Polish Geological Institute Special Papers, 24 (2008): 15–22
Proceedings of the Conference "The abiotic environment – evaluation of changes and hazards – case studies"

CADMIUM IN SEDIMENTS OF POLISH MAJOR RIVERS AND THEIR TRIBUTARIES

Izabela BOJAKOWSKA[1], Tomasz GLIWICZ[1]

Abstract. Since 1991 systematic geochemical investigations of water sediments in Poland have been conducted to the order of the Chief Inspector for Environmental Protection. River sediments monitoring network in Poland includes 301 sites. In 80 observation sites (the primary network) sediment samples have been collected once a year and in the remaining sites, once every three years. Several-year long monitoring has indicated a significant decrease in cadmium content in river sediments in Poland. Sediments in nearly 70% sites investigated in the last 3-year-investigation-cycle were characterized by cadmium contents lower than 0.5 mg/kg. The cadmium content higher than 1 mg/kg was observed only in 22.6% of the observation points. Rivers whose sediments are most cadmium polluted include the two Upper Silesian rivers: the Przemsza and the Chechło rivers and one Mazovian river – Jeziorka River. The main pollution source of the sediments of the Upper Silesian rivers, including the Upper Warta River and the Upper Vistula River, is wastewater discharged from zinc and lead mines and smelters and industrial plants utilizing zinc and its compounds. Another cause of high cadmium contents in sediments are the wastewater discharges from metallurgical, electric, electronic, dye and paint and plastics plants. It can be observed in the Wieprz River, which receives a wastewater from Lublin via the Bystrzyca, the Jeziorka and the Warta rivers.

Key words: monitoring, pollution, cadmium, Vistula River, Odra River.

Abstrakt. Systematyczne geochemiczne badania osadów wodnych Polski są prowadzone na zlecenie Głównego Inspektora Ochrony Środowiska od 1991 roku. Sieć obserwacyjna obejmuje 301 punktów, spośród których w 80 lokalizacjach próbki pobierane są co roku, a w pozostałych raz na trzy lata. Kilkunastoletnie badania wykazały wyraźny spadek zawartości kadmu w osadach rzecznych w Polsce. Blisko 70% zbadanych osadów w ciągu ostatnich trzech lat charakteryzowało się zawartością kadmu niższą niż 0,5 mg/kg. Zawartość kadmu wyższą niż 1 mg/kg stwierdzono w 22,6% zbadanych próbek. Najwyższe zawartości kadmu odnotowywane są w osadach dwóch rzek górnośląskich: Przemszy i Chechle oraz mazowieckiej rzece – Jeziorce. Głównym źródłem zanieczyszczenia osadów rzek Górnego Śląska, włącznie z górną Wisłą i Wartą, są ścieki odprowadzane z kopalń, hut i zakładów przemysłowych wykorzystujących cynk i jego związki w produkcji. Inną przyczyną wysokich zawartości kadmu w osadach są ścieki odprowadzane z zakładów metalurgicznych, elektrycznych, elektronicznych, zakładów produkujących barwniki i farby oraz wytwarzających plastiki. Jest to obserwowane w osadach Wieprza, który jest odbiornikiem ścieków z Lublina (poprzez dopływ Bystrzyca), Jeziorce i Warcie.

S³owa kluczowe: monitoring, zanieczyszczenie, kadm, Wisła, Odra.

INTRODUCTION

Most heavy metals mobilized to the environment as a result of both natural processes and human economic activity are immobilized in sediments by physical and biochemical processes, and chemical reactions. High concentrations of hazardous components are usually noted in sediments close to pollution sources including sewage discharges from metal ore processing plants, chemical, metallurgical, electric and electronic plants, and waste disposal sites and lagoons located in river valleys (Birch *et al*., 2001; Brack *et al*., 2001; Lindstrom, 2001; Marques *et al*., 2001; Mecray *et al*., 2001; Reiss *et al*. 2004; US EPA, 1997). The water sediments are not only the sink of potentially toxic metals and metalloids and persistent organic pol-

[1] Polish Geological Institute, Rakowiecka 4, 00-975 Warszawa, Poland; e-mails:izabela.bojakowska@pgi.gov.pl; tomasz.gliwicz@pgi.gov.pl

lutants, but also the living site of different water organisms, which influence both circulation of nutrients and mobilization or fixation of toxic components (Bourg, Loch, 1995; Smal, Salomons, 1995; Hansen, 1996; Reichardt, 1996; McLaren *et al*., 2004). The negative influence of polluted sediments on the inhabitant organisms and the adjacent water environment can occur even when the level of pollution in the overlying water column does not exceed the allowable quality criteria. The polluted waters may reduce or eliminate many useful and ecologically significant animal species and may be dangerous to a human being. The highly toxic sediments may be the secondary pollution source for surface waters through remobilization induced by favourable physical and chemical processes. During floods and high water levels these sediments are transported down the river and deposited in other unpolluted sites. They may also become a pollution source for vegetation growing along the polluted rivers as well as soils in flood plains (Bojakowska, Sokołowska, 1995; Weng, Chen, 2000; Gabler, Schneider, 2000; Bordas, Bourg, 2001).

