Chemicals

Diuron, isoproturon, and chlorotoluron (see Table 1 for chemical structure of PUHs and metabolites) were obtained from Riedel-de-Haën (Seelze, Germany). All N-dealkylated metabolites as well as all isotope labeled compound were purchased from the Doctor Ehrensdorfer Laboratory (Augsburg, Germany). The formamide derivatives and the para-hydroxylated diuron were prepared according to Tixier et al. [26]. Dry sodium hydride (NaH), 95%, was purchased from Aldrich (Milwaukee, WI, USA). Dimethylsulfoxide (DMSO), puriss. dried over molecular sieve, and iodoethane, puriss., were obtained from Fluka AG (Buchs, Switzerland). Nitrogen and Helium gas were supplied by Carbagas (Rümlang, Switzerland). Deionized water was further purified with a Nanopure water purification device (NANO-

Table 1
Investigated pesticides: structures, ions monitored and retention times

Common name	Abbreviation	$-R_1$	$-R_2$	$-R_3$	$-R_4$	Masses[a] (m/z)	Ret. time[b] (min)
Analytes							
Parent compounds							
Isoproturon	IPU	$-CH(CH_3)_2$	$-H$	$-CH_3$	$-CH_3$	**234**, 72	21.86
Chlorotoluron	CT	$-CH_3$	$-Cl$	$-CH_3$	$-CH_3$	**240**, 242	23.37
Diuron	DIU	$-Cl$	$-Cl$	$-CH_3$	$-CH_3$	**260**, 262	26.43
Metabolites							
	DMIPU	$-CH(CH_3)_2$	$-H$	$-CH_3$	$-H$	**248**, 162	22.75
	DMCT	$-CH_3$	$-Cl$	$-CH_3$	$-H$	**254**, 256	24.36
	diu-OH-(p)	$-OH$	$-Cl$	$-CH_3$	$-CH_3$	**270**, 272	30.66
Internal standards							
d_6-isoproturon		$-CH(CH_3)_2$	$-H$	$-CD_3$	$-CD_3$	**240**, 225	21.77
d_6-chlorotoluron		$-CH_3$	$-Cl$	$-CD_3$	$-CD_3$	**246**, 248	23.26
d_6-diuron		$-Cl$	$-Cl$	$-CD_3$	$-CD_3$	**266**, 268	26.43
Further metabolites[c]							
		$-CH(CH_3)_2$	$-H$	$-H$	$-H$	162, 262	23.20
		$-CH_3$	$-Cl$	$-CH_3$	$-CHO$	–[d]	–[d]
		$-CH_3$	$-Cl$	$-H$	$-H$	268, 270	24.80
		$-Cl$	$-Cl$	$-CH_3$	$-H$	274, 276	27.66
		$-Cl$	$-Cl$	$-H$	$-H$	288, 290	28.13
		$-Cl$	$-Cl$	$-CH_3$	$-CHO$	–[d]	–[d]

[a] Bold number, mass used for quantification, other mass used for confirmation.
[b] Temperature program for SPME injection.
[c] Metabolites which could be determined qualitatively (see text).
[d] Converted to corresponding demethylated metabolite during derivatization (see text).

pure 4, Skan, Basle, Switzerland). All other chemicals were either from Fluka (Buchs, Switzerland) or from Merck (Darmstadt, Germany).

2.2. Sampling and sample preparation

All water samples were collected in 1 l glass bottles and immediately filtered in the laboratory with the high pressure filtration equipment MD142-5-3 (Schleicher & Schuell, Germany) using cellulose nitrate filters NC 55 (pore size 0.45 μm, diameter 142 mm; Schleicher & Schuell, Germany). After filtration, the samples were kept in the dark at 4°C.

Before SPE extraction, water samples were allowed to reach room temperature. They were spiked with a mixture of internal standards (10 μl toluene containing 10 ng/μl of internal standards). For calibrations with Nanopure water and standard additions to matrix samples, a mixture of all analytes was added. Samples were shaken vigorously after spiking.

