ELSEVIER

Journal of Chromatography A, 733 (1996) 171–183

JOURNAL OF CHROMATOGRAPHY A

Occurrence and determination of organic pollutants in tap and surface waters of the Gdańsk district

M. Biziuk*, J. Namieśnik, J. Czerwiński, D. Gorlo, B. Makuch, W. Janicki, Ż. Polkowska, L. Wolska

Faculty of Chemistry, Technical University of Gdansk, 11/12 G. Narutowicza Street, 80-952 Gdańsk, Poland

Abstract

The results of the determination of different classes of organic pollutants (trihalomethanes, polycyclic aromatic hydrocarbons (PAHs), pesticides, volatile hydrocarbons and phenols) in ground water and drinking water sampled at different sites in the Gdańsk District are presented. Different methods were used to determine organic compounds in water: direct aqueous injection or sorption on solid sorbent (XAD-4) and extraction with pentane followed by a gas chromatography–electron capture detection (GC–ECD) for determination of volatile organohalogen compounds; purge and trap with a gas chromatography–flame ionization detection for determination of volatile hydrocarbons; sorption on solid sorbent XAD-4 or C_{18}, elution with organic solvent and GC–ECD for determination of pesticides; sorption on solid sorbent C_{18}, elution with organic solvent and a gas chromatography–mass spectrometry for determination of PAHs and sorption on solid sorbent C_{18}, elution with organic solvent and high performance liquid chromatography–ultraviolet determination of phenols. The proposed methods have been used successfully for the determination of organic compounds in samples of tap, swimming pool, river and sea waters.

The content of analysed organic compounds in the water delivered to the water supply system for Gdańsk from the surface water intake in Straszyn and from other selected intakes satisfies Polish, EC and WHO standards. The surface water bodies, i.e., rivers, sea and lakes in the Gdańsk District are not very polluted by anthropogenic compounds originating from municipal and industrial sewages and from agriculture.

Keywords: Water analysis; Environmental analysis; Pesticides; Phenols; Organohalogen compounds; Polynuclear aromatic hydrocarbons; Hydrocarbons, volatile; Trihalomethanes

1. Introduction

The importance of organic matter in aquatic systems has clearly been recognized during the past 30 years [1]. Organic matter often controls geochemical processes by acting as a proton acceptor and pH buffer, by affecting the transport and degradation of pollutants and by participating in mineral dissolution/precipitation reactions. Dissolved and particulate organic materials may also serve as substrates for microbially mediated reactions. The determination of organic contaminations in different types of water (sea water, ground water, drinking water etc.) is fundamental to the solution of environmental protection problems. At present, about 60 000 organic substances are being used by

* Corresponding author.

0021-9673/96/$15.00
SSDI 0021-9673(95)00905-1

mankind [2] and presumably some thousands of these substances are being transferred into the aquatic ecosystem. Therefore, it would appear to be hopeless to aim at a comprehensive analysis of all biogenic and anthropogenic organic pollutants present in water. First of all, because most of these compounds are present at microgram per litre (ppb) levels or less in water, an isolation and/or preconcentration step is necessary prior to the quantitation and identification of individual contaminants. Strategies based on identification of individual compounds within mixtures may provide less useful information when there are several sources of contaminated effluents containing identical compounds. Indeed, for pollution control purposes, the chemist is often required to "fingerprint" the identity of all the organic compounds in the mixture before determining the degree of contamination.

There are three routes for evaluating the degree of pollution of water samples by organic compounds:

(1) semiquantitative and comparative analysis based on "fingerprint" technique:
(2) quantitative analysis based on the determination and identification of each organic constituent (speciation analysis);
(3) quantitative analysis based on the determination of so-called "sum parameters", e.g., total organic carbon (TOC), total organic halogen (TOX).

But independently of how the problem of determination of organic pollutants in different types of water is approached, there is a need to choose a proper technique of isolation and/or preconcentration of trace organic compounds prior to their final determination. These techniques have been described in many review papers [3–5].

In this paper we present the methods and results of determination of different classes of organic pollutants [trihalomethanes (THMs), polycyclic aromatic hydrocarbons (PAHs), pesticides, volatile hydrocarbons and phenols] in samples of ground water and drinking water from different sampling sites in the Gdańsk District.

2. Experimental

2.1. Sampling

Our investigations concerned the determination of organic compounds in:

(1) nine underground water intakes for Gdańsk, (2) one surface water intake from Radunia river, (3) one drainage intake from Pręgowo, (4) five rivers in the Gdańsk District (Vistula, Radunia, Motława, Kacza, Rozwójka), (5) Lake Borowo, 20 km away from Gdańsk, and (6) sea water from Gdynia-Orłowo and Sopot.

THMs were also determined in tap water from different districts of Gdańsk and swimming-pool water from the Technical University of Gdańsk.

Samples of natural water have been collected from a depth of 1 m and stored in glass bottles. The bottles were filled to the brim, closed with a glass stopper and transported to the laboratory. Before the isolation and preconcentration step, samples were stored in the refrigerator at 4°C.

Samples of water for determination of volatile compounds were drawn into the glass flasks with the ground glass seals in such a way that no air was left in the flasks.

2.2. Determination of volatile organohalogen compounds

For the determination of volatile organohalogen compounds (trichloromethane, bromodichloromethane, dibromochloromethane, tribromomethane, tetrachloromethane, trichloroethane, tetrachloroethene, dichloromethane, 1,1,1-trichloroethane, 1,2-dichloroethane and 1,1-dichloroethene) direct aqueous injection (DAI) into a capillary column and electron capture detection (ECD) were used [6–12]. We have used a Carlo Erba (Italy) Vega 6180 gas chromatograph equipped with an electron capture detector (ECD 40/400). The chromatographic conditions were as follows: a 30 m × 0.32 mm I.D. fused-silica capillary column, coated with bonded 5 μm apolar DB-1 phase (J&W Scientific); 2 m × 0.32 mm I.D. fused silica precolumn; temperature program, 102°C isothermal-

ly; injection system, cold on column with secondary cooling; detector, ECD operated at 350°C with pure nitrogen (99.999%) as a make-up gas (30 ml min^{-1}); carrier gas, hydrogen at 0.4 m s^{-1}; injection volume, 2 μl. The detection limits of the DAI–ECD method, which were dependent on the species being determined, may be estimated at ca. 0.01 $\mu g\ l^{-1}$ on average and the standard deviation varied between 1.74% and 3.02%.