The cadmium is an element scattered in the Earth's crust. Its content in the lithosphere varies from 0.10 to 0.20 mg/kg. Cadmium minerals are scarce, because of their geochemical properties similar to zinc. The highest concentrations of this element occur in sphalerite (ZnS) that contains from 0.1 to 0.5% Cd and smitsonite ($ZnCO_3$) – up to 5% Cd (Stoeppler, 1991). The average cadmium content in fossil sediments and in recent unpolluted land sediments (soils, river and lacustrine sediments) is within the range of 0.4–0.8 mg/kg. Recent data of rivers sediments polluted by wastewater generated in mining and metallurgy of zinc-lead ores shows cadmium concentration sometimes even of a few hundred mg/kg (Stoeppler, 1991; Ciszewski, 1994). Apart from the mercury and lead, the cadmium belongs to the most dangerous metals due to its high-level of harmfulness to human beings and animals and a high degree of bioaccumulation caused by its easy absorption and relatively long retention in the organism. The PEL (probable effect levels) value for cadmium in sediments above which harmful effects to water organisms can often be observed, was determined as 3.5 mg/kg for the freshwater sediments and 4.2 mg/kg for the marine deposits (CMCE, 1999). Due to its attractive qualities cadmium is used in numerous branches of industry, above all in a production of nickel/cadmium batteries and dyes and pigments, in anticorrosive coatings of metal products, as a component of alloys and a stabilizing agent for plastics (mainly for PCV). The cadmium enters the environment via many routes, for example through mining and metallurgy processes of non-ferrous metals such as zinc, lead or copper, burning of coal, through the application of fertilizers.

METHODS AND SCOPE OF STUDIES

Since 1991 geochemical studies of water sediments in Poland aimed at controlling concentrations of heavy metals and some persistent organic pollutants in rivers and lakes have been conducted to the order of the Chief Inspector for Environmental Protection. The State Environmental Monitoring network of river sediments includes 301 sites. In 80 observation points (primary network) the sediment samples have been collected annually and in the remaining points – every three years. Sediment samples have been collected in summer within a riverbank zone where fine-grained suspended matter is deposited below the water surface. A grain fraction of <0.2 mm was used for chemical analyses of sediment samples. This fraction well reflects the trace element contents in the geological formation of a catchment area of a given river. The samples were analyzed for 20 elements (including cadmium) with an ICP-AES method after sample digestion in *aqua regia*. Sediment samples were digested in *aqua regia*, because only the share of element load, which is easily mobilized into the surface water, is interesting for purposes of evaluation of environmental pollution with heavy metals.

The Vistula River (length – 1048 km, basin area – 194 424 km^2), the longest river of Poland, receives huge amounts of sewages from the Upper Silesian coal and zinc-lead mines, smelters, industrial plants and cities located along the river (e.g. Oświęcim, Cracow, Tarnobrzeg, Sandomierz, Dęblin, Warsaw, Toruń, Bydgoszcz, Grudziądz). Another sources of the Vistula River pollutions are its tributaries, as well as leakages from industrial and municipal landfills located in the river valley. Monitoring observation points are located in:

- 23 sampling points along the course of the Vistula River (in following localities: Kiezmark, Tczew, Opalenie, Grudziądz, Fordon, Toruń, Nieszawa, Włocławek, Płock, Wyszogród, Warszawa, Góra Kalwaria, Gołąb, Piotrawin, Sandomierz, Tarnobrzeg, Nowy Korczyn, Niepołomice, Kraków, Tyniec, Oświęcim and Goczałkowice);
- 21 sampling points at mouth of the left sided tributaries of the Vistula River (Wierzyca, Wda, Brda, Zgłowiączka, Bzura, Jeziorka, Pilica, Radomka, Zagożdżonka, Iłżanka, Kamienna, Czarna Staszowska, Nida, Nidzica, Szreniawa, Prądnik, Rudawa, Chechło, Przemsza, Gostynia and Pszczynka);
- 21 sampling points at the mouth of the right sided tributaries of the Vistula River (Liwa, Osa, Drwęca, Mień, Skrwa, Wkra, Narew, Świder, Wilga, Wieprz, San, Łęg, Trześniówka, Wisłoka, Breń, Dunajec, Raba, Skawa, Soła, Biała and Iłownica; Fig. 1).

