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Non-Regulated Organic Compounds (NROC's) in the Odra River Water Samples

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Abstract

Within the framework of the research described here, an attempt was made to identify volatile and semi-volatile Non-Regulated Organic Compounds present in samples of riverine water. Twenty-five samples, collected from the Odra River during the eighth sample collection in October 2000 within the framework of the International Odra Project, have been analyzed using the PT-TD-GC-MS technique.

A computerized analysis with the use of a mass spectrometer pointed to the presence of organic compounds of natural and anthropogenic origin. The concentrations of chloroorganic compounds, i.e. saturated and unsaturated aliphatic aromatic hydrocarbons and chlorinated bis-isopropyl ether, in samples of water collected near Brzeg Dolny amounted to about 1 ppb. A slightly narrower spectrum of chloroorganic compounds occurring at lower concentrations was identified in samples of water collected in Głogów. The most likely source of these compounds was the "Rokita" Chemical Plant.

Keywords: Odra River, Water Samples, Non-Regulated Organic Compounds, NROC's, Screening Speciation

Introduction

A wide spectrum of different pollutants originating from natural and anthropogenic emission sources occurs in the aquatic environment. The number of pollutants as well as the loads delivered into the aquatic environment due to human activities are increasing.

Novel organic compounds appear in the environment as a result of:

- reactions of synthesis conducted in many laboratories,
- use of new types of compounds on the industrial scale.

The classification of organic compounds which can contribute to the pollution of the natural environment is presented in Table 1.

According to estimates [1], each year over 1000 new compounds appear in the environment due to the ever intensifying industrial activities of humans, and that, undoubtedly, lead to increased toxicological and ecotoxicological risks. The dimensions of these risks are difficult to evaluate because legal regulations describing respective admissible concentrations are still lacking. Such a situation occurs world-wide because research aimed at establishing numeric values for the respective standards is labor- and time-consuming, and the process of legislation formulation tends to protract.

In response to the increase in chemical pollution levels of the environment, an intensive development of analytical sciences has taken place [2, 3], which allows us to detect and identify novel – unknown until now – types of compounds in environmental samples.

This may give a strong push to speed up ecotoxicological research as well as legislative works. In literature, an increasing amount of information on the subject of such analytical research can be found. This information can be classified as analytical screening speciation [4, 5, 6].

The scientists from the Organic Chemistry Institute in Hamburg identified, with the use of SCAN GC-MS, new families of compounds in water samples collected

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Table 1. Classification of organic compounds that may contribute to environmental pollution.

No.	Parameter on which classification was based	Examples
1.	Compound structure	- hydrocarbons - organohalogens - carbonylic acids and their esters - other oxygen-containing compounds, i.e. ketones, aldehydes, ethers & alcoholes - organometalic compounds
2.	Volatility	- Very Volatile Organic Compounds (VVOC) - Volatile Organic Compounds (VOC) - Semi-Volatile Organic Compounds (SVOC) - Non-volatile organic compounds (Particulate Organic Matter, POM)
3.	Polarity	- Polar compounds - Non-polar compounds
4.	Emission sources	- Biogenic compounds - Compounds of anthropogenic origin
5.	Compartment	- Compounds dissolved in water - Compounds bound to particulate matter
6.	Identification method	- Parameters based on pooled component values (TOC, DOC, POC etc.) - Individual speciation analysis
7.	Availability of standards in reference to the occurrence of specific compounds in a researched environmental compartment	- Regulated Organic Compounds (ROC's) - Non-Regulated Organic Compounds (NROC's)

from the Elbe River. The possible impact of these substances on live organisms and the surrounding environment remains unknown. Moreover, researchers have demonstrated the presence of 250 organic compounds, among which 130 originated from industrial plants and reached the Elbe and its tributaries as drainage waters and leaks. Samples were characterized by the particularly pronounced concentrations of bis-propyl ethers [7]. One year earlier, other German scientists detected in the same river only 145 organic compounds; however, at that time, halogenated ethers were present at high concentrations. The obtained results in reference to amounts of compounds determined were based on German quality standards for surface waters. From among 28 standardized organic pollutants, concentrations of only 4 compounds exceeded the admissible limits [8, 9]. Although it has to be stressed that halogenated ethers were not included in the quality standards.

