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Polar, hydrophilic compounds in drinking water produced from surface water

Determination by liquid chromatography–mass spectrometry

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ABSTRACT

Drinking water produced from surface water may contain many polar, hydrophilic compounds in spite of different treatment steps such as soil filtration, ozone treatment and activated carbon filtration. Little is known about these compounds. The objectives of this work were the detection and identification by means of tandem mass spectrometry (MS–MS) coupled on-line by a thermospray interface with liquid chromatography. Quantification is possible if standard compounds are available. The different compounds in the water extracts were not only separated by means of an analytical column but also using MS–MS after loop injection bypassing the analytical column. Molecular weight information in the loop spectra (overview spectra) and collisionally induced dissociation (CID) made possible the identification of some of these compounds which cannot be eliminated in the drinking water treatment process. Identification was not only done by interpretation of the recorded daughter- and parent-ion spectra but also by comparing them with a laboratory-made daughter-ion library of polar, hydrophilic pollutants. Direct mixture analysis using MS–MS allows the detection and identification of some of the pollutants if they reach the drinking water in the course of the surface water treatment process because of their biochemical and chemical persistence and/or non-sorbability during the soil or activated carbon filtration process. The proposed method for the analysis of water for polar, non-volatile and/or thermolabile organic substances is a quick, specific and powerful technique which makes it possible to detect and identify these substances without any chromatographic separation or derivatization.

INTRODUCTION

Effluents from municipal and industrial biological waste water treatment plants contain plenty of non-biodegradable compounds when they reach rivers and streams used as receiving waters. These surface waters may serve not only for shipping and cooling purposes but also for drinking water preparation before they reach the ocean. Drinking water preparation requires various treatment steps such as biochemical, chemical and physico-chemical treatment to make this water, polluted by waste water treatment plant effluents, potable. However, in spite of all treatment steps, many non-biodegradable polar compounds cannot be eliminated completely by soil filtration [1], ozone treatment or activated carbon filtration processes because of their resistance against microbial attack and ozone treatment or non-adsorbability on acti-

vated carbon. Therefore, these compounds reach the drinking water nearly unchecked where they can be detected by specific and/or sensitive analytical methods. Complete enrichment from water for analytical purposes seems possible only by using special techniques such as solid-phase extraction combined with lyophilization or partitioning in aqueous two-phase systems.

Most of the organic compounds in effluents from waste water treatment plants are polar [2] and/or thermolabile because of their metabolic or anthropogenic origin. Assessments of the proportion of volatile compounds in the effluents from waste water treatment plants range from 10 to 30% [3–5]. Some of these pollutants are medium- to high-molecular weight substances such as fulvic and humic acids. However, size-exclusion chromatographic studies on river Rhine samples have shown [6], nearly 40% of these polar substances are low-molecular-weight substances. Analytical methods that require volatility for the separation and detection of polar water pollutants fail [2] in this instance, *i.e.*, detector systems that work well when coupled with gas chromatographic separation systems should not be used.

Nevertheless, so far mainly gas chromatography (GC) has been used in water and waste water analysis, combined with conventional detector systems such as the flame ionization detector (FID), electron-capture detector (ECD) and photoionization detector (PID). A mass spectrometer has also been used. For the reasons mentioned above, methods that require volatility for separation and detection are useful only for non-polar compounds but unsuitable for the mainly polar pollutants occurring in water.

Liquid chromatography coupled with a specific detector such as mass or tandem mass spectrometer would help to overcome some of these problems with polar, hydrophilic pollutants. Sample pretreatment is very important here. However, high-performance liquid chromatographic (HPLC) separation of waste and surface water extracts, even after selective desorption by varying eluents with increasing polarity and selective collection of the eluates from solid-phase extraction cartridges, is hardly successful because of matrix and co-elution effects [1,7]. Normally used detector systems such as UV-VIS, fluorescence, refraction and conductivity types are unsuitable because of insufficient specificity. Even selective detectors such as the mass spectrometer are only suitable if soft ionization techniques are used. Generation of fragments in the course of the ionization process cannot be tolerated because differentiation of molecular and cluster ions and also fragment ions is not possible and leads to misinterpretation of the recorded spectra.

Coupling of HPLC on-line with thermospray ionization and mass spectrometry ensures soft ionization and the generation of mainly molecular or cluster ions. The cluster ions produced were ammonia adduct ions when ammonium acetate was used for ionization purpose.

Only few results exist from comparable analytical studies of waste waters [1,2,7–9]. A little work on surface waters has been done using grab samples [1,7,10–14]. Rivera and co-workers [10–14] analysed in detail activated carbon extracts from filters of a drinking water treatment plant in Barcelona. They used off-line fast atom bombardment mass spectrometry (FAB-MS) and collisionally induced dissociation mass-analysed ion kinetic energy spectrometry (CID-MIKE). The examinations carried out so far confirm the observation that results obtained with detection methods such as FID, ECD and PID after GC separation only pretend clean water, drinking,

surface and waste water, and polar compounds could not be detected.

The aim of this work was to use on-line coupling of LC with tandem mass spectrometry by thermospray (LC-TSP-MS-MS) for the analysis of surface water being used for drinking water preparation. The pollutants dissolved in this water should be detected and identified as completely as possible during surface water treatment by soil filtration, ozone treatment and activated carbon filtration.

EXPERIMENTAL

Materials

Water pollutants were extracted using solid-phase extraction cartridges from Baker (Deventer, Netherlands). Solid-phase extraction materials were conditioned as prescribed by the manufacturer. Glass-fibre and membrane filters used for the pre-treatment of the water samples were obtained from Schleicher & Schüll (Dassel, Germany). Before use the glass-fibre and membrane filters were heated to 400°C or were treated with ultra-pure water obtained with a Milli-Q system (Waters Assoc., Milford, MA, USA) for 24 h and then washed with 100 ml of the same water. Hexane, diethyl ether, methanol and dichloromethane used for the desorption of water pollutants from the solid-phase material were Nanograde solvents from Promochem (Wesel, Germany). Nitrogen for drying of solid-phase cartridges was of 99.999% purity (Linde, Germany). All surfactant standards were gifts from the producers (Hüls, Marl; Hoechst, Frankfurt; BASF, Ludwigshafen; and Rewo, Steinau, Germany) and were of technical grade.

