



ELSEVIER

Journal of Chromatography A, 763 (1997) 315–321

JOURNAL OF
CHROMATOGRAPHY A

Ultrafiltration: a technique for determining the molecular-mass distribution of group parameters of organic pollutants in natural waters

Urte Ludwig^{a,*}, Thomas Grischek^a, Peter Neitzel^b, Wolfgang Nestler^a

^a*Institute for Technology and Economics Dresden, Department of Civil Engineering and Architecture, 01069 Dresden, Germany*

^b*Dresden University of Technology, Institute for Groundwater Management, 01062 Dresden, Germany*

Abstract

The heterogeneity of dissolved organic matter of natural waters and its different interactions cause particular analytical problems. As a result, a less specific parameter such as dissolved organic carbon (DOC) is often used to describe the sources and fate of organics in aquatic systems. The ion-paired organic-bounded sulfur (IOS) is a new parameter, and presently includes an important group of sulfur-containing components such as organic sulfonic acids. Natural waters have been characterised using ultrafiltration in combination with the determination of DOC and IOS concentrations. The determination of group parameters for different mass fractions (>10 000, 10 000–1000, <1000 g/mol) is a sensitive approach to obtaining further insight into the fate of dissolved organics in aquatic systems.

Keywords: Ultrafiltration; Water analysis; Dissolved organic carbon; Ion-paired organic-bound sulfur; Sulfur-containing compounds

1. Introduction

In recent years several analytical methods have been developed to investigate the composition of dissolved organic matter in natural waters [1–5]. However, the heterogeneity of organic matter and its different interactions can cause particular analytical problems. For example, humic substances are an important component of dissolved organic matter and comprise a complex system of related organic macromolecules exhibiting broad molecular-mass distributions and structural composition. Until now only a few percent of individual substances have been identified and quantified. Therefore, less specific parameters such as dissolved organic carbon (DOC), which includes a variety of dissolved or-

ganic substances, are often used to describe the sources and fate of organics in aquatic systems.

The organic group parameters, including organic substances with carbon as a common structural component, can provide important but limited information. Using fractionation methods, for example GPC (gel permeation chromatography), in combination with the detection of specific organic group parameters, gives enhanced information about the dissolved organic matter without determining individual substances [1,6]. The composition of the group parameters DOC and the spectral absorption coefficient (SAC) given in terms of the molecular-mass distribution has been investigated by Fuchs [7] using GPC. The parameter SAC₂₅₄ includes all substances with structures absorbing UV-light at 254 nm such as aromatics and substances with conjugated double bonds. The characterisation of natural

*Corresponding author.

waters using ultrafiltration in combination with the determination of organic group parameters is a suitable and time-saving approach to obtain more information about the composition and the behaviour of dissolved organic matter and specific groups of organic components.

For chemical and physical characterisation of aquatic humic substances, ultrafiltration is often used for fractionation of natural organic substances [8,9]. The fractionation can be performed for large volumes of solution without producing artefacts when compared with other techniques (for example GPC or solid-phase extraction). Therefore, ultrafiltration is suitable to the investigation of groundwater with a low content of organic substances for a wide range of molecular-mass. Using ultrafiltration possible problems must be considered:

(i) The size and the shape of the molecules are affected by the chemical structure and the micro-environmental conditions, such as the pH-value and the ionic strength of the initial solution. To calibrate the ultrafiltration the properties of the standards must correspond to fractionated soluble substances. During ultrafiltration no changes of the pH were observed because the concentration of molecules of low-molecular-mass stay nearly stable in both solutions, the concentrate and the filtrate.

(ii) Because of interactions between molecules aggregates could be built. The aggregation of molecules causes an increase in the portion of the high-molecular-mass fractions which could be different to the portion at sampling time.

(iii) Due to sorption interactions between the membrane material and solute losses of solute are possible. This disadvantage was minimized by developing new membranes (Amicon, Beverly MA, USA).

(iv) The existing distribution of molecular-mass of higher molecular and of pore size of the membranes lead to a S-shape of solute rejection curves. Therefore a factor of 10 between the limits of molecular-masses is necessary for the complete separation of higher molecular-mass substances [10].

The organic group parameters determined here are the DOC and the ion-paired organic bounded sulfur (IOS). The new parameter IOS includes an important group of sulfur-containing components like organic sulfonic acids [11–13]. The IOS records sulfur-containing substances which are capable of forming ion

pairs. The method for determination of IOS in natural waters was developed by Schullerer in 1992 [12]. However, only a few results concerning sources and fate of IOS in natural waters are known [11]. The majority of sulfur-containing organic components are of an anthropogenic origin from the production of dyes, tensides and textiles. Therefore, it should be possible to determine additional anthropogenic sources with the IOS parameter.

