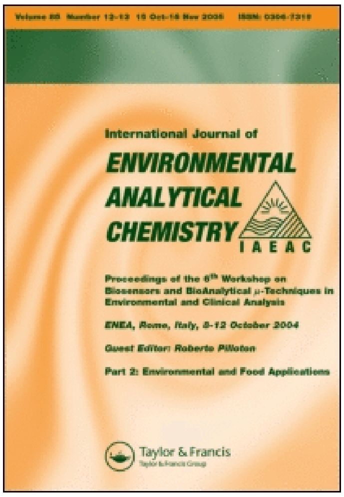

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Clofibric Acid and N-(Phenylsulfonyl)-Sarcosine in Sewage, River and Drinking Water

Th. Heberer[a]; H. -J. Stan[a]
[a] Institute of Food Chemistry, Technical University of Berlin, Berlin, Germany

To cite this Article Heberer, Th. and Stan, H. -J.(1997) 'Determination of Clofibric Acid and N-(Phenylsulfonyl)-Sarcosine in Sewage, River and Drinking Water', International Journal of Environmental Analytical Chemistry, 67: 1, 113 — 124
To link to this Article: DOI: 10.1080/03067319708031398
URL: http://dx.doi.org/10.1080/03067319708031398

Intern. J. Environ. Anal. Chem., Vol. 67, pp. 113-124
Reprints available directly from the publisher
Photocopying permitted by license only

DETERMINATION OF CLOFIBRIC ACID AND N-(PHENYLSULFONYL)-SARCOSINE IN SEWAGE, RIVER AND DRINKING WATER

TH. HEBERER* and H.-J. STAN

Institute of Food Chemistry, Technical University of Berlin, Gustav-Meyer-Allee 25, D-13355 Berlin, Germany

(Received 2 September 1996; In final form 6 December 1996)

Two polar compounds, the drug metabolite clofibric acid (2-(4)-chlorophenoxy-2-methyl propionic acid) and N-(phenylsulfonyl)-sarcosine, were detected as organic contaminants in groundwater samples from sewage farm areas near Berlin at maximum concentrations of 4 µg/l and 150 µg/l, respectively. Contaminations by these two compounds were also found in most of the drinking water samples collected from the 14 waterworks in the Berlin area. The maximum concentrations in drinking water samples were 270 ng/l for clofibric acid and 105 ng/l for N-(phenylsulfonyl)-sarcosine. The analytical results obtained correlate well with the percentage values of artificial groundwater enrichment and bank filtrate used by any particular water treatment plant in drinking water production. Thus, it can be assumed that both polar contaminants commonly leach into drinking water and are not eliminated by the drinking water treatment used by the Berlin waterworks. Positive findings in screening analyses of surface water samples outside Berlin as, for example, the river Danube in Germany and the river Po in Italy indicate that the occurrence of clofibric acid and N-(phenylsulfonyl)-sarcosine in environmental water samples is not just a local phenomenon.

Keywords: Clofibric acid; N-(phenylsulfonyl)-sarcosine; gas chromatography-mass spectrometry; artificial groundwater enrichment and bank filtration; drinking-water contamination

INTRODUCTION

In recent years, the occurrence of polar contaminants in the aqueous environment has become a subject of public concern. Polar pesticides have, especially, been considered as a potential source of ground water contamination due to their widespread use in agriculture and their high mobility in the subsoil. Thus, many investigations have focused on the analysis of pesticide residues in order to

---

* Corresponding author: Fax: +49-30-314-72922 ; E-mail : hebe1 330@mailszrz.zrz.tu-berlin.de.

check the maximum tolerances of only 100 ng/l in drinking water set by the European Union Commission[1].