2.3. Solid phase extraction

SPE was carried out according to di Corcia et al. and Berg et al. [24,25]. Di Corcia et al. reported excellent recoveries around 100% on Carbopack B for PUHs. Briefly, the Carbopack cartridges (Envi-Carb (Carbopack B), 250 mg, Supelco, Bellafonte, CA, USA) were conditioned with 8 ml of methylene chloride/methanol (80:20, v/v), 4 ml of methanol, 20 ml of ascorbic acid solution (10 g/l, in Nanopure water acidified with HCl to pH 2), and 10 ml of Nanopure water. Samples (1 l) were then drawn

through the cartridges at a flow-rate of ca. 15 ml/min. Thereafter, the solid-phase was washed with 0.5 ml of methanol and air dried under vacuum for 30 min to remove as much water as possible. Elution was performed with 1 ml of methanol and 6 ml of methylene chloride/methanol (80:20, v/v) into conical glass vials (7.5 ml, Supelco, Bellafonte, CA, USA). Then 0.15 ml of DMSO was added and the methylene chloride–methanol mixture was carefully evaporated under a gentle stream of nitrogen at room temperature until the volume was about 2 ml. The volume was further reduced to 0.15 ml (of DMSO) at 60°C for approximately 20 min. The PUHs were derivatized by adding 50 μl of iodoethane immediately followed by 150 μl DMSO containing 0.03 g NaH. The use of iodoethane instead of iodomethane, as described in Refs. [11–13], allowed the differentiation between parent compounds and the N-demethylated metabolites. After 10 min, the reaction was stopped with addition of 6 ml water containing 0.5 *M* phosphate buffer (pH 7) and 5 *M* sodium chloride. Samples were stirred until no more iodoethane was visible (60 h). Samples, which finally were introduced to the GC by liquid injection, were processed as follows after derivatization. The reaction was stopped by adding 5 ml water containing 0.5 *M* phosphate buffer (pH 7). These solutions were transferred to 20 ml vials and the conical vials were rinsed twice with 4 ml of the stopping solution. Then, 1 ml of hexane was added and the samples were vigorously shaken for 2 min. The samples were placed at −20°C over night and subsequently the liquid hexane phase was collected. Finally, the hexane was concentrated to 100–150 μl under a gentle stream of nitrogen.

2.4. SPME, GC, and MS: instruments and settings

The GC–MS system consisted of a HRGC 8060, a MD 800 mass spectrometer (Fisons Instruments, Beverly, MA, USA) and a Combi PAL autosampler (CTC Analytics, Zwingen, Switzerland). SPME extraction of 3 ml of the derivatized sample was done during 50 min at 50°C with a polyacrylate coated fiber (85 μm film thickness) from Supelco (Bellafonte, PA, USA). The fibers were conditioned according to the manufacturers instructions and were replaced after ca. 50 injections. During extraction, the fiber was rotated in the sample at 250 rounds per minute by the Combi PAL auto-sampler, changing the direction of rotation every 5 s. Desorption in the split/splitless injector was performed with closed split valves during 6 min at 280°C. Liquid injection was performed with a split/splitless injector at a temperature of 250°C. The injection volume was 2 μl and splitless time was 1.5 min. A fused-silica column DB17-MS (I.D.=0.25 mm, l=30 m, d_f= 0.25 μm) from J&W (Folsom, CA, USA) was used for gas chromatography together with a deactivated pre-column (2.5 m, 0.32 mm I.D.) and a transfer capillary (1.5 m, 0.18 mm I.D.).

The GC oven was programmed as follows: 6 min at 60°C (1.5 min for liquid injection), first ramp 12°C/min to 170°C, second ramp 2°C/min to 206°C, third ramp 20°C/min to 290°C, 2 min at 290°C. The GC–MS interface temperature was kept at 295°C and the ion source at 220°C.

The mass spectrometer was run in the positive electron impact mode at 70 eV. Single ion monitoring (SIM) was used to quantify the compounds (m/z: see Table 1). Dwell times varied from 0.06 to 0.2 ms depending on the selected masses for each compound and the amount of compounds in each SIM window. Manual tuning with a reference gas was performed before each series, aimed at maximum sensitivity and unit mass resolution.

2.5. Calculations, quantification, and confirmation criteria

LOD were calculated according to the method described in DIN 32645 [27], which uses calibration data (standard addition) of low amounts of compounds to estimate the LOD.

Environmental samples were quantified by using calibration data of spiked nanopure samples, which were processed at the same time as the samples. Calibrations were done by linear regression of the ratio between the signals of a compound and the corresponding internal standard (isotope labeled parent compound) versus the ratio of the spiked amounts of a compound and the internal standard. For every compound, two ions were acquired with the MS and evaluated separately. The mass with the best signal-to-noise ratio was taken as quantification ion. Confirmation was positive, if the result of the

confirmation ion was within ±20% of the quantification ion. In addition, the difference of the retention times between the analyte and the internal standard in a sample had to be within ±1 s of the difference of the retention times found in standard samples.