Ultrafiltration in combination with the determination of organic group parameters has been applied to determine the composition of molecular-mass fractions of dissolved organic matter in Elbe river water and the changes along a flowpath in a river bank infiltration scheme [14]. The Elbe river is polluted by many different types of industrial and municipal waste water as well as diffuse inputs from superficial runoff. For the purpose of drinking water supply derived from river bank infiltrate, it is important to know details of the raw water composition.

2. Methods

Water samples were taken from the Elbe river and groundwater within the catchment of a waterworks near Torgau, Germany (Fig. 1a and b). The selected sampling points are along a flowpath of river infiltrate to the production well.

2.1. Ultrafiltration

Ultrafiltration was performed with the stirred cell UF2000A (Amicon) with a water volume of 2 l at 0.3–0.35 MPa. The water samples were fractionated in the molecular-mass ranges <10 000 g/mol and <1000 g/mol using the membranes YM10 (10 000 g/mol) and YM1 (1000 g/mol) UF2000A (Amicon). In order to test the separation capability of membranes, the DOC molecular-mass distribution of several polymer standards was determined [4]. Fig. 2 shows the modified ultrafiltration procedure.

2.2. Determination of group parameters

2.2.1. DOC [German standard method 38 409 Part 3]

For DOC determination, the dissolved organic

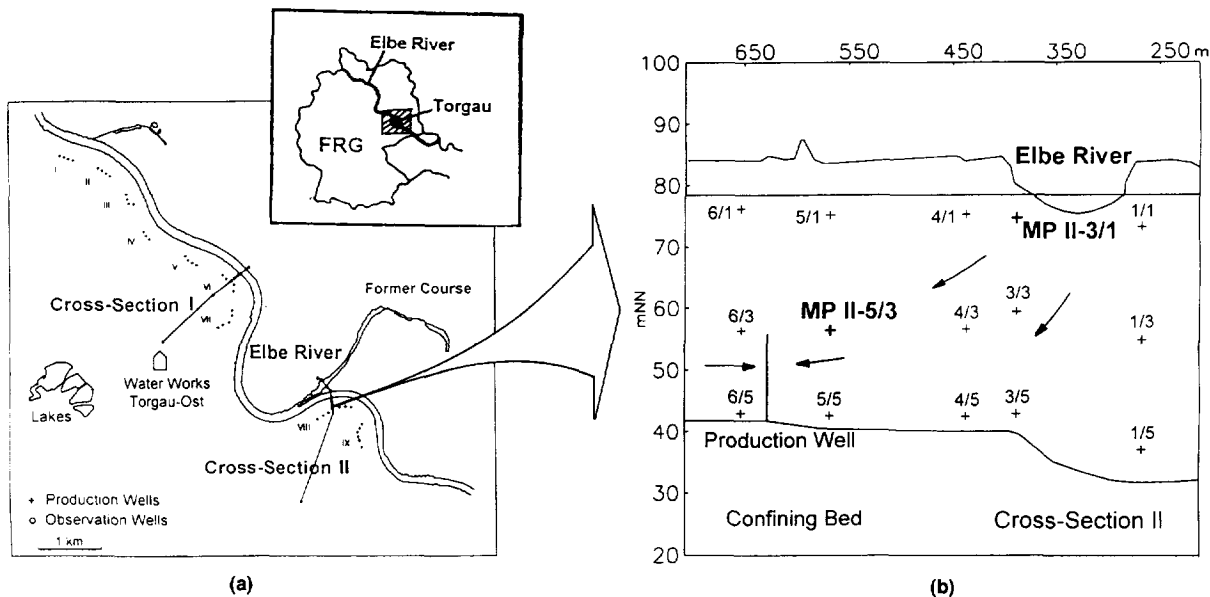


Fig. 1. (a) Location of river bank infiltration site at Torgau-Ost. (b) Cross-section II, Torgau Aquifer.

substances were combusted in an oxygen stream and subsequently detected with an infra-red detector using a Dohrmann TOC Analyser (Model DC-190, Rosemount GmbH, Hanau, Germany) with a detection limit of 0.2 mg/l C.