The Odra River, the second river in Poland (after Vistula) with its length of 854 km and the basin area of 118 861 km^2 is a recipient of colossal amounts of sewage, as well. Wastewaters are supplied from mines, coke works, steelworks and chemical plants of Ostrava–Karvina district (Czech Republic), and from mines and smelters and power plants of the Upper Silesia and the Legnica–Głogów copper district on the territory of Poland. Huge amounts of sewage are discharged from cities and industrial plants situated on the river (Szczecin, Schwedt, Frankfurt, Eisenhüttenstadt, Zielona Góra, Nowa Sól, Głogów, Brzeg Dolny, Wrocław, Brzeg, Kędzierzyn-Koźle, Racibórz, Ostrava). The monitoring observation points are placed in:

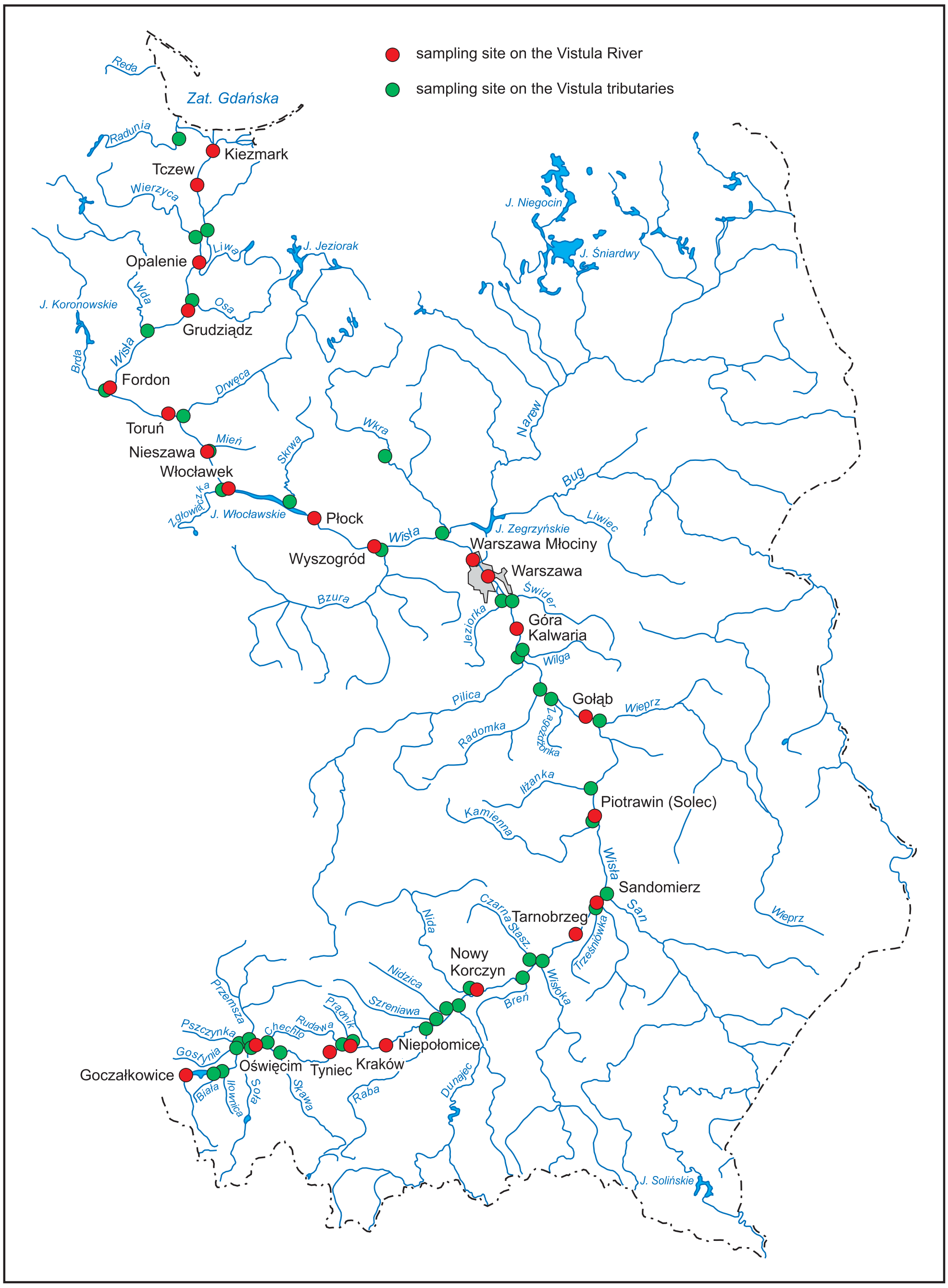

Fig. 1. Sampling sites on the Vistula River and its tributaries

- 17 points along the course of the Odra River (Chałupki, Racibórz, Koźle, Wróblin, Brzeg, Wrocław, Brzeg Dolny, Ścinawa, Biechów, Nowa Sól, Krosno Odrzańskie, Świecko, Kostrzyn, Gozdowice, Krajnik Dolny, Kołbaskowo and Police);
- 20 points at mouth of the tributaries of the Odra River (Ina, Płonia, Myśla, Warta, Nysa Łużycka, Bóbr, Obrzyca, Krzycki Rów, Rudna, Barycz, Ślęża, Oława, Stobrawa, Nysa Kłodzka, Mała Panew, Osobłoga, Kłodnica, Bierawka, Ruda and Olza; Fig. 2).