3. Results and discussion

3.1. Preparation of the extract for SPME after derivatization

After the derivatization, excess iodoethane built a second phase in the derivatization solution, which was visible as suspended small droplets directly after buffer addition and later as bigger droplets at the bottom of the vessel. However, this second phase of iodoethane was destroyed by nucleophilic substitution of iodine by chlorine within 60 h under continuous stirring. The resulting chloroethane did not form a visible second phase. Adsorption on teflon stirring bars was tested by exposing 6 ml derivatization solution to a large teflon surface (three bars, 40 mm×8 mm). A loss of 5% to 10% was observed for the parent compounds and between 5% and 35% for the metabolites, which are less polar than parents after derivatization. Therefore, hand-made stirring bars with a glass surface were used to avoid adsorption. Further parameters of the derivatization which influence the SPME injection are discussed in Table 2 and below.

3.2. SPME injection

The distribution of the compounds between the derivatization solution and the SPME fiber can be described by Eq. (1) [28]. The fraction on the fiber increases with increasing partitioning coefficient ($K_{\text{fiber/SPME solution}}$) and volume of the fiber (V_{fiber}) and decreasing extraction volume ($V_{\text{SPME solution}}$), which may be only a part of the whole derivatization solution ($V_{\text{derivatization solution}}$):

$$\text{fraction}_{\text{on fiber}} = \frac{1}{1 + \frac{1}{K_{\text{fiber/SPME solution}}} \frac{V_{\text{SPME solution}}}{V_{\text{fiber}}}} \cdot \frac{V_{\text{SPME solution}}}{V_{\text{derivatized solution}}} \cdot 100\% \quad (1)$$

Table 2 lists and discusses important parameters that influence the distribution of the compounds. A set of parameters that yields a high fraction on the fiber was evaluated based on literature and theoretical considerations. In addition to these general criteria, the following two conditions were considered. More phosphate than sodium hydride had to be added to assure a neutral pH and two independent measurements of each sample had to be possible.

3.3. Partitioning coefficient and transferred amount

The partitioning coefficients between the derivatization solution and the fiber ($K_{\text{fiber/SPME solution}}$) were measured to be between 2000 and 2100 for the parent compounds under the given extraction conditions. The determination of the partitioning coefficient ($K_{\text{fiber/SPME solution}}$) was done according to the method of Urruty et al. [29], which uses the exponentially decreasing signal of a repeatedly extracted sample (Correlation coefficients of exponential regression were all >0.99). Inserting this partitioning coefficient into Eq. (1) reveals that 13% of the parent compounds were transferred to the fiber ($V_{\text{SPME solution}}=3$ ml, $V_{\text{fiber}}=0.52$ μl [30], $V_{\text{derivatization solution}}=6.3$ ml).

3.4. Chromatography

Fig. 2 presents chromatograms of all quantification ions in different matrices using SPME. Chemical interferences increased from nanopure water (see Fig. 2a) to lake water (b) and further to WWTP effluent (c) leading to increasingly noisy base lines.

This chemical noise rarely causes failures of identification based on the criteria mentioned above in the case of river and lake water samples. In contrast, low results of WWTP effluents (i.e. <20 ng/l) often had to be rejected.

Fig. 3 reveals that the chromatography was stable over the extraction and injection of 40 identical dirty environmental samples. The ratio of the peak areas of diuron (m/z 262) and d_6-diuron (m/z 268) remained constant over the whole series ($\sigma=0.6\%$). Therefore, quantification was independent on sample

Table 2
Parameters influencing the distribution between the derivatization solution and the SPME fiber [28,35]

