Polish Journal of Environmental Studies Vol. 11, No. 6 (2002), 663-668

Distribution of Pollutants in the Odra River System Part III. Organic Pollutants in Bottom Sediments

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

Abstract

Within the framework of the International Odra Project, the organic pollution level, i.e. with pesticides, volatile organic compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, chlorobenzenes, in Odra river sediment was studied by a scientific team from Gdańsk University of Technology. From August 1997 to May 2000 seven sample collections were conducted, among others one immediately after the flood in 1997 (for sampling sites see map in Part I).

The results of multi-annual investigations indicate that Odra river sediments are not polluted with pesticides, polychlorinated biphenyls (PCBs) and volatile organic compounds.

The main problem, particularly in the upper course of the Odra river, is caused by polycyclic aromatic hydrocarbons (PAHs) present in sediments.

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

Introduction

The structure and extensive surface area of bottom sediments predestines them to the role of a natural sorbent filtering out a variety of components, such as heavy metals, volatile organohalogen compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phenols, and pesticides [1-6]. Due to the accumulation of the above-mentioned compounds, the sediment itself may become a secondary source of pollution and keep contaminating over-lying water for many years, even after pollution inflow from primary sources has been cut off [7].

Bottom sediments are an important element of aquatic ecosystems. They constitute ecological niches supporting benthic organisms, i.e. animals and plants living on the bottom of bodies of water, and are a source of nutrients for aquatic organisms such as small invertebrates and protozoans.

An assessment of the effect of pollution on life in water bodies requires the sources and concentrations of the pollutants to be determined. In this respect, bottom sediments are very useful material for investigation, because they act as sorption column and provide a clear picture of events taking place in the overlying water. This study presents the results of investigations on benthic sediments collected from the Odra river in the years 1997-2000 within the framework of the International Odra Project (IOP). The study constitutes a logical continuation of the previous work, i.e. of Parts I and II.

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Experimental

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

Approximately 100 g of sediment was lyophilized at -50°C under a pressure of 0.67 Pa for 8 - 24 h, depending on the type of sample (sand, sludge, etc.). The dry sediment was sieved manually through a 2 mm mesh.

A 1 g sample of the dry sediment was soaked in acetone and internal standard (deuterated compounds: naphthalene-d8, benzo(a)anthracene-d12; PCB209) were added. After 24 h, 5 ml of dichloromethane was added. The mixture of the sample and solvent was shaken for 24 h at room temperature. The obtained extract was decanted and combined with 2 ml of dichloromethane used to wash an extraction vial. The extracts were evaporated to reduce the volume to approximately 1 ml.

For sample clean-up, a short column packed with SiO_2 and 1 g of activated copper powder in the upper layer was used. The extract introduced into the column was eluted with 10 ml of dichloromethane. The eluate volume was reduced to 1 ml under a stream of nitrogen gas.

This concentrate was analysed for PAH content by means of gas chromatography-mass spectrometry (GC-MS) under conditions described in Part II.

In the case of PCB analysis the procedure was the same as for PAH, up to the step of obtaining the eluate, which was then evaporated to dryness under a stream of nitrogen. The solid residue was dissolved in 100 µl of dried pentane and then extracted three times with volumes of 100 µl for 5 min each time, in an ultrasonic bath. Individual extracts were combined and introduced to a glass column (120 mm long, 5 mm I.D.) packed with 500 mg of silica gel. Dry pentane was used for elution. An eluate portion of 6 ml was collected and evaporated to dryness under a stream of nitrogen and later the solid residue was dissolved in 30 µl of hexane. The final extract was analysed by GC-MS under conditions described in Part II.

Volatile Organic Compounds (VOC)

Following the procedure described in Part II, volatile sulphur compounds, aliphatic and aromatic hydrocarbons and chloroorganic compounds have been analyzed in supernantant water from sediment samples.

Chlorobenzenes

The sediment samples were prepared in the following way:

- wet sediments were spiked with international standards (deuterated 1,2-dichlorobenzene) and dried by adding Na_2SO_4 ,
- extraction was performed with dichloromethane using the shake-flask method for 24 h at room temperature,
- the obtained extracts were decanted,
- extracts were cleaned up using a short silica gel column with activated copper powder in the upper layer,
- analytes were eluted with 10 ml of dichloromethane,
- eluate was evaporated under a stream of nitrogen to a volume of about 0.3 ml,
- 4-bromofluorobenzene as an injection standard was added.