RESULTS AND DISCUSSION

Fifteen-year-long monitoring studies have indicated a significant decrease in the cadmium content in river sediments in Poland. This tendency is especially significant in sediments of high polluted rivers (Fig. 3). Cadmium concentrations in the Vistula bottom sediments varied within a very wide range of concentrations: from <0.5 (geochemical background value) to

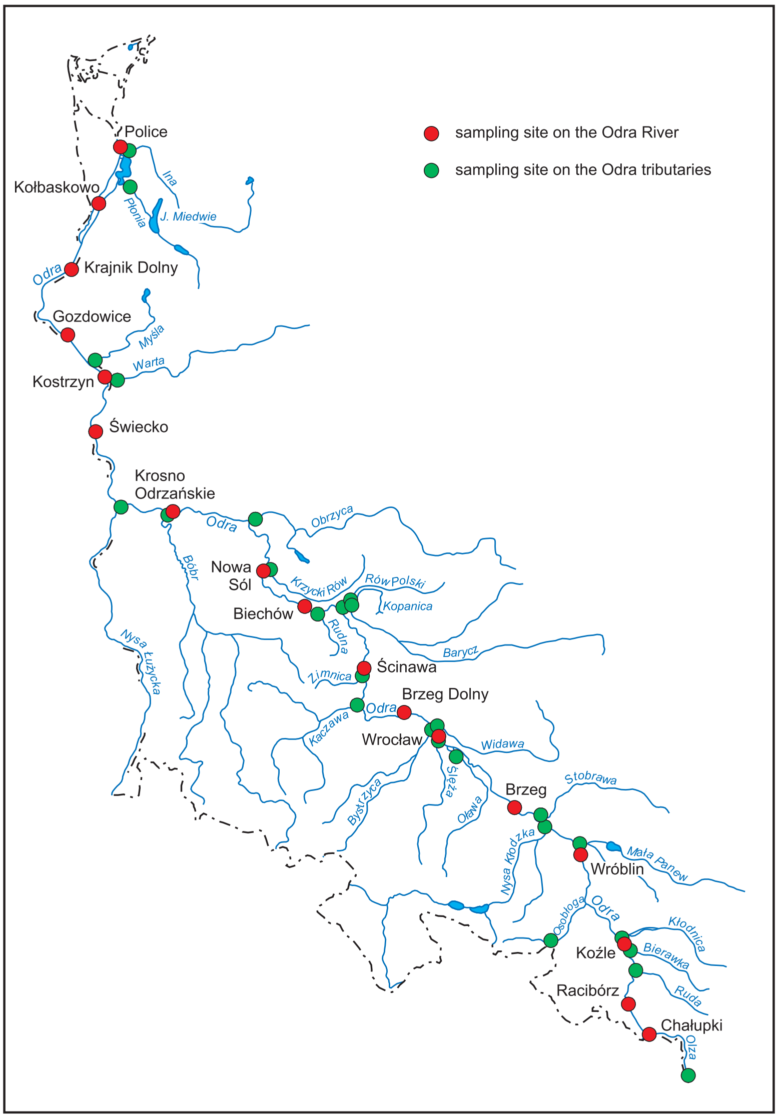

Fig. 2. Sampling sites on the Odra River and its tributaries

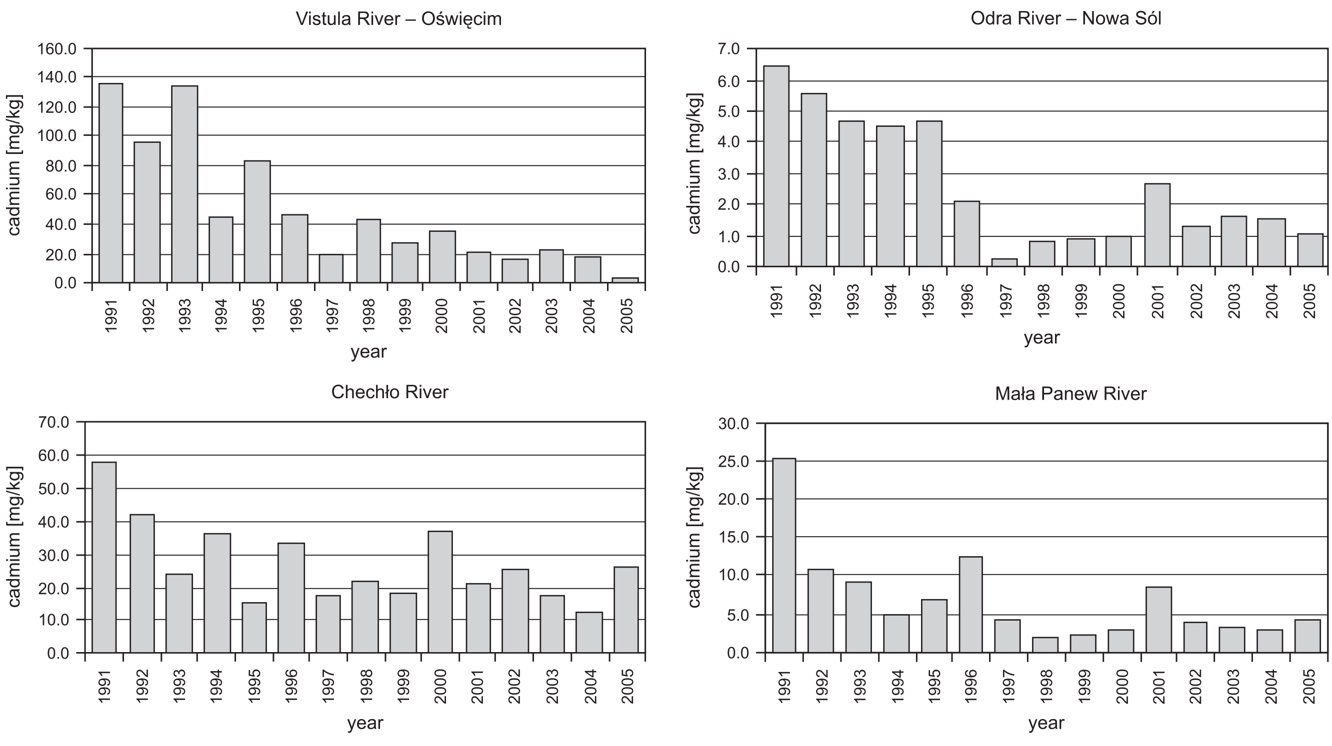

Fig. 3. Changes of cadmium concentration in sediments (1991–2005)

135 mg/kg. Its mean and median values are 7.1 mg/kg and 1.4 mg/kg, respectively. In the observation points situated along the course of the Vistula River the average cadmium concentrations in sediments are much diversified. In sediments of upper and middle course of the river – from Oświęcim to Wyszogród – high and increased cadmium contents are observed (Fig. 4). The highest cadmium concentrations are noticed in Oświęcim, below the Przemsza River inflow, and in Tyniec and Niepołomice (49.5, 16.2, 16.7 mg/kg, respectively). In the lower part of the Vistula River, especially below the Włocławek Lake dammed up on 675 km of the Vistula river course, the cadmium contents in the sediments higher than 1 mg/kg is seldom observed. Increased cadmium contents in the lower part of the Vistula River are noticed only in the sediments taken from the river in Tczew. The significant amounts of suspended materials and heavy metals transported by the Vistula River are stopped in the Włocławek Lake. Sediments of the Włocławek Lake are characterized by high contents of the cadmium up to 12.8 mg/kg. The average Cd content in the lake silts is 2.8 mg/kg (Bojakowska *et al.*, 2000). The observed decrease in the cadmium content in the sediments of the lower course of the Vistula River is caused as well by a major inflow of the Narew River waters which flow into the Vistula River on 550 km of its course. The average water flow in the Vistula River above the Narew River mouth is 570 m^3/s, and the average water flow in the Narew River is 291 