Parameter	Theoretical influence on the fraction of derivatized PUHs on the fiber		Comment	Selected parameter
Fiber material	Equilibrium partitioning	Apolar fibers are suited for apolar compounds — polar fibers are suited for more polar compounds.	Polyacrylate fibers (PA) efficiently extract compounds with properties similar to PUHs [35].	PA fiber
Salt concentration	”	Aqueous activity coefficient increases exponentially with increasing NaCl concentration. Therefore, the partitioning constant increases exponentially with increasing salt concentration.	Selected concentrations should be close to saturation.	5 *M* NaCl and 0.5 M phosphate buffer (pH 7)
Co-solvent and $V_{\text{derivatization solution}}$ (stopping solution and DMSO)	”	Aqueous activity coefficient decreases with increasing content of organic co-solvent [36]. Increasing volume of the stopping solution dilutes the solution and hence decreases the fraction on the fiber, but decreases as well the concentration of the co-solvent DMSO.	0.3 ml of DMSO are required for the derivatization procedure. Six ml of stopping solution are needed (to add sufficient phosphate buffer) to neutralize the NaH. At 5% of DMSO the decrease of the aqueous activity coefficient is expected to be lower than two [36,37].	5% DMSO in 6.3 ml (6 ml stopping solution and 0.3 ml DMSO)
Part of the derivatization solution that is used for one SPME extraction	”		Two independent measurements have to be possible.	ca. 1/2 (i.e. 3 ml out of 6.3 ml)
Agitation	Time to approach equilibrium	Stirring enhances the transfer of the molecules from solution to fiber.	Maximum frequency of autosampler is 250 rounds per minute.	250 rounds per minute
Extraction temperature	Time to approach equilibrium and equilibrium partitioning	Increasing temperature decreases time to reach partitioning. The equilibrium partitioning itself is decreased by increasing temperature [28].	Selected parameter has to be a compromise between the two effects.	50°C
Extraction time	Time to approach equilibrium	Difference to equilibrium partitioning decreases exponentially with time [28].	Equilibrium should be approached to more than 80%.	50 min

number and order. However, the absolute peak area decreased slightly over time, most probably due to aging of the fiber. To avoid a significant loss in sensitivity, a new fiber was used after about 50 injections. Symmetry and shape of the peaks were also unaffected by sample number (see Fig. 3). Obviously, no compound that causes a deterioration of the chromatographic system was injected. The positive effect of SPME is that only the hydrophobic fraction of the extract is injected onto the column. The advantages of such a second partitioning between water and an organic phase were recently also described by Vandecasteele et al. [31].

3.5. Detection limit, quantification limit, and reproducibility

For the SPME injection method, the LOD for Nanopure water, lake water, and WWTP effluent were between 0.3 and 1.0 ng/l for the parent compounds (see Table 3). These values were in the same order of magnitude as those obtained using the most sensitive LC–MS–MS method [20]. The standard deviations were lower than 10% for multiple extracted samples at a level of 4 ng/l ($n=3$ or 4). Using the liquid injection method, the LOD were around 7 times higher. This difference reflects the