These (low) maximum tolerances constituted a real challenge to analysts working in the field of pesticide residue monitoring. The improvement in the methods for the detection of pesticides at these trace level concentrations led to the discovery of other contaminants in water that did not originate from agricultural use. In the course of the monitoring of ground water for acidic herbicides in the Berlin area an unknown phenoxyalkanoic acid was detected and finally identified as clofibric acid (2-(4)-chlorophenoxy-2-methyl propionic acid)[2]. This compound is the active metabolite of the drugs clofibrate, etofyllinclofibrate and etofibrate, which are used as blood lipid regulators in medical care. At that time, the contamination was thought to originate from a point source, namely a pharmaceutical production plant. An improvement of the detection sensitivity of the analytical methods[3-5] allowed extended screening with the result that clofibric acid could be detected in some river water samples and also in all tap water samples collected in Berlin in 1993 and 1994[6]. These findings led to the conclusion that clofibric acid represents a compound of high persistence in the environment that enters the water compartment via municipal sewage treatment plants. As early as 1976, clofibric acid was found by Garrison et al.[7] at concentrations up to 2 μg/l in raw and treated sewage waters. One year later, these results were confirmed by Hignite and Azarnoff[8] who found up to 10 μg/l of clofibric acid in the effluent of the Big Blue River Sewage Treatment Plant in Kansas City, USA. The instrumental detection limits were at that time not sufficient to screen for clofibric acid in river or drinking water.

The development of a new analytical method applying solid phase extraction (SPE), derivatization with pentafluorobenzyl bromide (PFBBr) and detection by capillary gas chromatography-mass spectrometry (GC-MS) with selected ion monitoring (SIM) enabled the reliable trace level determination of more than 30 acidic herbicides and clofibric acid in water samples[3-5]. In this method, 2-(4-chlorophenoxy)-butyric acid, a structural isomer of clofibric acid, is used as surrogate standard and was found to work excellently to control the analytical procedure[5]. The analytical method originally developed for the investigation of drinking water has also been successfully applied to ground, surface and even sewage water with analyte concentrations at the low ng/l (ppt) level[5].

Applying this method to sewage, drainage and ground water samples collected from sewage farm areas near Berlin, clofibric acid was found to be a potential organic indicator of sewage contamination in sewage farm ground water[9-11]. Clofibric acid proved to be almost persistent and leaches easily through the sewage farm subsoil[11]. In the course of these investigations, another hitherto unknown polar contaminant was found in ground water samples from the sewage farm area. Its structure was identified by GC-MS and confirmed by synthesis of all possible isomers as N-(phenylsulfonyl)-sarcosine[12]. Meanwhile, both polar contaminants N-(phenylsulfonyl)-sarcosine and clofibric acid were found in river and drinking water samples in Berlin[11,13,14].

In this paper, positive findings of N-(phenylsulfonyl)-sarcosine and the drug clofibric acid are presented based on investigations of water samples from the Berlin area and also from rivers inside and outside Germany.

EXPERIMENTAL

Material

All solvents were Pestanal products from Riedel de Haen Seelze, Germany. Pentafluorobenzyl bromide was obtained from Aldrich, Steinheim, Germany, triethylamine from Merck, Darmstadt, Germany. Sample vials, screw caps and septa were purchased from Zinsser, Frankfurt, Germany, 200 µl inserts for the sample vials from CS-Chromatographie Service, Langerwehe, Germany. Clofibric acid was of analytical purity, purchased from Sigma, Deisenhofen, Germany. N-(phenylsulfonyl)-sarcosine and 2-(4-chlorophenoxy)-butyric acid were synthesized according to procedures described elsewhere[2,11]. The structural formulae of these compounds are given in Figure 1. Stock solutions of all compounds were prepared in methanol. Solid phase extraction (SPE) was carried out