m^3/s. The results obtained during 15 year observations show a decrease in the cadmium level in the Vistula River sediments during that period. It was found, however, that flood in 1997 increased Cd concentration in the sediments deposited near Tarnobrzeg and Piotrawin due to wash out and transporting of the earlier deposited sediment in the upper river course.

Among 42 studied tributaries of the Vistula River, the average Cd concentrations are higher than background concentration value in the sediments of 17 tributaries, and in the deposits of 10 tributaries the average Cd contents are higher than 1 mg/kg. The most cadmium-polluted Vistula tributaries are the Przemsza and Chechło rivers of highly urbanized Upper Silesia and Jeziorka River (Fig. 5). Their sediments contain average of 78.9, 29.3 and 36.1 mg/kg of cadmium, respectively. The raised levels of cadmium average concentrations characterized the sediments of Wieprz (6.5 mg/kg), Biała (5.9 mg/kg), Gostynia (3.6 mg/kg) and Bzura rivers (3.0 mg/kg) (Figs. 5, 6). Mean Cd contents higher than 1 mg/kg were also noted in deposits in Rudawa, Pszczynka and Breń. The main source of the cadmium pollution of the Przemsza and Chechło River sediments are wastewaters discharged from the mining industry and processing of zinc-lead ores and wastewaters discharged from Upper Silesian industrial plants using zinc and its compounds in production (zinc and its compounds contain admixture of cadmium). The high Cd concentrations observed in sediments of the Jeziorka River (tributary of the Vistula River on its 494 km) are caused by discharging wastewaters from Piaseczno and Konstancin-Jeziorna, in the Biała River sediments – by wastewaters from Bielsko-Biała and Czechowice-Dziedzice, in the Gostynia River – by wastewaters from Tychy and in the Wieprz River – by wastewaters from Lublin. In these sediments, the cadmium pollution is caused by wastewaters discharged from the electronic, electrical, paint and metallurgical industries. To some degree sediment pollution by cadmium is also due to a common use of zinc galvanizing pipes and a white paint containing zinc oxide.