The results of the determination of volatile organohalogen compounds for water intakes are given in Table 1; for different districts of Gdańsk in Table 2; for surface water and swimming-pool water in Table 3.

2.3. Determination of volatile hydrocarbons

For the determination of volatile hydrocarbons (heptane, benzene, isooctane, nonane, decane, undecane, xylene, toluene) and chlorobenzene, purge and trap technique, sorption on solid sorbent (Tenax TA) followed by thermal desorption and gas chromatography–flame ionization detection (GC–FID) were applied [12–14]. The stream of purified argon was passed in the form of bubbles through a sample at a flow-rate of 30–40 ml min^{-1} for 10 min. Liberated volatile compounds were dried by the Nafion drier and trapped on the solid sorbent Tenax TA. Subsequently, after turning on the six-port switching valve, compounds were desorbed in a stream of helium (20 ml min^{-1}) at a temperature of 250°C for 2 min, and were then analysed by GC–FID. The volume of the purging device was 20 ml, the volume of the water sample was 10 ml, and the mass of the sorbent bed was 120 mg. The chromatographic conditions were as follows: a Hewlett-Packard 5830A gas chromatograph; a 10% Dexil 300 coated on Chromosorb WAW DMCS (80–100 mesh) packed column (2 m × 3 mm I.D.); FID detector working at 150°C. Samples were analysed at the following temperature conditions: 75°C (2 min) → 6°C min^{-1} → 130°C (1 min). The detection limit of this method was about 0.05 $\mu g\ l^{-1}$.

The results for volatile hydrocarbon determination for water intakes are given in Table 4, for surface water in Table 5.

2.4. Determination of selected organohalogen particles

Solid-phase extraction (SPE) was used and the extraction was performed by passing 1 l of the water sample through C_{18} extraction cartridges (J.T. Baker) at a rate of ca. 10 cm^3 per minute. Cartridges were conditioned prior to use (washed) with 2 × 5 cm^3 of methanol (high purity grade) and 2 × 2 cm^3 of "zero" water. The trapped compounds were extracted from the sorbent cartridge with a mixture (2 × 2.5 cm^3) of *n*-pentane and dichloromethane (1:1, v/v). The two extracts were combined and evaporated to a volume of 0.5 cm^3. The final extracts were analysed by a GC–ECD method. Because multiple injections of the extracts on a gas chromatograph are possible, this method enables complex examination of the extract using various techniques of final determination. The determination of volatile organohalogen compounds was conducted using the following analytical conditions: GC 6180 VEGA Carlo Erba-Fisons; extract injection, 1–2 μl (cold on-column); capillary column (30 m × 0.32 mm I.D.) coated with apolar stationary phase DB-5 (J&W); film thickness, 0.25 μm; temperature program: from 40°C to 120°C at 10°C min^{-1} then to 270°C at 5°C min^{-1}; precolumn, 2 m × 0.32 mm I.D. deactivated; ECD working in constant current mode; detector temperature, 350°C; carrier gas, hydrogen (0.4 m s^{-1}); make-up gas, nitrogen (99.999%) 50 cm^3 min^{-1}. The detection limit of this method was about 1 ng l^{-1}.

The results of selected organohalogen pesticide determination in drinking water intakes and surface waters are given in Tables 6 and 7.

2.5. Determination of PAHs

PAHs were determined from the same extracts as organochlorine pesticides by gas chromatography–mass spectrometry (GC–MS) technique

using a GC-8000 Fisons gas chromatograph equipped with 30 m × 0.32 mm I.D. fused-silica capillary column, coated with bonded 0.25 μm apolar DB-5 phase (J&W), and detector MSD-800 in the selected-ion monitoring mode. Temperature program: from 40°C to 120°C at 40°C min^{-1}, then to 280°C at 5°C min^{-1} and 10 min at 280°C. The detection limit of this method was about 0.5 ng l^{-1}. The results of selected PAH determination in drinking water intakes are given in Table 8.

2.6. Determination of volatile organohalogen compounds and selected organohalogen pesticides after sorption on XAD-4 sorbent layer

The compounds were concentrated from 0.5 l of water at flow-rate of 15 ml min^{-1} on sorbent bed composed of 0.8 g of XAD-4 [5,15]. The trapped compounds were extracted with 10 ml of reagent grade pentane at 0.5 ml min^{-1}. The extracts were analysed by GC–ECD technique. Because multiple injections of the extracts to a chromatograph are possible, this method enables determination of volatile organohalogen compounds and pesticides. Volatile organohalogen compounds were determined as follows: GC 6180 VEGA Carlo Erba-Fisons; extract injection, 1–2 μl (cold on-column); capillary column (30 m × 0.32 mm I.D.) coated with apolar stationary phase PS-255; film thickness, 5 μm; isothermal conditions, 85°C; precolumn, 2 m × 0.32 mm I.D. deactivated; ECD working in constant current mode; detector temperature, 350°C; carrier gas, hydrogen (0.4 m s^{-1}); make-up gas, nitrogen (99.999%) 50 cm^3 min^{-1}. The detection limit of this method was about 0.05 μg l^{-1}.

Table 9 contains the results for the determination of volatile organochlorine compounds in the Vistula river, Borowo lake, Straszyn lake (water intake from Gdańsk) and the swimming pool of the Technical University of Gdańsk.

