



## TRACE METALS IN SEDIMENTS OF THE WARTA RIVER BASIN

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**Abstract.** The geochemical studies of water sediments in Poland, which aim is controlling concentrations of heavy metals and some harmful organic compounds in the environment, have been realized since 1991 after the order of the Chief Inspector for Environmental Protection. In the Warta River drainage basin 43 observations sites are localized, from which 18 sites are located along the Warta River. Sediment samples have been analyzed for 19 elements (Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, V and Zn) after acid digestion. Results of these studies indicated that the Warta recent sediments are characterized by considerable increased contents of Ag, Cd, Cr, Cu, Hg, Pb and Zn in compared to their geochemical background values, especially at the river section from Konin to its inflow to the Odra River at Kostrzyń and its upper-stream part. Among samples from the examined Warta 11 tributaries, an excessive amount of heavy metals is observed in sediments of the Ner River (Cd, Cr, Cu, Hg, Pb, Zn), which is the wastewater receiver from the Łódź urban-industrial centre, in the Stradomka River (Cd, Hg, Ni, Pb, Zn), which is charged with sewages from Częstochowa, in the middle part of the Noteć River (Cu, Pb, Zn) and in the middle part the Prosna River (Cu, Pb). The fifteen years monitoring of sediments from the Warta River drainage basin has indicated the decrease of some element concentrations in sediments of the Warta River and the most heavy metal polluted Warta tributaries such as, Stradomka and Ner rivers.

**Key words:** water sediments, trace elements, pollution, Warta River.

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**Abstrakt.** Badania geochemiczne osadów wodnych Polski, których celem jest kontrolowanie stężenia metali ciężkich i trwałych zanieczyszczeń organicznych, są prowadzone od 1991 roku na zlecenie Głównego Inspektora Ochrony Środowiska. W zlewni Warty zlokalizowane są 43 punkty obserwacyjne, spośród których 18 rozmieszczonych jest wzdłuż Warty. W próbkach osadów, roztwarzanych kwasowo, oznaczana jest zawartość 20 pierwiastków. Wyniki tych badań wykazały, że współczesne osady Warty charakteryzują się znacznie podwyższoną zawartością Ag, Cd, Cr, Cu, Hg, Pb i Zn w porównaniu do wartości ich tła geochemicznego, zwłaszcza na odcinku od Konina do ujścia rzeki do Odry w Kostrzynie oraz w górnym odcinku rzeki. W osadach spośród badanych 11 dopływów Warty podwyższone zawartości metali ciężkich są obserwowane w osadach rzeki Ner (Cd, Cr, Cu, Hg, Pb, Zn), która jest odbiornikiem ścieków z Częstochowy, w osadach środkowej Noteci (Cu, Pb, Zn) i w osadach środkowej Proсны (Cu, Pb). Kilkunastoletnie badania monitoringowe osadów w zlewni Warty wykazały obniżenie zawartości niektórych badanych pierwiastków w osadach rzeki Warty oraz w silnie zanieczyszczonych dopływach Warty takich jak Ner i Stradomka.

**Słowa kluczowe:** osady wodne, pierwiastki śladowe, zanieczyszczenia, Warta.

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## INTRODUCTION

Most of heavy metals introduced to the surface waters by natural processes as well as by a human activity are trapped in sediments due to physical and biochemical processes and chemical reactions, proceeding in the water environment. Contents of metals in sediments is significant for the quality of surface water environment because the water sediments are not only a “repository” of stable and toxic pollutions but also the habitat of numerous groups of water organisms. Contaminated sediments influence on reduction or elimination of many animal species and are dangerous for peoples and wild animals eating fishes from places with sediments of high concentrations of harmful components. Part of these substances could be redistributed into the water by chemical and biochemical processes acting within the sediments or by their mechanical replacement resulted from a current action, transport and dredging (Smal, Salomons, 1995; Bordas, Bourg 2001). Sediments with a high contents of harmful components are also the potential source of environmental pollution e. g during floods the soils of flood terraces could be replaced or transported down stream and accumulated in other places formerly free of contaminations (Bojakowska, Sokołowska, 1995; Weng, Chen, 2000).