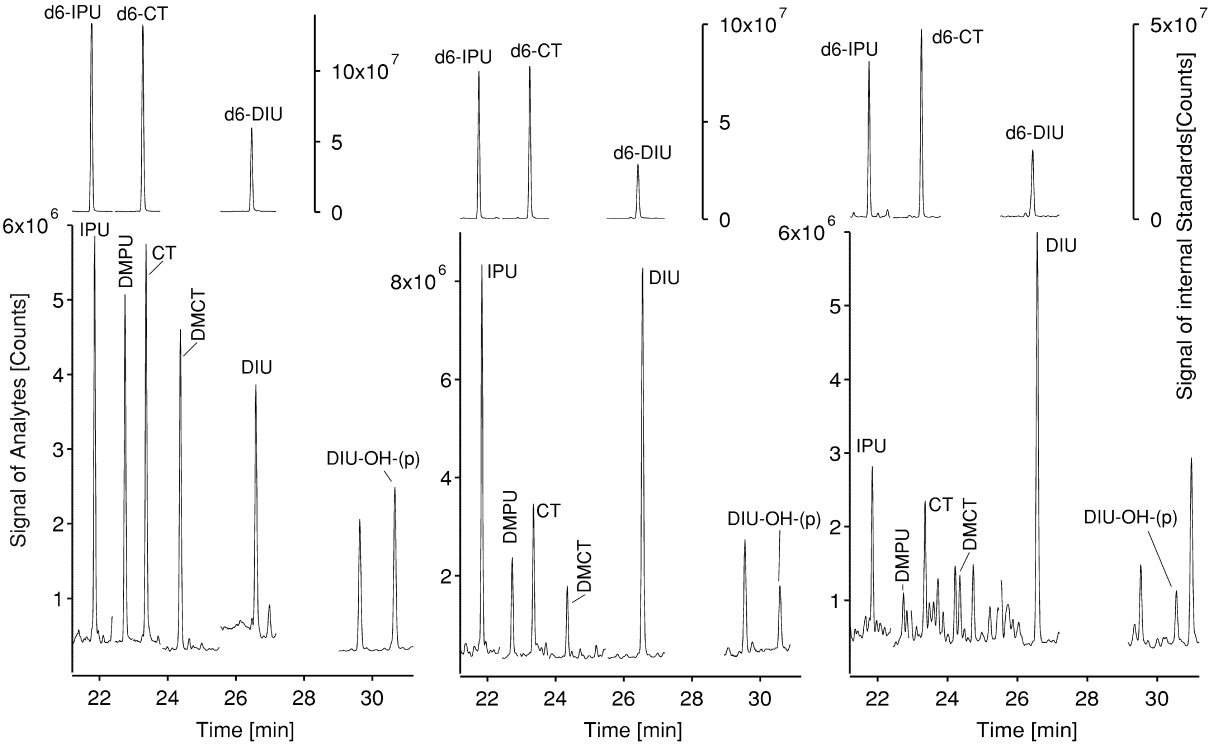

Fig. 2. Chromatograms of all quantification ions in three different matrices spiked with 4 ng/l [(a) nanopure water, (b) lake water, (c) WWTP effluent]. Some of the compounds were already present in the unspiked samples: Lake water: IPU 6.2 ng/l, CT 1.2 ng/l, DIU 18.7 ng/l; WWTP effluent: IPU 3.6 ng/l, DIU 20.8 ng/l.

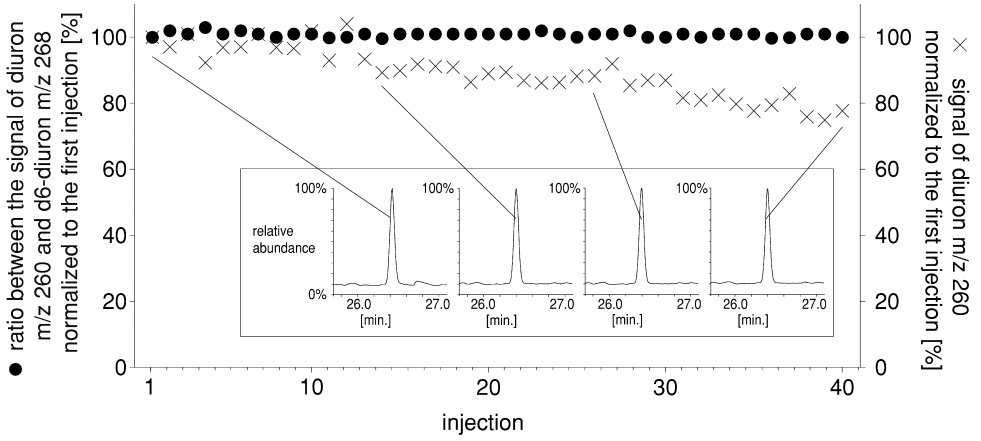

Fig. 3. Chromatograms (diuron m/z 260, 18 ng/l) and signals compared over 40 injections of identical samples. These 40 samples were prepared by mixing 20 derivatization solutions from lake samples with 20 derivatization solutions of WWTP effluent samples.

Table 3
Limits of detection (LOD), standard deviations (σ) and response ratios of PUHs in different matrices

Compound	SPME										Liquid injection		
	LOD[a] [ng/l]			σ (4 ng/l spiked) $n=3$, [ng/l]			Response ratio				LOD[b] [ng/l]		
							Response	σ response	Response	σ response			
	Nanopure	Lake	WWTP	Nanopure	Lake	WWTP	Lake/Nanopure	Lake/Nanopure	WWTP/Nanopure	WWTP/Nanopure	Nanopure	Lake	WWTP
IPU	0.3	0.3	0.3	0.1	0.008	0.08	1.00	0.02	1.01	0.01	2.5	2.5	2.1
CT	0.5	0.5	1.0	0.06	0.2	0.3	0.99	0.02	0.99	0.02	3.2	1.9	3.3
DIU	0.3	0.3	0.5	0.05	0.04	0.05	1.03	0.02	0.99	0.02	3.0	2.4	1.2
DMIPU	2.4	2.0	4.2	0.2	1.3	0.1	0.9	0.11	0.7	0.17	29	10	4.6
DMCT	2.2	2.2	2.0	6.0	5.9	5.4	0.85	0.11	0.7	0.1	6.6	1.7	9.2
diu-OH-(p)	1.2	0.9	0.3	0.2	0.4	0.1	1.01	0.06	1.09	0.04	6.0	3.6	3.2