GC analyses were done on a DB-17 fused-silica column (J&W Scientific, Folsom, CA, USA) and helium (Linde) was used as the carrier gas. HPLC separations were done on a μ Bondapak C₁₈ (5 μ m) column (30 cm \times 3.9 mm I.D.) (Waters). The mobile phase was methanol (HPLC grade) from Promochem and Milli-Q purified water. The ammonium acetate for thermospray ionization was of analytical-reagent grade from Merck (Darmstadt, Germany).

Sampling and sample preparation

All samples from the waste water treatment plant, surface waters and the drinking water treatment plant were taken as grab samples in glass bottles. The bottles were rinsed carefully with several portions of the same water that was subsequently stored in them. The storage temperature was 4°C.

Depending on the degree of pollution, different amounts of water were used for solid-phase extraction. Water samples were forced through the solid-phase extraction cartridges after passage through a glass-fibre filter. To ensure complete adsorption, the water samples were forced through two cartridges in series. The adsorbed pollutants were desorbed separately. Solvents of different polarities (hexane, hexane-diethyl ether, diethyl ether, water-methanol, methanol and dichloromethane) were used for this purpose. All eluates except those with methanol and methanol-water were evaporated to dryness with a stream of nitrogen and the residue was dissolved in methanol. The samples were rinsed into glass bottles after solid-phase extraction, and freeze-drying was applied to enrich non-C₁₈-adsorbable compounds. Samples containing high chloride concentration were mixed with silver ions to precipitate and separate the silver chloride before lyophilization. After freeze-drying, the samples

were dissolved in methanol and used for MS investigations. Loaded activated carbon from filters from the waste water treatment plant was dried by lyophilization and extracted with methanol.

Quantification

A 19-l volume of drinking water was enriched on a C₁₈ solid-phase extraction column. Elution was effected with different eluents of increasing polarity. The combined eluates were evaporated to dryness under a stream of nitrogen and the residue was dissolved in a known volume of methanol.

Flow-injection analysis (FIA) for quantification was applied, recording mass spectra beginning at m/z 350 and ending at m/z 800 for quantification of nonanol polypropylene glycol ether. The compositions of the mobile phases for FIA were as follows: mobile phase I, methanol–water (60:40); mobile phase II, 0.1 M ammonium acetate in water. The overall flow-rate was 1.5 ml/min with a ratio of 0.8 ml/min of mobile phase I and 0.7 ml/min of mobile phase II.

Areas under the peaks of the mass traces of the cluster ions of m/z 394, 452, 510 and 568 from water extracts were determined and compared with a calibration graph obtained with standard solutions of 0.1, 0.5 and 1.0 mg/l of the surfactant mixture Degressal in methanol.

Gas chromatographic system

A Varian (Darmstadt, Germany) Model 3400 GC system with a fused-silica capillary column was used. The conditions were as follows: carrier gas, helium; linear gas velocity, 15 cm/s; injector temperature, 250°C; transfer line temperature, 250°C; column, DB-17, film thickness 0.25 μm , 30 m \times 0.25 mm I.D.

Combined with GC, electron impact (EI) ionization was applied with an ionization energy of 70 eV. Under these conditions the pressure in the ion source was 8×10^{-6} Torr and in the manifold 3×10^{-2} Torr. The electron multiplier was operated at 1200 V with a dynode voltage of 5 kV. The temperature in the ion source was 150°C.

Liquid chromatographic system

LC separations coupled with MS, MS–MS and UV detection were achieved with a Waters Assoc. (Milford, MA, USA) Model 600 MS system. A Waters Model 510 pump was used for post-column addition of 0.1 M ammonium acetate solution in the TSP mode. A Waters Model 490 MS UV detector was connected in-line with the TSP interface. The conditions in FIA bypassing the analytical column were as given above. The chromatographic conditions for separations on the analytical column varied and are specified in the legends of the figures.

Direct chemical ionization (DCI)

For DCI spectra a triple-stage quadrupole mass spectrometer (TSQ 70) from Finnigan MAT (San Jose, CA, USA) was used. The temperature at the beginning of the DCI experiments was 50°C and at the end 450°C, with a gradient of 800°C/min.