Similar studies were conducted by a scientific team from the Department of Analytical Chemistry, Gdańsk University of Technology, within the framework of the International Odra Project (IOP) [10]. This international project was financed by the German Ministry of Research, Technology, Education and Science, and by the Foundation for Polish-German Cooperation. Research activities within the project started in May 1997. Within the IOP there were 12 sub-projects conducted by 5 German and 7 Polish teams. Besides the input for European integration and, particularly, development of trilateral Polish-German-Czech cooperation [11], important goals of conducted activities were:

- investigations on transport of pollutants in specific compartments of the aquatic environment, i.e. water, suspended particulate matter and sediments
- identification and characterization of sources, modes of transport and sedimentation of pollutants
- elucidation of transport mechanisms and changes in different types of pollutants
- determinations of particular pollutants and evaluation of their impact on the ecosystem in the Odra basin and Odra mouth
- investigations on accumulation and remobilization of pollutants in samples of sediments transported by flood waters
- establishment of qualitative criteria for different areas around the Odra, i.e. populated and industrial areas, drinking water abstraction areas, and natural and landscape parks
- development and assessment of needed analytical techniques [http://odra.ifd.uni.wroc.pl]

The first undertaking within the project's framework was the international research study conducted immediately after the 1997 flood. The aim of the study was to investigate the impact that the flood has had on water quality in the Odra, and to determine the amounts of noxious substances accumulated in the flooded areas. Particular attention was given to the investigations of flooded areas in the industrial regions, and in the vicinity of dump sites and wastewater treatment plants. Since the occurrence of flood, the Odra basin has been monitored twice a year by collecting samples from over 100 sampling sites.

Also, within the IOP a series of international conferences on the subject of the Odra has been started. Until then, data on the pollution level in the Odra basin were incomplete and incoherent. Therefore, systematic investigations, with the use of appropriate analytical methods that had been validated, were conducted within the IOP.

In the period 1997-2000, samples of water, benthic sediments and suspended particulate matter were collected during eight sampling collections. In the collected and

Table 2. Conditions for analyte determinations using the PT-TD-GC-MS technique.

Elements of measuring system	System's working condition
Gas chromatograph	GC, 8000, FISONS
Column	RTX – 624 Restek Corporation, 60m × 0,32 mm ID fused silica: D_f – 1,8 μm: 6% cyanopropylphenyl, 94% dimethylpolyoxosilane
Detector	Mass spectrometer (SCAN: 10-450)
Injector	Thermal desorber connected to sorption microtrap; Purging gas: argon at 20 m^3min^{-1}; Purge time: 10 min
Microtrap	Sorbent: 80 mg Tenax TA/30 mg Carbosieve III; Desorption temperature: 250°C for 60 s
Carrier gas	Helium: 100 kPa, ~ 2 cm^3min^{-1}
Temperature settings	35°C for 2 min, 5°C min^{-1} to 100°C, 10°C min^{-1} to 250°C, 250°C for 10 min.

properly prepared samples a wide spectrum of organic as well as inorganic compounds were determined.

Studies on the subject of a wide spectrum of Regulated Organic Compounds, realized by the scientific team from the Chemical Faculty, Gdańsk University of Technology, have been described in a number of publications [12, 13, 14, 15].

This paper presents the outcome of attempts made to detect non-regulated organic compounds in water samples.

Materials and Methods

Collection of Water Samples for Analysis

Samples of water from the Odra were collected in October 2000 during the eighth sample collection organized within the IOP. Twenty-five samples from the upper course of the Odra, namely, from Chałupki, Krapkowice, Brzeg Dolny, Głogów and Połęcko, were collected for further analysis (Fig. 1).

Samples were taken directly from the river in the following general locations: near the right (R) and left (L) river bank, and mid-stream (M). Also, samples of water from bore holes at depths of 1, 2, 3 and 4 meters and at the approximate distance of 10 meters from the river bank, were collected.

Samples were stored in the refrigerator at 4°C until further processing. The analysis took place 4 to 10 days after sample collection.

Equipment

- Purge and Trap (PT) system for concurrent washing out and sorption of analytes on the sorbent.

In this study, a system constructed in the Department of Analytical Chemistry, Gdańsk University of Technology [16] for isolation and enrichment of analytes in water samples was used. The system can be connected to the gas chromatograph in an "on-line" mode.

- Gas chromatograph, GC. The working conditions are given in Table 2.