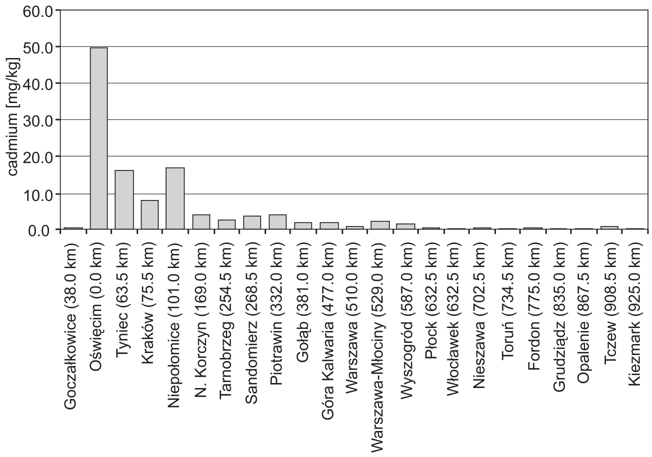

Fig. 4. Average cadmium contents in the Vistula River sediments (1991–2005)

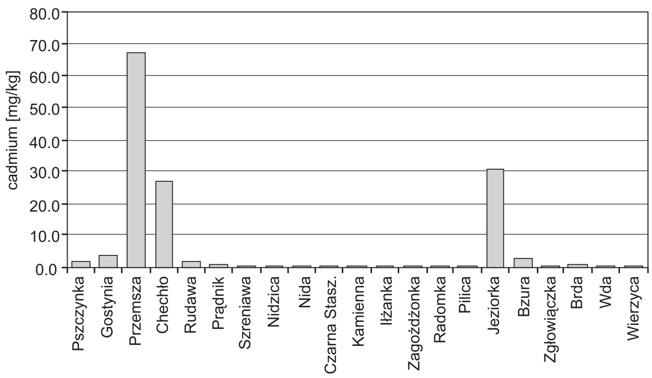

Fig. 5. Average cadmium contents in sediments of the right-sided Vistula River tributaries (1991–2005)

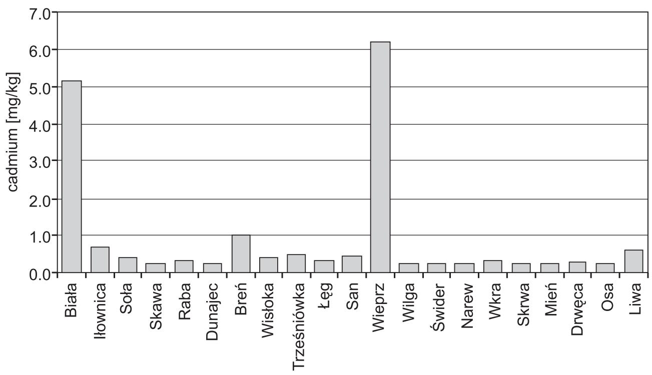

Fig. 6. Average cadmium contents in sediments of the left-sided Vistula River tributaries (1991–2005)

The cadmium concentration in the sediments of the Odra River is within a concentration range of from <0.5 (geochemical background value) to 7.2 mg/kg and its mean and median values correspond to 2.1 mg/kg and 1.6 mg/kg, respectively. These val-

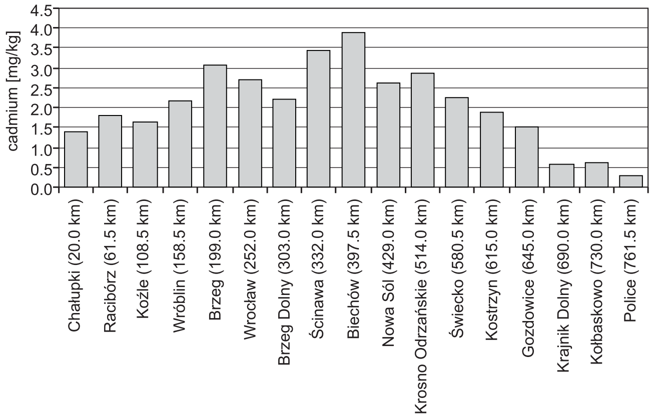

Fig. 7. Average cadmium contents in the Odra River sediments (1991–2005)