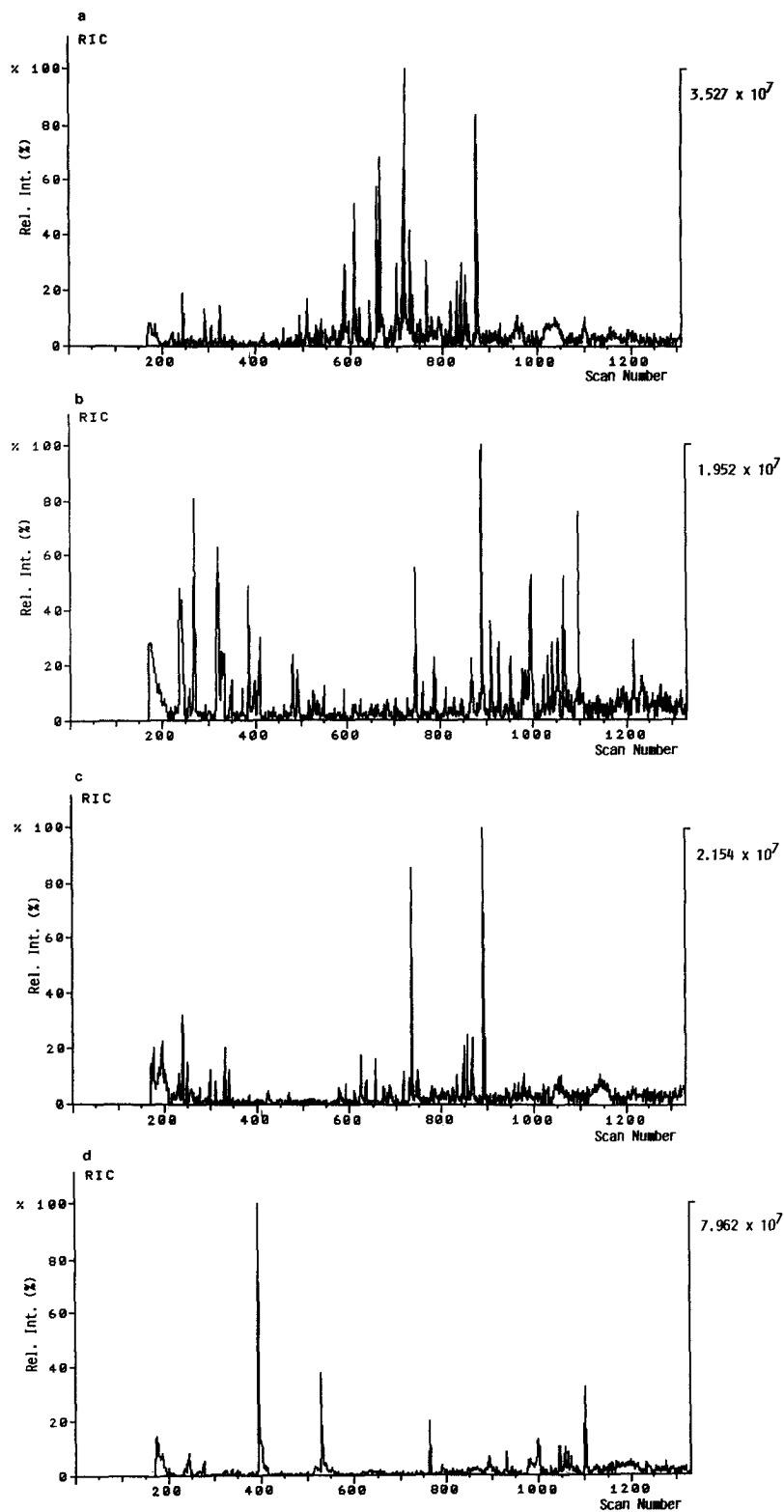


Fig. 1. GC-MS total ion current traces for (a) river Rhine water, (b) soil filtrate, (c) ozone-treated soil filtrate, (d) activated carbon filtrate drinking water. C_{18} solid-phase extract; eluent, methanol.

MS and MS-MS systems

The mass spectrometer was a TSQ 70 combined with a PDP 11/73 data station. The TSP interface was obtained from Finnigan MAT. For coupling the HPLC system with the mass spectrometer, the following conditions were chosen: vaporizer temperature, 90°C; jet block temperature, 200°C; aerosol temperature, 190°C. The conditions varied during the analytical separations. Under the above conditions the ion source pressure was 0.5 Torr and the pressure in the manifold was $2 \cdot 10^{-5}$ Torr.

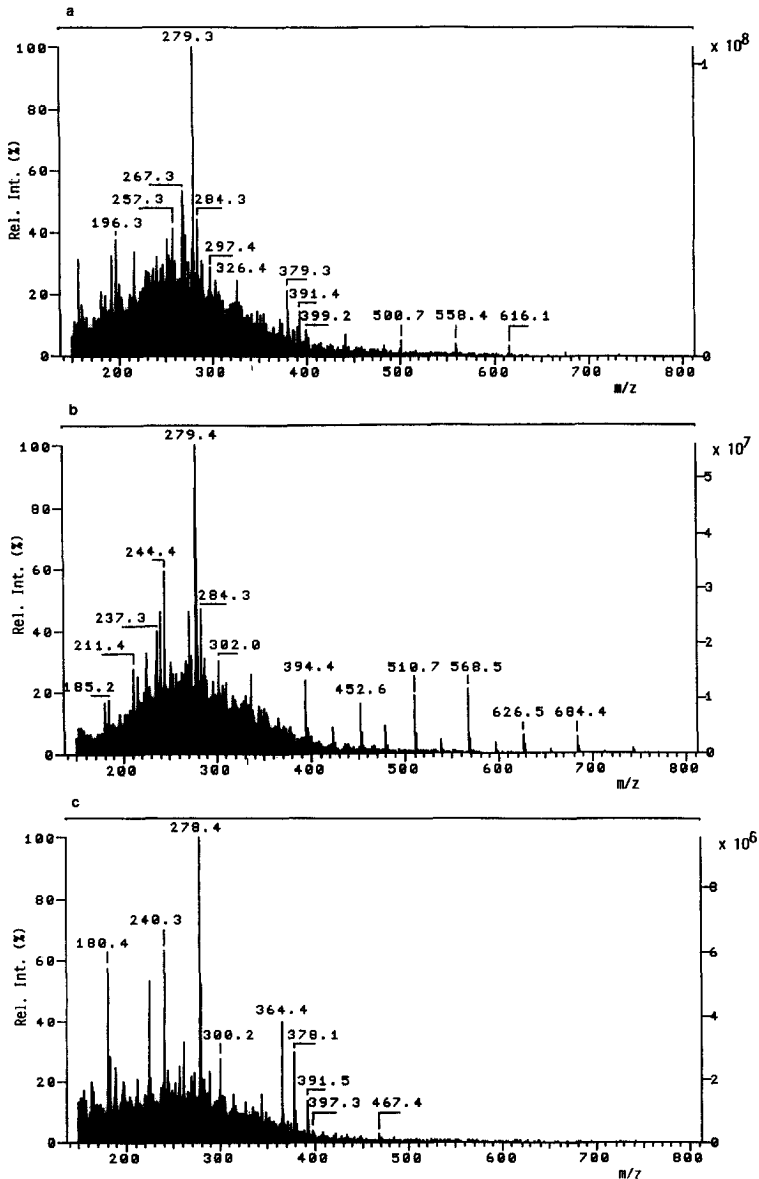


Fig. 2.

