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Geochemical characteristics of bottom sediments in the Odra River estuary — Roztoka Odrzańska (north-west Poland)

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Roztoka Odrzańska is the last section of the Odra River estuary. Both in 1996, and in 1999 concentrations of Zn, Cu, Pb, Cd and Hg in the surface waters of Roztoka Odrzańska were within the limits for I class of purity. Maps of the heavy metal distributions in bottom sediments resemble those of TOC distribution in the < 0.20 mm fraction. Overall, 58.3% of the bottom sediments of Roztoka Odrzańska in 1996, as regards concentrations of Cd, Zn, Pb, Cu and Hg, belonged to class IV of purity; 14.6% belonged to class III; 18.8% belonged to class II and 8.3% to class I at all research stations. The excessive pollution the Roztoka Odrzańska sediments is controlled mainly by Cd and Zn concentrations and, to a much lower degree by Pb. Analyses in 1999 showed similar average concentrations of Cu, Zn and Pb, but less than half the content of cadmium. Concentrations, though, of cobalt (1.8x) and especially mercury (22.7x) were higher than the 1996 average levels. The observed concentrations fall within the concentration limits recorded in 1996 for Cu, Zn, Pb, Cd and Co, but they exceed these limits considerably for Hg.

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INTRODUCTION

The problem of polluted estuaries and coastal zones has been widely identified and since these ecosystems are important for the natural environment many regional and interregional studies have addressed this issue (e.g. Hyland *et al*., 1998). It was estimated in the USA that potentially medium levels of toxicity could be found in about 75% of coastal biotopes and estuaries, with 5% showing high toxicity levels (Daskalakis *et al*., 1995). More recently, the incidence of high toxicity biotopes has increased markedly; for example in 1994 and 1995 over 50% of estuaries in the south-east USA continued to show medium contamination levels, but a dramatic increase (from 12 up to 30%) in the incidence of highly contaminated areas was recorded over the same period of time (Hyland *et al*., 1998).

Estuaries, especially those located in areas of intensive agriculture, face the largest potential risks and suffer most from the toxic effects of exposure to many pollutants; the deleterious effect of those compounds is especially acute on molluscs and fish, and, eventually, on human health as a result of fish and mollusc consumption (Fulton *et al*., 1999; Hyland *et al*., 2000; Yuan *et al*., 2001).

Metals in rivers are transported both in solution and as a solid phase. Transitions between the two are possible as a result of precipitation and of adsorption and desorption processes. Precipitation of metals from solutions is controlled mainly by changes in pH and Eh. In sorption processes the key role is played by molecules with large active surface e.g. organic matter, oxides and hydroxides of Mn and Fe, and silt-fraction minerals (Salomons and Förstner, 1984). A substantial threat to the condition of a water ecosystem is posed by organic compounds with hydrophobic properties, which can combine with sediments, organic matter and suspensions (Cox *et al*., 1994). The mobility, toxicity and bioavailability of heavy metals in a given ecosystem depends on the way they are fixed in the sediments. The metal fraction absorbed at the surface of solid bodies is the most labile and bioaccessible one; in this fraction, metals are bound by processes of physical and chemical sorption and ion exchange, and interchange easily with other positive ions. Increases in concentrations of hydrogen, calcium and magnesium ions result in the displacement of metals from their sorption centres, usually in the form of simple, toxic ions (Sunda and Gillespie, 1979; Petersen, 1982; Peterson *et al*., 1984; Baccini,

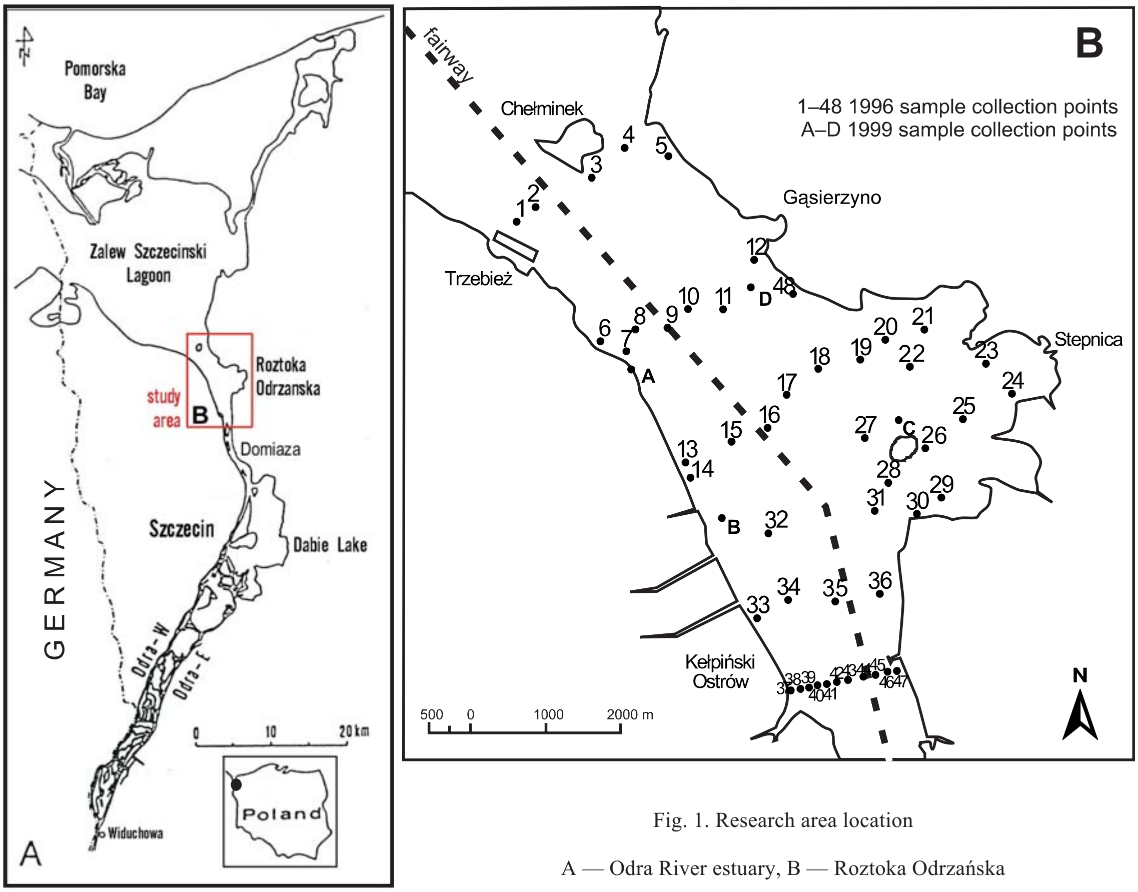

Fig. 1. Research area location

A — Odra River estuary, B — Roztoka Odrzańska

1985). Concentrations of heavy metals fixed in this form clearly correlate with concentrations of metals in organisms living in the sediment (Lum and Gammon, 1985; Tessier and Campbell, 1987).

The accumulation of pollutants in river sediments is controlled mainly by hydrological and sedimentation-related factors, namely grading of grains according to their size and density, the mixing the pollutants with sediments derived from tributaries and riverside erosion, and deposition on alluvial plains (Macklin, 1996). In the river-beds of the temperate climatic zone the highest concentrations of pollutants can be observed in fine-grained sediments along the river banks and in small bays, whereas in the main stream the concentrations of these compounds are usually lower (Bubb *et al*., 1991); moreover, increased pollutant levels are observed in sediments of the lower course of a river (Rostad *et al*., 1994).

Most of such pollutants are a threat to human health through their carcinogenic, mutogenic and teratogenic actions. The inflow of such substances changes the orginal biocenoses and causes environmental destruction. It diminishes biological diversity; the biomass of some species increases at the expense of others, which are squeezed out. These changes are unfavourable economically (Wiktor, 1976). Recent years have witnessed increased pathological changes in organisms, especially fish and molluscs, inhabiting polluted estuaries and marine inshore waters, as compared to those inhabiting unpolluted areas (Bengtsson, 1974; Förstner and Wittman, 1981).

