Polish Journal of Environmental Studies Vol. 11, No. 6 (2002), 655-661

Distribution of Pollutants in the Odra River System Part II. Organic Pollutants in Odra River Water

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Received: 13 May, 2002
Accepted: 16 July, 2002

Abstract

Within the framework of the International Odra Project, organic pollution (pesticides, volatile organic compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, chlorobenzenes) of the Odra river and its tributaries were studied by a team from Gdaρsk University of Technology. From August 1997 to May 2000 seven sample collections were conducted, i.e. one directly after the flood in 1997 (for sampling sites see map in Part I).

During the study period the pollution of Odra river water with PAH, PCBs and pesticides in general did not exceed allowable levels.

The highest concentration of volatile chloroorganic compounds was found in the sample from Brzeg Dolny.

Keywords: organic pollutants, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, volatile organic compounds, pesticides, surface water.

Introduction

Within the framework of the International Odra Project (IOP) sampling of water from the Odra river was conducted (see map in Part I).

The investigations focused on pollutants which belonged to the following classes of organic compounds:

Polycyclic Aromatic Hydrocarbons – PAHs [1-5]

PAHs are common organic pollutants of natural and anthropogenic origin; they are products of incomplete combustion of organic substances, including fuels. PAHs are regarded as very harmful because of their carcinogenic and toxic properties. Due to lyophilic properties and slow degradation, they are widely distributed in the environment and undergo bioaccumulation, especially in species that occupy higher levels in the food chain. PAH pollution of the Odra river and its tributaries was studied in the period from August 1997 to May 2000. Within this period, seven sample collections were conducted, i.e. one directly after the flood in 1997, and the remaining four at six-month intervals. Generally, 16 individual PAHs recommended by the US EPA were determined to assess PAH pollution.

Polychlorinated Biphenyls – PCB's [6-11].

Though PCBs were never produced inPoland they have been widely used in the power industry (transformer oils, insulating liquids in capacitors), as plasticizers in paints and lacquers and also as hydraulic fluids. They can occur as contaminants when pesticides, chlorophenols and other wood preservatives are produced.

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They are also formed in the process of pulp bleaching and water disinfection with chlorine. They were found to form during incineration of municipal wastes and wood. Polychlorinated aromatic compounds, including PCBs, are formed from inorganic chlorine and organic material, especially under limited oxygen content conditions and in the presence of copper, iron and aluminium.

Volatile Organic Compounds [12-16]

Volatile organic sulphur compounds. Organic sulphur compounds may occur in different aquatic environments as a consequence of industrial spills or natural reduction processes in the presence of high amounts of organic matter and sulphate. Volatile S – organic compounds are considered to be toxic species. Furthermore, their environmental implications concern bad odour nuisances. The determination of organosulphur compounds in water provides useful information on source input, e.g. a relation of spills to redox processes.

Aliphatic and aromatic hydrocarbons. Opposite to aromatic hydrocarbons, which are strongly toxic, aliphatic hydrocarbons are not considered to be such. Particularly strong toxic and carcinogenic properties are displayed by benzene, ethylbenzene and xylenes which have all been listed by the US EPA as hazardous ectotoxins.

Chloroorganic compounds (VOCl). Chloroorganic compounds are the most harmful among VOCs. Pollution chiefly originates from anthropogenic sources (solvents, water treatment processes, pulp bleaching).

Chlorobenzenes

Chlorobenzene is used to produce materials for dye industry and as a solvent for polymeric plastics while dichlorobenzene is used in the cosmetics industry.

Pesticides [5, 17-20]

The common use of pesticides makes them widely distributed in all compartments of the environment, i.e. air, water, plants and soil. Due to high values of the octanol : water coefficient for most of the pesticides, they are easily sorbed on soil and sediments. The problems which might be caused in the nearest future by the presence of pesticides should be a subject of special attention since a lot of these substances tend to bioaccumulate. Even worse, due to the persistence of pesticides in the environment and their lypophilic character they also tend to biomagnify in the food chain. Therefore, many laboratories attempt to monitor pesticide concentrations in soil and sediments.

Experimental

Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs)

The water samples were spiked with standards and subjected to solid phase extraction (SPE). A sample volume of 0.5 l with added internal standards (naphthalene - d8, benzo(a)anthracene - d12, and PCB 209), was percolated through a sorbent bed at a controlled rate of about 5 ml/min. The sorbent bed drying was carried out in a gentle air stream. The analytes were eluted from the sorbent with dichloromethane (5x2 ml). The eluate was evaporated to 0.3 ml in the stream of nitrogen.