Results and Discussion

25 samples of water collected from the upper Odra river basin were analyzed (Fig. 1). On average, each chromatogram displayed 30 peaks of different sample components. Compounds were identified by comparing their spectra with those of standards in the National Institute of Standards and Technology, NIST, library. Overall, 77 volatile organic compounds were identified at concentrations in the range of ppb and ppt, on the basis of all chromatograms.

In Table 3, the analytical results from samples collected sequentially at sampling sites are presented. Names of the organic compounds identified in specific samples, and the respective retention times are given. The results of quantitative determinations, i.e. a peak area of the identified compound expressed as a percentage of the internal standard peak area, are shown in columns (the amount of 4-bromo-1-fluorobenzene as an internal standard was 133 ng per 10ml of water sample).

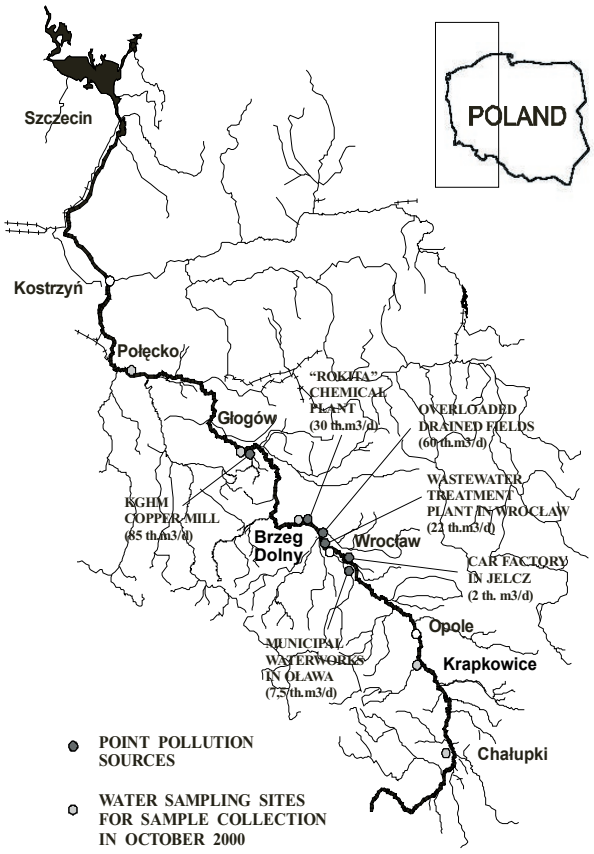

Fig. 1. Location of water sampling sites and chosen point pollution sources.

Table 3. Results of PT-TD-GC-MS screening analysis of water samples.
Ch - Chałupki, K - Krapkowice, B - Brzeg Dolny, G - Głogów, P - Połęcko, R - right river bank, M - mid-stream, * - compound identified in samples which are not listed in this table, Degree of compatibility - 1, 2.

Lp.	Retention time	Detected compounds		Site of sample handling						
		Chloroorganic compounds	Other organic compounds	Ch bore hole	K R	B R	B M	G R	G bore hole (2m)	P bore hole (1m)
1	8.48		hexane *							
2	10.30	1,1 - dichloroethene					2			
3	11.73		benzene	**17**	(4,5)		4	8	5	5
4	12.00	1,2 - dichloroethane				**18**	**31**			
5	12.17		heptane *							
6	13.19	trichloroethylene				8	8	5		
7	14.00	1,2 - dichloropropane				**24**	**25**	**11**		
8	15.78		dimethyldisulfide						2	
9	16.28		toluene					*1*	6	**13**
10	17.30	tetrachloroethylene				3	3	2		
11	18.10		acetic acid, butyl ester					*(1)*		
12	18.20		hexanal *							
13	19.46	chlorobenzene				3	2		*1*	
14	19.56		o - xylene *							
15	19.60		p - xylene						3	6
16	19.83		ethylbenzene			*(1)*	*1*	*1*	7	**17**
17	19.69		nonane							*1*
18	20.77		styrene					*1*	**23**	**38**
19	21.25		heptanal							2
20	22.23		propylbenzene				*(1)*		*1*	2
21	22.40		decane						4	5
22	22.58		1,2,3 - trimethylbenzene						*1*	2
23	22.99		1-ethyl-4-methylbenzene						*1*	3
24	23.06		alpha - methylstyrene						*1*	2
25	23.32		1,3,5 - trimethylbenzene				*1*	*1*	5	**10**
26	23.53		5-hepten-1-one, 6-methyl-	9	3	5	9	*1*		4
27	23.58		benzaldehyde					3	2	
28	23.81		octanal			2	2	2	*1*	6
29	23.97	1,3 - dichlorobenzene				2	2	*1*		
30	24.14	1,4 - dichlorobenzene				4	3	*1*		
31	24.19		1,2,4 - trimethylbenzene						2	
32	24.45		2-ethyl-1-hexanol				*(1)*	*(1)*	*1*	
33	24.52		benzonitrile				*(1)*	2	3	

Table 3 continues on next page...