Heavy metal concentrations in various parts of the Odra River estuary have long been researched by the Institute of Marine Sciences, University of Szczecin. The monitoring of changes in heavy metal concentrations in the soft tissues and shells of freshwater molluscs as compared to the concentrations recorded in the sediments and surface water is a particular area of research (Piotrowski, 1999*b*; 2000*a*, *b*; 2003*a*–*d*; Piotrowski and Wiertlewska, 1999*a*, *b*).

The planned output of the research conducted in the Odra River estuary is a classification of these bottom sediments as regards concentrations of heavy metals, polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), chloroorganic pesticides, polycyclic aromatic hydrocarbons (PWA), and oil-derived hydrocarbons (Piotrowski, 2003*a*, *d*).

Annually the Odra River (the 1995–1996 data) carries away 2.607 tons of phosphate phosphorus, 527.703 tons of suspended matter, and organic substances shown by means of the BOD_5 ratio (the latter amounting to 41.978 tons of O_2) to the Baltic Sea (Cydzik *et al.*, 1997). Moreover, it is estimated that every year 0.776 tons of mercury, 1.799 tons of cadmium, 54.576 tons of copper, 30.360 tons of lead and 299.562 tons of zinc flow down the Odra River and into the sea (the 1.11.1995–31.10.1996 data acc. to sea (Cydzik *et al.*, 1997).

Comparison of the Odra River water quality assessments made annually by Environmental Protection Inspector's Office for Szczecin Province shows that the contamination of the Odra River waters is permanent while water quality deterioration in the Szczecin urban area continues, resulting from the discharge of crude domestic and industrial sewage (Landsbery-Uczciwek, 1995; Cydzik *et al*., 1997).

This paper provides, as for as currently possible, a comprehensive profile of the Roztoka Odrzańska bottom sediments, especially as regards their concentration of the heavy metals

Cd, Zn, Pb, Cu, Co and Hg. The first five of these are classified as posing a considerable potential threat and cobalt is considered to pose a medium potential threat. 97% of Pb, 89% of Cd, 72% of Zn, 66% of Hg (Walker *et al*., 2002) and over 90% of Cu and 30% of Co (Kabata-Pendias and Pendias, 1979, 1993) in river and reservoir sediments in industrial areas come from anthropogenic pollutants. In practical terms, characterisation of the overall physical and chemical characteristics of the Roztoka Odrzańska sediments can be translated directly into guidelines for maintaining the Szczecin–Świnoujście water lane navigability. Analysis of the data collected helps direct future research into the geochemistry of the Odra River estuary.

So far, no comprehensive paper has been published on the contemporary bottom sediments in this area, except for papers on individual segments of the Odra River estuary (Majewski, 1980) or selected research problems (Piotrowski, 1997; Lis and Pasieczna, 1998; Adamiec and Helios-Rybicka, 2002*a*, *b*; Helios-Rybicka *et al*., 2002*a*, *b*; Wolska and Namieśnik, 2002*a*, *b*).

RESEARCH AREA

The Odra River estuary consists of a complex lower Odra River water course system, Lake Dąbie, Roztoka Odrzańska, Szczecin Bay, the Piana, Świna and Dziwna River straits and a part of Pomerania Bay (Jasińska, 1991). This area is subject to complex hydrological processes including:

— water exchange between the sea and the inland area. The backwater of the Odra River and demersal infusions of saline sea water reach an average distance of 100 km from the seashore (Majewski, 1966), but they may be observed as far as 160 km maximally from the coast (Buchholz, 1989);

— a complex system of rivers and canals in the Widuchowa–Trzebież section;

— high retention in the area resulting from the presence of superficial reservoirs (Szczecin Bay, Lake Dąbie) and the geology of the adjacent areas (peat plains);

— considerable changes of hydrological values, mainly water levels.

In Widuchowa the Odra River forks into the eastern Odra and western Odra, the two arms divided by the area of Międzyodrze. Near Szczecin the eastern Odra flows into a large Lake Dąbie and after it the river rejoins, via Iński Nurt, the western Odra and together they flow (as Domiąża) northwards to Roztoka Odrzańska and Szczecin Bay, after which they reach the Baltic Sea via three straits (Buchholz, 1993).

Roztoka Odrzańska is the last section of the Odra River estuary (Fig. 1A). This is the area where fresh and brackish waters mix. The area is limited to the south by the estuaries of two smaller rivers (the Gunica and Krępa) flowing into the Odra River; this is the boundary between Roztoka Odrzańska and Domiąża. The northern boundary of the research area is the island of Chełminek behind which the Odra River flows into Szczecin Bay (Buchholz, 1993). The area of Roztoka Odrzańska is 26.3 km^2. The length of the research area is 9 km from north to south and its width varies from 1.1 km in its southern part to 2.8 km in the north and 5.7 km in the central part of the area. The average depth of Roztoka, apart from the Szczecin–Świnoujście water lane trough, is 3.5 m. The water lane depth is maintained at a level of 12 m below the surface of the water (Fig. 2). Domiąża, results from which are compared with the results reported here, connects naturally with Roztoka Odrzańska, and its southern boundary is delimited by Iński Nurt where the waters of the western and eastern Odra rejoin. The natural hydrological system of Roztoka Odrzańska and Domiąża has been considerably modified by the construction of the Szczecin–Świnoujście Seaway. In Domiąża, it runs through Szeroki Nurt (Piotrowski and Stolarczuk, 1999; Piotrowski and Łaba-Mydłowska, 2003).

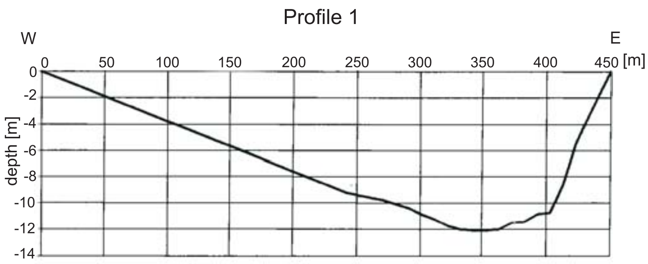

Fig. 2. Variations in depth in Roztoka Odrzańska along the southern research profile (points No 37–47)

MATERIAL AND METHODS

The field research was conducted in September 1996 along five research profiles. 48 samples of bottom sediments were collected by means of bottom sediments Van Veen dredging equipment (Fig. 1B). This sampler made it possible to collect samples from sampling areas of 0.0625m^2 and from depths of up to 15 cm.

The sampling points were located by means of the Trimble Navigation GPS satellite navigation system.

The pH of the sediments was measured according to the Polish Standard PN-91/C-04540/05 immediately after collection.

Under laboratory conditions the > 2 mm grain size fraction of the sediments was separated for mineralogical and petrographical examination.

The < 2 mm fraction was divided into four parts. One of them was frozen and treated as an archive sample. The following analyses were carried our on the second one:

— percentage content of dry matter (DM); the calculations were based on the percentage mass loss of the sample after drying at 105^{o}C to solid matter as compared to the mass of the sample in its natural state, assumed to be 100%;

— percentage mass loss on ignition at 600^{o}C (LOI);

— percentage content of calcium carbonate in dry matter ($CaCO_3$) — determined by the Scheibler method;

— percentage content of organic carbon in dry matter (TOC) — determined by Tiurin method.

From the third one, the < 0.20 mm fraction was separated by screen washing. Contents of TOC (%) and heavy metals (mg/kg): Cu, Zn, Pb, Co, Cd and Hg, were determined for the < 0.20 mm fraction. The concentrations of Cu, Zn, Pb, Co and Cd were determined by ICP-AES using a Varian plasma spectrometer, and mercury was determined by means of a hydrides generator (cold fumes method): CV-AAS.

The fourth sample was used to determine the grain size distribution by screen washing.

Certified standard solutions of metals and concentrated nitric acid made by Merck, as well as redistilled and initially deionised water were used in the analyses.