[a] Derived from standard addition of 0, 2, 4, 6, 8, and 10 ng/l.
[b] Derived from standard addition of 0, 10, 20, 30, 40, and 50 ng/l.

increased fraction of the total analyte molecules that was transferred to the GC–MS {i.e. 13% with SPME [26% of the half (splitted) derivatization solution] compared to approximately 2% for liquid injection [2 μl of 100–150 μl (transfer rate of liquid–liquid extraction step was >80%)]}.

3.6. Calibration and quantification

Correlation coefficients (r^2) for standard additions were all higher than 0.99 for both methods and all matrices. The slopes of the regressions were equal for the three different matrices (Table 3). Therefore, it was possible to use calibrations with spiked Nanopure water for the quantification of natural waters.

3.7. Metabolites

The results for the metabolites differed largely in quality. For the hydroxylated diuron [diu-OH-(p), for structure see Table 1] a good performance was established (Table 3). During derivatization the formamide intermediates of IPU and CT were found to be converted into the DMIPU and DMCT. Therefore, when analyzing real samples, the result for the demethylated metabolite represented always the sum of the demethylated and the formamide derivative and are thus only qualitative in nature. However, the linearity and the detection limits of DMIPU and DMCT were good (Table 3). The other metabolites could not be quantified due to scatter in the data, which was most probably caused by incomplete derivatization. However, it was still possible to qualitatively identify these metabolites.

3.8. Performance of the method: illustrative examples

The usefulness of the presented procedure for monitoring the concentrations of PUHs and studying their fate in the aquatic environment is illustrated with samples from two environmental systems and one technical system. Fig. 4 shows a vertical concentration profile from Lake Murtensee (Switzerland). Due to the sharp density gradient at around 9 m, the upper lake compartment (epilimnion) and the lower compartment (hypolimnion) can be considered as separated but well mixed boxes [32]. In fact, concentrations between 1 m and 5 m, as well as between 12 m and 40 m were nearly the same. Detailed results on the fate of PUHs in lakes will soon be presented in another paper [33].

As a second illustration of the analytical performance, samples from a drinking water treatment plant (Murten, Switzerland) are presented in Table 4. This plant purifies water from the hypolimnion of the same lake mentioned above. The water is treated twice with an ozone dosage of approximately 0.7 mg/l. The concentration at the entry of the plant is equal to the concentration of the lake at the depth, in which the water is collected (30–40 m). During

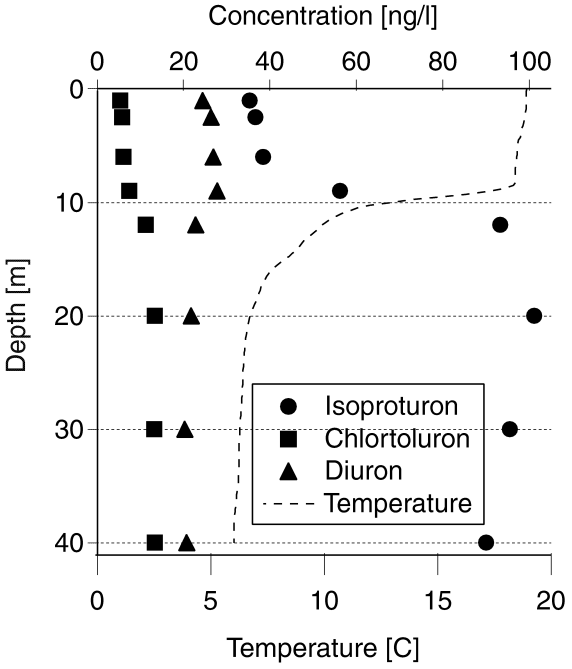

Fig. 4. Vertical profile of Lake Murtensee, July 13, 2000.

ozone treatment, all three compounds were readily degraded, with isoproturon showing the highest apparent degradation rate followed by chlorotoluron and diuron. This order is in agreement with the different second order rate constants for reaction with ozone [34]. Diu-OH-(p) was found as a degradation intermediate. The third example illustrates the possibility to trace the transport of the compounds to remote areas such as the North Sea. Sampling locations and results are presented in Fig. 5. Note the good agreement between samples analyzed in duplicate and the decrease of concentrations with increasing distance from the coast.