From the same extracts pesticides were determined using different GC conditions, different apparatus in Poland and Belgium (Laboratory of Organic Chemistry, University of Ghent). GC conditions for the determination of pesticides were as follows: GC 6180 VEGA Carlo Erba-Fisons; extract injection, 1–2 μl (cold on-column); a capillary column (60 m × 0.32 mm I.D.) coated with an apolar stationary phase DB-5; film thickness, 0.25 μm; temperature program, 50°C → 15° min^{-1} → 170°C → 5° min^{-1} → 260°C (15 min); precolumn, 2 m × 0.32 mm I.D. deactivated; ECD. The detection limit of this method was about 1 ng l^{-1}.

The results of determinations are given in Table 10.

2.7. Determination of phenols

Phenols were determined in all water intakes after sorption on solid sorbent (C_{18} cartridge). Before sorption, each column was conditioned with 5 ml of methanol and then with 10 ml of 0.01 *M* HCl containing 0.5% isopropanol. Water samples (1 l) were adjusted to pH 2 with 0.01 *M* HCl and 0.5% of isopropanol and 40 g of NaCl were added. Phenols were eluted from the sorbent bed with 1 ml of methanol. A 20-μl sample of the eluate was analysed directly by HPLC technique. The column was packed with LiChrospher RP-18e; mobile phase, methanol–0.001 *M* H_3PO_4 (45:55, v/v). A Merck-Hitachi liquid chromatograph, equipped with UV–Vis detector Type L 4250, was used. Pentachlorophenol was detected at 300 nm and all other phenols were detected at 280 nm. The detection limit of this method was about 0.5 μg l^{-1}.

3. Results and discussion

Several different methods were used for determination of organic compounds in water:

(1) direct aqueous injection (Tables 1–3) or sorption on solid sorbents (XAD-4) and extraction with pentane (Table 9) with GC–ECD for determination of volatile organohalogen compounds;

(2) purge and trap with GC–FID for determination of volatile hydrocarbons (Tables 4 and 5);

(3) sorption on solid sorbent XAD-4 or C_{18},

Table 1
Determination of volatile organohalogen compounds ($\mu g\ l^{-1}$) in the water intakes for drinking water for Gdańsk

Water intake	Sampling date	$CHCl_3$	$CHBrCl_2$ + C_2HCl_3	$CHBr_2Cl$	$CHBr_3$	THM	CCl_4	C_2Cl_4	CH_2Cl_2
Straszyn	20.07.93	0.01	0.01	n.d.[a]	n.d.	0.4	n.d.	–	–
lake	7.06.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	30.11.94	0.3	n.d.	n.d.	n.d.	0.3	0.03	n.d.	n.d.
	2.03.95	0.05	0.03	0.01	n.d.	0.1	0.05	0.01	0.03
Straszyn	18.03.93	24.0	10.1	0.9	n.d.	35.0	–	–	–
(treated)	20.07.93	2.1	2.5	2.5	0.3	7.4	0.2	0.2	2.4
	7.06.94	2.5	3.4	2.6	n.d.	8.5	0.1	n.d.	n.d.
	30.11.94	2.4	3.3	n.d.	n.d.	5.7	n.d.	n.d.	n.d.
	2.03.95	8.4	5.7	2.4	n.d.	16.5	1.0	0.1	0.3
Pręgowo	22.12.93	2.3	2.2	1.3	n.d.	5.8	nd.	–	–
(treated)	19.04.94	0.4	3.0	0.6	n.d.	4.0	0.4	0.9	2.4
	7.06.94	0.6	0.5	n.d.	n.d.	1.1	n.d.	n.d.	n.d.
	2.03.95	3.1	2.1	0.8	n.d.	6.0	n.d.	0.1	0.2
Lipce	20.07.93	0.07	0.03	n.d.	n.d.	0.1	n.d.	0.84	0.76
(treated)	2.03.95	0.9	0.2	0.5	n.d.	1.6	n.d.	0.1	n.d.
Bitwy pod	8.07.93	0.1	5.4	n.d.	n.d.	5.5	n.d.	n.d.	n.d.
Płowcami	12.04.94	0.2	1.9	n.d.	n.d.	2.1	n.d.	–	–
(treated)	7.06.94	0.2	8.5	n.d.	n.d.	8.7	n.d.	n.d.	n.d.
Chełm	8.07.93	0.1	0.04	n.d.	n.d.	0.1	n.d.	–	–
(treated)	25.11.94	0.3	1.9	n.d.	n.d.	2.2	n.d.	n.d.	–
	1.03.95	9.6	5.9	2.1	n.d.	17.6	1.1	0.1	0.1
Dolina	8.07.93	n.d.	0.04	n.d.	n.d.	0.5	n.d.	n.d.	n.d.
Radości	12.04.94	0.02	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.
(treated)	6.06.94	0.06	0.01	n.d.	n.d.	0.07	n.d.	0.02	0.32
Zaspa	8.07.93	0.3	0.06	n.d.	n.d.	0.4	n.d.	n.d.	n.d.
(treated)	6.07.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	30.11.94	0.4	0.05	n.d.	n.d.	0.4	n.d.	n.d.	n.d.
	2.03.95	n.d.	0.3	0.2	n.d.	0.5	n.d.	0.1	0.2
Czarny	8.07.93	0.13	0.14	n.d.	n.d.	0.3	n.d.	–	–
Dwór	7.06.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
(treated)	30.11.94	0.1	0.05	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
	2.03.95	0.1	0.1	0.1	n.d.	0.3	n.d.	0.1	0.3
Grodza	20.07.93	0.1	0.02	n.d.	n.d.	0.1	n.d.	–	–
Kamienna	22.12.93	0.3	n.d.	n.d.	n.d.	0.3	n.d.	–	–
(treated)	30.11.94	0.2	n.d.	n.d.	n.d.	0.2	0.02	n.d.	n.d.
Jasień	20.07.93	0.9	n.d.	n.d.	n.d.	0.9	n.d.	–	–
Osowa	20.10.93	0.1	0.1	n.d.	n.d.	0.2	n.d.	–	–

1,1,1-Trichloroethane, 1,2-dichloroethane and 1,1-dichloroethene were not detected at any of the sampling sites.
[a] Not detected.