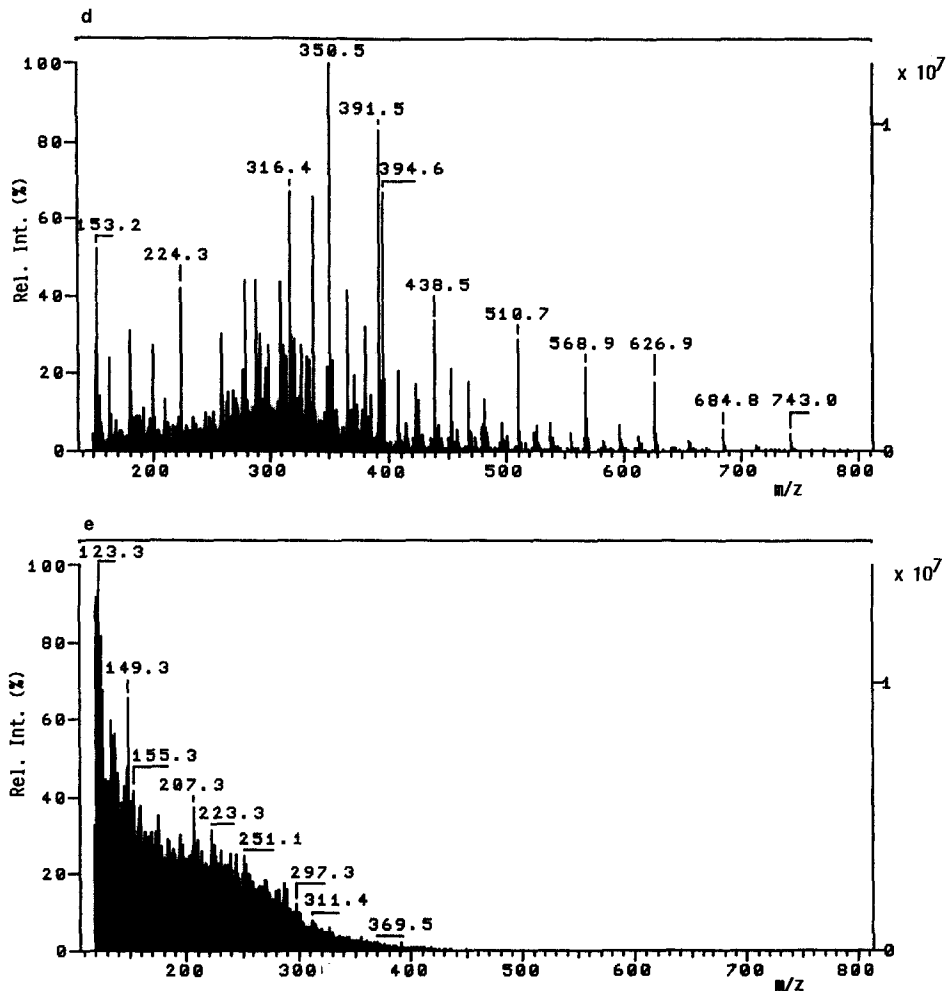


Fig. 2. LC-TSP-MS loop injection spectra (bypassing the analytical column) of solid-phase extracts of (a) river Rhine water, (b) soil filtration, (c) ozone-treated soil filtrate and (d) activated carbon filtrate (drinking water). (e) DCI spectrum of a drinking water extract. Compare Figs. 1d and 2d.

The electron multiplier was operated at 1200 V and the dynode at 5 kV. In the MS-MS mode the ion source pressure was also 0.5 Torr. Under CID conditions the pressure in quadrupole 2 (collision cell) was 1.3 mTorr. The electron multiplier voltage in quadrupole 3 was 1500 V with a dynode voltage of 5 kV.

RESULTS AND DISCUSSION

Water samples were taken from a drinking water treatment plant of a German city located on the river Rhine. During the drinking water preparation process, grab samples taken from the river Rhine, soil-filtered water, soil-filtered and ozone-treated water and drinking water after activated carbon filtration were analysed.

The Rhine is polluted by numerous volatile and non-volatile organic compounds. Fig. 1a, the GC-MS total ion current profile of a river Rhine extract, shows the volatile compounds. Many of these pollutants can be identified by a library search using the NBS library of electron impact spectra.

Many more compounds appear if a LC-MS overview spectrum of this extract is generated, bypassing the analytical column (Fig. 2a). The TSP soft ionization process generates mainly molecular and cluster ions of defined chemical substances differing from each other only in their ratio of mass to charge (m/z).

To obtain molecular weight information, the pollutants occurring in the drinking water preparation process were detected by LC-TSP-MS. Identification was achieved by LC-TSP-MS-MS, generating the daughter ions essential for structural information. For comparison purposes the same extracts were also analysed by direct chemical ionization (DCI-MS).

A library of daughter-ion spectra for LC-MS research work comparable to the NBS EI mass spectral library of volatile compounds was not available. Therefore, identification has to be achieved by standard retention time comparisons after chromatographic separation and/or by the difficult process of interpreting the daughter-ion spectra.