The sediment samples were mineralised by means of concentrated nitric acid (65%) in a microwave system; 10 ml of acid was used per sample. The total metal content was determined in the water samples, without preliminary filtration of the sample; undissolved metals, if any, were dissolved by evaporation (almost to dryness) of a water sample acidified with concentrated nitric acid (0.5 ml of the acid was used for every 100 ml of water) and the residue was dissolved in 1 ml of concentrated nitric acid for every 100 ml of the sample collected for analysis. The correctness of the analyses of the sediment was monitored by means of analysing a soil sample with known contents of Cu, Zn, Pb, Cd, Co and Hg with every series of measurements; water analyses were monitored by analysing control water samples with known metal contens made by the Promochem Company (symbol RT QCI-034) with every series of measurements.

The detection limits of the equipment for individual metals are given below: Cu — 0.005 ppm, Pb — 0.020 ppm, Zn — 0.002 ppm, Cd and Co — 0.003 ppm and Hg — 0.050 ppm.

In September 1999 bottom sediments were collected at four points (A, B, C and D) to determine concentrations of heavy metals in the < 0.20 mm grain size fraction, using the methodology of sample collection, preparation and analysis as described above.

In 1996 water samples were not collected, but water samples from Roztoka Odrzańska, collected by the Provincial Environment Protection Inspectorate, were analysed. In 1999, the four research stations, water samples from 1 m below water level were collected from using Nurek sampler.

The research results were processed by means of *Microsoft Excel* software; analysis of pile-ups (agglomeration method: of the simple bond; distance measure: Euclid's distance; lack of data removed by random) and principal component analysis were carried out using *Statistica* software (version 5). Non-metric multidimensional scaling (MDS), based on √√√-transformed abundances and Bray-Curtis similarities,was carried out using *Primer* software (version 5) developed by Plymouth Marine Laboratory, UK. Distribution maps for key parameters of the sediments examined and their concentrations of heavy metals were produced using the kriging method by means of *Surfer* (version 7.0) and *Corel Draw* (version 7.0) software.

Excel software was highly effective in creating and managing the data sheets, performing the basic statistical calculations and operating the data base.

The *Statistica* software cooperated well with the *Excel* spreadsheets and enabled multi-spectral analyses, in this case mainly the analyses of pile-ups (agglomeration method — the purpose of the algorithm obtained is to join objects into bigger and bigger bundles, using some measure of similarity or distance. A typical result of such grouping is the hierarchic tree (=dendrogram) and the Principal Components Analysis (PCA), i.e. the linear dimension reduction technique, allowing identifying mutually orthogonal dimensions of the highest variance within the framework of the original data and performing the data projection into the space with the lower number of dimensions created from the subset of constituents with the highest variance).

Primer software enabled the following; the purpose of MDS can thus be simply stated: it constructs a “map” or “configuration” of the samples, in a specified number of dimensions, which attempts to satisfy all the conditions imposed by the rank (dis)similarity matrix, e.g. if sample 1 has a higher similarity to sample 2 than it does to sample 3 then sample 1 will be closer on the map to sample 2 than it is to sample 3. *Surfer's* main purpose is to create contour and surface maps. It has been equipped also with the tools to perform several operations on the data introduced, as well as effectively presenting the results.

Corel Draw contains the software to prepare the vector graphics, type documents, edit pictures, and to create animations. It improves the presentation of the maps created using the *Surfer* programme.

The Kriging method is optimal for small data sets (< 250 observations); Kriging with the default linear variogram, or Radial Basis Function with the multiquadric function, produce good representations of most data sets.

RESULTS AND DISCUSSION

Detailed discussion of changes in the basic physical and chemical parameters of the Roztoka Odrzańska sediments is beyond the scope of this paper and is discussed elsewhere.

Considering all the parameters analysed in these sediments the highest similarity can be found between the concentration of hydrogen ions (pH) and the contents of TOC and $CaCO_3$. The LOI is related to these parameters to a smaller extent. The second group of similarities is formed by the sand content and the percentage of DM. The muddy-clayey and > 2 mm fractions are the most conspicuous parameters here.

Statistical parameters of the TOC and heavy metal distributions in the < 0.20 mm fraction show high variability relative to that of the key physical and chemical parameters of the > 2 mm fraction (Table 1). The highest similarity in this sediment fraction concerns the concentrations of Co, TOC, Cd and Hg. Another group of similarities has been found for the concentrations of Cu and Pb, which show a strong relationship to the first group. The concentrations of Zn in the Roztoka Odrzańska sediments, however, differ substantially from all these. But the coefficients of the Pearson correlation (Table 2) among the elements analysed demonstrate high values, significant in all cases (positive correlation).

The content of TOC in the < 0.20 mm fraction shows a significant negative correlation with the sand content positive correlations with the muddy-clayey content, the LOI and the content of TOC in the < 2 mm fraction. On average the TOC concentrations are 1.5 times lower than in the < 2 mm fraction. The highest concentrations are found east and west of the

Table 1

Statistical distribution parameters for organic carbon (TOC %) and heavy metals (mg/kg) in Roztoka Odrzańska bottom sediments

Parameters	TOC [%]	Cu	Zn	Pb	Co	Cd	Hg
		[mg/kg]					
$X_{arith.}$	4.54	98	844	83	5	7.9	0.06
$X_{geo.}$	3.08	73	487	57	4	5	0.05
median	4.80	90	742	85	5	6.9	0.07
SD	2.97	64.9	705.7	57.26	2.68	5.9	0.032
CI	0.84	18.36	199.64	16.2	0.757	1.668	0.009
CV	65.5	66.1	83.6	68.9	56.7	75.1	54.1
skewness	–0.078	0.447	0.688	0.344	0.232	0.319	–0.487
Kurtosis	–1.468	–0.892	–0.463	–0.949	–0.267	–1.351	–1.416
minimum	0.22	8	38	4	< 1	0.4	< 0.01
maximum	9.30	209	2034	175	12	15.9	0.1

Fraction < 0.20 mm, n = 48; $X_{arith.}$ — arithmetic mean, $X_{geo.}$ — geometric mean, SD — standard deviation, CI — confidence interval, CV — coefficient of variation (SD/$X_{arith.}$ x 100)

Szczecin–Świnoujście water lane, and the lowest TOC content is typical for sediments in the river bank zone (Fig. 3).

Maps of the heavy metal distributions are similar in outline to the TOC distribution in the < 0.20 mm fraction. Differences relate mainly to the location and shape of, mainly, the maxima and minima.

Maximal Cd concentrations are located on the eastern side of the Szczecin–Świnoujście seaway along the Chełminek Island–Adamowa Island line. The second maximum appears in the southern part of the area, also to the east from the seaway. Locations of minimum Cd concentrations are the area north of the Kiełpiński Ostrów Island, the Trzebież region and two coastal areas east of Roztoka (Fig. 4).

The Zn concentrations are very similar to the Cd concentrations in distribution. Differences relate particularly to the location and shape of the maxima (Fig. 5).

The Pb distribution is similar too, and here the maxima are smaller in area, while bottom areas characterised by low Pb concentrations are larger (Fig. 6).

Compared to these, the Cu distribution, differs markedly. In this case we can see two concentration maxima. One situated in the northern part, on both sides of the seaway, and the second lies in the SE part. The latter has two areas of increased concentrations, one near Kiełpiński Ostrów, on the western part of the seaway, and the second close to Adamowa Island. Regions of low Cu values overlap similar regions for the metals described above (Fig. 7).

Yet more different are cobalt concentrations. Regions of Co maxima are grouped only on the eastern part of the seaway and they comprise four local centres: one near Gąsierzyno, the second in the area of Adamowa Island, with smaller centres around Stepnica and NW of that port respectively (Fig. 8).

The mercury distribution is more uniform. However, it has been assumed the number of classes similar as for the previous metals. The spatial variability of Hg differs little from the absolute values. A large area of Hg maxima extend from Trzebież to Adamowa Island, where three local points of high concentrations were additionally determined. High Hg concentrations were found around the port in Stepnica and in the south near the border with Domiąża (Fig. 9).