2.2.2. IOS

The enrichment of the ion-paired sulfur-containing components was performed with ion-pairing solid-phase extraction using Tetrabutylammonium bromid (J.T. Baker, Phillipsburg, USA) as the ion-pairing agent [15]. After washing and drying steps, the analytes were eluted with methanol. The eluate was then dried using a vacuum evaporator. The amount of sulfur of the ion paired components was determined by ICP-OES (Spectro A.I. GmbH, Kleve, Germany). The difference between the amount of sulfur and the amount of sulfate (determined with an ion chromatograph from Metrohm AG, Herisau, Switzerland) yields the parameter IOS [11]. The detection limit was found to be 20 µg/l S for IOS and 5 µg/l S for sulfate-bound S.

2.2.3. SAC₂₅₄ [German standard method 38 404 Part C3]

The absorption of dissolved organic substances at 254 nm was measured using a UV-VIS Spectrometer

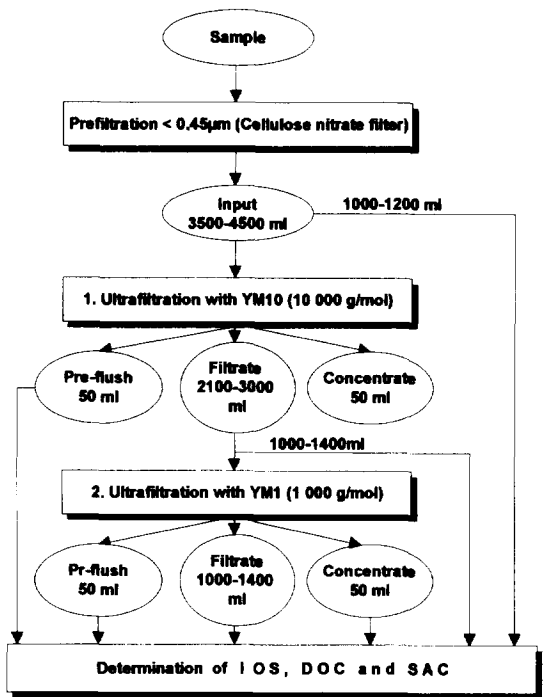


Fig. 2. Flow diagram of the ultrafiltration procedure.

Table 1
Compilation of mean values of group parameters analysed

Water sample	Parameter	Initial water	>10 000 g/mol	10 000–1000 g/mol	<1000 g/mol
Elbe	DOC (mg/l)	5.9	0.9	2.0	3.0
	IOS ($\mu\text{g/l}$)	152	13	74	65
	SAC (1/m)	15.3	1.3	5	9
	DOC/IOS (mgC/mgS)	38.8	69.2	27	46
	SAC/DOC (m^2/g)	2.5	1.4	2.5	3.0
MP II-3/1	DOC (mg/l)	3.9	0.5	1.2	2.2
	IOS ($\mu\text{g/l}$)	105	19	50.5	35.5
	SAC (1/m)	10.5	1.5	4.5	4.5
	DOC/IOS (mgC/mgS)	37.1	27.9	23.7	62
	SAC/DOC (m^2/g)	2.7	3	3.8	2.1
MP II-5/3	DOC (mg/l)	2.9	0.1	0.3	2.5
	IOS ($\mu\text{g/l}$)	73	5	25	43
	SAC (1/m)	6.6	0.7	1.7	4.2
	DOC/IOS (mgC/mgS)	39.7	20	12	58.1
	SAC/DOC (m^2/g)	2.3	7.0	5.7	1.7

Lambda 11 (Perkin-Elmer GmbH, Überlingen, Germany) in order to obtain the amount of SAC₂₅₄.

2.2.4. HPLC

The chromatographic system comprised an HP 1090 series II liquid chromatograph with a 1040 UV-VIS-diode-array detector and a 1046A fluorescence detector. The system was controlled by a ChemStation computer (all from Hewlett-Packard, Palo Alto, CA, USA)

3. Results and discussion

Table 1 gives a compilation of the mean values of the group parameters determined for the natural waters investigated. The DOC content in the Upper Elbe river amounts to 6 mg/l. Only 50% of the dissolved organic substances have molecular-mass values of <1000 g/mol (Table 2). This means that greater than 50% of the analysed fraction is in the

range of molecular-mass values where classical analysis fails. The main components of high-molecular-mass fraction of DOC are humic and fulvic acids with molecular-mass values in the range 1000–3000 g/mol, with part >10 000 g/mol. The higher molecular-mass fractions may include substances from anthropogenic sources such as lignin sulfonates, modified celluloses and water soluble synthetic polymers. It is difficult or even impossible to identify and quantify the natural and synthetic macromolecules as individual substances (Table 3).