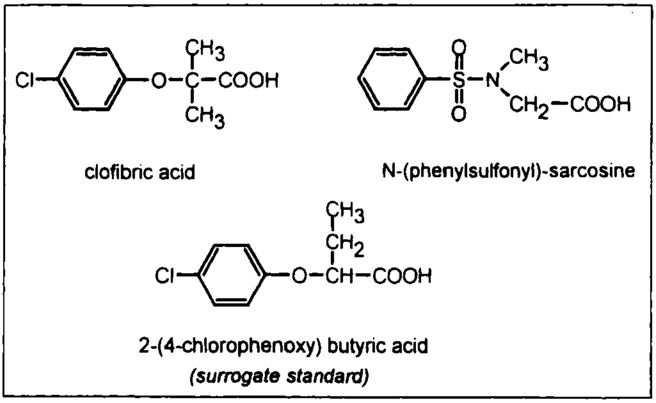

FIGURE 1 Structural formulae of clofibric acid, N-(phenylsulfonyl)-sarcosine and 2-(4-chlorophenoxy)-butyric acid used as surrogate standard in sample preparation

with cartridges of polypropylene with a volume of 6 ml and BAKERBOND Polar Plus RP-C18 material from Mallinckrodt Baker, Griesheim, Germany. Adjustable transferpettors (1-10µl and 10-100µl) were from Brand, Wertheim, Germany.

Sample Preparation

A water sample of 1 L was mixed with 100 µl of a solution of 2-(4-chlorophenoxy) butyric acid in methanol (1 mg/l) as surrogate standard to give a concentration of 100 ng/l. The sample was then acidified to pH <2 with HCl. Each SPE-cartridge was filled with 1 g of RP-C18 adsorbent. Conditioning was performed successively with 10 ml acetone, 10 ml methanol and finally 10 ml of distilled, deionized water (pH <2). The solvents were drawn through the cartridge by means of a gentle vacuum and the cartridge was not permitted to run dry during the whole conditioning procedure. Then the spiked water sample was percolated through the cartridge at a maximum flow rate of approximately 8 ml/min by applying a low vacuum.

After drying the cartridge for 2-3 hours under a gentle stream of nitrogen, the analytes were eluted with 2.5 ml of methanol. The eluate from the SPE-cartridge containing the target compounds was mixed with 100 µl of a solution of 2,4 dichlorobenzoic acid in methanol (2 mg/l) as internal standard. Then the eluate was dried under a gentle stream of nitrogen. (Meanwhile, the internal standard 2,4-dichlorobenzoic acid has been replaced by pentafluorophenoxy acetic acid)

Derivatization

Derivatization was performed at 110°C for one hour using 100 µl of pentafluorobenzylbromide (2% in toluene) and 2 µl of triethylamine as catalyst as previously described[3,5]. The derivatized sample was then dried under nitrogen and finally dissolved in 100 µl of toluene.

GC-MS Parameters

All mass spectrometric measurements were performed with an Hewlett-Packard HP 5970 MSD combined with an HP 5890 gas chromatograph fitted with a 25 m × 0.2 mm i.d. × 0.33 µm HP-5 capillary column and a 1.5 m × 0.32 mm i.d. × 0.33 µm HP-5 pre-column. Carrier gas was helium (purity: 99.999%) set to a carrier gas flow of 28 cm/s at the initial temperature. The oven temperature was held at 100°C for 1 min following injection, then programmed at 30°C/min to

150°C, which is held for 1 min, then at 3°C/min to 205°C followed by 10°C/min to 260°C and finally held for 23 min. Injection port and transfer line temperatures were 210°C and 250°C, respectively. 2μl quantities of sample were injected by means of an HP 7673 autosampler using hot splitless injection with the split closed for 0.9 min. Using SIM, three or four characteristic ions were selected for each compound as shown in Table I and scanned with corresponding time windows between one and five minutes with dwell times of 150 to 300 ms per ion. Chromatograms are presented as multiple ion detection (MID) chromatograms, which means there was a summation of all ions in the corresponding time window. Peak identity is confirmed by checking the individual indicative ion profiles and their ion intensity ratios. Mass spectrometer tuning was performed weekly using the auto-tuning macro. Pre-column and insert liner were exchanged at least after 50 injections.