4. Conclusion

SPME as an injection tool for the analysis of enriched and derivatized phenylurea herbicide in water samples proved to be an excellent method to routinely and precisely determine concentrations below 1 ng/l in natural waters. We think that SPME could also be a good GC injection method for ultratrace level analysis of other compounds in enriched samples (i.e. triazines, neutral pharmaceuticals etc.). However, chemical noise is a limiting factor, when working with complex matrices. This problem could be reduced by the use of high-resolution mass spectrometry or tandem MS systems.

Compared to LC–MS–MS methods the presented approach affords less expensive instrumentation and requires less instrumental knowledge and maintenance-time. On the other hand the derivatization step is time consuming and prevents the quantification of some metabolites which are measurable by LC–MS methods [21]. In addition LC–MS can be combined with on-line enrichments techniques (e.g. [22]) which enables the very rapid quantification of

Table 4
Concentrations after different treatment steps in the drinking water treatment plant of Murten[a]

	Isoproturon [ng/l][b]	Chlorotoluron	Diuron	diu-OH-(p)
Lake Murtensee 30 m[c]	95	13.1	20	<0.9
Drinking water treatment plant — before first treatment	98	13.3	20	<0.9
After first ozonation — ozone dose 0.7 mg/l	11.8	4.5	13.1	2.4
After second ozonation — ozone dose 0.8 mg/l	0.7	0.9	2.7	5.4
First filtration (sand, carbon)	<0.3	<0.5	0.7	1.4
Second filtration (carbon)	<0.3	<0.5	<0.3	<0.9

[a] Samples collected July 17, 2000.
[b] One sample per treatment step; RSD<5% for concentrations >8 ng/l, RSD<10% for concentrations >4 ng/l, RSD<30% for concentrations below 4 ng/l.
[c] Samples collected July 13, 2000.

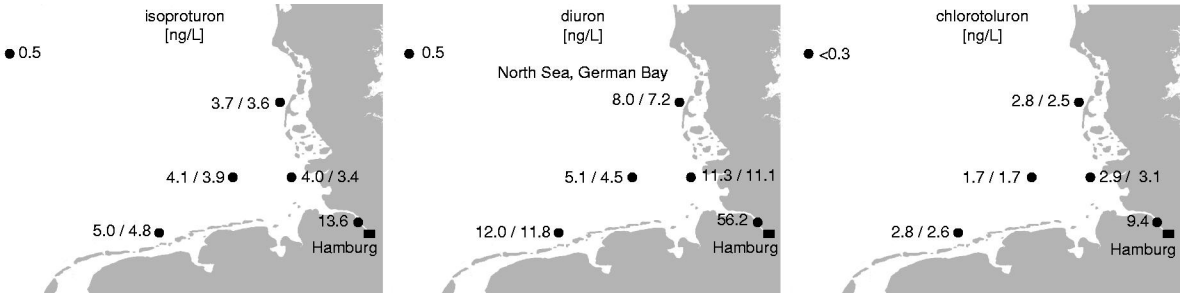

Fig. 5. PUHs concentration in samples (partly analyzed in replicate) from the North Sea (collection cruise mid-July 2000, sampling depth 5 m). Concentrations of metabolites were below LOD.

PUHs and other compounds even with smaller sample volumes (i.e. 10–30 ml).

Acknowledgements

We thank Doctor N. Theobald and his team (Federal Maritime and Hydrographic Agency, Hamburg, Germany) for kindly providing the samples from the North Sea. We are indebted to Marc Suter, Torsten Schmidt and Michael Berg for reviewing this manuscript and for their helpful comments.