The determination of the parameters SAC₂₅₄ and IOS of individual fractions provide more information about the composition of DOC. The measurement of the SAC₂₅₄ shows that the percentage distribution of UV-active compounds is comparable to the DOC concentration. The amount of SAC₂₅₄ increases with the decrease of the molecular-mass range. The main portion of sulfur-containing substances were found in the middle molecular-mass fraction range (10 000–1000 g/mol). We assume that sulfonated polypep-

Table 2
Percentage composition of molecular mass fractions contained in Elbe river water

	>10 000 g/mol	10 000–1000 g/mol	<1000 g/mol
SAC ₂₅₄ (%)	8	33	59
DOC (%)	15	34	51
IOS (%)	9	49	42

Table 3
Potential and identified organic sulfurous organic substances of polluted natural waters

	Range of molecular mass		
	>10 000 g/mol	10 000–1000 g/mol	<1000 g/mol
Potential sulfurous organic substances	Sulfonated polysaccharides e.g., starch, cellulose derivatives, hemi-celluloses, lignin; sulfonated humic- and fulvic acids	Sulfonated polypeptides; polypeptides with thioamino acid; hydrolysed lignin sulfonates; sulfonated humic- and fulvic acid	Arylsulfonates; thioaminocarbon-acid (cysteine, cystine, methionine); sulfonated gallacid; alkylsulfonates; alkylether-sulfonates; alkylbenzenesulfonates; alcoholsulfonates (anionactive tensides); sulfur-containing pesticides; sulfonated mono- and disaccharides
Identified sulfurous organic substances with HPLC (in Elbe river water)	–	–	Aromatic sulfonic acids (dyes) [13,16]; alkylbenzenesulfonates (surfactants) [17]; S-containing herbicides (S-triazines, thioacetic acid amides, thiourea derivatives, thiolcarbamic acids) [18,19]; S-containing insecticides (thiophosphoric acids) [19]

tides, hydrolysed lignin sulfonates and sulfonated humic and fulvic acids form this portion (Table 3), e.g., resulting from paper mill wastes.

The fate of dissolved organic matter in the Elbe river and during infiltration were the subject of investigation between 1991 and 1995 [9]. Up to 50% of the decrease in DOC concentration occurs in the first few centimetres of the flowpath within the biologically-active river bed sediments. Sorption processes are also important. The rates of attenuation are different for the individual molecular-mass fractions. During infiltration, a shift in molecular-mass distribution from high (>10 000 g/mol) to lower molecular-mass fractions (<1000 g/mol) was observed. The values of the carbon specific absorption coefficient SAC_{254}/DOC (Table 1) show that the higher molecular-mass substances with UV-active structures, such as aromatics, are clearly less attenuated compared with other substances given their greater biological stability. Compared to the changes in the individual molecular-mass fractions, changes in the carbon specific absorption coefficient

(SAC_{254}/DOC) of organic substances as a whole are small.

In contrast, along the investigated flowpath the attenuation of IOS is most significant for the middle molecular-mass fraction (10 000–1000 g/mol) (Table 1). The decrease in IOS concentration of the middle molecular-mass fraction leads to a change in the molecular-mass distribution such that at the end of the investigated flowpath the highest IOS content was found in the low-molecular-mass fraction (<1000 g/mol).

The relation between DOC and IOS provides information about the component of organic-bounded sulfur determined by IOS (Table 1). In all water samples, the ratio of organic-bounded sulfur DOC/IOS is approximately equal along the flowpath. However, for individual molecular-mass fractions, differences are observed. During infiltration, in the high-molecular-mass fraction amounts of bounded sulfur decreased significantly, and in the low-molecular-mass fractions the amount increased. The attenuation (decomposition/sorption) of low-molecu-

Table 4

Comparison between the amount of sulfur of determined sulfonic acid (HPLC) and the parameter IOS

	09.10.1995		06.11.1995		06.02.1996	
	Arylsulfonates ($\mu\text{g/l}$)	IOS ($\mu\text{g/l}$)	Arylsulfonates ($\mu\text{g/l}$)	IOS ($\mu\text{g/l}$)	Arylsulfonates ($\mu\text{g/l}$)	IOS ($\mu\text{g/l}$)
Elbe	3.48	169	2.98	162	7.74	136
MP II-3/1	–	–	1.08	120	0.90	90
MP II-5/3	–	–	1.36	69	1.48	62

lar-mass sulfur-containing components is more comparable to that of the DOC components as a whole. Substances of the molecular-mass fraction <1000 g/mol like arylsulfonates come to only a very low part of the parameter IOS (Table 4). The higher molecular-mass sulfur-containing components (>1000 g/mol) are more stable than the other DOC components. The decomposition of individual organic sulfurous substances such as organic sulfonic acids in aquatic systems was the subject of other investigations [20,21].