TABLE I GC and MS data of the PFB derivatives of the target compounds. In brackets the relative intensity of the charged mass fragment in the EI mass spectrum with the basepeak = 100

PFB-ester	*t_R [min]*	*Selected Ions (rel. abund.)**
clofibric acid	24,54	128 (100);130 (32);394 (13)
2,4-dichloro benzoic acid (internal standard)	24,78	173 (48);370 (42); 372 (28)
mecoprop	25,64	142 (59);169 (100); 394 (94)
2-(4-chlorophenoxy)-butyric acid (surrogate standard)	25,84	128 (93); 169 (70); 394 (77)
dichlorprop	27,07	162 (65); 414 (46); 416 (32)
1-naphthylacetic acid	28,45	115 (19); 141 (100); 366 (84)
N-(phenylsulfonyl)-sarcosine	31,11	77 (88); 141 (75); 184 (100); 268 (29)

* relative abundances of the corresponding masses in the full mass spectrum.

RESULTS AND DISCUSSION

Sewage Farm Ground Water

In the course of a project on the leaching behavior of compounds applied with municipal waste water to sewage farms south west of Berlin, clofibric acid and N-(phenylsulfonyl)-sarcosine have been found as major polar contaminants with high leaching potential. In the subsoil of the sewage farms, samples were taken down to the fourth and in a few cases fifth ground water aquifer in a depth of more than 125 meters. Most of the samples have, however, been taken from the first ground water aquifer with some special locations with parallel sample wells allowing sampling from all four (five) existing aquifers[11-13].

Clofibric acid was found to pass unchanged through the microbiological treatment in the sewage treatment plants before the sewage is applied to the sewage farms. In the sewage farms, clofibric acid showed a remarkable persistence and was found to be a major contaminant present in most of the ground water wells at concentrations ranging from 1 ng up to 4 μg per liter[11]. Outside the sewage farm area, the samples of the first ground water aquifer were found to be free of clofibric acid with the exception of those from wells having a groundwater connection to the sewage farms[11]. High concentrations of clofibric acid in the second and third ground water aquifers at depths of more than 70 meters indicate that this compound is not retarded significantly in the sewage farm subsoil[11].

The distribution pattern of clofibric acid in the ground water aquifers of the sewage farms showed that in the first ground water aquifer clofibric acid is almost shifted vertically. In contrast, in the second and third ground water aquifers which are used in drinking water production by the neighboring water works clofibric acid is also shifted horizontally. All these trends were established in seven sampling series from 1992 to 1995 and clofibric acid turned out to represent an organic tracer compound for easy detection of possible organic contamination of the ground water resources by sewage water[11].

Additionally, N-(phenylsulfonyl)-sarcosine, a hitherto unknown polar contaminant, was found in ground water samples from the sewage farm area in the sampling series of winter 1993 to 1994[11-13]. Its structure was established by several different derivatization procedures applying gas chromatography-mass spectrometry with different ionization techniques such as electron ionization (El), positive chemical ionization (PCI) and negative chemical ionization (NCI)[11-13]. Finally, one of the structures postulated was confirmed by synthesis of all possible isomers[11].

N-(phenylsulfonyl)-sarcosine was detected in sewage farm ground water sample at concentrations up to 150μg/l[11]. A typical MID-chromatogram of a pentafluorobenzylated extract of a sewage farm ground water samples is shown in Figure 2. In this case, the sample contained 990 ng/l of clofibric acid and more than 15 μg/l of N-(phenylsulfonyl)-sarcosine. This example also demonstrates that the analytical method can be applied over a wide concentration range. The target compounds exhibit an almost linear response over four orders of magnitude from 5 ng/l to 50 μg/I.