34	24.54		beta-methylstyrene							4
35	24.63		1,4 - diethylbenzene						*1*	2
36	24.69		undecane				2	(2)	*1*	2
37	24.85	1,2 - dichlorobenzene				5	2	*1*		
38	25.01		1-methyl-4-propylbenzene							*1*
39	25.13		phosphonic acid, (p-hydroxyphenyl)-		2	3	(3)	4		2
40	25.15		1-ethyl-3,5-dimethylbenzene						(5)	
41	25.26		2,5-dimethyl-1-hepten-4-ol							3
42	25.36		2-ethyl-1,3-dimethylbenzene						2	2
43	25.41	bis(2-chloroisopropyl) ether				7	6	6		
44	25.84		3,7-dimethyl-1,6-octadien-3-ol *							
45	25.97		nonanal	8	2	5	3	5	6	**30**
46	26.06		acetophenone		*1*	*(1)*		3		
47	26.10		1,2,3,4 - tetramethylbenzene						2	*1*
48	26.18		benzoic acid, methyl ester *							
49	26.67		2,7 - dimethyloctane					*(1)*		
50	27.01		1-ethenyl-4-ethylbenzene						*1*	
51	27.22		N - ethylbenzenamine		3		*1*		*1*	
52	27.87		decanal	**33**	9	**18**	**15**	**12**	**11**	**55**
53	28.25		naphthalene						2	
54	28.57		benzoic acid		**10**	**15**	2		6	
55	29.30		3,6 - dimethylundecane *							
56	29.60		undecanal	(6)		5	4	3	2	8
57	29.65		bornyl acetate *							
58	30.07		branched alkane C13	6	**13**	**14**	6	5	5	4
59	30.25		branched alkane C13-15						*1*	
60	31.40		dodecanal	5	(3)	4	2	3	2	7
61	31.67		2-ethenylnaphthalene						2	3
62	31.84		branched alkane C15	5	7	**11**	4	4	6	4
63	31.93		diphenyl ether						6	4
64	32.45		6,10-dimethyl-5,9-undecadien-2-one	**42**	8	9	**27**	7	3	**10**
65	32.57		alpha, farnesene							2
66	33.05		dibutyl phthalate *							
67	33.40		1,2-dihydro -2,2,4-trimethylquinoline		(3)	6	**12**	5	9	3
68	33.58		butylated hydroxytoluene	13	12	7	**36**	**10**	**13**	**11**
69	33.74		alpha, isomethyl ionone *							

Table 3 continues on next page...

70	33.83		hexadecane		2	6	3	(3)	(3)	
71	34.79		lilial *							
72	35.80		propanoic acid, 2-methyl-,1-(1,1-dimethylethyl)-2-methyl-1,3-propanodiyl ester	**(13)**	3	4			2	
73	36.21		heptadecane			2				
74	37.03		diethyl phthalate *							
75	37.40		1 - octadecene *							
76	38.61		methyl dihydrojasmonate *							
77	41.37		isopropyl myristate						4	

The certainty of compound identification was coded as follows: a high degree of compatibility between the standard and compound spectra was not marked, while lower compatibility was marked in parentheses. Some compounds present in the samples were not identified; however, a general class or family of compounds to which they might belong has been assigned.

The font type symbolizes the amount of a given compound in a specific sample as evaluated by the percentage of the standard peak area. A three-stage scale was used, as follows:

italic: ≤ 1; normal: 1-10; **bold:** $\geq$ **10**.

In all analyzed water samples a large number of organic compounds of probably natural origin (saturated and unsaturated alcohols, aldehydes and ketones) were found. They were decomposition products originating from dead aquatic flora and fauna.

However, some of these compounds can be synthesized and used by the industry, for example:

- decanal – used for enhancing the taste and smell of food
- dodecanal – a smell enhancer used in food.

A significant group among the identified compounds is formed by the substances of anthropogenic origin, such as:

- saturated and unsaturated chlorinated aliphatic hydrocarbons,
- chlorinated aromatic hydrocarbons (dichlorobenzenes),
- chlorinated bis(isopropyl) ether.