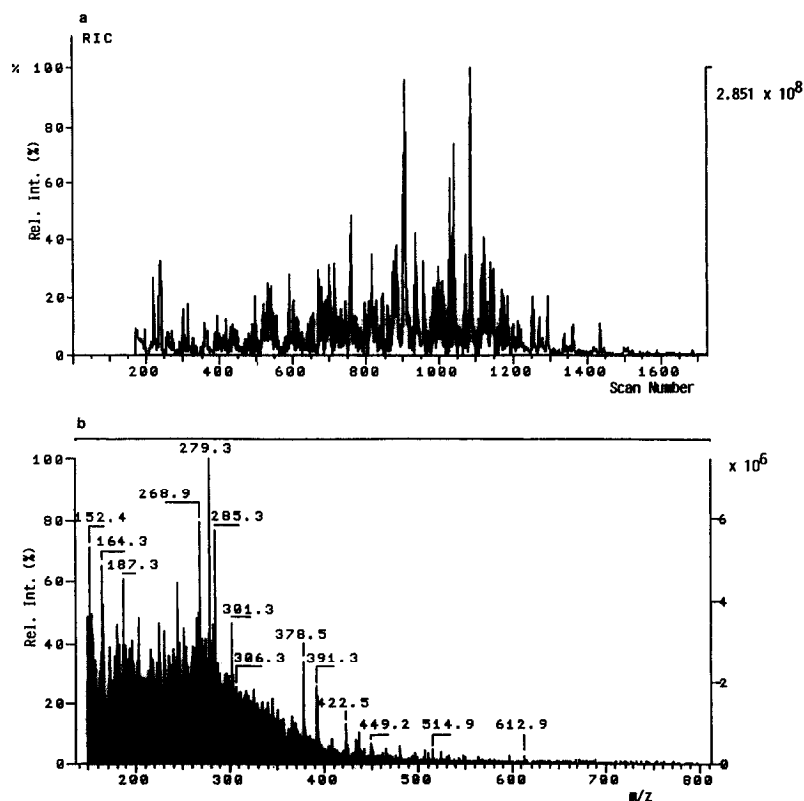


Fig. 3. (a) GC-MS total ion current trace and (b) LC-MS loop injection spectrum (bypassing the analytical column) of activated carbon filter extract. Solvent, methanol.

LC-TSP-MS is a selective ionization technique especially for polar molecules. Therefore, not all compounds in the extracts will be ionized, but as polar molecules are the dominant compounds in waste and surface waters, this ionization technique seemed to be very appropriate to the present research. Estimates of concentrations can only be made after calibration with standard compounds:

Phthalate esters can be recognized in Fig. 2a, the LC-MS overview spectrum of a river Rhine extract, at m/z 279 and 391. Compounds at m/z 442, 500, 558 and 616 can be identified as polypropylene oxide-containing pollutants because of their equidistant masses of $\Delta m/z = 58$.

The concentrations and number of the TSP-active pollutants decrease from one step to the next in the treatment process, *i.e.*, soil filtration, ozone treatment and activated carbon filtration (Fig. 2a-d). This applies to the volatile substances, the GC-MS profiles of which are shown in Fig. 1a-d. In the LC-MS overview spectra only the concentration decreases but the actual number of compounds does not change obviously.

Unfortunately, it was impossible to take time-successive samples, beginning with the river Rhine via the different stages of water treatment, and ending with drinking water. So the advance of the pollutants in the different stages of water treatment in relation to the retention time could not be followed.

As mentioned before, the number of slightly polar and non-polar compounds decreases whereas the number of polar compounds does not change (see Fig. 2a-d). Therefore, the signals of the polar compounds now arise from the background after the disappearance of those for slightly polar and non-polar compounds and then dominate the appearance of the overview spectra.

Comparison of DCI-MS with LC-TSP-MS analysis using ammonia gas or ammonium acetate, respectively, to generate the same ions from the same extract showed that TSP ionization is a softer ionization technique than DCI. More undesirable fragmentations and none of the higher molecular weight compounds could be observed in the DCI spectrum (Fig. 2e). Therefore, LC-TSP-MS was to be preferred for solving our problems with polar, thermolabile compounds.

As GC-MS and LC-MS demonstrate (compare Fig. 1a with 1b and Fig. 2a with 2b), adsorption effects and biochemical degradation seem to be the dominating effects in soil filtration. In this way many non-polar compounds were retained and/or metabolized by bacteria and became more polar. Activated carbon filtration eliminates many non-polar volatile compounds, as the GC profile of the activated carbon extracts shows (Fig. 3a). The LC-MS overview spectrum of the same extract (Fig 3b) is also crowded by many signals.

Phthalate esters can be identified immediately in this activated carbon filter at m/z 279 and 391. Polar compounds containing ethoxylate or propoxylate chains such as non-ionic surfactants cannot be observed in the full-scan spectra because these hydrophilic compounds were hardly adsorbed on activated carbon. Although they were adsorbed at low concentrations, the signals in the overview spectra were suppressed by the strong signals of non-polar and slightly polar compounds that were well adsorbed by the activated carbon. Normally these very hydrophilic compounds pass through activated carbon filters unchecked.

As it was difficult to identify the compounds in the LC-MS overview spectra in Fig. 2a-d, we tried to separate these mixtures of pollutants on an analytical column.

In this way it might perhaps be possible to concentrate some of these compounds by focusing and to make identification by CID easier.

Although the chromatographic conditions were varied systematically by changing the analytical columns from C_2 via C_8 to C_{18} and the composition of the mobile phases (gradient elution with 5, 10 and 20% of acetonitrile), the separation compared with the GC-MS profiles remained poor. As an example, Fig. 4a shows one of these LC-MS profiles for the different water treatment stages (extract of soil filtrate) recorded after time-consuming optimization efforts.

The appearance of the LC-MS profile shown is bad, but the UV trace at 220 nm (Fig. 4b), recorded parallel to LC-MS total ion current measurement, is worse. It is notable, however, that many of the TSP-active compounds show only little absorbance at 220 nm and the drinking water extract does not show any absorbance in the UV region at 254 nm. None of these polar and hydrophilic pollutants has any chro-