All extracts were analysed by GC-MS method in a SIM mode. The identification was based on retention parameters of peaks recorded for characteristic ion masses of the analysed chlorobenzenes (Tab. 1).

Method characteristics:

- Method Detection Limit (MDL): 1µg/kg (for 1 g of sample)
- Relative Standard Deviation (RSD): : 2-20 % depending on chlorobenzene

Pesticides

Procedure with Shaking.

A wet sample was stored in the refrigerator at 0 - 6°C prior to treatment. Approximately 100 g of sediment was lyophilized at -50°C under a pressure of 0.67 Pa for 8 - 24 h, depending on sample type (sand, sludge, etc.). Dry sediments were sieved manually through a 2 mm mesh. Two-to-ten gram samples of dry sediment were mixed with dichloromethane (3 volumes of solvent to 1 volume of sample) and shaken for 24 h at room temperature. The obtained extract was decanted and sediment was washed out two times with 1.5 ml of dichloromethane for 3 min each time, in an ultrasonic bath. All extracts were combined, evaporated to dryness and the residue was dissolved in acetonitrile (2x1.5 ml) in an ultrasonic bath for 3 min. The extract was then transferred onto the SPE column which had been packed manually with alumina, copper and sodium sulfate. The pesticide fraction was eluted with acetonitrile. After evaporation under a stream of nitrogen, the residue was dissolved in 0.5 ml of methanol and analyzed. The whole procedure was repeated with a pesticide standard added to the sample in order to evaluate the recovery.

Table 1. GC run parameters for chlorobenzene analysis.

Element of analytical system:	Parameters:
Gas chromatograph:	GC 8000, Fisons
Column:	Rtx 624 fused silica column (60 m x 0.30 mm); film thickness 0.18 µm
Detector:	MD 800 (Mass Detector), with EI;operation in SIM mode
Injection system:	On-column
Carrier gas :	Helium: 70 kPa
Oven temperature program:	40°C to 250°C (7°/min), to 280°C (10°/min), 280°C for 5 min.

Method characteristics:

- Method Detection Limit (MLD) = approx. 1 ng/g
- Relative Standard Deviation (RSD) = below 23 %

Procedure with Accelerated Solvent Extractor.

Sediment samples from the Odra were lyophilized. Before the analysis, a 5 g sample was mixed with sodium sulfate and the internal standard, PCB 209, was added. The sample was kept in an extraction vial at room temperature until solvent evaporated. The vial was then placed in an Accelerated Solvent Extractor. The operating conditions were as follows: solvent - dichloromethane/acetone (1:1), 5 min heating time, 1 min static extraction time, temperature of 100°C, pressure of 2000 psi. The extract was then evaporated to dryness and the clean-up procedure as the one described previously, was applied.

Method characteristics:

- Method Detection Limit (MLD): approx. 1 ng/g
- Relative Standard Deviation: 10-35 %

Standard deviation was calculated for the results of pesticide determination in 7 samples to which the internal standard had been added.

Results

Policyclic Aromatic Hydrocarbons – PAHs

The pollution of sediments with PAHs along the course of the Odra river for the 5 sample collections is given in Fig. 1. The pollution of sediments in the Odra catchment area, collected just after the flood, ranged from below the detection limit of 1 μg/kg to ca. 50 mg/kg. The highest values were found for the upper course of the Odra river. In samples collected later the concentrations of PAHs in sediment were relatively low, i.e. below 30 mg/kg, although in the sediment samples from November 1997, PAHs were determined at noticeably higher concentrations of usually 30-60 mg/kg.

In general, the differences in concentration among different sampling periods were not high, although in some cases the increased concentrations were determined. A comparison of data for different areas indicated that pollution with PAHs is much higher in the upper course of the Odra river. The explanation of this phenomenon can be the same as in the case of water samples, i.e. that the pollution is influenced by the presence of highly urbanized regions between Skorogoszcz and Oława, and in the north of the Czech Republic as well as by the large heat- and power-generating plants, with the biggest one close to Opole, which are located in the southern part of the Odra river catchment area.

According to Polish recommendations, soil containing PAHs such as those found in many samples in this study, is regarded as polluted or strongly polluted. For protected areas the total PAH MAC is 1 mg/kg, a value much lower than PAH concentration in sediment samples from the majority of studied areas. Moreover, benzo(a)pyrene concentration also exceeded MAC for soils in the protected areas (0.01 mg/kg according to the guidelines of MOŚZNiL from 1994).