The distribution pattern of N-(phenylsulfonyl)-sarcosine in the different ground water aquifers of the sewage farms confirmed those results already deter-

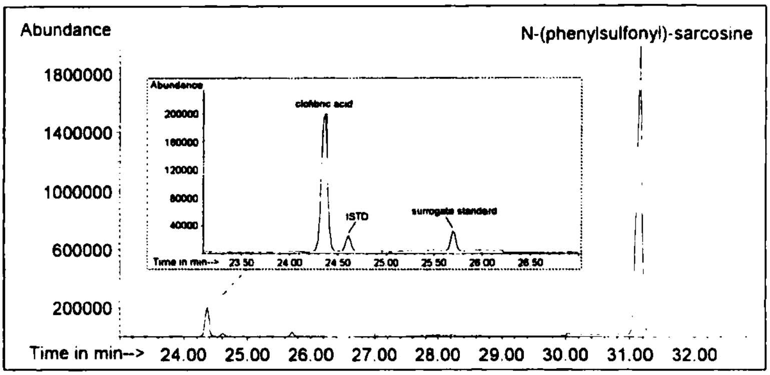

FIGURE 2 MID-chromatogram of a pentafluorobenzylated extract of a sewage farm ground water sample (LWL 14/67) collected from a ground water well of the first ground water aquifer at a depth of 17 m. The sample contained 990 ng/l of clofibric acid and 15250 ng/l of N-(phenylsulfonyl)-sarcosine. Sample volume: 500 ml; 93% recovery of the surrogate added at a concentration of 200 ng/l

mined for clofibric acid[11]. In the first ground water aquifer it is shifted almost vertically, whereas in the lower ground water aquifers an increased horizontal shift was observed.

N-(phenylsulfonyl)-sarcosine was, however, only found at low concentrations in the sewage applied to the sewage fields. This indicated that this compound is only a metabolite of a precursor compound which is degraded in the sewage farm subsoil. Recently, this assumption was also confirmed by Knepper and Haberer[15] who found N-(phenylsulfonyl)-sarcosine mainly in industrial but also in municipal waste water. They postulated that N-(phenylsulfonyl)-sarcosine is a metabolite of N-(phenyl-sulfonyl)-capronic acid which is used as corrosion inhibitor for the treatment of metals[16-20] but this path needs further confirmation.

Berlin drinking water

In a monitoring study of drinking water samples from the various plants of the Berlin waterworks carried out from 1992 to 1995[6,11,14], clofibric acid and N-(phenylsulfonyl)sarcosine were found at maximum concentrations of 270 ng/l and 105 ng/l, respectively. In Figure 3, the MID-chromatogram of a pentafluorobenzylated extract of a Berlin drinking water sample containing 55 ng/l of clofibric acid and 35 ng/l of N-(phenylsulfonyl)-sarcosine is shown as an example. A review of the water sources of all Berlin water plants was carried out in order to support the assumption made for the path of the two contaminants into the drinking water. Drinking water collected from those wells with contact to surface water by bank filtration or artificial ground water enrichment should show higher

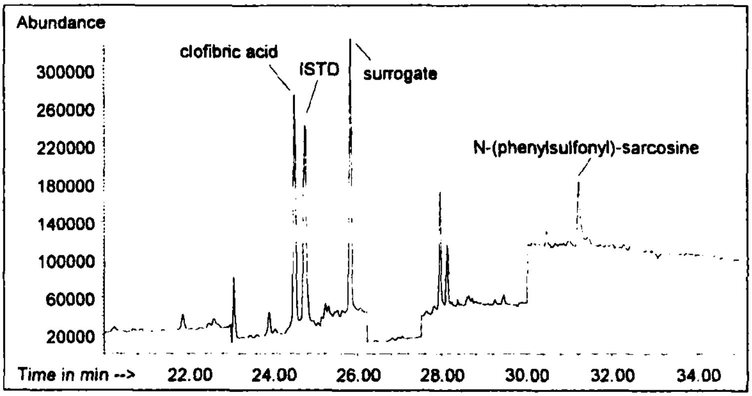

FIGURE 3 MID-chromatogram of a pentafluorobenzylated sample taken from water works in Tiefwerder. Sample spiked with 100 ng surrogate standard and 200 ng internal standard (ISTD) per liter. 55 ng/l of clofibric acid and 35 ng/l of N-(phenylsulfonyl)-sarcosine were found in this sample