Table 2
Determination of volatile organohalogen compounds ($\mu g\ l^{-1}$) in the tap water from different districts of Gdańsk

District	Sampling date	$CHCl_3$	$CHBrCl_2$ + C_2HCl_3	$CHBr_2Cl$	$CHBr_3$	THM	CCl_4	CH_2Cl_2	C_2Cl_4
Wrzeszcz,	6.05.93	16.8	8.1	1.2	n.d.[a]	26.1	–	–	–
Traugutta str.	25.06.93	0.7	0.5	n.d.	n.d.	1.2	n.d.	–	–
	8.09.94	1.4	1.9	1.0	n.d.	4.3	n.d.	n.d.	n.d.
	01.03.95	8.3	4.7	1.6	n.d.	14.6	0.7	0.8	n.d.
Zaspa,	6.05.93	1.9	1.3	n.d.	n.d.	3.2	–	–	–
Pilotów str.	25.06.93	3.0	0.3	n.d.	n.d.	3.3	0.2	–	–
	8.09.94	3.2	4.1	2.6	n.d.	9.9	n.d.	n.d.	n.d.
	01.03.95	0.1	0.1	n.d.	n.d.	0.2	n.d.	0.8	0.04
Niedźwiednik,	6.05.93	24.8	8.9	0.8	n.d.	34.5	–	–	–
Góralska str.	25.06.93	6.2	2.6	0.8	n.d.	9.6	0.2	–	–
	8.09.94	5.5	6.5	2.5	n.d.	14.5	0.1	n.d.	n.d.
	01.03.95	11.4	5.7	1.7	n.d.	18.8	n.d.	n.d.	n.d.
Morena,	6.05.93	23.0	5.9	0.4	n.d.	29.3	–	–	–
Arctowskiego	25.06.93	1.6	1.3	0.8	n.d.	3.7	0.2	–	–
str.	8.09.94	5.7	8.0	6.1	2.0	19.8	n.d.	n.d.	n.d.
	01.03.95	11.1	6.5	2.3	n.d.	19.9	1.1	0.5	n.d.
Down Town,	25.06.93	3.6	1.7	0.4	n.d.	5.7	0.2	–	–
Toruńska	8.09.94	2.6	2.5	3.4	n.d.	8.5	n.d.	n.d.	n.d.
str.	01.03.95	0.2	0.2	0.1	n.d.	0.5	n.d.	0.3	n.d.
Orunia	25.06.93	1.3	0.6	n.d.	n.d.	1.9	n.d.	–	–
	10.12.93	0.56	0.86	n.d.	n.d.	1.42	n.d.	–	–
Stogi	25.06.93	0.1	n.d.	n.d.	n.d.	0.1	n.d.	–	–
	08.09.94	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.
	01.03.95	3.1	n.d.	n.d.	n.d.	3.1	n.d.	0.3	0.2
Chełm, Chału-	6.05.93	0.8	0.3	n.d.	n.d.	1.1	–	–	–
bińskiego str.	25.06.93	1.5	1.3	0.6	n.d.	3.4	0.1	–	–
	01.03.95	9.6	5.9	2.1	n.d.	17.6	1.1	0.5	0.1
Żabianka,	6.05.93	6.1	3.4	0.3	n.d.	9.8	–	–	–
Wejhera str.	25.06.93	0.5	12.7	n.d.	n.d.	13.2	n.d.	–	–
	08.09.94	2.5	16.7	0.3	n.d.	19.5	0.1	n.d.	n.d.
	20.03.95	0.9	4.0	n.d.	n.d.	4.9	n.d.	n.d.	0.3
Przymorze,	6.05.93	0.5	1.4	n.d.	n.d.	1.9	–	–	–
Kołobrzeska	25.06.93	2.1	0.1	n.d.	n.d.	2.2	n.d.	–	–
str.	10.03.95	2.3	1.8	0.6	n.d.	4.7	n.d.	0.1	0.1
Suchanino,	6.05.93	32.0	10.6	0.8	n.d.	43.0	–	–	–
Kurpińskiego	25.06.93	2.7	1.4	0.1	n.d.	4.2	0.2	–	–
str.	08.09.94	6.0	8.4	5.8	n.d.	20.2	0.2	n.d.	n.d.
	01.03.95	9.0	5.6	2.0	n.d.	16.6	0.7	0.4	0.1

1,1,1-Trichloroethane, 1,2-dichloroethane and 1,1-dichloroethene were not detected at any of the sampling sites.
[a] Not detected.

Table 3
Determination of volatile organohalogen compounds in natural waters ($\mu g\ l^{-1}$)