Because of their toxicity to humans and the environment, these compounds are presented in a separate column.

The widest variety and, at the same time, the highest concentrations of chloroorganic compounds were observed in water samples collected near Brzeg Dolny, namely 1,1-dichloroethene (0.25 ppb), 1,2-dichloroethane (2,7 ppb), trichloroethene (1 ppb), 1,2-dichloropropane (3 pbb), tetrachloroethene (0.4 ppb), chlorobenzene (0.4 ppb), (1,3)-dichlorobenzene (0.25 ppb), (1,4)-dichlorobenzene (0.4 ppb), (1,2)-dichlorobenzene (0.4 ppb), and bis(2-chloroisopropyl) ether (0.8 ppb).

The highest concentrations of the aforementioned compounds were determined in water samples collected directly from the river near its right bank (marked P). The most probable source of the emitted chloroorganics was “Rokita” Chemical Plant in Brzeg Dolny. The plant is on a list of 80 top environmental polluters. According to the report by WIOŚ Wrocław (Voivodship Inspectorate for Environmental Protection), this plant is a source of free chlorine, and aliphatic and aromatic hydrocarbons. Phenols and chlorophenols were determined in wastewater released into the river by “Rokita,” while 27% of wastes produced in the plant have been classified as very hazardous. The pollution with chloroorganic compounds of only one river bank can be connected to the location of the plant on the right bank.

A similar variety of chloroorganics, although at lower concentrations, was determined in water samples collected in Głogów, located 120 km away from Brzeg Dolny. The most likely emission source of these compounds, as based on spectral analysis, was also “Rokita;” however, additional local sources have not been ruled out. The wastewater treatment plant in Chobień, “Cedynia” Copper Mill in Orsk, “Rudna” Mining Company in Polkowice, Waste Processing Plant in Głogów, MZWiK municipal waterworks in Głogów and Copper Mill in Głogów are all located in the Głogów area. To prove that any of the above-mentioned plants also emit chloroorganics is difficult and requires further research.

Among the identified compounds, a particular attention should be turned to bis(2-chloroisopropyl) ether (CAS:39638-32-9). This group of compounds was detected for the first time in the early ‘90s in samples of water from the Łaba River [17]. A possible impact of bis(propyl) ethers on live organisms and the environment has not yet been sufficiently researched. In the Odra, this compound was identified in samples collected directly from the river at sites in Brzeg Dolny and Głogów. Based on the internal standard peak area, the mean concentration of bis(2-chloroisopropyl) ether in the analyzed samples was determined to be 0.8 ppb.

In water samples from bore holes collected close to the Odra at sites in Głogów and Połęcko, high concentrations of toluene (0.5-1.7 ppb), ethylobenzene (0.5-2.3 ppb), styrene (0.7-5 ppb) and trimethylbenzenes (0.25-1.3 ppb) were determined. The concentrations were much higher than those in samples of water collected directly from the river. Toluene and ethylobenzene, both belonging to the BTEX group, have been listed by the U.S. Environmental Protection Agency (EPA) as hazardous substances. It is difficult to point out the emission source of the above--mentioned mono-aromatic compounds. A coring device has been ruled out as a possible source because the compounds were identified only in samples collected at very specific locations.

Conclusions

The following conclusions can be drawn based on research results:

1. A computerized spectral analysis, obtained with the use of mass spectrometer as a detector, has demonstrated that many organic compounds of natural and anthropogenic origin were present in samples of riverine water collected from the upper course of the Odra during the eighth sampling collection within the IOP.
2. Among the identified compounds, saturated and unsaturated aliphatic hydrocarbons, aromatic hydrocarbons and chlorinated bis(isopropyl) ether constituted a significant group of substances in reference to toxic impact on humans and the environment.
3. The widest spectrum and, at the same time, the highest concentrations (0.25-3 ppb) of chloroorganic compounds were determined in water samples collected near Brzeg Dolny. The most likely emission source of these compounds was "Rokita" Chemical Plant.
4. A slightly narrower spectrum of chloroorganics, occurring at lower concentrations (0.1-1.5 ppb), was found in Głogów. The identification of emission sources of these compounds was difficult, however, based on the results of spectral analysis, it can be assumed that they also originated from "Rokita" Chemical Plant.
5. Bis(2-chloroisopropyl) ether was identified in water samples collected directly from the river near Brzeg Dolny and Głogów. The possible impact of this chemical on live organisms and the environment has not been yet elucidated.
6. High concentrations (0.25-5 ppb) of mono-aromatic hydrocarbons were determined in water samples from bore holes collected in the Głogów and Połęcko areas. The source of these compounds remains unknown.