4. Conclusions

The determination of different less-specific group parameters in selected molecular-mass fractions of natural waters provides more detailed information about the composition of dissolved organic matter and their changes. Ultrafiltration is a useful method for the fractionation of organic matter in water samples. Large volumes of water can be fractionated in a short time without extreme conditions (for example, pressure <0.4 MPa) and use of organic solvents leading to artifacts.

The technique has been successfully applied to determine the content of ion-paired sulfur-containing organic substances (IOS) in dissolved organic matter (DOC) and its changes along a flowpath of Elbe river water infiltrate towards a production well.

With the application of this technique information can be obtained about the molecular composition of the DOC and its changes along a flowpath without knowledge of individual substances. Parameters such as IOS could be useful in recording anthropogenic impacts on river water quality and transformations

during infiltration, and in assessing risks to drinking water supply.

Acknowledgments

This work was financially supported by the German Ministry of Education, Science, Research and Technology (No. 02WT9454) and the “Deutsche Forschungsgemeinschaft (DFG)” (No. NE432/1-2). The authors would like to thank the Fernwasserversorgung Elbaue-Ostharz GmbH for support during sampling of their groundwater cross-sections.

References

- [1] J. Oleksy-Frenzel and M. Jekel, *Anal. Chim. Acta*, 319 (1996) 165.
- [2] S.A. Huber and F.H. Frimmel, *Environ. Sci. Technol.*, 28 (1994) 1194.
- [3] U. Müller, B. Wricke and H. Sontheimer, *Vom Wasser*, 81 (1993) 371.
- [4] H.-J. Neu, W. Ziemer and W. Merz, *Fresenius J. Anal. Chem.*, 340 (1991) 65.
- [5] H.F. Schröder, *Fresenius J. Anal. Chem.*, 353 (1995) 93.
- [6] S.A. Huber, A. Balz and F.H. Frimmel, *Fresenius J. Anal. Chem.*, 350 (1994) 496.
- [7] F. Fuchs, *Vom Wasser*, 65 (1985) 93.
- [8] P. Burba, V. Shkinev and B.Y. Spivakov, *Fresenius J. Anal. Chem.*, 351 (1995) 74.
- [9] G. Abbt-Braun, F.H. Frimmel and P. Lipp, *Z. Wasser-Abwasser-Forsch.*, 24 (1991) 285.
- [10] M. Cheryan, *Ultrafiltration Handbook*, Technomic Publishing, Lancaster, Pennsylvania, 1986.
- [11] S. Schullerer, G. Koschensch, H.J. Brauch and F.H. Frimmel *Vom Wasser*, 78 (1992) 229.
- [12] S. Schullerer, PhD-Thesis, University Karlsruhe, Germany, 1992.

- [13] P. Neitzel, U. Ludwig, W. Nestler, T. Grischek and J. Dehnert, *LC-GC*, 14 (1996) 416.
- [14] T. Grischek, J. Dehnert, W. Nestler, P. Neitzel and R. Trettin, in A.G. Brown (Editor), *Geomorphology and Groundwater*, Wiley, 1995, New York, pp. 21–35.
- [15] P.L. Neitzel, W. Nestler, in B.V. Mallinckrodt Baker (Editor), *Bakerbond Application Note EN-517: Extraction of Arylsulfonates from Water by Ion Pair-Extraction Using Bakerbond SDB-1, Bakerbond spe* Application Handbook*, Deventer, Netherlands, 1996.
- [16] S. Fichtner, F.T. Lange, W. Schmidt and H.-J. Brauch, *Fresenius J. Anal. Chem.*, 353 (1995) 57.
- [17] A. Kreißelmeier, M. Schoester and G. Kloster, *Fresenius J. Anal. Chem.*, 353 (1995) 109.
- [18] P.L. Neitzel, W. Nestler, T. Grischek and J. Dehnert, *Wiss. Z. Techn. Univers. Dresden*, 44 (1995) 52.
- [19] S. Franke, S. Hildebrandt, J. Schwarzenbauer, M. Link and W. Franke, *Fresenius J. Anal. Chem.*, 353 (1995) 39.
- [20] H. Greim et al., *Chemosphere*, 28 (1994) 2203.
- [21] R.M. Wittich, M.G. Rast and H.J. Knackmuss, *Appl. Environ. Microbiol.*, 54 (1988) 1842.