TABLE II Clofibric acid and N-(phenylsulfonyl)-sarcosine in drinking water samples collected from the Berlin water works[11,14]. Correlation between bank filtration (BF), artificial ground water enrichment (GWE) and the level of drinking water contamination

Water works	*BF[1] in %*	*GWE[2] in %*	*clofibric acid in ng/l[5]*	*NPS[3] in ng/l[5]*	*SWC[4]*
Beelitzhof	66	7	60	105	+
Buch	0	0	< 5	-	+
Friedrichshagen	82	0	10	25	o
Johannisthal	62	0	170	105	++
Jungfernheide	52	43	45	-	+
Kaulsdorf	0	0	-	-	-
Kladow	68	0	6	17	+
Köpenick	74	0	6	8	o
Riemeisterfenn	17	0	11	70	+
Spandau	30	48	-	-	-
Stolpe	unknown	+	13	-	(-)
Tegel	54	27	25	-	+
Tiefwerder	61	0	55	35	+
Wuhlheide	58	0	75	-	+

[1]BF : bank filtration; [2]GWE : artificial ground water enrichment; [3]NPS : N-(phenylsulfonyl)-sarcosine; [4]SWC : degree of contamination of the neighboring watercourse; [5]-: below the limit of detection of 1 ng/l for clofibric acid or 2 ng/l for N-(phenylsulfonyl)-sarcosine.

contamination levels than that collected from ground water wells without direct influences from contaminated neighboring watercourses.

* As can be seen from Table II, the analytical results obtained for the drinking water samples collected from all fourteen Berlin water works were found to correlate well with the individual percentage contributions to the ground water which originate from artificial groundwater enrichment and bank filtration[11,14].

The geographical situation of the water works and the relative contamination of any neighboring watercourse used as a source for ground water enrichment are decisive for the concentrations of both polar contaminants[11,14]. Both compounds, according to present results, commonly leach into drinking water and are not eliminated by the drinking water treatment used by the Berlin waterworks[11,14].

Surface water outside Berlin

The results obtained for clofibric acid and N-(phenylsulfonyl)-sarcosine in the Berlin area encouraged further investigations outside Berlin. Thus, we collected a few surface water samples to spot check for both compounds in several German rivers. Of course, these samples were not representative but the purpose of these investigations was to show that the occurrence of both polar contaminants in environmental water samples is not a local phenomenon. Up to 220 ng/l of clofibric acid and 490 ng/l of N-(phenylsulfonyl)-sarcosine were detected in various locations in Germany [6,11].

In Figure 4, the MID-chromatogram of a surface water sample is shown which was collected in July 1994 from the river Danube near Ulm in Germany. In this

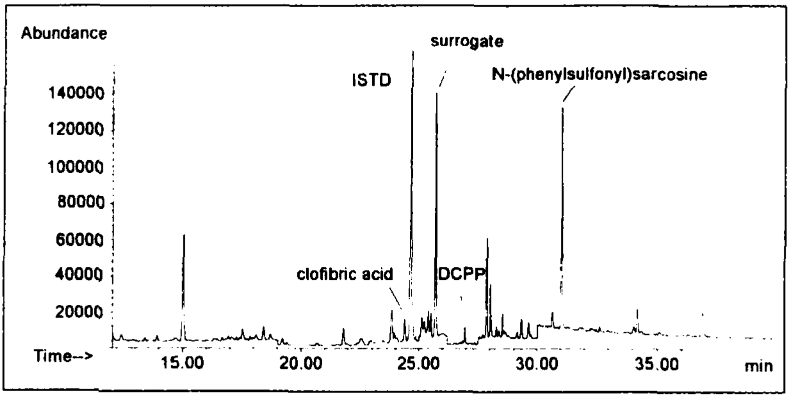

FIGURE 4 MID-chromatogram of a pentafluorobenzylated sample taken from the river Danube near Ulm (21/7/94). Sample spiked with 200 ng surrogate standard and 400 ng internal standard (ISTD) per liter. 17 ng/l of clofibric acid, 30 ng/l of dichlorprop (DCPP) and 105 ng/l of N-(phenylsulfonyl)-sarcosine were found in this sample