Polychlorinated Biphenyls - PCB's

Sediments were analysed for total content of all PCBs and 7 individual PCBs (congeners no 28, 53, 101, 118, 138, 153 and 180) used for characterisation of PCB pollution. The total concentrations of 7 selected PCBs in sediments for each sampling period at different sites along the Odra river are presented in Fig. 2.

In general, the content of PCB's was below 20 μg/kg, and often even below 10 μg/kg, which are considered low values. As a rule the higher concentrations were observed in the region where pulp and paper industry is situated. The highest determined value was 77 μg/kg.

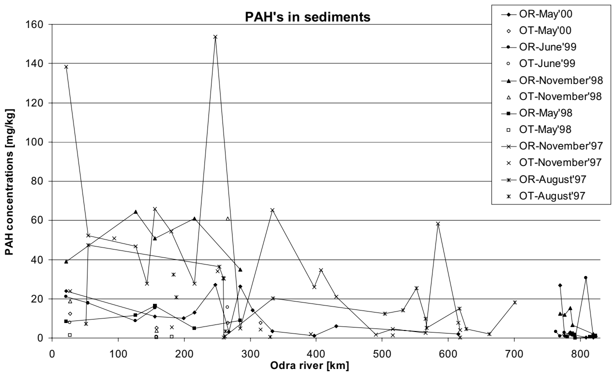

Fig. 1. PAH concentrations along the course of the Odra river (OR) and its tributaries (OT).

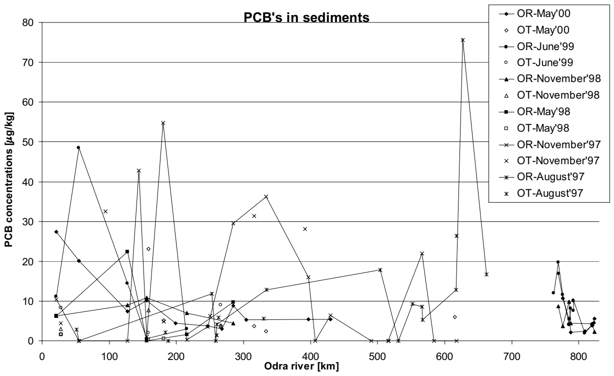

Fig. 2. PCB concentrations along the course of the Odra river (OR) and its tributaries (OT).

In Poland, total PCBs maximum allowable concentration (MAC) for sediments has not been established yet, but in the developed countries MAC is set at the level of 100 µg/kg. According to these standards the studied sediments can be regarded as non-polluted.

Volatile Organic Compounds

Volatile organic sulphur compounds. Organic sulphur compounds in the sediment samples, i.e. in sediment-overlaying supernatant water, were present at higher levels than in water samples, especially in the upper course of the river. The concentrations ranged from a detection limit to ca. 60 µg/kg (Fig. 3). The highest level was observed in the samples from June 1999 and May 2000. The increased concentrations were also observed in the Szczecin Lagoon in June 1999 (about 5 µg/kg) and in May 2000 (around 10 µg /kg).

It was hypothesized that, similar to the case of water samples, VOS pollution might have originated from human activities, but the natural processes were its main source.

Aliphatic and aromatic hydrocarbons. In sediments, specifically in supernatant water, aliphatic and aromatic hydrocarbons were detected at higher levels than in water, but generally their concentrations did not exceed 70 µg/l (Fig. 4). The only exception was the occurrence of toluene in supernatant water at a relatively high concentration of above 20 µg/l, in samples from the vicinity of Chałupki, a site close to the Polish-Czech border. This phenomenon was observed for each sampling period. The fact that toluene occured only in sediments suggests that it might be a biodegradation product of other anthropogenic organic pollutants.

Chloroorganic compounds (VOCl). The concentration of chloroorganic compounds in sediments was ca. 100 times lower as compared to the concentrations in water (Fig. 5). The highest concentrations of ca. 2 µg/l were found in the upper course of the Odra river. This finding correlated with the increased concentration of VOCl in water in the same region. Exceptionally high concentrations of tetrachloroethene were determined in the Szczecin Lagoon at all sampling sites in June '99.

This can be regarded as incidental pollution probably caused by spills from tankers.