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References

1. DOJLIDO J.R. Chemia wód powierzchniowych. Wydawnictwo Ekonomia i Środowisko: Białystok, pp 195, **1995**.
2. NAMIEŚNIK J. Trends in environmental analytics and monitoring. Crit. Rev. Anal. Chem. **30**, 221, **2000**.
3. NAMIEŚNIK J. Modern trends in monitoring and analysis of environmental pollutants. Pol. J. Environ. Stud. **10**, 127, **2001**.
4. KOT A., NAMIEŚNIK J. The role of speciation in analytical chemistry. Trend Anal. Chem. **19**, 69, **2000**.
5. WASIK A., ŁOBIŃSKI R., NAMIEŚNIK J. An automated speciation analyser of organometallic compound content. Instrum. Sci. Technol. **29**, 393, **2001**.
6. MARCZAK M., WOLSKA L., NAMIEŚNIK J. Wykorzystanie przesiewowej analityki specjacyjnej w badaniach środowiska. Chem. Inż. Ekol. **9**, 1097, **2002**.
7. FRANKE S., HILDEBRANDT S., SCHWARZBAUER J., LINK M., FRANCKE W. Organic compounds as contaminants of the Elbe River and ist tributaries. Fresenius J. Anal. Chem. **353**, 39, **1995**.
8. GÖTZ R., BAUER O.H., FRIESEL P., ROCH K. Organic trace compounds in the water of the River Elbe near Hamburg. Part 1. Chemosphere. **36**, 2085, **1998**.
9. GÖTZ R., BAUER O.H., FRIESEL P., ROCH K. Organic trace compounds in the water of the River Elbe near Hamburg. Part 2. Chemosphere. **36**, 2103, **1998**.
10. WOLSKA L., WARDENCKI W., WIERGOWSKI M., ZYGMUNT B., ZABIEGAŁA B., KONIECZKA P., POPRAWSKI L., BIERNAT JAN F., NAMIEŚNIK J. Evaluation of pollution degree of the Odra River basin with organic compounds after the 1997 summer flood - general comments. Acta Hydrochim. Hydrobiol. **27**, 343, **1999**.
11. HELIOS-RYBICKA E., KNÖCHEL A., MEYER A.K., PROTASOWICKI M., POPRAWSKI L., WOLSKA L., NAMIEŚNIK J. Distribution of pollutants in the Odra River system. Part 1. General description of the International Odra Project. Pol. J. Environ. Stud. **11**, 649, **2002**.
12. WARDENCKI W, STANISZEWSKA M, WOLSKA L, JANICKI W, NAMIEŚNIK J. Evaluation of pollution degree of the Odra River basin with organic compounds after the 1997 summer flood. Part 2. Determination of volatile and semivolatile compounds in post-flood sediments of the Odra basin. Chem. Anal. **45**, 291, **2000**.
13. GALER K., ZYGMUNT B., K.L., NAMIEŚNIK J. Evaluation of pollution degree of the Odra River basin with organic compounds after the 1997 summer flood. Part 3. Determination of pollution of post-flood sediments with polychlorionated biphenyls and polycyclicaromatioc hydrocarbons. Chem. Anal. **45**, 297, **2000**.
14. WOLSKA L., STANISZEWSKA M., JASTRZĘBSKA A., KONIECZKA P., NAMIEŚNIK J. Determination of chlorobenzenes in water and sediment samples collected from Odra River. Chem. Inż. Ekol. **8**, 959, **2001**.
15. ZYGMUNT B., WOLSKA L., NAMIEŚNIK J. Sources and concentration of organic pollutants in the Odra River. Chem. Inż. Ekol. **8**, 973, **2001**.
16. JANICKI W., WOLSKA L., WARDENCKI W., NAMIEŚNIK J. A simple device for permeation removal of water vapour from purge gases in the determination of volatile organic compounds in aqueous samples. J. Chromatogr. **654**, 279, **1993**.
17. GARCIA K.L., DELFINO J.J., POWELL D.H. Non-regulated organic compounds in Florida sediments. Wat. Res. **27**, 1601, **1993**.