sample 17 ng/l of clofibric acid and 105 ng/l of N-(phenylsulfonyl)-sarcosine were found, respectively. Additionally, the sample contained 30 ng/l of the phenoxyalkanoic acid dichlorprop (2-(2,4-dichlorophenoxy) propionic acid) one of the most frequently used herbicides in Germany. Actually, the drug clofibric acid is a structural isomer of mecoprop (2-(4-chloro-o-tolyloxy) propionic acid), another important phenoxyalkanoic acid used as a herbicide in Germany. Clofibric acid has, however, no herbicidal potential and has therefore to our knowledge never been used as a herbicide in agriculture.

Meanwhile, positive results for clofibric acid and N-(phenylsulfonyl)-sarcosine were confirmed by other working groups who found both compounds in the river Rhine, its tributaries and in other German rivers at varying concentration levels up to the µg per liter level[15,21-23].

Surface water outside Germany

Positive results obtained with only a few samples collected from rivers in Italy indicate that the occurrence of both polar contaminants is not a singularly German phenomenon. Especially, N-(phenylsulfonyl)-sarcosine was detected at concentrations up to 60 ng/l in surface water samples collected in Venice, in the Lago Maggiore and in the river Po. Clofibric acid was also found in the river Po at a concentration of 30 ng/l.

The unequivocal confirmation of a positive finding of 60 ng/l N-(phenylsulfonyl)-sarcosine in the river Po (Italy) is demonstrated in Figure 5 by the indicative ion traces of the corresponding PFB-ester at m/z 77, 141, 184 and 268. All the

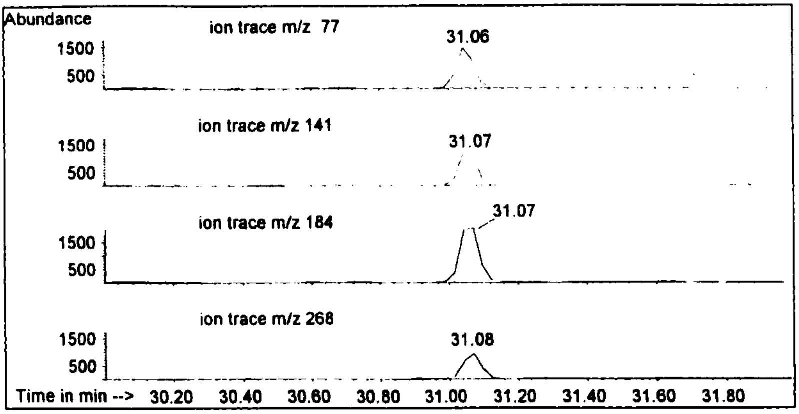

FIGURE 5 Ion traces for m/z 77, 141, 184 and 268 of the PFB-ester of N-(phenylsulfonyl)-sarcosine extracted from the MID chromatogram of a river water sample which was collected from the river Po in Italy. 60 ng/l of N-(phenylsulfonyl)-sarcosine were found in this sample

ion traces give clear peak signals at the expected retention time with peak area ratios fitting the relative abundances of the standard compound as given in Table I.

CONCLUSION

The drug clofibric acid and N-(phenylsulfonyl)-sarcosine found in municipal sewage water were also detected in surface, ground and drinking water. Both contaminants were found in Berlin drinking water samples and can be expected wherever contaminated surface water is used for artificial groundwater enrichment and/or bank filtration in drinking water production. The occurrence of clofibric acid and N-(phenylsulfonyl)-sarcosine in environmental water samples is neither a local nor a national phenomenon as they have also been found in surface water samples at different locations in Germany and Italy.

Acknowledgements

The authors thank the state government of Brandenburg and the Landesumweltamt Brandenburg for their financial aid within the project "Rieselfelder südlich Berlin - Altlasten, Grundwasser, Oberflächengewässer", the Berliner Wasser Betriebe (BWB), Mrs. G. Fricke for her practical assistance and Mr. R. Hatton for his help in checking the manuscript.