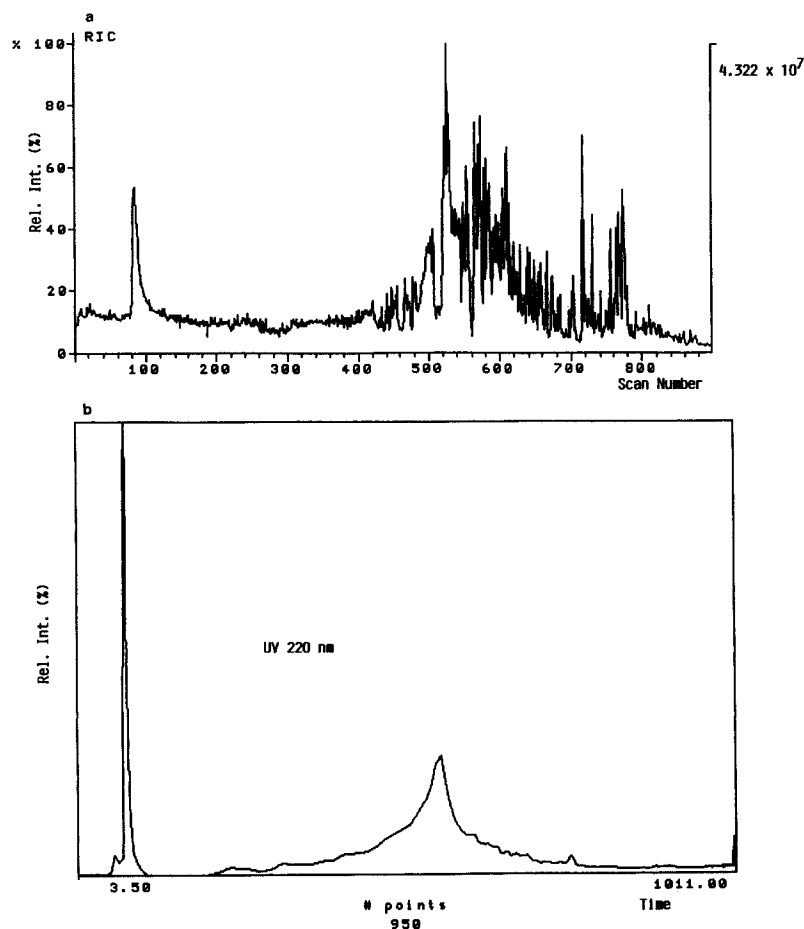


Fig. 4. (a) LC-TSP-MS total ion current trace from extract of Fig. 1b. Soil filtration; C_{18} column; mobile phase, methanol-water, gradient from 100% water to 100% methanol in 30 min. (b) UV (220 nm) trace of soil filtration extract; compare with (a). LC conditions as in (a).

mophore active in the higher UV ranges, which is essential for absorbance. This makes LC-TSP-MS analysis very useful for the detection of polar pollutants in water. On the other hand, non-polar but volatile compounds are sensitive to UV radiation but cannot be ionized by TSP. Therefore, the method of choice for volatile compounds is GC-MS, whereas LC-TSP-MS or electrospray (ESP) is very specific to polar and slightly polar compounds. Using these ionization techniques is often the only way to detect these substances.

A well established and useful method for the analysis of pollutants separated and detected by GC-MS or LC-MS may be analysis by mass chromatograms. In our investigations this seemed to be the only way to follow pollutants in river Rhine water or after soil filtration, up to the stage of drinking-water after activated carbon filtration. In this way mixtures of poorly separated compounds may be analysed more easily.

The ineffectiveness of the different treatment steps with some of these pollutants is notable. In LC-MS overview spectra of soil filtration and drinking water extracts (Fig. 2a and d), ions at m/z 394 and 452 are present, *i.e.*, ozone treatment and activated carbon filtration of the raw water are inefficient in eliminating these pollutants. Owing to this behaviour, in Germany these compounds are called "drinking water relevant compounds", which resist all purification efforts. Even the non-specific but strong oxidizing agent ozone fails to destroy these molecules.

This behaviour was also observed when waste water containing non-ionic surfactants was treated with ozone [7]. Further, the 44 a.m.u. spaced ion series pointed to widely used non-ionic surfactants with poly(ethylene oxide) chains which are non-biodegradable and, as shown here, poorly degradable by ozone. The oxidation in this type of anthropogenic molecule has proceeded to the maximum extent and seems to prevent further oxidation.

After the detection of the pollutants and tentative identification of these polar, hydrophilic compounds which cannot be eliminated in the drinking water treatment process, the possibilities for identification will now be discussed.

To identify these pollutants with the proposed LC-TSP-MS-MS system, different approaches were possible:

(1) Separation of the mixture of pollutants on an analytical column and comparison of retention times with those of standards, if available. Not only MS but also UV detection could be employed. However, a lack of standards and perhaps missing chromophores in the pollutants, respectively, would prevent these identification methods from being used.

(2) If this separation were successful, we should obtain information about retention times and, as the TSP soft ionization technique is used, about molecular weight. Generation of daughter ions by CID from column-separated pollutants would have given structural information for the identification of unknown compounds.

(3) The most promising alternative with regard to time and manpower was the analysis of mixture using MS-MS. Samples with complex matrices [15,16] and/or environmental samples [1,2,7,9,17] have been analysed using CID and series of neutral loss and parent-ion scans under data system control on a triple-stage quadrupole instrument. The mixtures were volatilized directly into the ion source of the MS-MS instrument, whereas we used a TSP interface between the liquid chromatograph and

the triple-stage quadrupole mass spectrometer. To solve the problems of polar pollutants in this work we used the mass filter in quadrupole 1 to separate the ions after loop injection bypassing the analytical column. CID was done in quadrupole 2. In quadrupole 3 daughter and parent ions and neutral loss scans could be recorded to obtain structural information.

As mentioned before, lack of standards would prevent the first approach to identification. However, even if standards were available, a complex matrix in these mixtures could also prevent separation, as observed with a polyethylene glycol (PEG)-containing sample. Although the more sensitive and selective procedure of generating mass traces was applied, no separation could be observed. Co-elution effects disturbed the chromatographic separation of PEG on a C_{18} column, as shown in Fig. 5a. In contrast, Fig. 5b shows a very good LC-MS profile of PEG separation under the same chromatographic conditions.