As regards parameters of the < 0.20 mm fraction we can distinguish two groups of similar stations. The first one, which

Table 2

Values of Pearson coefficients of correlation between the chemical elements analysed in the Roztoka Odrzańska bottom sediments

	Corg.	Cu	Zn	Pb	Co	Cd	Hg
Corg.	X	0.594	0.821	0.774	0.633	0.862	0.781
Cu		X	0.729	0.793	0.642	0.737	0.604
Zn			X	0.917	0.653	0.941	0.769
Pb				X	0.722	0.897	0.732
Co					X	0.692	0.602
Cd						X	0.802
Hg							X

Fraction < 0.20 mm, n = 48

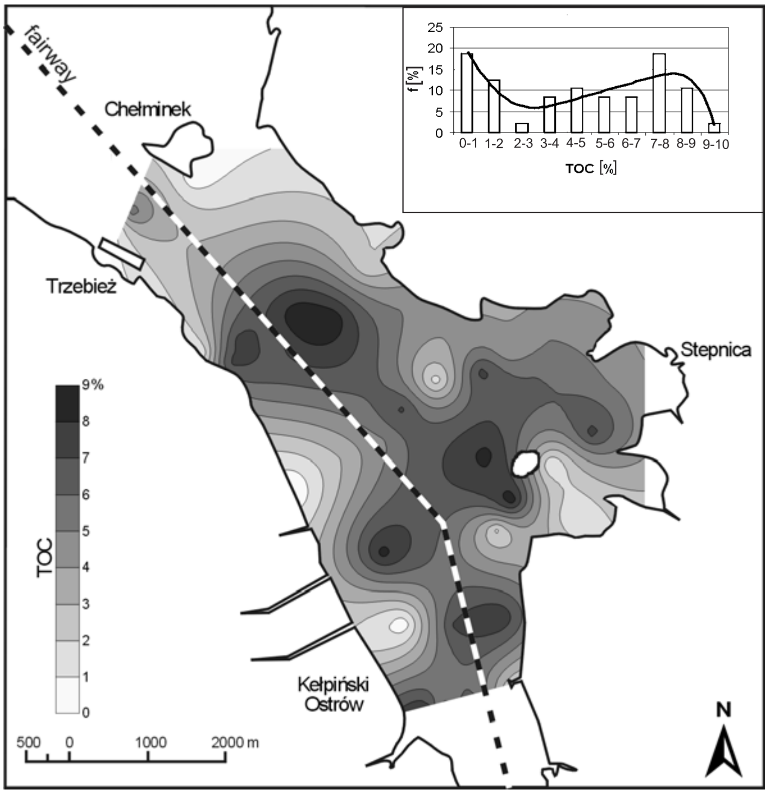

Fig. 3. Distribution map and histogram and compensation curve for distribution of organic carbon, fraction < 0.20 mm

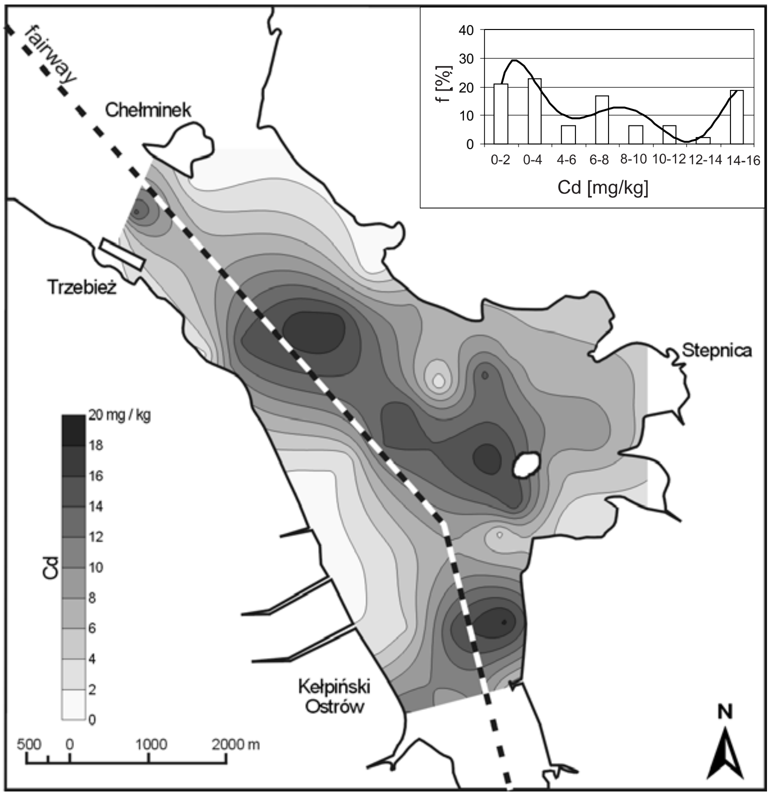

Fig. 4. Distribution map and histogram and compensation curve for distribution of cadmium, fraction < 0.20 mm

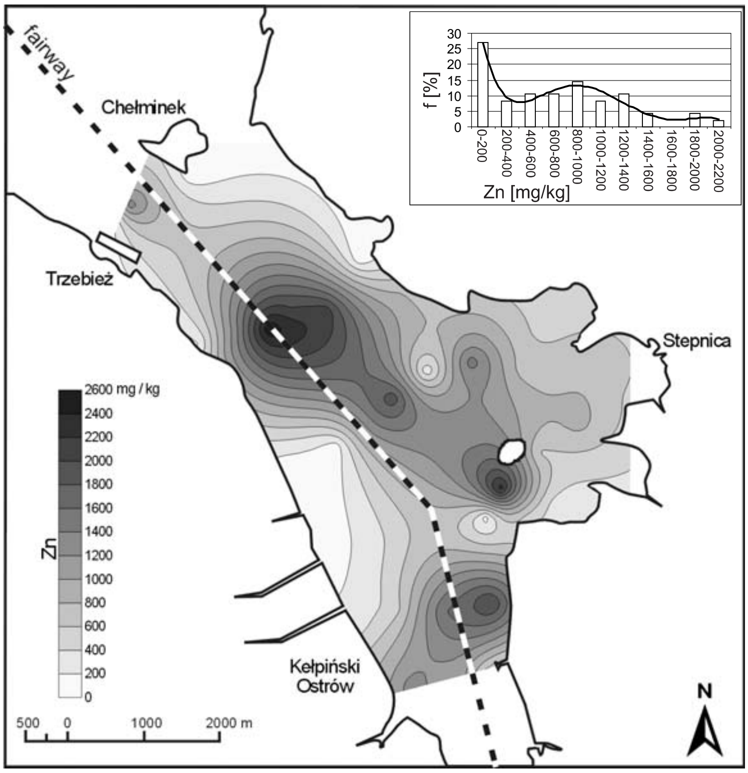

Fig. 5. Distribution map and histogram and compensation curve for distribution of zinc, fraction < 0.20 mm

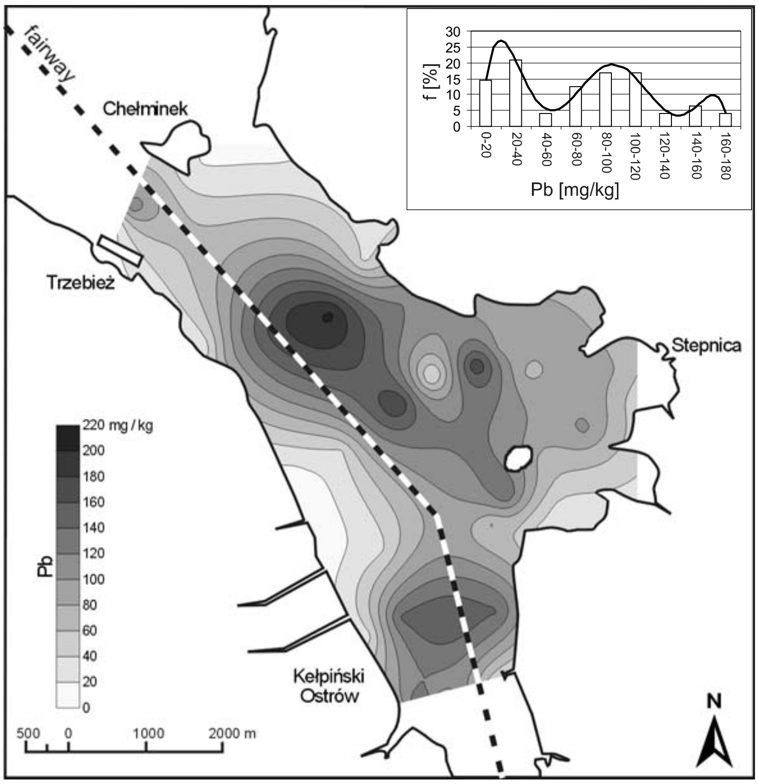

Fig. 6. Distribution map and histogram and compensation curve for distribution of lead, fraction < 0.20 mm