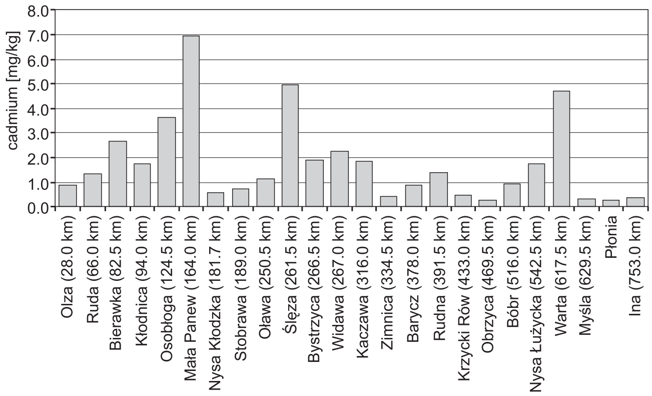

Fig. 8. Average cadmium contents in sediments of the Odra River tributaries (1991–2005)

ues are significantly smaller and less diversified than the values observed in the Vistula River. Average cadmium concentrations higher than 2 mg/kg are noticed in sediments deposited in the river from Wróblin to Kostrzyn with the uppermost values for sediments deposited in Biechów (Fig. 7). In the lower course of the Odra River, below the Warta River mouth, cadmium contents exceeding 1 mg/kg are seldom observed and average Cd contents lesser than 1 mg/kg are observed in the sediments of that part of the river course (Fig. 7). The observed decrease in the cadmium contents in the sediments of the lower Odra River is caused by a major inflow of the Warta River waters which influx into the Odra River in 617.6 km of its course. The average water flow in the Odra River above the Warta River mouth is 240 m^3/s, and the average water flow in the Warta River is 180 m^3/s. Cadmium is transported to the Odra River also in industrial and municipal wastewaters discharged from the cities located upon the river, such as: Racibórz, Kędzierzyn, Opole, Brzeg, Wrocław, Brzeg Dolny, Głogów, Nowa Sól.

Among 24 studied tributaries of the Odra River in the sediments of 18 tributaries the average Cd concentration are higher than the background concentration value. The most cadmium-polluted tributaries are Mała Panew, Ślęża, Warta and Osobłoga (Fig. 8), with the average cadmium concentration of 6.9, 5.0, 4.7 and 3.6 mg/kg, respectively. The raised levels of cadmium concentrations are also noticed in the sediments of Widawa (2.2 mg/kg) and Bierawka (2.7 mg/kg). Average Cd contents higher than 1 mg/kg were also noted in deposits in Ruda, Kłodnica, Oława, Bystrzyca, Kaczawa, Rudna, and Nysa Łużycka. The main source of the cadmium pollution of the Mała Panew River sediments are wastewaters discharged from mining industry and processing of zinc-lead ores and wastewaters discharged from the Upper Silesian industrial plants situated in the catchments area of this river. The high Cd concentrations observed in sediments of the Warta River are anthropogenic and result from a supply of communal and industrial sewages from cities located at the river, first of all from Poznań, Konin and Częstochowa. The increased cadmium contents in the sediments of Ślęża, Oława and Bystrzyca is caused by wastewater discharged from industrial plants localised in Wrocław. The increased Cd concentration in the sediments of the Ruda and Bierawka rivers are connected with discharging wastewaters from the Upper Silesian mines and towns, enlarged values of cadmium in the Kaczawa and Rudna River sediments are the result of discharging wastewaters from the Legnica–Głogów district.

CONCLUSION

The cadmium content in the Vistula River sediments is determined by the cadmium amount entering the environment by the industrial and municipal wastewater discharged to the Vistula River by cities located by the river and amount of cadmium inflowing to the Vistula River from its tributaries: Przemsza, Chechło, Gostynia, Biała, Wieprz and Jeziorka rivers. The observed decrease in the cadmium content in the sediments of the Lower Vistula River is caused by a major inflow of less polluted Narew River and a deposition of transported pollutants in the Włocławek Lake.

The cadmium is transported to the Odra River by industrial and municipal wastewaters discharged by the cities located by the river. The increased cadmium contents in the Odra River sediments are caused also by the discharge of wastewaters to the upper and middle part of the Odra River and its tributaries mainly the Mała Panew, Kłodnica, Bierawka, Kaczawa, Rudna and Zimnica rivers. Wastewaters are generated during the exploitation of raw material deposits and the processing of mineral raw materials and coals in the Upper and Lower Silesia. Significant amounts of cadmium are transported to the Odra River by its tributary – the Nysa Łużycka River.

Data from monitoring studies revealed a gradual decrease of the cadmium content in the river sediments during last 15 years. This tendency is clearly visible despite variations caused by differences in amounts of precipitation among years influencing amounts of terrigenic material entering water as a result of erosion, which, in turn, has an impact on concentration of the pollutants in the sediments. Undoubtedly the observed drop of cadmium contents in the sediments is caused mainly by the decrease in the amount of pollutants entering surface waters due to the reduced extraction of natural resources and industrial production in Poland as well as by starting new wastewater treatment plants and modernization and development of the old ones. The decrease in the amount of pollutants entering river waters with surface discharge is connected with a considerable reduction of emission of air pollutants by industrial plants.