Final analysis. Final analysis was carried out by GC-MS (SIM mode). The parameters of GC-MS runs are given in Table 1.

Method characteristics:

- Method Detection Limit (MDL): 1-5 ng/l
- Relative Standard Deviation (RSD): 10-20 %

Volatile Organic Compounds (VOC)

A volume of 10 ml of water from each sample was transferred into the purging vessel. The purge gas, argon, was passed through the vessel at a flow-rate of 20 ml min^{-1} for 10 min. Purged analytes were trapped on microtrap sorbent bed (80 mg Tenax TA / 30mg Carbosieve III) at ambient temperature. Then the analytes were desorbed and transferred by carrier gas (1 min.) onto the front of a capillary column. The trap was heated to a final temperature of 250 ^{0}C.

Final analysis. In water analysis, volumes of 10 cm^3 of the original water samples were introduced into a purge vessel, while in sediment analysis, 10 cm^3 of supernatant water was subjected to purging.

The purged analytes were focused in a sorbent trap at ambient temperature. In the next step, the trapped analytes were thermally desorbed, transferred by carrier gas into a capillary chromatographic column for separation and finally detected by MS.

The chromatographic parameters are shown in Table 2.

Method characteristics:

- Method Detection Limit (MDL*)*: 1 ng/l
- Relative Standard Deviation (RSD): <10 %

Pesticides

The analysis of pesticides in water was based on solid phase extraction (SPE - RP C18), elution with dichloromethane and final determination using gas chromatography with the thermoionic detector (NPD) and the electron capture detector (ECD). Pesticides were extracted from sediments by shaking with solvent or by accelerated solvent extraction. The extract was then cleaned up using an SPE alumina column and analysed by GC – MS, GC – ECD and GC – NPD .

Samples were stored in a cool and dark place for some days, but not longer than 2 weeks. The SPE column (reversed phase octadecylsilane RP- C_{18} – 500 mg Bakerbon SPE, JT Baker) was conditioned by adding methanol (5x2 ml) and deionized water (2x2 ml) before extracting the pesticides from aqueous solution. Attention was paid not to dry sorbent bed during column conditioning because of the possibility of functional group deactivation. Then,

Table 1. GC run parameters for PAH and PCB analysis.

Element of analytical system:	Parameters:
Gas chromatograph:	GC 8000, Fisons
Column:	SPB-5™ fused silica column (30 m x 0.25 mm); film thickness 0.25 µm
Detector:	MD 800 (Mass Detector), with EI;Operation in SIM mode
Injection system:	On-column
Carrier gas :	Helium at 70 kPa
Oven temperature program:	40° C to120°C (40° / min) to 280°C (5°/min); 280°C for 17 and 5 min for PAHs and PCBs, respectively

Table 2. Chromatographic run parameters for determination of VOC.

Elements of analytical system:	Parameters:
Gas chromatograph:	GC 8000, Fisons
Column:	Rtx-624 Restek Corporation, 60 m x 0.32 mm ID fused silica; df - 1.8 µm.: 6% cyanopropylphenyl, 94% dimetylpolisiloxane
Detector:	MD 800 (Mass Detector), with EI;Operation in SCAN mode: 10 - 450
Injection system:	thermal desorber coupled to a system for purging an analyte from a liquid sample; purge gas, argon, flowing at 20 cm^3 min^{-1}; purge time: 10 min
Microtrap:	Sorbent: 80 mg Tenax TA / 30 mg Carbosieve III; desorption temperature: 250°C; desorption time: 60 sec.
Carrier gas :	Helium at 100 kPa and ~2 cm^3 min^{-1}
Oven temperature program:	35 °C for 2 min; 5 °C $min^{-1}$to 100 °C; 10 °C min^{-1} to 250 °C; 250 °C for 10 min.

the analytes in a 0.5 l aqueous sample were pre-concentrated on the sorbent surface at controlled speed (about 5 ml/min). Sorbent bed drying was carried out in a gentle air stream. The analytes were desorbed from the bed with dichloromethane (5x2 ml). The extract was evaporated to dryness in the stream of nitrogen, and then 1 ml of methanol was added.