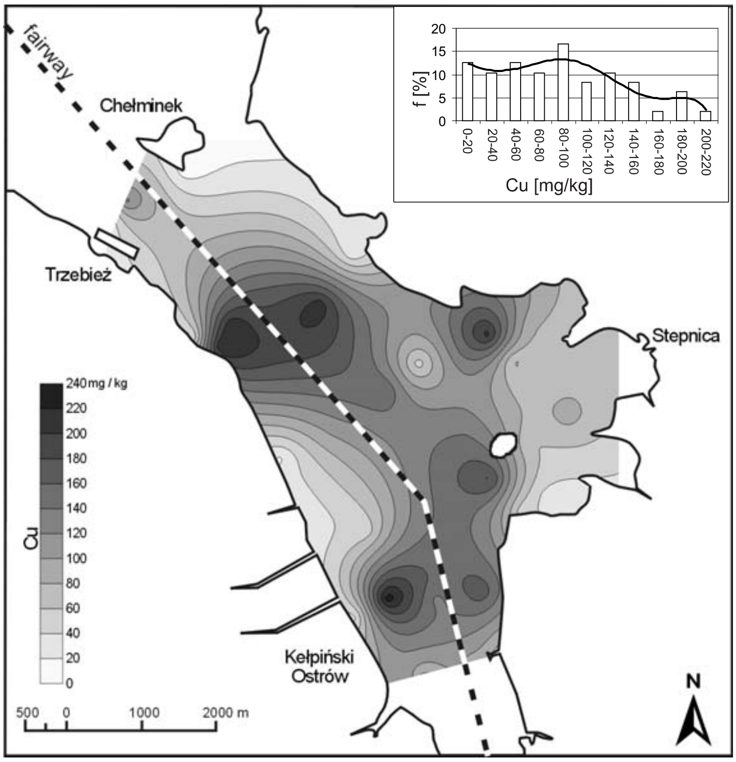

Fig. 7. Distribution map and histogram and compensation curve for distribution of copper, fraction < 0.20 mm

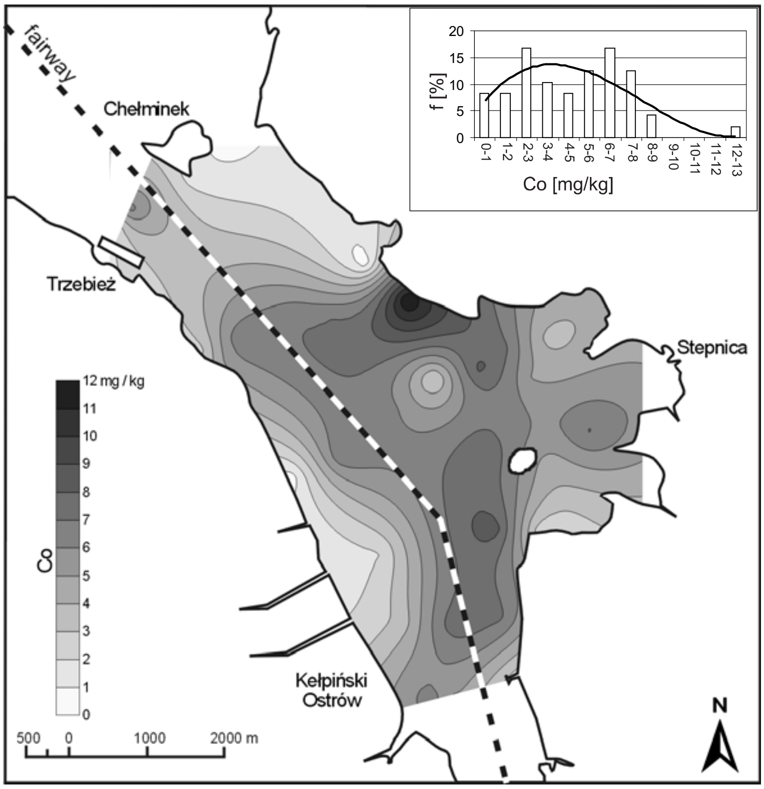

Fig. 8. Distribution map and histogram and compensation curve for distribution of cobalt, fraction < 0.20 mm

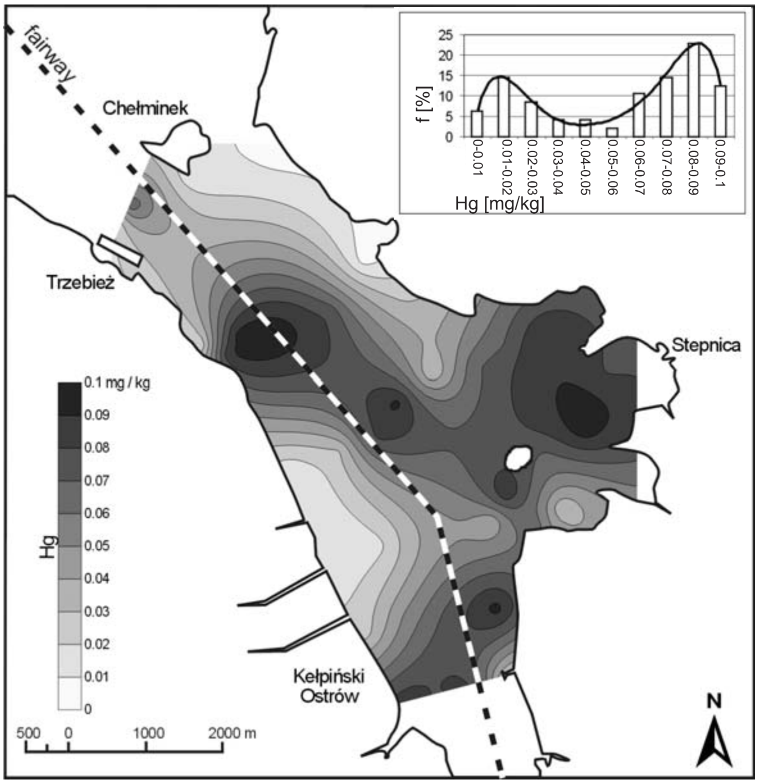

Fig. 9. Distribution map and histogram and compensation curve for distribution of mercury, fraction < 0.20 mm

comprises three distinct subgroups, covers the southern stations (nearby the border with Domiąża), the northern stations (bordering the Zalew Szczeciński) as well as the stations close to the shore. The second group comprises the stations 9–11, 17, 28, 36 and 39, close to the seaway. This pattern reflects the hydrological system of Roztoka, which contrasts with that in the southern part of the area, nearby the boundary with Domiąża, where the Odra flows quickly. On flowing into the funnel-shaped area of Roztoka it loses a part of its transporting power, and loses a further part where the Szczecin–Świnoujście seaway changes its direction. The northern area, nearby the boundary with Zalew Szczeciński also shows hydrodynamic variations, with higher salinities on our side, and increases in water circulation on the other. Additionally, that area is divided by Chełminek Island, east of which is situated the seaway. After having flowed through all of Roztoka, part of the sediment carried by the river has already been already deposited and therefore in the northern part the sediments are generally more pure as a rule. Stations close to the shore are generally affected by strong wave action, both wind-formed and generated by intense vessel traffic. This holds especially for places situated close to the Szczecin–Świnoujście seaway as well as to entrances to the ports of Trzebież and Stepnica. In those areas there is an outflow of the finer fractions, which locally accumulate in that highly complicated waterway. That system is additionally modified by the fishing nets placed there. The separate group is composed of the central stations situated relatively close to the seaway. In those areas the accumulation of pollutants and sediment materials is largely determined by the vessels which navigate through the seaway. Each such passage results in the remobilisation of sediments not only in the seaway channel, but also outside it through wave generation. Additionally, the situation is complicated by dredging.