Sampling site	Sampling date	$CHCl_3$	$CHBrCl_2$ + C_2HCl_3	$CHBr_2Cl$	$CHBr_3$	C_2Cl_4	CCl_4
Sea water	07.03.94	2.2	1.44	0.55	0.02	n.d.[a]	0.11
Orłowo	14.03.94	0.37	0.12	0.19	0.11	n.d.	0.01
	24.11.94	0.6	0.49	0.22	n.d.	n.d.	0.02
Kacza river	07.03.94	1.28	0.86	0.36	0.01	n.d.	0.01
	14.03.94	0.91	0.15	0.26	0.21	n.d.	0.01
	21.11.94	0.74	n.d.	n.d.	n.d.	n.d.	0.04
Vistula river	07.03.94	1.44	0.08	0.14	0.04	0.03	0.03
	14.03.94	0.84	0.06	0.05	0.02	0.01	0.01
	10.06.94	0.88	0.02	n.d.	n.d.	n.d.	0.02
	21.11.94	0.17	0.03	n.d.	n.d.	0.01	n.d.
Motława river	07.03.94	0.26	0.02	n.d.	0.02	0.02	0.03
	14.03.94	0.11	0.04	n.d.	n.d.	0.01	0.01
	21.11.94	0.04	0.02	n.d.	n.d.	n.d.	0.01
Rozwójka river	07.03.94	0.65	0.06	n.d.	0.01	0.02	0.28
	14.03.94	0.37	0.11	n.d.	n.d.	0.01	0.01
	22.04.94	0.05	0.02	n.d.	n.d.	0.01	n.d.
	10.06.94	0.35	0.03	n.d.	n.d.	0.04	n.d.
	21.11.94	0.04	0.02	n.d.	n.d.	n.d.	0.04
Radunia river	07.03.94	0.23	0.03	n.d.	n.d.	0.02	0.02
	14.03.94	0.16	0.15	n.d.	n.d.	0.01	0.01
	10.06.94	0.04	0.12	n.d.	n.d.	n.d.	n.d.
	21.11.94	0.09	0.02	n.d.	n.d.	n.d.	n.d.

[a] Not detected.

elution with organic solvent and GC–ECD for determination of pesticides (Tables 6, 7 and 10);

(4) sorption on solid sorbent C_{18}, elution with organic solvent and GC–MS for determination of PAHs (Table 8).

(5) sorption on solid sorbent C_{18}, elution with organic solvent and HPLC–UV method for determination of phenols.

These compounds were determined in the water intakes (Tables 1, 4, 6, 8), tap water (Table 2), surface water (Tables 3, 5, 7, 9 and 10) and swimming pool water (Table 9).

The concentrations of organic compounds (volatile organohalogen compounds, PAHs, pesticides, volatile hydrocarbons and phenols) in the water delivered to the water supply system from the surface water intake in Straszyn and from other selected ground water intakes satisfy Polish, EC and WHO standards. The Polish and WHO standards were exceeded in the first half of 1993 for trichloromethane in the drinking water sampled on 6.05.1993 in the Suchanino district (Table 2: 32 $\mu g\ l^{-1}$ compared to the acceptable level of 30 $\mu g\ l^{-1}$) with simultaneous high content of trichloromethane in all districts supplied by the surface water intake of Straszyn (intake where the water is treated by chlorination). This limit was not exceeded during the following series of analysis: 26.06.93, 29.07.93, 6.08.93, 20.10.93, 21.12.93, 22.12.93. Since the end of June 1993 there has been a noticeable and significant drop of THM contents in the drinking waters (Table 2) in all the districts of Gdańsk supplied by the Straszyn intake (Morena, Suchanino, Niedźwiednik, Siedlce). This was probably caused by filtration of the water in the Straszyn

Table 4
Determination of volatile hydrocarbons ($\mu g\ l^{-1}$) in the water intakes for drinking water for Gdańsk

Water intake	Sampling date	Hexane	Benzene	Xylene	Isooctane	Toluene	Nonane	Decane	Undecane	Chlorobenzene
Straszyn (treated)	18.03.93	n.d.[a]	0.65	n.d.	n.d.	0.84	0.66	0.34	0.48	n.d.
	19.04.94	3.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	30.11.94	n.d.	0.67	0.35	n.d.	0.64	n.d.	n.d.	n.d.	n.d.
Straszyn lake	20.07.93	n.d.	n.d.	n.d.	n.d.	0.90	2.10	3.2	6.40	n.d.
	19.04.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	30.11.94	n.d.	0.83	0.1	n.d.	0.52	n.d.	n.d.	n.d.	n.d.
Pręgowo	22.12.93	n.d.	0.11	n.d.	n.d.	0.08	n.d.	n.d.	n.d.	n.d.
	19.04.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Lipce	20.07.93	n.d.	2.90	n.d.	n.d.	0.80	1.30	2.00	4.60	n.d.
	19.04.94	n.d.	8.20	n.d.	n.d.	0.13	n.d.	0.20	n.d.	n.d.
	07.06.94	n.d.	23.2	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	n.d.
Bitwy pod Płowcami	22.12.93	n.d.	n.d.	n.d.	n.d.	0.43	n.d.	n.d.	n.d.	n.d.
	20.07.93	n.d.	n.d.	n.d.	n.d.	0.92	1.58	3.45	1.26	n.d.
	07.09.94	n.d.	n.d.	n.d.	n.d.	3.32	9.4	n.d.	n.d.	n.d.
Czarny Dwór	20.07.93	n.d.	2.02	n.d.	3.74	5.40	5.5	n.d.	0.26	n.d.
	30.11.94	n.d.	0.7	0.6	n.d.	1	n.d.	n.d.	n.d.	n.d.
Zaspa	20.07.93	n.d.	n.d.	n.d.	n.d.	0.53	1.22	2.27	1.58	n.d.
	06.06.94	n.d.	0.80	n.d.	n.d.	0.10	n.d.	n.d.	n.d.	n.d.
	30.11.94	n.d.	0.81	1.4	n.d.	2.4	n.d.	n.d.	n.d.	n.d.
Grodza Kamienna	20.07.93	n.d.	3.10	n.d.	n.d.	1.40	2.60	3.50	2.80	n.d.
	06.06.94	n.d.	0.50	n.d.	n.d.	0.20	n.d.	n.d.	n.d.	n.d.
	30.11.94	n.d.	0.63	0.28	n.d.	0.51	n.d.	0.06	n.d.	n.d.