Final analysis. The final determination was carried out by gas chromatography connected with the thermoionic detector (NPD) sensitive to nitrogen and phosphorus containing compounds or with the electron capture detector (ECD) sensitive to compounds with high electron affinity (e.g. organochlorine pesticides) or with MS detector. The GC run parameters are given in Table 3.

Method characteristics:

- Method Detection Limit (MDL): 3-70 ng/l
- Relative Standard Deviation (RSD): below 17 %

Results

Polycyclic Aromatic Hydrocarbons - PAHs

Water pollution with PAHs in the Odra river, based on measurements from five sample collections, is given in Fig. 1. The total content of 16 PAHs in water from the Odra river and its tributaries was in the range from below the detection limit of 1 ng/l to 1.5 µg/l for all samples apart from the post-flood ones, for which PAH concentrations at quite a few sampling sites were in the range from very low values to 2.0-2.4 µg/l. There was one case for the sampling period in May'98 for which PAH content was relatively high at 3.35 µg/l. For the majority of cases, i.e. for a given sampling period and a given sampling site, the concentrations were rather low, that is, slightly below or slightly above 0.5 µg/l.

- Generally, higher PAH concentrations were found in the upper course of the Odra river. This might have resulted from the fact that the region between Skorogoszcz and Oława is highly urbanized, the north of the Czech Republic is highly industralized and large heat- and power-generating plants, with the biggest one close to Opole, are located in the southern part of the Odra river catchment area.
- In Poland total PAH maximum allowable concentration (MAC) for surface water has not yet been established. However, for benzo(a)pyrene, which is a strongly carcinogenic compound, MAC was established at a value of 0.2 µg/l for all surface water quality classes. For all the analyzed samples benzo(a)pyrene concentration was lower than MAC.
- Pollution with PAHs was found to depend on river stage, i.e. lower pollution at higher river water levels.
- In general, during the study period, PAH pollution of Odra water did not exceed allowable levels, and therefore was not critical.

Polychlorinated Biphenyls - PCBs

In the majority of cases, PCBs were detected in water samples from the whole Odra basin at concentration level below 10 ng/l, and quite often even below the method detection limit of 1 ng/l (Fig. 2). Except for a few cases, the measured concentrations were even lower than the maximum allowable concentration for underground waters of 10 ng/l.

Taking into account data from all the sample collections, it can be concluded that water pollution with PCBs in the Odra river and its tributaries is negligible.

Table 3. GC run parameters for determination of pesticides in water and sediments.

Elements of analytical system:	Parameters:		
Gas chromatograph:	GC 8160, Fisons	GC 6000, Fisons	HP-5890 Hewlett Packard
Column:	RTX - 35 Restek Corporation fused silica column (30 m x 0.25 mm), film thickness 0.25 µm (35% diphenyl, 65 % dimethyl polysiloxane -PDMS)	RTX - 5 Restek Corporation fused silica column (60 m x 0.25 mm), film thickness 0.25 µm (5% diphenyl, 95 % dimethyl polysiloxane -PDMS)	HP 5 or CP - Sil 8MS;30 m x 0.5 mm x 0.25 mm (5% diphenyl, 95% dimethyl polysiloxane - PDMS)
Detector:	NPD (Nitrogen Phosphorous Detector)	ECD (Electron Capture Detector)	MS HP - 5972
Injection system:	Split/Splitless mode 250 °C	Cold on-column	Split/Splitless mode 240 °C
Carrier gas:	Hydrogen at ~2 ml/min	Hydrogen at ~2 ml/min	helium
Oven temperature program:	60°C to 180°C(40°C/min); to 200°C (30°/min); to 260°C (17°C/min)	60°C to180°C(30°C/ min); to 280°C (10°C/min); 280°C for 13 min	50°C for 1.5 min; to 180°C (30°C/min); to 275°C (10°C/min); 275°C for 12 min

Volatile Organic Compounds

Volatile organic sulphur compounds. The concentration of organic sulphur compounds (VOSs) during the entire sampling period varied from a detection limit to ca. 2 µg/l (Fig. 3). In the middle course of the Odra river, 300-600 km downstream from the riverhead, the concentration was generally below 0.1 µg/l. Higher VOS concentrations of usually about 0.5 µg/l were observed in the upper course of the river (up to 300 km from the riverhead) while during the November'97 sampling, after the flood, it reached a value of about 2 µg/l. The highest level of 2.5 µg/l was observed in the Szczecin Lagoon in June'99 .