References

[1] EEC Drinking Water Guideline, 80/779/EEC, EEC No. L229/11-29, EEC, Brussels, August 30th, 1980

[2] H.-J. Stan and M. Linkerhägner, *Vom Wasser*, **79**, 75-88 (1992).

[3] Th. Heberer, S. Butz and H.-J. Stan, *J. AOAC Int.*, **77**, 1587-1604 (1994).

[4] S. Butz, Th. Heberer and H.-J. Stan, J. Chromatogr. A, **677**, 63-74 (1994).

[5] Th. Heberer, S. Butz and H.-J. Stan, *Intern. J. Environ. Anal. Chem.*, **58**, 43-54 (1995).

[6] H.-J. Stan, Th. Heberer and M. Linkerhägner, *Vom Wasser*, **83**, 57-68 (1994).

[7] A.W. Garrison, J.D. Pope and F.R. Allen, In: *Identification and Analysis of Organic Pollutants in Water* (C.H. Keith ed., Ann Arbor Science Publishers Inc.,1976)517-566.

[8] Ch. Hignite and D.L. Azamoff, *Life Sciences*, **20**, 337-342 (1977).

[9] Th. Heberer and H.-J. Stan, Investigation of trace organic contaminants in sewage farm areas near Berlin. Poster at the "24th Symposium on Environmental Analytical Chemistry" in Ottawa (Canada), May 16-19, 1994.

[10] Th. Heberer and H.-J. Stan, Investigation of acidic herbicides and related polar contaminants in sewage farm areas near Berlin. Poster at the II Eighth IUPAC International Congress of Pesticide Chemistry in Washington, DC (USA), July 4-9, 1994.

[11] Th. Heberer, Identification and Quantification of Pesticide Residues and Environmental Contaminants in Ground and Surface Water Applying Capillary Gas Chromatography - Mass Spectrometry, TU Berlin thesis (in German), Berlin: Wissenschaft & Technik Verlag 1995; 437 p.

[12] Th. Heberer and H.-J. Stan, *Fresenius' Environ. Bull.*, **3**, 639-643 (1994).

[13] Th. Heberer and H.-J. Stan, *GIT Fachz. Lab.*, **39**, 718-720 (1995).

[14] Th. Heberer and H.-J. Stan, *Vom Wasser*, **86**, 19-31 (1996).

[15] T.P. Knepper and K. Haberer, *Vom Wasser,* **86**, 263-276 (1996).

[16] H. Diery et. al., Water-misable corrosion inhibitor. Ger. Offen. DE 2840112 790329 (1979).

[17] H. Peters and E.Surma, Cooling fluid containing anticorrosion and anticavitation additives. Eur. Pat. Appl. EP 48429 A1 820331 (1982).

[18] W. Ritschel and H. Lorke, Reaction products from boric acid, diethanolamine, and monoethanol amines and their use as corrosion inhibitors. Ger Offen. DE 3304164 A1 840809 (1984).

[19] J. Geke and B. Stedry, Agent and spray method for cleaning and passivating metals. Ger Offen. DE 3316724 A1 841108 (1984).

[20] J. Geke and B. Stedry, Use of carboxylic acids or their salts as corrosion inhibitors in media for surface treatment of metals. Ger Offen. DE 4323907 A1 950119 (1995).

[21] T.P. Knepper, A. Weber and K. Haberer, *Vom Wasser*, **85**, 271-284 (1995).

[22] W. Abke, H. Korpien and B. Post, In: *Jahresbericht der Arbeitsgemeinschaft Rhein-Wasserwerke (ARW)* 1994, Karlsruhe: self-published 1995; 81-91.

[23] M. Stumpf, T.A. Ternes, K. Haberer, P. Seel and W. Baumann, *Vom Wasser*, **86**, 291-303 (1996).