Heptane was not detected at any of the sampling sites.
[a] Not detected.

intake using a carbon filter prior to the chlorination, as well as by the elimination of the preliminary chlorination step of water treatment during which THMs were formed by the chlorination of humic compounds. On the GC–ECD chromatogram a peak consisting of both bromodichloromethane and trichloroethylene was found. Bromodichloromethane is a typical product of humic acid chlorination, very often present in addition to large amounts of trichloromethane while trichloroethylene is a frequently occurring pollutant in municipal sewage and industrial wastes. In our case it was necessary to identify the nature of this pollution, especially in the case of the deep water intake at Bitwa pod Płowcami Street (Table 1) and the district using water from this intake (Żabianka, Table 2). The analysis carried out with the mass spectrometer (GC 800 and MD 800 from Fisons) confirmed our assumption that the compound responsible is trichloroethylene, and hence the intake at Bitwa pod Płowcami Street is probably polluted by municipal sewage or industrial wastes. Trichloroethylene is also present in the tap water from other districts, but in no case does it exceed the acceptable level. The highest concentration of trichloroethylene found was 16.7 $\mu g\ l^{-1}$ in the water sampled in Żabianka district on 08.09.94 (Table 2). In the other deep water intakes and the reservoir of Radunia river in Straszyn no

Table 5
Determination of volatile hydrocarbons in natural waters ($\mu g\ l^{-1}$)

Sampling site	Sampling date	Hexane	Heptane	Benzene	Toluene	Nonane +Xylene	Decane	Undekane	Chlorobenzene	Isooctane
Vistula	07.03.94	n.d.[a]	n.d.	0.78	2.14	n.d.	n.d.	n.d.	0.89	n.d.
river in	14.03.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Kiezmark	22.04.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	10.06.94	n.d.	n.d.	n.d.	n.d.	0.35	n.d.	0.16	n.d.	0.23
	12.10.94	n.d.	n.d.	4.34	10.11	n.d.	6.54	0.8	3.25	n.d.
	21.11.94	n.d.	n.d.	0.96	0.92	3.27	n.d.	1.7	n.d.	n.d.
Radunia	07.03.94	n.d.	n.d.	1.08	1.23	n.d.	3.14	n.d.	0.38	n.d.
river in	14.03.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Straszyn	12.10.94	n.d.	n.d.	5.41	3.91	n.d.	n.d.	n.d.	n.d.	n.d.
	21.11.94	n.d.	n.d.	1.5	0.84	3.52	5.6	0.44	3	n.d.
Motława	07.03.94	n.d.	n.d.	0.83	1.22	n.d.	4.04	1.87	n.d.	n.d.
river in	14.03	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.
Gdańsk	22.04.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	10.06.94	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	0.18	n.d.	n.d.
	21.11.94	n.d.	n.d.	1.53	0.68	2.27	2.91	1.7	n.d.	n.d.
Kacza	07.03.94	n.d.	n.d.	0.18	0.93	n.d.	n.d.	n.d.	n.d.	2.05
river in	14.03.94	n.d.	n.d.	0.08	0.6	n.d.	n.d.	n.d.	n.d.	n.d.
Orłowo	21.11.94	n.d.	n.d.	0.64	0.3	0.9	0.97	0.4	n.d.	n.d.
Rozwójka	07.03.94	n.d.	n.d.	33.7	0.07	n.d.	48.8	n.d.	31.3	n.d.
river (near	14.03.94	n.d.	n.d.	22.3	n.d.	n.d.	22.5	6.7	n.d.	n.d.
Refinery)	22.04.94	n.d.	n.d.	25.9	15.2	34.4	9.9	2.9	n.d.	n.d.
	09.06.94	296	n.d.	165.0	n.d.	0.1	0.03	n.d.	0.03	n.d.
	12.01.94	n.d.	n.d.	4.37	2.7	n.d.	6.2	1.23	2.9	n.d.
Sea water	07.03.94	n.d.	n.d.	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	n.d.
(Orłowo)	14.03.94	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	n.d.	n.d.	n.d.
	22.04.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	21.11.94	n.d.	n.d.	0.07	0.16	0.58	0.67	0.3	n.d.	n.d.

[a] Not detected.

significant concentrations of THMs were noted. In 1994 the increase of THMs in the tap waters was noted and a high concentration of tetrachloromethane was detected, in addition to compounds (tetrachloroethylene; dichloroethane) which had never been observed before. This might be caused by use of the active carbon bed for too long or by inappropriate bed regeneration. In all intakes vestigial contents of crude oil type hydrocarbons were noted but their amounts have significantly dropped compared to the results of test series from the first nine months of 1993. This can probably be linked to seasons of the year and slower penetration of these compounds to the underground waters. Studies have shown that the methods for isolation and determination of the volatile organic compounds in drinking waters and their intakes are very useful in their applications. The studies have also shown rising levels of pollution caused by volatile hydrocarbons and trichloroethylene in the water from the underground water intakes. This may indicate anthropogenic pollution of the waters by municipal sewage and industrial wastes. The occurrence of different amounts of THMs in the tap water from the different dis-

Table 6
Determination of organochlorine pesticides in drinking water intakes from the Gdańsk District (ng l^{-1}) after sorption on C_{18} extraction cartridges

Sampling site	Sampling date	Lindane	*p,p'*-DDT	Methoxychlor
Bitwy pod	19.04.94	n.d.[a]	n.d.	n.d.
Płowcami	07.09.94	1	n.d.	n.d.
Dolina Radości	08.07.93	n.d.	n.d.	n.d.
	12.04.94	10	n.d.	n.d.
Zaspa	07.06.94	2	4	n.d.
	02.03.95	n.d.	n.d.	n.d.
Czarny Dwór	08.07.93	n.d.	n.d.	n.d.
	07.06.94	11	n.d.	n.d.
	02.03.95	n.d.	n.d.	n.d.
Pręgowo	21.12.93	76	n.d.	n.d.
	06.06.94	n.d.	n.d.	n.d.
Straszyn	22.12.93	77	34	n.d.
(reservoir)	07.06.94	19	n.d.	8
	02.03.95	33	19	n.d.
Straszyn	22.12.93	n.d.	n.d.	n.d.
(treated)	07.06.94	2	n.d.	n.d.
	02.03.95	n.d.	n.d.	n.d.