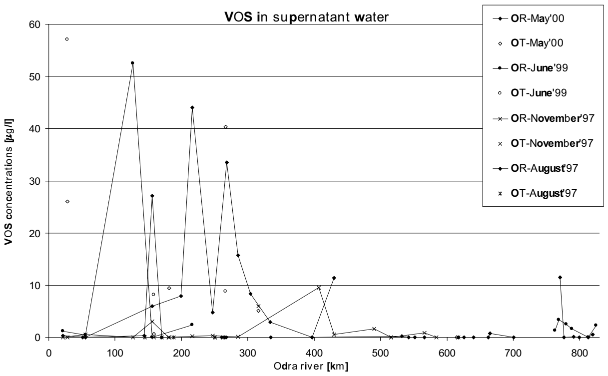

Fig. 3. Volatile Organic Sulfur compounds concentrations along the course of the Odra river (OR) and its tributaries (OT).

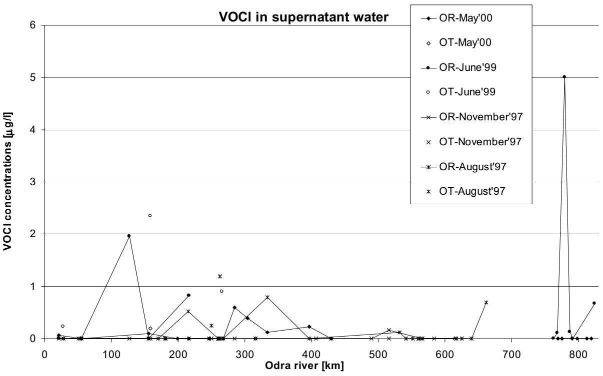

Fig. 5. Volatile Organochlorine compounds concentrations along the course of the Odra river (OR) and its tributaries (OT).

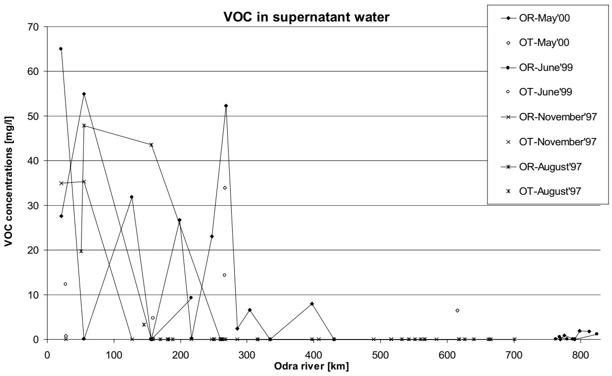

Fig. 4. Volatile Organic Hydrocarbons concentrations along the course of the Odra river (OR) and its tributaries (OT).

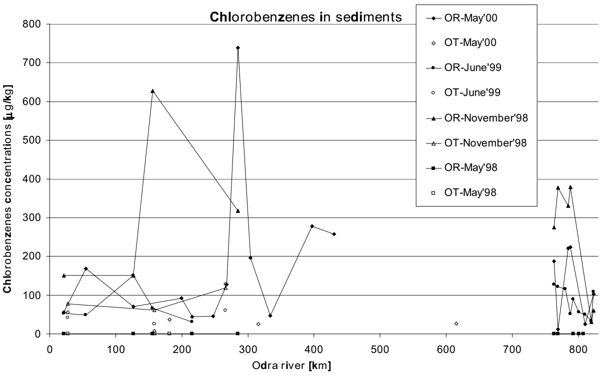

Fig. 6. Chlorobenzenes concentrations along the course of the Odra river (OR) and its tributaries (OT).

Chlorobenzenes

The concentration of chlorobenzens in sediments was considerably higher in comparison to water samples, ranging from a detection limit to ca. 750 µg/kg at Brzeg Dolny in May '00 (Fig.6) .

Increased concentration of chlorobenzene in sediments was observed in the same regions of the Odra river as for water samples, i.e. in sediment samples from the begining course of the Odra river (values from 150 to 650 µg/kg), in samples from Brzeg Dolny and at sampling sites downstream from Brzeg Dolny, and also in the Szczecin Lagoon (values from ca. 100 to about 400 µg/kg).

The results confirmed the conclusions drawn previously for water samples. The same sources are responsible for pollution in the above-mentioned parts of the Odra river, i.e. releases from transboundary sources in the Czech Republic, chemical plant at Brzeg Dolny and ships in Szczecin harbour.