In 1996 the concentrations of Zn, Cu, Pb, Cd and Hg in the surface waters of Roztoka Odrzańska were lower than the boundary values for river water (Rozporządzenie..., 1991) and may be categorised as class I of purity. In Poland, Co concentrations are not covered by standards. According to the 1999 researches the waters of Roztoka should also be classified as class I of purity because of the low concentrations of Zn (0.0074–0.0223 mg/l), Cu (0.0046–0.0066 mg/l), Pb (0.0012–0.0017 mg/l), Cd (< 00001 mg/l) and Hg (0.0001–0.0004 mg/l).

In the geochemical profile situated at the boundary of Roztoka Odrzańska and Domiąża (Figs. 1b and 2) the research stations were placed as follows: station 44 was sited in the central part of the seaway; stations 43 and 45 were arranged at the boundary of the seaway route; station 41 was sited on the production of Wąski Nurt (Domiąża), and the station 39 was situated on the production of the mouth of the River Krępa and the Jasienica Channel. Parameters for the < 0.20 mm fraction reach, in the axis of Szczecin–Świnoujście seaway, medium values for the profile. That station does not differ from the majority of the stations along the profile. The lowest concentrations of Cd, Zn, Pb and Co are found in the stations sited east of the seaway. The border stations, in particular, sitted close to the shore, are characterised by metal concentrations close to zero. This is evidently caused by the vessel traffic and by waves generated by them, which, moving along the shore, cause the outflow of fine fractions into more sheltered places. This pattern holds also for the distribution of Cu and Hg. Relatively high

Table 3

Level of heavy metals [mg/kg] subconcentration in Roztoka Odrzańska bottom sediments as compared to the geochemical background of Polish water sediments and selected water reservoirs

Water sediments	Cu	Zn	Pb	Co	Cd	Hg
	[mg/kg]					
geochemical background of water sediments in Poland*	16.4	13.2	7.6	2.4	>15.7	>1.2
water sediment of Poland**	4.7	3.4	1.2	1.2	2.8	0.5
Odra River***	3.2	5.6	1.3	1.2	8.7	0.3
Lake Dabie ***	5.2	3.8	2.0	0.9	5.6	0.3
Zalew Szczeciński lagoon***	4.1	5.0	1.5	0.8	4.6	0.3
Odra River — Domiąża****	0.9	1.1	1.1	1.2	0.8	1.1

Calculations were based on average levels of metals concentration as per: * — Bojakowska *et al.*, 1996; ** — Lis and Pasieczna, 1995; *** — Lis and Pasieczna, 1998; **** — Piotrowski and Łaba-Mydłowska (2003); in all cases the grain fraction < 0.20 mm was analysed

concentrations of Cu were are observed at station 46, though the other two eastern stations show low concentrations, typical for the metals described above. High concentrations of Hg were seen at station 45, sited on the boundary of the seaway; the border stations show low concentrations. TOC concentrations show the same pattern as the first group of metals. Another characteristic feature of that profile is the relatively high values of metal and TOC concentrations at the western border stations, typically a little above the average for the profile. The minimum values west of the seaway were found at the station 41, sited on the production of Wąski Nurt of Domiąża. These results show the significance of the distribution of the sand and muddy-clayey fractions. Sand accumulates in those places where we can observe low concentrations of metals and TOC. The location of the maximum concentrations may relate to the delivery of those substances by the River Krępa and Jasienicki Channel waters, although this seems improbable because of the purification of the outflow from the adjoining phospho-gypsum storage yard of ZCh “Police”. An other possibility, acting by itself or in tandem with the above, pH and Eh where the Wąski Nurt waters and the Krępa and Jasienicki Channel mounts meat. This question needs further study.

According to the draft subaqueous sediment classification system (Bojakowska and Sokołowska, 1998; Bojakowska, 2001) only in 1996 were the concentrations within the limits for the first class of sediment purity.

However, if to the maximum recorded values of metal diconcentrations were taken as the criterion, the sediments of Roztoka Odrzańska should be regarded as class IV in the case of concentrations of Cd, Zn and Pb, and as class III for Cu.

In the draft sediment classification given by Bojakowska (2001) Co concentrations are not quoted, though using the previous draft sediment classification system (Bojakowska and Sokołowska, 1998) where parameters of its distribution such as: $x_{arith.}$, $x_{arith} + SD$, Q_{75} would place the sediments in to class I, the maximum values being within the limits for class II of purity.

Levels of heavy metal pollution of the bottom sediments of Roztoka Odrzańska can be shown by the percentage share of the research stations in particular classes of purity, specified for the analysed metals (classification according to Bojakowska, 2001). The worst situation as regards the purity of the sediments examined concerns concentrations of Cd: 58.3% of the stations show concentrations equivalent to class IV of purity. 6.3% of stations may be assigned to class III, 25% to class II and 10.4% to class I. The other metal strongly polluting the sediments of Roztoka Odrzańska is Zn, for which the share of stations referable to class IV was 37.4%, with 31.3% class III 6.3% in class II and in 25% in class I. As regards Pb, 2.1% of stations could be referred to class IV, 37.5% to classes III and II and 22.9% to class I. For Cu, no concentrations referable to class IV were recorded; 45.8% could be assigned to class III, 41.7% to class II and 12.5% to class I. For mercury, all concentrations found at all stations are within the limits for the class I of purity.

To sum up, the bottom sediments of Roztoka Odrzańska, in 1996, expressed as concentrations of Cd, Zn, Pb, Cu and Hg, could be classified (*cf.* Bojakowska, 2001; which excluded Co concentrations), at 58.3% of the research stations as class IV of purity; 14.6% could be referred to class III, 18.8% to class II and 8.3% to class I. Excessive pollution of the sediments of Roztoka Odrzańska, defined here as the share of the stations assignable to class IV of purity, was determined mainly by the concentrations of Cd and Zn as well as, to a lower degree, by Pb. The purest sediments as regards heavy metal concentrations, are in the northern part of Roztoka, on the borderline with Zalew Szczeciński — stations 1, 3 and 4 as well as station 47 in the south, close to the shore. The stations characterised by class II of purity are those in the central part of the area situated west of the Szczecin–Świnoujście seaway (stations 6, 13, 14 and 15) as well as the stations situated east of the seaway, located both close to the shore and some distance from it.

In 1999, we observed by comparison some changes in the sediments of Roztoka Odrzańska though it should be emphasised that any comparison is tentative as only 4 samples were collected in 1999. At those four stations Cu and Pb concentrations demonstrated values referable to class II of purity, Zn and Cd concentrations were within the standards for class III, and Hg concentrations were within class IV *cf.*

Table 4

Concentrations of heavy metals [mg/kg] in Roztoka Odrzańska bottom sediments in 1999

Parameters	Cu	Zn	Pb	Co	Cd	Hg
	[mg/kg]					
$X_{arith.}$	87	794	82	9	3.8	1.34
minimum	75	757	77	8	3.6	1.15
maximum	95	841	89	10	4.1	1.59

fraction < 0.20 mm, *n* = 4

Bojakowska, 2001). Cobalt concentrations did not exceed the limits for class I (vide Bojakowska and Sokołowska, 1998). Thus all four stations of 1999 should be classified as highly polluted, class IV sediments, because of the excessive Hg concentrations.