The above concentration levels were not generally dangerous to animals or plants.

Pollution by VOSs can originate from human activities but its main source is natural processes. The increased VOS pollution observed in the samples from June'99 might be related to higher ambient temperature and hence faster reduction processes.

Aliphatic and aromatic hydrocarbons. Aliphatic and aromatic hydrocarbons were detected in water samples only occasionally at concentrations below 10 µg/l (Fig. 4).

Surprisingly high concentrations of aliphatic and aromatic hydrocarbons were found in water samples collected in the upper course of the river in May'00, reaching at some sites the level between 50 and 60 µg/l. Also, in June'99 in the Szczecin Lagoon, the concentration was slightly increased, reaching the level of 10 µg/l. This might possibly be attributed to the presence of ships and barges in the area.

Chloroorganic compounds (VOCl). The chloroorganic compounds were detected mainly in water samples at concentrations ranging from the detection limit to about 835 µg/l (Fig. 5). This can be connected to a relatively high solubility of VOCl in water and their poor adsorption on particulate matter.

During sample collection in August'97, the highest concentrations of up to 835 µg/l and the widest spectrum of chloroorganic compounds were found at Brzeg Dolny; starting from this site the concentration of chloroorganics gradually decreased downstream the Odra river. The Chemical Plant "Rokita", which is on the list of 80 plants of the highest environmental nuisance, is located in Brzeg Dolny - ca. 27% of the plant effluent has been classified as very harmful waste. According to the Provincial Inspectorate of Environmental Protection (Wojewodzki Inspektorat Ochrony Środowiska - WIOŚ) in Wrocław, "Rokita" emits to the environment free chlorine as well as aliphatic and aromatic hydrocarbons.

A similar situation was observed in June'99, with the highest concentration of VOCls about 30 km downstream from Brzeg Dolny. The concentration of VOCls in the samples from the last sampling periods was ca. 100 times lower than the highest concentration in August'97. It should be noticed that the water level in the Odra river was very high at the time.

Chlorobenzenes

For all sample collections the total content of chlorobenzenes in water from the Odra river and its tributaries was in the range from below a detection limit to 318 µg/l (Fig. 6). The highest concentration of ca. 318 µg/l was found in Brzeg Dolny in August'97. Starting from this particular site, concentrations slowly decreased along the course of the river reaching several µg/l at the distance of 300 km downstream. Chlorobenzenes were detected in nearly all water samples from Brzeg Dolny, where the chemical plant is located.

The increased concentration of chlorobenzes was also sporadically observed in the Odra river tributaries (ca. 8µg/l), in the upper Odra (less than 1 µg/l), and in the Szczecin Lagoon (several µg/l).

Pollution of the upper course Odra river can be attributed to sources located abroad, i.e. across the Polish-Czech border, whereas pollution of the lagoon might be related to periodic cleaning of ships and barges.

On the basis of the obtained results it can be stated that generally waters in the Odra river are not polluted with chlorobenzenes, except for Brzeg Dolny.

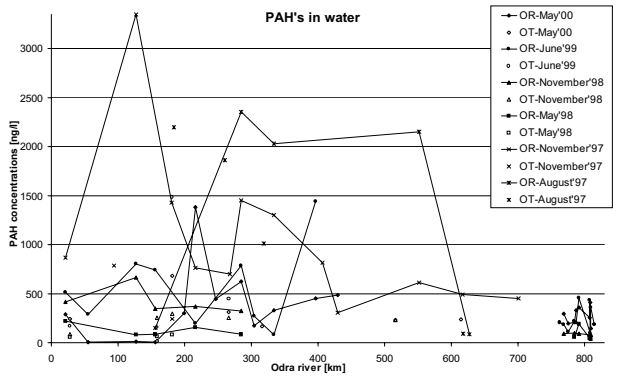

Fig. 1. PAH concentrations along the course of the Odra river (OR) and its tributaries (OT).