Pesticides

The concentrations of pesticides in sediments were much lower than the proposed Dutch standards for soils of 2-6 mg/kg dry weight of soil (Fig. 7). The total concentrations of the nitrogen- and phosphorous-containing pesticides in sediments varied from 0 to 132 µg/kg, while the concentrations of organochlorine pesticides varied from 0 to 33 µg/ kg.

The highest concentrations were found in sediments near Oława in May '98. This sampling site is situated in the centre of the agricultural region, not far from the river mouths of Mała Panew, Nysa Kłodzka, Stobrawa and Oława as well as from the illegal pesticide waste disposal site in Wronów. This can also explain relatively high concentrations of modern pesticides, e.g. nitrogen and phosphoroorganic, in water and sediments taken from the sampling sites situated in this region. The high concentrations of pesticides in sediments found in the region of Szczecin and the Szczecin Lagoon (approx. 30 µg/kg in the Pomeranian Bay I, and approx. 26 µg/kg in Świna near Świnoujście, in May '98) indicate that this area is the most polluted one. The pollution might be caused by the waste disposal sites situated in the region. The high total inflow of water from the Odra river to the Pomeranian Bay (which aids the accumulation of pesticides in sediments and their relatively high concentration in water), may be another causative factor.

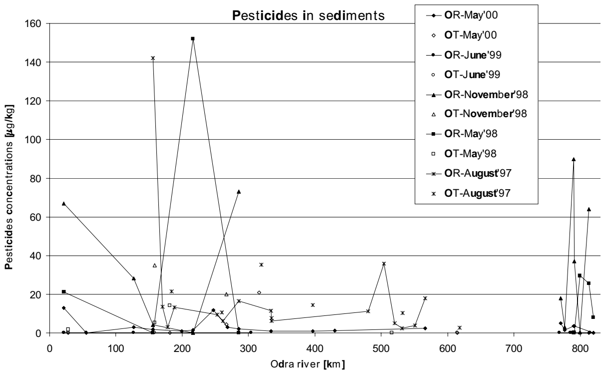

Fig. 7. Pesticides concentrations along the course of the Odra river (OR) and its tributaries (OT).

A correlation was found between the high concentration of pesticides in water and sediments taken from the same sampling sites, i.e. Olza, Kłodzko, Siechnice, Ścinawa, Czerna, Świerkocin and Kaleńsko. In the region where high concentrations of pesticides were detected during the spring sample collection in May '98 and autumn collection in November '98, the high concentrations of pesticides were also determined in sediments.

Conclusion

The results of multi-annual investigations indicate that the Odra river sediments are not polluted with pesticides, polychlorinated biphenyls (PCBs) and volatile organic compounds. The main problem, particularly in the upper course of the Odra river, is caused by polycyclic aromatic hydrocarbons (PAHs) present in sediments.

The conducted investigations resulted in large data sets of analytical measurements, which will require further analysis. It will also be necessary to pool all the results obtained by the separate research teams who took part in the International Odra Project. Only then will the in-depth assessment of the condition of water environment in the Odra river basin be possible.

Literature data contain a lot of similar information which concern studies on other riverine systems [8-12].

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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Poznań,

8-9 maja 2003 r. - XII Poznańskie Konwersatorium Analityczne „Nowoczesne metody przygotowania próbek i oznaczania śladowych ilości pierwiastków”

7 maja 2003 r. - Szkoła Naukowa

Organizatorami spotkania są:

Zakład Chemii Analitycznej Wydziału Technologii Chemicznej Politechniki Poznańskiej;
Komisja Nieorganicznej Analizy Śladowej
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Konwersatorium poświęcone będzie analizie śladowej, metodom przygotowania próbek analitycznych, technikom absorpcyjnej, emisyjnej i fluorescencyjnej spektrometrii atomowej oraz sprawdzaniu (walidacji) metod analitycznych. Przed Konwersatorium, w dniu 7 maja 2003 roku, planowana jest jednodniowa Szkoła Naukowa.

Przewiduje się również prezentację aparatury, urządzeń, odczynników, literatury fachowej i materiałów pomocniczych związanych tematycznie z programem naukowym Konwersatorium.

W ramach Konwersatorium i Szkoły Naukowej planowana jest wystawa aparatury, sprzętu, odczynników i literatury fachowej.

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