If the time-consuming separation of pollutants was successful and could be verified by mass chromatograms, CID of focused pollutants should be carried out to obtain daughter-ion spectra of unknown compounds. Comparing one of the CID spectra from the column separation (Fig. 6a) with library spectra in our laboratory-made library on the Finnigan TSQ 70 generated from hydrophilic, polar compounds, the identification was successful. The plot of the library search gives three alternatives

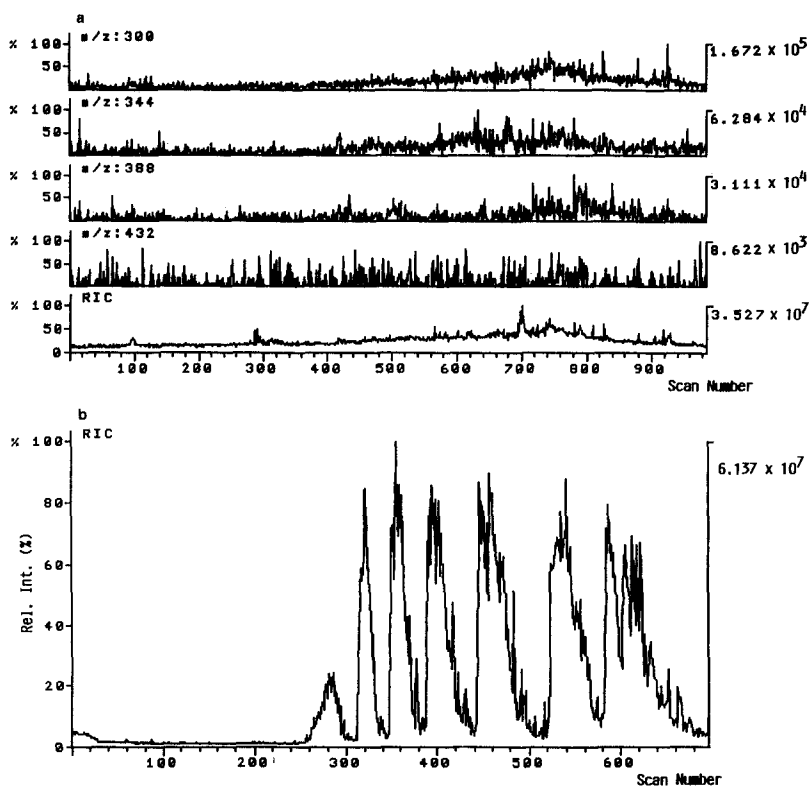


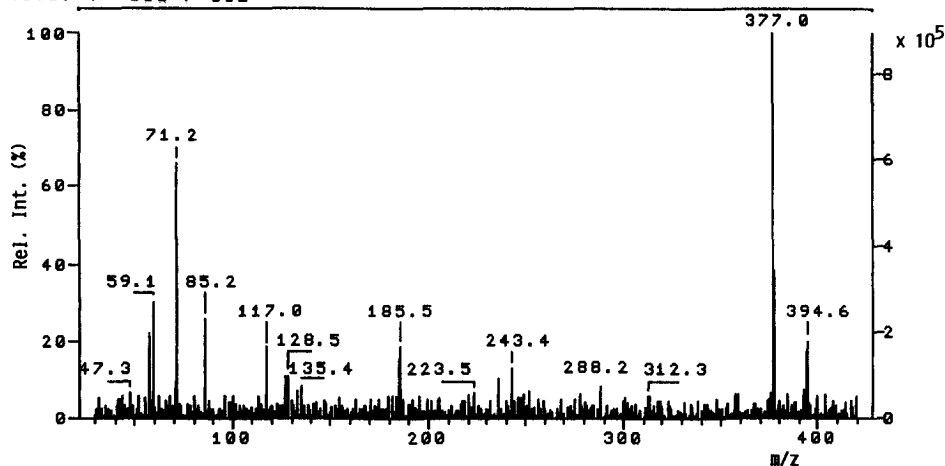
Fig. 5. LC-TSP-MS mass traces and total ion currents of (a) drinking water extract (C_{18}) and (b) polyethylene glycol standard. LC conditions as in Fig. 4a.

a

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SPEC: THD ver 5 on UIC 2 4          25-JAN-90 DERIVED SPECTRUM      9
Samp: 3 E I                          Start : 13:39:00      10
Conn: COLUMN / DAU 1.3
Mode: TSP +DAU 394.5 @ -30eV LMR SYNTH GAS UP LR
Oper: RS                               Inlet :
Base: 377.0                           Inten : 892985      Masses: 30 > 420
Norm: 377.0                           RIC : 14666139     # peaks: 487
Peak: 1000.00 muu
Data: + 653 > 662

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b

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LIBR: THD ver 5 on UIC 2 4          25-JAN-90 DERIVED SPECTRUM      9
Samp: 3 E I                          Start : 13:39:00      10
Conn: COLUMN / DAU 1.3
Mode: TSP +DAU 394.5 @ -30eV LMR SYNTH GAS UP LR
Oper: RS                               Inlet :
Base: 377.0                           Inten : 892985      Masses: 30 > 420
Srch: purity                          Samp mass: all      Libr ut: all
Libr: ABC                              Defect: 0 @ 1, 300 @ 1000
Data: + 653 > 662

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1	8	DEGRESSAL							5D	20
		Purity: 312	Fit: 844	Rfit: 343	mu: 394	bp: 377.0				
		CAS#:								
2	87	PLURAFAC							LF	120
		Purity: 189	Fit: 701	Rfit: 223	mu: 394	bp: 377.0				
		CAS#:								
3	110	TRITON							DF	20
		Purity: 121	Fit: 416	Rfit: 272	mu: 378	bp: 378.0				
		CAS#:								

Fig. 6. Results of library search in laboratory-made library. (a) Daughter-ion spectrum from water extract; (b) proposed list for identification.

(Fig. 6b) for the compound which had to be identified. The pollutant, an anthropogenic, non-ionic surfactant, was a mixture of nonanol polypropylene glycol ethers. This could additionally be proved using the standard for generating the daughter ions and comparing them with the daughter ions of the unknown compound.