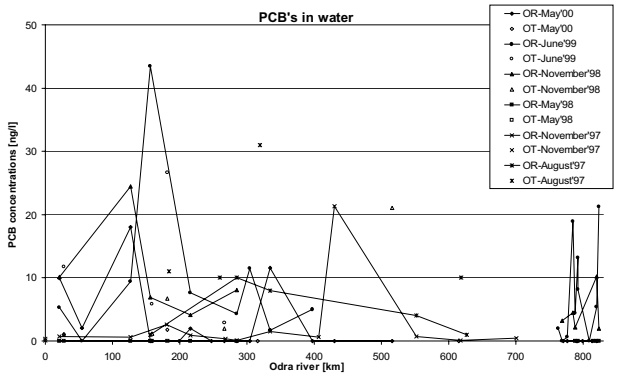

Fig. 2. PCB concentrations along the course of the Odra river (OR) and its tributaries (OT).

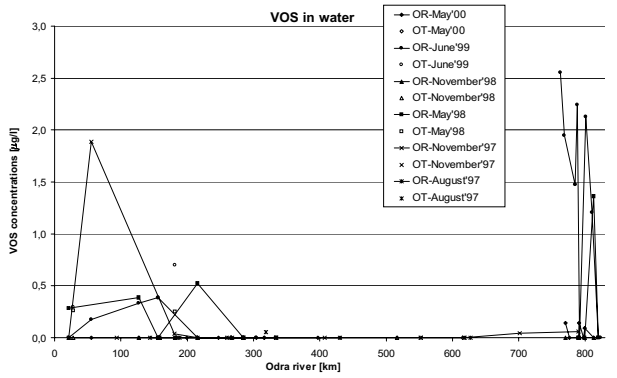

Fig. 3. Volatile Organic Sulfur compounds concentrations along the course of the Odra river (OR) and its tributaries (OT).

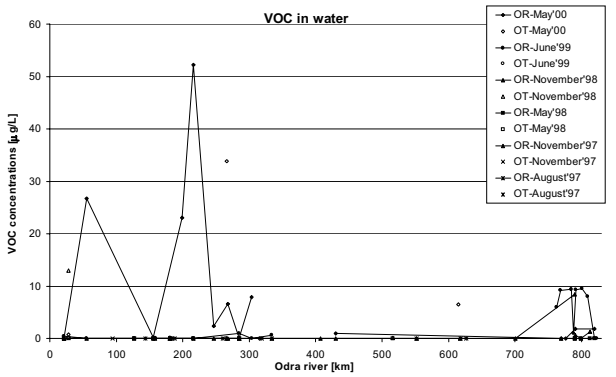

Fig. 4. Volatile Organic Hydrocarbons concentrations along the course of the Odra river (OR) and its tributaries (OT).

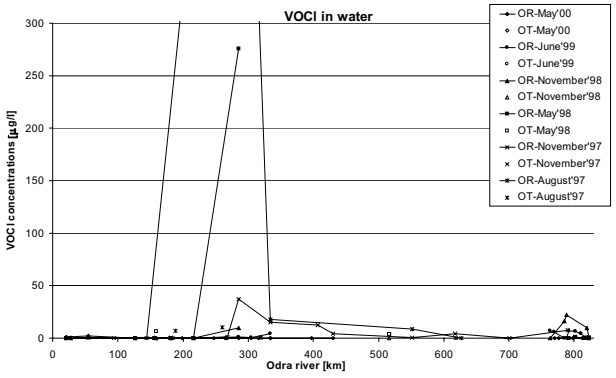

Fig. 5. Volatile Organochlorine compounds concentrations along the course of the Odra river (OR) and its tributaries (OT).

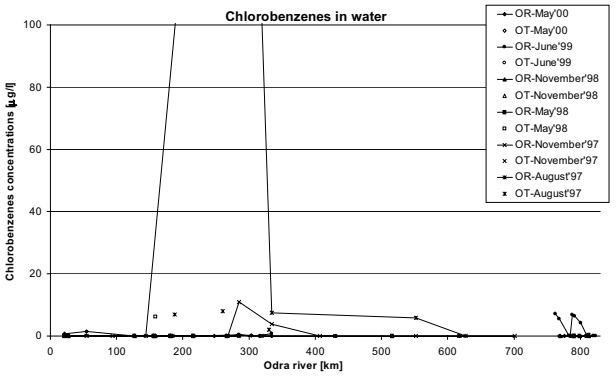

Fig. 6. Chlorobenzenes concentrations along the course of the Odra river (OR) and its tributaries (OT).