[a] Not detected.

tricts of Gdańsk indicates not only the mixing proportions of the treated water by the chlorination from Radunia river (Straszyn intake) with the underground waters which do not need chlorination, but also the correctness of the method, of carrying out the water treatment process of the Straszyn intake.

The concentrations of volatile hydrocarbons and volatile halogeno-organic compounds in surface waters (Tables 3 and 5) were very low. This shows that anthropogenic pollution of the Gdańsk District by volatile organic compounds is low. Relatively low concentrations of volatile organohalogen compounds were found in Radunia river and Motława river; a slightly higher concentration in the Rozwójka river flowing near the Oil Refinery of Gdańsk and the highest in the Vistula river, Kacza river and sea waters of Gdynia Orłowo near the outlet of Kacza River. The Vistula river is the biggest Polish river transporting pollutants from half of Poland. The Kacza river flows across the densely populated districts of Gdynia, that do not have a good sewage system, and also transports a lot of municipal and industrial sewages to the Baltic Sea. This is demonstrated clearly in our results. We have identified relatively high levels of trichloroethylene, a typical industrial pollutant in the Kacza river. This could explain why trichloroethylene was found also in sea water in Gdynia Orłowo and Sopot.

High levels of benzene, decane, chlorobenzene and hexane were found in the Rozwójka river flowing near the Refinery (Table 5). Other rivers and sea waters were not much polluted by these compounds. Although the series of analyses listed in Tables 3 and 5 were performed in the same week (7.03.94 till 14.03.94), we have noted very large differences in the levels of the analysed compounds. During this week in our district there was a lot of wind. It shows the big influence of weather conditions on the levels of

Table 7
Determination of organochlorine pesticides in surface water from the Gdańsk District (ng l^{-1}) after sorption on C_{18} extraction cartridges

Sampling site	Sampling date	Lindane (ng l^{-1})	*p,p'*-DDT (ng l^{-1})	Metoxychlor (ng l^{-1})
Vistula river in Kiezmark	07.03.94	43	n.d.[a]	29
	14.03.94	60	16	30
	09.07.94	24	13	n.d.
	12.10.94	26	15	28
	21.11.94	22	n.d.	23
Motława river in Gdańsk	09.07.94	18	8	4
	12.10.94	11	n.d.	11
	21.11.94	n.d.	n.d.	11
Radunia river in Straszyn	09.07.94	17	n.d.	4
	12.10.94	11	n.d.	13
	21.11.94	22	n.d.	12
Sea water Orłowo (quay)	07.03.94	31	n.d.	20
	14.03.94	35	12	19
	12.10.94	20	n.d.	22
	21.11.94	22	n.d.	26
Kacza river in Orłowo	07.03.94	12	n.d.	23
	14.03.94	n.d.	n.d.	24
	12.10.94	20	n.d.	22
	21.11.94	9	n.d.	17
Rozwójka river (near Refinery)	07.03.94	10	12	23
	14.03.94	14	8	24
	12.10.94	27	n.d.	12
	21.11.94	19	12	17

[a] Not detected.

analysed volatile compounds in the surface water.

The results do not show very high pollution levels in analysed waters by volatile compounds, with the exception of trichloroethylene in the Kacza river and in the sea water of Orłowo or of hydrocarbons in the Rozwójka river. However, all analysed compounds are very dangerous for humans and for nature and permanent control of water pollution by municipal and industrial sewages containing these compounds is necessary.

Owing to the simplicity and short time of preconcentration, minimum water adsorption and the absence of solvent background we have used the adsorption on solid sorbents for preconcentration of nonvolatile (Tables 6–8 and 10) and volatile (Table 9) organic compounds from water (Tables 6–10). The compounds adsorbed can be released from the sorbent layer by (i) thermal desorption for the determination of the group parameter volatile organic halogen — expressed as chlorine (VOX) which can serve as an indicator of anthropogenic pollution of water by organohalogen compounds [15–17] or by (ii) solvent extraction [6,15] for individual determination of compounds (Tables 6–10).

Pesticides were found in the surface water intake in Straszyn, the drainage water intake in Pręgowo and even in the underground water intakes (Table 6). We have also found rather high concentrations of lindane and metoxychlor in the Vistula river and also a relatively high

Table 8
Determination of PAHs (ng l^{-1}) in the water intakes for drinking water for Gdańsk

Compound	Straszyn					Zaspa		Czarny Dwór			Pręgowo	
	Lake			Treated								
Sampling date	07.06.94	07.09.94	30.11.94	07.09.94	30.11.94	19.04.94	30.11.94	07.06.94	07.09.94	30.11.94	19.04.94	07.09.94
Acenafthene	3.3	0.1	1.2	0.3	0.7	0.2	2.2	n.d.[a]	n.d.	4.5	1.1	3.8
Fluorene	1.8	0.1	1.3	0.3	0.7	0.1	1.3	n.d.	0.1	1.1	0.7	2.2
Acenafthylene	0.6	0.1	1.2	n.d.	n.d.	0.1	0.8	n.d.	n.d.	0.2	0.3	1.4
Phenanthrene	8.6	1.0	5.5	0.6	2.2	1.7	1.9	n.d.	2.3	4.1	3.7	2.6
Anthracene	0.6	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	n.d.	0.2
Fluoranthene	3.6	n.d.	1.1.	0.2	n.d.	1.2	n.d.	n.d.	3.6	n.d.	0.3	0.3
Pyrene	1.8	0.4	0.5	0.1	n.d.	1.2	n.d.	n.d.	9.2	n.d.	0.1	0.3
Chrysene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.3	n.d.	n.d.	n.d.
Benzo[*b*]-fluoranthene	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	n.d.
Naphtalene	4.3	0.1	4.5	1.0	3.6	0.1	28.9	9.4	n.d.	54.2	13.9	24.4

Benzo[a]pyrene, benzo[a]anthracene, benzo[*k*]fluoroanthene, dibenzo[*ah*]anthrazene, indeno[1,2,3-*cd*]pyrene and benzo[*g,h,i*]perylene were not detected at any of the sampling sites.
[a] Not detected.

concentration of this analyte in the sea water in Gdynia Orłowo (Tables 7 and 10). The analysis has been carried out after sorption in laboratory-made columns packed with Amberlite XAD-4 (Table 10) but also on Supelclean LC-C_{18} commercially available cartridges (Table 7). The results obtained for XAD and C_{18} are comparable.