In contrast to this time- and manpower-consuming method of separation on an analytical column, direct mixture analysis [18,19] of the same extracts was done using MS-MS function. In this way ions of m/z 394 in the extract of soil-filtered water and m/z 452 in drinking water were separated by mass filtration. Daughter-ion spectra of m/z 394 (Fig. 7a) and m/z 452 (Fig. 7b) generated by CID do not show a very clean

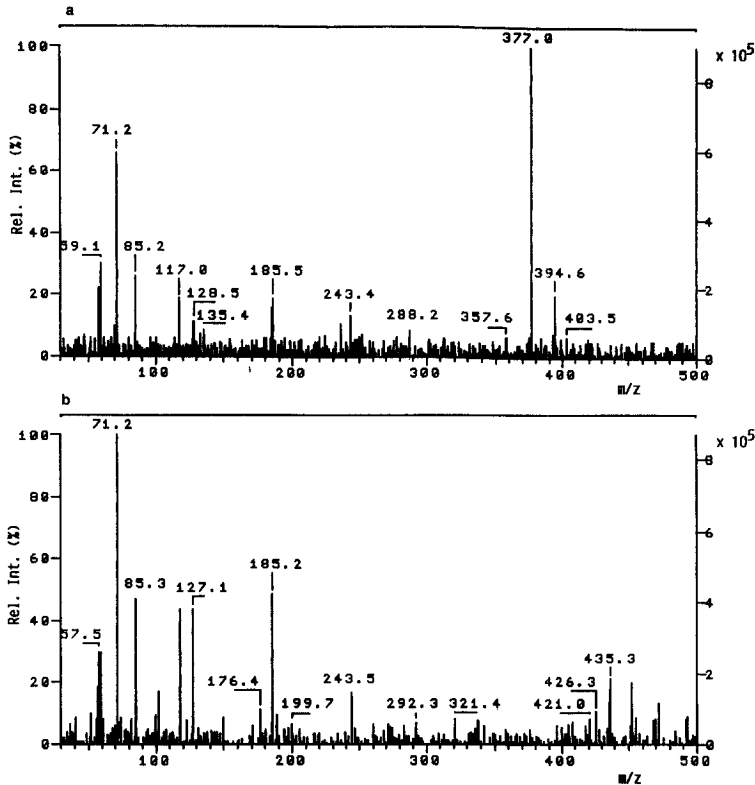
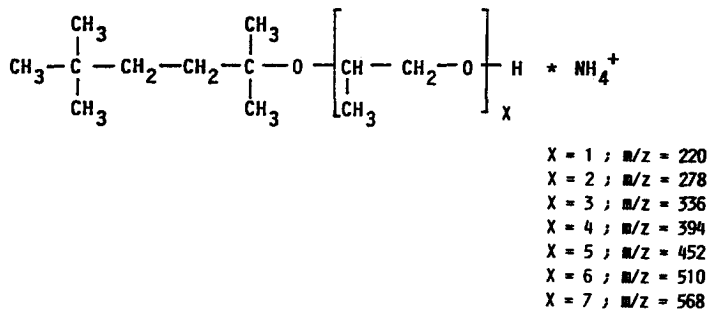



Fig. 7. TSP-MS-MS (daughter-ion spectrum bypassing the analytical column) of (a) m/z 394 (soil filtration extract) and (b) m/z 452 (drinking water extract).

background, although both spectra correspond well with the daughter-ion spectra of the standard in our laboratory-made library. The fragmentation behaviour under CID conditions and the safety data sheet of the producer confirmed the result of the interpretation of the daughter-ion spectrum, as shown in Fig. 8. The identification of this nonanol polypropylene glycol ether by mixture analysis was done in 10 min using the MS-MS function of the tandem mass spectrometer for daughter-ion generation and comparison of the recorded daughter-ion spectra with the library spectra.

In contrast, chromatographic separation before fixing the conditions for daughter-ion generation and the subsequent separation with simultaneous CID of the selected ions took 3.5 h.

FIA, bypassing the analytical column, allows the quantification of the identified mixture of nonanol polypropylene glycol ethers in drinking water. Peak areas under the mass traces of the cluster ions of m/z 394, 452, 510 and 568 from the drinking water extract were compared with the results for the same ions of a standard (Degresal) using a calibration graph. In this way we found 5 $\mu\text{g/l}$ of the above ether in the mixed eluates (diethyl ether-hexane, diethyl ether and methanol) after C_{18} enrichment. Calculations relating to the dissolved organic carbon (DOC) content of the drinking water showed that about 0.1% DOC is induced by this polypropylene glycol ether mixture.





**Collisionally Induced
Dissociation (CID)**

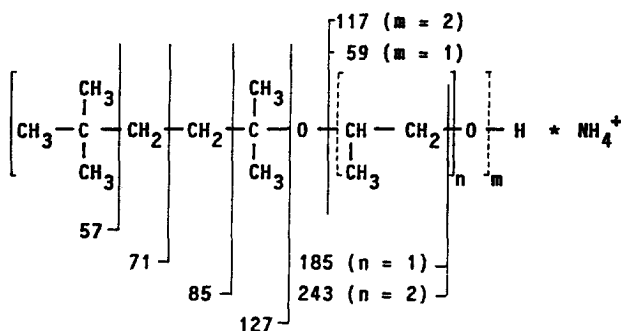


Fig. 8. Molecular ion (cluster ion) and fragmentation pattern of nonanol polypropylene glycol ether under CID conditions. Argon pressure, 1.3 mTorr.

CONCLUSIONS

LC separations of polar, hydrophilic water pollutants can be very difficult because of the complex matrix in these samples. Direct mixture analysis by LC-MS-MS for unknown polar, thermolabile compounds is an excellent and powerful method that is able to detect and identify many compounds from complex matrices without time-consuming derivatization and separation. Soft ionization of the compounds is essential for identification in order to obtain mainly molecular or cluster ions. After identification, quantification by mixture analysis is easy if standards for calibration are available.

Working in the MS-MS mode, daughter ions of the parent ions which have been selected by mass filtration give structural information because of their fragmentation behaviour under CID conditions. On the other hand, DCI is not suitable

for these problems because of extensive fragment generation. Soft ionization interfaces such as TSP can be used to suppress this fragmentation in the ionization process. Even slight fragmentation in this process can make chromatographic separation necessary or may lead to misinterpretation of the spectra.

The use of GC-MS for waste-, surface- and drinking water examinations is successful only with volatile compounds. In GC-MS analysis derivatization is essential for the chromatographic separation of the polar compounds, but this procedure discriminates non-reactive molecules.

Many compounds could still be detected in drinking water samples in spite of all previous efforts to eliminate them. So far only a few could be identified and recognized as anthropogenic substances. Their toxicological and ecotoxicological potential under chronic use must be checked.

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