Pesticides

Concentrations of pesticides in water (Fig. 7) are generally lower than the Polish standards for sewage (0.5 μg/l for organochlorine insecticides and 10.0 μg/l for organophosphorous and carbamate insecticides), for surface water (0.05 μg/l for organochlorine insecticides and 1.0 μg/l for organophosphorous and carbamate insecticides) and tap water (0.5 μg/l for the sum of pesticides and 0.1 μg/l for individual pesticide). The sum of the nitrogen containing pesticides, mainly triazines, varied from 0 to 1.9 μg/l and the highest concentrations of more than 1 μg/l were observed in August'97 in the Odra at Klopot (1.9 μg/l) and at Brzeg Dolny (1.6 μg/l); in May'98 in the Szczecin Lagoon (1.4 μg/l); in June 99 in Odra at Malczyce (1.6 μg/l); and in May'00 in Odra at Raciborz (1.7 μg/l). The sum of the phosphorus-containing pesticides, mainly fenitrothion and bromophos ethyl, varied from 0 to 2.8 μg/l and the highest concentrations of more than 1 μg/l were observed in May'98 in Odra at Nysa Kłodzka (1.1 μg/l) and in the Szczecin Lagoon (2.8 μg/l); and in June'99 in Odra at Chałupki (1.1 μg/l), Malczyce (2.1 μg/l) and Scinawa (2.0 μg/l). The sum of the organochlorine pesticides concentration varied from 0 to 5.1 μg/l and the highest concentrations of more than 1 μg/l were observed in May 1998 in the Odra at Mała Panew (1.0 μg/l) and in the Szczecin Lagoon (2.1, 1.5 and 5.1 μg/l), and in May 2000 in the Odra at Ścinawa (2.0 μg/l).

Due to agricultural operations the concentration of pesticides was much higher in the spring than in the autumn. The high concentrations of pesticides in water were found at two sampling sites: in Olza on the border with the Czech Republic and in Kłopot near the Nysa Łuzycka river mouth, on the border with Germany.

The high concentrations of pesticides in water were found in the region of Szczecin and the Szczecin Lagoon, including the Pomeranian Bay. This indicates that the region is highly polluted in comparison to other investigated areas.

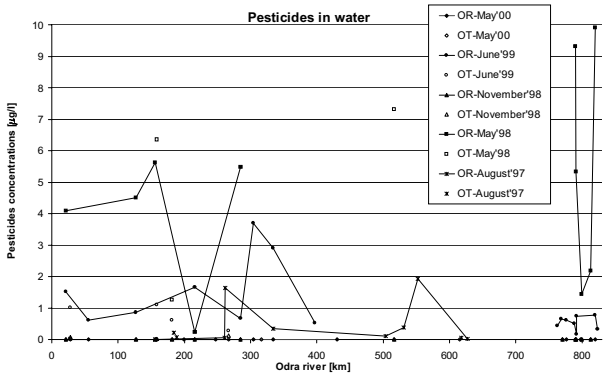

Fig.7. Pesticide concentrations along the course of the Odra river (OR) and its tributaries (OT).

Conclusion

Taking into account data from all sample collections, it can be concluded that water pollution with PCBs and pesticides of the Odra river and its tributaries is negligible. PAH pollution of the Odra water did not exceed the allowable levels and, therefore, was not critical.

The highest concentration of volatile chloroorganic compounds and chlorobenzenes in water were found in Brzeg Dolny. Starting from this site, the concentration slowly decreased along the course of the river. As a possi ble explanation for this phenomenon it has to be said that in Brzeg Dolny there is the Chemical Plant "Rokita", which was on the list of 80 plants of the highest environmental nuisance in Poland.

Exceptionally high concentrations of tetrachloroethene were determined in the Szczecin Lagoon. This can be regarded as incidental pollution, probably caused by leakage from tankers.

In this part of the study only analyses concerning water samples were described. The results of sediment analyses were presented in a separate study because of the large amount of data (see Part III). The next stage of work will involve pooling of all the results which should allow for a complex evaluation of the pollution level in the aquatic environment of the Odra river basin.

Literature data contain a lot of similar information which concern studies on other riverine systems [21-23].

Acknowledgements

The authors would like to express their deepest gratitude to the team members from Department of Analytical Chemistry Chemical Faculty, Gdańsk University of Technology, for performing analyses.

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