During analyses in 1993 and 1994 we did not find phenol, *o*-nitrophenol, *p*-nitrophenol, 2,4-dinitrophenol, *o*-chlorophenol, *m*-chlorophenol, *p*-chlorophenol, 2,6-dichlorophenol, pentachloro-

Table 9
Determination of volatile organochlorine compounds in surface waters and in the swimming pool at Technical University of Gdańsk after sorption on XAD-4 solid sorbent ($\mu g\ l^{-1}$)

Sampling site	Sampling date	$CHCl_3$	C_2HCl_3	CCl_4	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
Vistula river	17.10.90	0.41	0.07	0.05	n.d.[a]	n.d.	n.d.
in Kiezmark	25.06.90	0.57	0.24	0.03	n.d.	n.d.	n.d.
Borowo lake	28.06.90	0.15	0.13	0.05	n.d.	n.d.	n.d.
	23.07.90	0.22	0.44	0.14	n.d.	n.d.	n.d.
	12.10.90	0.16	0.55	0.05	n.d.	n.d.	n.d.
Straszyn	25.06.90	0.36	1.38	0.08	n.d.	n.d.	n.d.
reservoir	25.07.90	0.62	1.16	0.38	n.d.	n.d.	n.d.
	19.10.90	0.15	0.5	0.02	n.d.	n.d.	n.d.
	07.12.90	0.35	1.31	0.17	n.d.	n.d.	n.d.
Swimming pool,	03.04.90	43.6	11.1	0.9	–	–	24.3
	14.03.91	93.4	27.4	7.6	14.6	0.3	0.1
Technical University	23.09.91	43.6	11.1	4.2	2.3	0.2	n.d.
Gdańsk	19.12.91	35.7	8.8	5.7	2.5	n.d.	0.1

[a] Not detected.

Table 10
Determination of organochlorine pesticides in surface water and drinking water intakes from the Gdańsk district (ng l^{-1}) after sorption on XAD-4 solid sorbent

Sampling site	Sampling date	Lindane	*p,p'*-DDT	Methoxychlor
Vistula river in	03.05.92	19	n.d.[a]	21
Kiezmark	17.09.92	11	n.d.	13
	07.03.94	48	<10	24
	14.03.94	56	<10	32
Sea water from	03.05.92	6	1	0.3
Orłowo (quay)	17.09.92	4	1	n.d.
	07.03.94	27	12	17
	14.03.94	33	<10	21
Sea water from	03.05.92	3	n.d.	<1
Sopot (Quay)	17.09.92	3	n.d.	n.d.
Kacza river in	03.05.92	1	n.d.	1
Orłowo	17.09.92	1	n.d.	1

[a] Not detected.

phenol and 2,4-dichlorophenol in any water intakes. The concentrations of PAHs were very low (Table 8).

The surface waters, i.e. rivers, sea and lakes, in the Gdańsk District are not very polluted by anthropogenic compounds originating from municipal and industrial sewages and from agriculture. However all these compounds are very dangerous for humans and for nature and permanent monitoring of the water quality is needed along with changes in legislation and the development of new technologies to restrict this kind of pollution.

The proposed methods have been used successfully for the determination of organic compounds in tap water, rivers and the sea.

References

[1] G. Aiken and J. Leenheer, Chemistry and Ecology, 8 (1993) 135.
[2] H. Huhnerfuss and R. Kallenborn, J. Chromatogr., 580 (1992) 191.
[3] B. Charmas, A. Gierak and R. Leboda, Chem. Anal., 39 (1994) 1.
[4] C.J. Koester and R.E. Clement, Crit. Rev. Anal. Chem., 24 (1993) 263.
[5] J. Namieśnik, T. Górecki, M. Biziuk and L. Torres, Anal. Chim. Acta, 237 (1990) 1.
[6] M. Biziuk, J. Czerwiński and E. Kozłowski, Int. J. Environ. Anal. Chem., 50 (1993) 109.
[7] T. Loung, C.J. Peters, R.J. Young and R. Perry, Environ. Technol. Letters, 1 (1980) 299.
[8] I.F.M.M. Temmerman and D.J.M. Quaghebeur, J. High Resolut. Chromatogr., 13 (1990) 379.
[9] M. Biziuk and Ż. Polkowska, Pollutants in Environment, 3 (1993) 12.
[10] K. Grob, J. Chromatogr., 299 (1984) 1.
[11] K. Grob and A. Habich, J. High Resolut. Chromatogr. Chromatogr. Commun., 6 (1983) 11.
[12] M. Biziuk, Ż. Polkowska, D. Gorlo, W. Janicki and J. Namieśnik, Chem. Anal., 40 (1995) 299.
[13] W. Janicki, B. Zygmunt, L. Wolska, W. Chrzanowski and W. Wardencki, Chem. Anal., 37 (1992) 599.
[14] W. Janicki, L. Wolska, W. Wardencki and J. Namieśnik, J. Chromatogr. A, 654 (1993) 279.
[15] E. Kozłowski, M. Biziuk, T. Górecki and E. Sieńkowska-Zyskowska, Arch. Ochr. Środ., 1 (1992) 97.
[16] M. Biziuk and Ż. Polkowska, Analyst, 115 (1990) 393.
[17] M. Biziuk, E. Kozłowski and A. Błasiak, Int. J. Environ. Anal. Chem., 44 (1991) 147.