Sediments in nearly 70% investigated sites in the last 3-year-investigation-cycle were characterized by cadmium contents lower than 0.5 mg/kg. The cadmium content higher than 1 mg/kg was observed in 22.6% of observation sites.

REFERENCES

BIRCH G., SIAKA M., OWENS C., 2001 — The source of anthropogenic heavy metals in fluvial sediments of a rural catchment: Coxes River, Australia. *Water, Air and Soil Pollution*, **126**, 1–2: 13–35.

BOJAKOWSKA I., GLIWICZ T., SOKOŁOWSKA G., STRZELECKI R., WOŁKOWICZ S., 2000 — Pierwiastki śladowe i promieniotwórcze w osadach zbiornika włocławskiego. *Prz. Geol*., **48**, 9: 831–836.

BOJAKOWSKA I., SOKOŁOWSKA G., 1995 — Heavy metals in the Bystrzyca river flood plain. *Geol*. *Quart*., **40**, 3: 467–480.

BORDAS F., BOURG A., 2001 — Effect of solid/liquid ratio on the remobilization of Cu, Pb, Cd and Zn from polluted river sediment. *Water, Air, and Soil Pollution*, **128**: 391–400.

BOURG A., LOCH J., 1995 — Mobilization of heavy metals as affected by pH and redox conditions. *In*: Biogeodynamics of pollutants in soils and sediments: 87–102. Springer.

BRACK K., JOHANNESSON L., STEVENS R., 2001 — Accumulation rates and mass calculations of Zn and Hg in recent sediments, Göta älv estuary, Sweden. *Environ*. *Geol*., **40**: 1232–1241.

CCME (CANADIAN COUNCIL OF MINISTERS OF THE ENVIRONMENT), 1999 — Canadian Environmental Quality Guidelines: Canadian Sediment.

CISZEWSKI D., 1994 — Rozprzestrzenianie metali ciężkich w osadach dennych rzeki Chechło. *Prz*. *Geol*., **42**, 2: 116–121.

GABLER H., SCHNEIDER J., 2000 — Assessment of heavy metal contamination of floodplain soils due to mining and mineral processing in the Harz Mountains, Germany. *Environ*. *Geol*., **39**, 7: 774–781.

HANSEN P., 1996 — Bioassays on sediment toxicity. *In*: Sediments and toxic substances: 179–196. Springer.

LINDSTROM M., 2001 — Urban land use influences on heavy metals fluxes and surface sediment concentrations of small lakes. *Water, Air and Soil Pollution*, **126**, 3–4: 363–383.

MARQUES M., MARTINEZ-CODE E., ROVIRA J., ORDONEZ S., 2001 — Heavy metals pollution of aquatic ecosystems in the vicinity of a recently closed underground lead-zinc mine (Basque Country, Spain). *Environ*. *Geol*., **40**: 1125–1137.

MCLAREN R., KANJANAPA K., NAVASUMRIT P., GOONERATNE S., RUCHIRAWAT M., 2004 — Cadmium in water and sediments of the Chao Phraya River and Associated Waterways, Bangkok, Thailand. *Water, Air and Soil Pollution*, **154**, 1–4: 385–398.

MECRAY E. L., KING J. W., APPLEBY P. G., HUNT A. S., 2001 — Historical trace metal accumulation in the sediments of an urbanized region of the Lake Champlain Watershed, Burlington, Vermont. *Water, Air and Soil Pollution*, **125**, 1–4: 201–230.

REICHARDT W., 1996 — Ecotoxicity of certain heavy metals affecting bacteria-mediated biogeochemical pathways in sediments. *In*: Sediments and toxic substances: 159–178. Springer.

REISS D., RIHM B., THÖNI C., FALLER M., 2004 — Mapping stock at risk and release of zinc and copper in Switzerland – dose response functions for runoff rates derived from corrosion rate data. *Water, Air, and Soil Pollution*, **159**: 101–113.

SMAL H., SALOMONS W., 1995 — Acidification and its long-term impact on metal mobility. *In*: Biogeodynamics of pollutants in soils and sediments: 193–212. Springer.

STOEPPLER M., 1991 – Cadmium. *In*: Metals and their compounds in the Environment: 803–852. VCH Verlagsgesellschaft. Weinheim.

US EPA (US ENVIRONMENTAL PROTECTION AGENCY) 823-R-97-006, 1997 — The incidence and severity of sediment contamination in surface waters of The United States.

WENG H., CHEN X., 2000 — Impact of polluted canal water on adjacent soil and groundwater systems. *Environ*. *Geol*., **39**, 8: 945–950.