Heavy metal concentrations in the Roztoka Odrzańska sediments show a linear dependence, at a significance level of 0.05, with such parameters as:

— sand content (2–0.063 mm): negative correlation,

— mud content (< 0.063 mm), LOI and TOC in the < 2 mm fraction: positive correlations,

Typically, increased concentrations of the following elements are found in contaminated sediments: mercury, cadmium and silver up to several mg/kg, arsenic, chromium, copper, nickel and lead up to several hundred mg/kg, and zinc up to several thousand. However, their content in uncontaminated freshwater sediments is low; not exceeding several dozen mg/kg for zinc, 0.5 mg/kg for cadmium and 0.05 mg/kg for mercury (Faulth *et al*., 1985; British...., 1993; Bojakowska and Borucki, 1994; Lis and Pasieczna, 1995; Bojakowska *et al*., 1996, 1998; Bojakowska, 2001). Table 3 shows a breakdown of heavy metal concentrations in the Roztoka Odrzańska sediments compared both to the adjacent areas and the geochemical background of subaqueous sediments in Poland (Piotrowski and Łaba-Mydłowska, 2003; tables 2 and 5).

As compared to the Domiąża sediments, the area adjoining the research area, also studied in 1996 may show slightly elevated concentrations of cobalt, zinc, lead and mercury, and lower concentrations of cadmium and copper in the Roztoka Odrzańska sediments.

The highest metal concentrations in the Roztoka Odrzańska sediments are found in the specifications of the data with the values of the assumed geochemical background.

As compared to the Odra River sediments, the Roztoka sediments demonstrate, in particular, higher concentrations of cadmium, zinc and copper, insignificantly higher concentrations of lead and cobalt, and lower concentrations of mercury. They show a similar relationship to the sediments of Zalew Szczeciński and Lake Dąbie, though showing also lower concentrations of cobalt.

The 1999 results demonstrated insignificantly lower average concentrations of Cu, Zn and Pb, and less than half the content of cadmium. But the concentrations of cobalt (1.8x) and especially mercury (22.7x) were higher than the average levels in 1996 (Table 4). The observed concentrations fall within the concentration limits recorded in 1996 for Cu, Zn, Pb, Cd and Co, but they exceed these limits considerably for Hg. As in the case of the Domiąża sediments, the observed differences can be explained by a selective inflow of heavy metals into the research area after the 1997 flood (Piotrowski and Łaba-Mydłowska, 2003; Piotrowski, 2003*c*).

The accumulation of sediments contaminated with heavy metals and other substances, both in the river bed and outside it, is controlled mainly by sorting of grains by density and size, mixing with sediments delivered by tributaries, erosion of the banks and the volume of deposition on alluvial plains (Macklin, 1996). In river beds in temperate climates the highest metal concentrations are observed most frequently in fine-grained sediments close to the banks and in small bays, the concentrations being substantially lower in the mainstream zone (Bubb *et al*., 1991). This pattern is modified in case of the Domiąża and Roztoka Odrzańska sediments by:

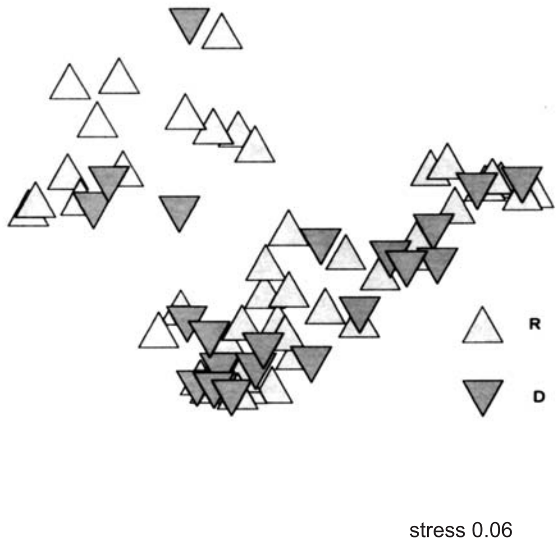

Fig. 10. Dispersion of the bottom sediment samples from Roztoka Odrzańska and Domiąża on the basis of MDS analysis

Key parameters in the < 2 mm fraction; R — Roztoka Odrzańska; D — Domiąża

— anthropogenic conversion of the natural river system,

— heavy river traffic,

— continuous dredging of the Szczecin–Świnoujście water lane and port canals and basins,

— deposition of contaminants from reloading activities in the Szczecin port.

Comparison of average values of the parameters analysed in the < 2 mm fraction and concentrations of TOC and heavy metals in the < 0.20 mm fraction does not reveal significant (at a significance level of 0.05) differences between the values calculated for the sediments of Domiąża and Roztoka Odrzańska — except for the content of $CaCO_3$ in the < 2 mm fraction. But comparison of the parameter distributions examined reveals distinct differences between the two areas, except for the ignition loss distributions which are comparable.

Dendrograms generated by the analysis of pile-ups do not demonstrate any important differences between the sediments of those two areas examined in 1996, creating one, partly homogeneous seaward section of the River Odra. Dendrograms developed both for the key parameters and concentrations of TOC and heavy metals in the < 0.20 mm fraction demonstrate a dispersion and mix of individual research points. In other words, the Domiąża and Roztoka Odrzańska points do not form separate and clearly distinct groups of similarities.

The same picture is shown by principal component analysis (PCA) of the parameters analysed in the < 2 mm fraction, where the samples from Domiąża agree with the field of grouping the samples from Roztoka Odrzańska. A clearer picture (although similar to that obtained by PCA) is produced by the non-metric multidimensional scaling method (MDS) on the diagram of which (Fig. 10) the points of both areas agree with each other. Stress < 0.1 corresponds to a good ordination with no real prospect of a misleading interpretation.

The points, taken together, from two groups on the diagram: a bottom one and an upper one. The upper group is made up of points 6, 7, 18, 21, 22, 24, 25, 26, 29, 30, 32, 33 and 34 in the Roztoka Odrzańska area and points 4, 5, 6 and 7 in the Domiąża area. The bottom group is made up of the remaining points from both areas. Although this division of the points into two groups is quite clear, it does not correspond to their spatial distribution. The upper group is represented by isolated points in the central part of Roztoka situated both east and west of the water lane and three points at Domiąża located on the narrow stream, and one point situated on the water lane adjacent to the Roztoka Odrzańska area. Moreover, a lack of clear differences between the sediments of Domiąża and Roztoka Odrzańska is shown by principal component analysis (PCA) made for concentrations of organic carbon and heavy metals in the < 0.20 mm fraction, in which only one factor is separated and thus we do not obtain a three-dimensional picture; nevertheless, it indicates little difference between the deposits of these two areas of the Odra, regardless of their location of deposition, and despite the hydrochemical differences between them.

CONCLUSIONS

The mobility, toxicity and bio-availability of heavy metals in a given ecosystem depends on the way they are fixed in the sediment. To predict this, the Tessier pattern is used most frequently (Tessier *et al*., 1979). This pattern shows that the first heavy metal fraction to be fixed by processes of physical and chemical sorption and ion exchange, is the most labile and bio-available one. An increase in concentration of hydrogen, calcium and magnesium ions results in displacement of metals from their sorption centres, usually in the form of simple and toxic ions (Sunda and Gillespie, 1979; Petersen, 1982; Peterson *et al*., 1984; Baccini, 1985). Concentrations of heavy metals fixed in this form clearly correlate with concentrations of metals in organisms living in the sediments (Lum and Gammon, 1985; Tessier and Campbell, 1987). The harmful influence of contaminated sediments on water organisms has been widely documented (Smal and Salomons, 1995; Calmano and Förstner, 1995; Reichardt, 1996; Hansen, 1996).