References

[1] M. Fielding, D. Barcelo, A. Helweg, S. Galassi, L. Torstensson, P. Van Zoomen, R. Wolter, G. Angeletti, Pesticides in Ground and Drinking Water, E. Guyot SA, Brussels, 1991.
[2] C. Tomlin (Ed.), The Pesticide Manual, The British crop protection council and the royal society of chemistry, Farnham, 1994.
[3] W. Paulus, Microbicides For the Protection of Materials, Chapmann & Hall, London, 1993.
[4] D.C.G. Muir, in: R. Grover, A.J. Cessna (Eds.), Environmental Chemistry of Herbicides, CRC Press, Boca Rotan, 1991, p. 1.
[5] M. Bach, A. Huber, H.-G. Frede, V. Mohaupt, N. Zullei-Seibert, Schätzung der Einträge von Pflanzenschutzmitteln aus der Landwirtschaft in die Oberflächengewässer Deutschlands, Umweltbundesamt, Berlin, 2000.
[6] Directive 98/83/EEC. Quality of Water Intended for Human Consumption, Brussels, 1998.
[7] D. Simon, S. Helliwell, K. Robards, Anal. Chim. Acta 360 (1998) 1.
[8] N. Voulvoulis, D. Scrimshaw Mark, N. Lester John, Chemosphere 38 (1999) 3503.
[9] I. Liska, J. Slobodnik, J. Chromatogr. A 733 (1996) 235.
[10] S. Hatrik, J. Tekel, J. Chromatogr. A 733 (1996) 217.
[11] S. Scott, Analyst 118 (1993) 1117.
[12] U. Oehmichen, A. Aimene, K. Haberer, Vom Wasser 76 (1991) 287.
[13] P. Seel, T.P. Knepper, S. Gabriel, A. Weber, K. Haberer, Vom Wasser 83 (1994) 357.
[14] H.-J. Stan, P. Klaffenbach, Fresenius, J. Anal. Chem. 339 (1991) 40.
[15] F.P.M. Karg, J. Chromatogr. 634 (1993) 87.
[16] I. Ferrer, D. Barcelo, J. Chromatogr. A 854 (1999) 197.
[17] E. Hogendoorn, P. van Zoonen, J. Chromatogr. A 892 (2000) 435.
[18] E. Baltussen, H. Snijders, H.G. Janssen, P. Sandra, C.A. Cramers, J. Chromatogr. A 802 (1998) 285.
[19] C. Crescenzi, A. di Corcia, E. Guerriero, R. Samperi, Environ. Sci. Technol. 31 (1997) 479.
[20] R. Steen, A.C. Hogenboom, P.E.G. Leonards, R.A.L. Peerboom, W.P. Cofino, U.A.Th. Brinkman, J. Chromatogr. A 857 (1999) 157.
[21] A. Di Corcia, A. Costantino, C. Crescenzi, R. Samperi, J. Chromatogr. A 852 (1999) 465.
[22] A.C. Hogenboom, W.M.A. Niessen, U.A.Th. Brinkman, J. Chromatogr. A 841 (1999) 33.
[23] C. Charrêteur, R. Colin, D. Morin, J.J. Péron, Analusis 26 (1998) 8.
[24] A. Di Corcia, M. Marchetti, Environ. Sci. Technol. 26 (1992) 66.
[25] M. Berg, S.R. Müller, R.P. Schwarzenbach, Anal. Chem. 67 (1995) 1860.
[26] C. Tixier, M. Sancelme, F. Bonnemoy, A. Cuer, H. Veschambre, Environ. Toxicol. Chem. 20 (2001) 1381.
[27] DIN, in DIN 32645, 1994.
[28] J. Pawliszyn, Solid Phase Microextraction: Theory and Practice, Wiley–VCH Inc, New York, 1997.
[29] L. Urruty, M. Montury, J. Chromatogr. Sci. 37 (1999) 277.
[30] J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, Cambridge, 1999.
[31] K. Vandecasteele, I. Gaus, W. Debreuck, K. Walraevens, Anal. Chem. 72 (2000) 3093.
[32] M.M. Ulrich, S.R. Müller, H.P. Singer, D.M. Imboden, R.P. Schwarzenbach, Environ. Sci. Technol. 28 (1994) 1674.

[33] A.C. Gerecke, S.R. Müller, S. Canonica, M. Schärer, R.P. Schwarzenbach, Environ. Sci. Technol., in press.
[34] J. De Laat, P. Maouala-Makata, M. Dore, Environ. Technol. 17 (1996) 707.
[35] J. Dugay, C. Miège, M.-C. Hennion, J. Chromatogr. A 795 (1998) 27.
[36] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, in: Environmental Organic Chemistry, Wiley, New York, 1993, p. 76.
[37] R. Batlle, C. Sanchez, C. Nerin, Anal. Chem. 71 (1999) 2417.