Visibly increased concentrations were observed in saline marshes and, to a slightly lesser extent, in "muddy" sediments (silts) due to the presence of molecules with large active surface areas, e.g. organic matter, oxides and hydroxides of Mn and Fe, and silty minerals (Van den Berg *et al*., 1999; Rate *et al*., 2000; Lee and Cundy, 2001). Taking into consideration the entire river system another pattern can be observed: the heavy metal concentration increases gradually from the riverhead to its estuary (Wright and Mason, 1999; Ronco *et al*., 2001). The concentration of heavy metals in sediments varies depending on seasonal changes and depends on seasonal changes in the biological production and hydrology of a given area. For example, in the River Humber increased concentrations of Cu, Pb and Zn were observed in winter, spring and summer, but such increases were only observed in winter in the Thames, Orwell and Stour Rivers (Wright and Mason, 1999; Turner, 2000).

Contamination of the bottom sediments in Domiąża and Roztoka Odrzańska is unquestionable, especially as regards cadmium, copper, zinc, lead and cobalt concentrations. Moreover, the sediments in the entire Odra River estuary area exceed the boundary values for some metals, e.g.: cadmium, zinc, copper, chromium, arsenic and lead.

The share of mobile forms of heavy metals in the bottom sediments of the Odra River estuary is very large and in some cases these forms account for as much as 80% of the total metal content (Protasowicki and Niedźwiedzki, 1991) creating a serious threat to organisms which inhabit this area.

An attempt to use the bottom sediments, extracted in the course of dredging work from the Odra River estuary, for agricultural purposes failed. In many cases increased heavy metal concentrations were found in the plants cultivated on these sediments (Niedźwiedzki and Tran van Chinh, 1990).

Contamination of the Odra River estuary environment with heavy metals has already been reflected in increased concentrations of some metals in planktonic organisms. From 1984 to 1988 decreased levels of mercury and zinc were observed along with increased concentrations of lead, cadmium and copper in these organisms. Increased contents of these toxic metals may affect the development of planktonic organisms and consequently impact on the trophic chain. So far, no increase in concentration of the metals examined has been observed in the tissues of molluscs and fish from the Odra River estuary (Protasowicki and Niedźwiedzki, 1991; Mutko, 1994; Piotrowski, 2000*a*, *b*).

Subsequent to the preparation of this work significant new work on the pollution of the Odra River ecosystem by heavy metals and other substances has been published (Adamiec and Helios-Rybicka, 2002*a*, *b*; Helios-Rybicka *et al.*, 2002*a*, *b*; Wolska and Namieśnik, 2002*a*, *b*). These results of the IOP (International Odra Project) are difficult to compare with the results outlined here because of the very different numbers of samples from Roztoka Odrzańska — here 48 in 1996 and 4 in 1999 while in the IOP programme only one sample from "Roztoka Orzańska" was analysed, and that without the cobalt content. In general, though, the results given here accord with the IOP results, as regards the high load of the Odra River ecosystem with Cd and Zn and to a lesser extent with Pb and Cu. The pattern obtained after the denser sampling of deposits of the Odra estuary shows some distinct phenomena, among which importantly are the estuary's geochemistry before the 1997 flood, during the flood and after the flood (Piotrowski, 2003*a*, *b*). Significant here is the high and very high pollution of the Odra River ecosystem with Cd and Zn observed throughout, while the Hg, Cu and Pb loads show regional differences (Helios-Rybicka *et al*., 2002*b*). Decreases in heavy metal concentrations have taken place in the northern part of the Odra estuary i.e. in Zalew Szczeciński (Adamiec and Helios-Rybicka, 2002*a*, *b*; Helios-Rybicka *et al*., 2002*a*, *b*; Wolska and Namieśnik, 2002*a*, *b*).

The IOP Programme showed that, in the Widuchowa profile, the highest metal contents were observed in the 1997 deposits, i.e. those formed during the "Flood of the Century". In deposits formed after the flood, the metal contents decreased to the same level as that before the flood. For instance, Hg contents have decreased by half and Zn by one third (Adamiec and Helios-Rybicka, 2002*a*, *b*; Helios-Rybicka *et al*., 2002*a*, *b*; Wolska and

Namieśnik, 2002*a*, *b*). These observations help explain the observed changes in heavy metal concentrations in deposits of the Odra estuary after the 1997 flood (Piotrowski, 2003*c*).

The management of contaminated sediments extracted in the course of dredging the Szczecin–Świnoujście water lane and the port basins and canals is a separate problem. Pollutants contained in the sediments, especially PAHs and heavy metals, may be released to the aqueous environment during dredging in locations where contaminated sediments are stored. At present many countries consider the sediments extracted from a river bottom to be waste which, depending on its chemical composition, can be freely re-introduced into the environment, or used with some restrictions or, if excessively contaminated, treated or deposited in a storage area (Bojakowska, 2001).

The Roztoka Odrzańska estuary has a highly complicated hydrology, where the surface layer of the bottom sediments is continuously remodelled and shifted. In this connection it should be anticipated that part of the dredging spoil should be polluted not only with heavy metals, but also with the WWA, PCB compounds and to a lesser degree with OCPs (Piotrowski, 2003*a*). Analyses of polynuclear aromatic hydrocarbon (PAHs) concentrations reveal very high concentrations of these compounds, typical of heavily contaminated soils.

The Odra River estuary sediments have not yet been fully investigated as regards their purity and toxicity to benthic organisms. Studies, commenced at the Institute of Marine Sciences a few years ago, aim to provide a detailed geochemical description encompassing concentrations of heavy metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), chloroorganic pesticides and oil derivative hydrocarbons in the sediments. Since there is a threat to the natural balance of the trophic chain, changes in heavy metal concentrations in soft tissues and shells of selected species of fresh water molluscs are watched closely and compared to their concentrations in the sediments and the surface layers of water (Piotrowski, 2000*a*, *b*).

Molluscs play an important role in the self-purification of aqueous environments by fixing heavy metals in shells, and so increased monitoring of the degree and kind of pollution of the sediments of the Odra River estuary and of their influence on the local organisms should be undertaken. Strategies to reduce the pollution of the sediments and to aid remediation would be desirable.

In 1996 and in 1999 concentrations of Zn, Cu, Pb, Cd and Hg in the surface waters of Roztoka Odrzańska were within the limits for class I of purity. The heavy metal distributions are similar in outline to TOC distribution in the < 0.20 mm fraction. Differences relate mainly to the concentration maxima and minima. The TOC content in the < 0.20 mm fraction shows a significant negative correlation with the sand content, a positive correlation with the mud content the LOI and the content of TOC in the < 0.20 mm fraction. On average the TOC concentrations are 1.5 times lower than in the < 2 mm fraction. The highest concentrations are found east and west of the Szczecin–Świnoujście water lane, and the lowest TOC content is typical for sediments in the riverbank zone. Overall, the bottom sediments of Roztoka Odrzańska, in 1996, expressed as concentrations of Cd, Zn, Pb, Cu and Hg, could be referred to class IV of purity (58.3%), to class III (14.6%), to class II (18.8%) and to class I (8.3%). The excessive pollution of the sediments of Roztoka Odrzańska is governed mainly by Cd and Zn and, to a lower degree, by Pb.

Concentrations of heavy metals in the Roztoka Odrzańska sediments show significant linear relationships, $\alpha = 0.05$: with sand content (negative correlation), with mud content, LOI and TOC in the < 2 mm fraction (positive correlations).

The 1999 results showed slightly lower average concentrations of Cu, Zn and Pb, and less than half the content of cadmium. But the concentrations of cobalt (1.8x) and especially mercury (22.7x) were higher than the average 1996 levels. The observed concentrations fall within the concentration limits recorded in 1996 for Cu, Zn, Pb, Cd and Co, but they exceed these limits considerably for Hg. As in the Domiąża sediments, the differences observed can be explained by a selective inflow of heavy metals into the research area after the 1997 flood.

There remains, as noted by the researches involved in the IOP project, an urgent need to monitor toxic pollutants in various parts of Odra River ecosystem, taking into account the Sediment Quality Assessment Triad — chemistry–toxicity–biota. Because of the specific, estuarine character of the area, with its strong anthropogenic influence, studies involving the appearance of metal species and of the stability of associated minerals, over a range of physical and chemical conditions, are desirable.

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