The Warta River, being the third river in Poland (after Vistula and Odra rivers) with its length of 808.2 km, takes its spring in the Silesian–Cracow Upland in Kromołów (380 m a.s.l) and it inflows into the Odra River at Kostrzyń. Its catchment area is 54,529 km<sup>2</sup> being 17.5% of whole country area. Almost the total Warta watershed is covered by Quaternary deposits (clays, glacial tills, silts, sands, gravels and peats) and locally the Tertiary rocks with a relatively low contents of potentially harmful trace elements. Only in the southern part of the basin, in the Silesian–Cracow Upland, the Mesozoic carbonate and clastic rocks are exposed, the part of which has the increased contents of zinc and lead, resulted from ore mineralization. Water pollution of Warta River and its tributaries results mainly from a direct supply of communal and industrial sewages generated by cities located along them. Most of sewages to Warta River are from Poznań (62 mln m<sup>3</sup>/year), Częstochowa (24 mln m<sup>3</sup>/year) and Konin (8 mln m<sup>3</sup>/year) but its tributaries receive the most of sewages from Łódź (to the Ner River – 95 mln m<sup>3</sup>/year) and from Kalisz (to the Proсна River – 12 m<sup>3</sup>/year).

## EXTENT AND METHODS

Studies of bottom river and lake sediments in Poland have been conducted since 1991 for the programme of State Environmental Monitoring and they have been focussed on control of content and fluctuations in time of chemical contaminations in the recently accumulating river and lake sediments. In the Warta River drainage basin are located 43 observation sites with 18 situated in the Warta River and others in its tributaries. For monitoring purposes the sediment samples are taken in 11 sites each year but in the other 32 sites – once per three years (Fig. 1).

In all samples of water sediments were defined – among others – the contents of following elements: arsenic, barium, cadmium, copper, chromium, cobalt, nickel, lead, strontium, vanadium and zinc, after digestion in aqua regia, applying the emission spectrometer with plasma activation ICP JY70 Plus Geoplasma by Jobin-Yvon, and the mercury content in a solid sample using the atomic absorption method with the analyser AMA 254 by Altec (Czech).

## RESULTS AND DISCUSSION

Fifteen years observations have evidenced the occurrence of decreased content of most studied elements in sediments of the Warta River and some of its tributaries. **Silver** in analysed sediments was noticed in range from <0.5 mg/kg to 6.9 mg/kg. Increased silver content was observed in sediments taken from the rivers Warta and Ner. In the middle course of the Warta River average Ag content in sediments at Poznań is 2.4 mg/kg, and at Koło – 3.0 mg/kg and in the upper course of river at Zawiercie – 2.9 mg/kg. In the Ner sediments average Ag content in sediments varied from 4.1 mg/kg in the upper course of river to 2.1 mg/kg near of the river mouth. Concentrations of **arsenic** in studied sediments varied from <5 mg/kg to 42 mg/kg. Increased content of arsenic was detected in samples taken from the

Stradomka River at Częstochowa, where the average As content was 16 mg/kg. **Barium** concentrations varied from 7 mg/kg to 530 mg/kg and its high average contents were noticed: in the Stradomka sediments (191 mg/kg), in the upper course of Ner deposits at Konstantynów Łódzki (164 mg/kg) and at Mirosławice (166 mg/kg), in sediments of the middle part of the Noteć at Ujście (184 mg/kg) and at Nakło (136 mg/kg), and in the upper course of the Warta River in sediments at Lgota (136 mg/kg) and in lower course of that river at Wronki (104 mg/kg) and at Kostrzyń (96 mg/kg). Contents of **cadmium** in sediments fluctuated from <0.5 mg/kg to 71 mg/kg and its high concentrations were observed mainly in the Warta sediments in the section from Poznań to Kostrzyń and in sediments accumulated in the

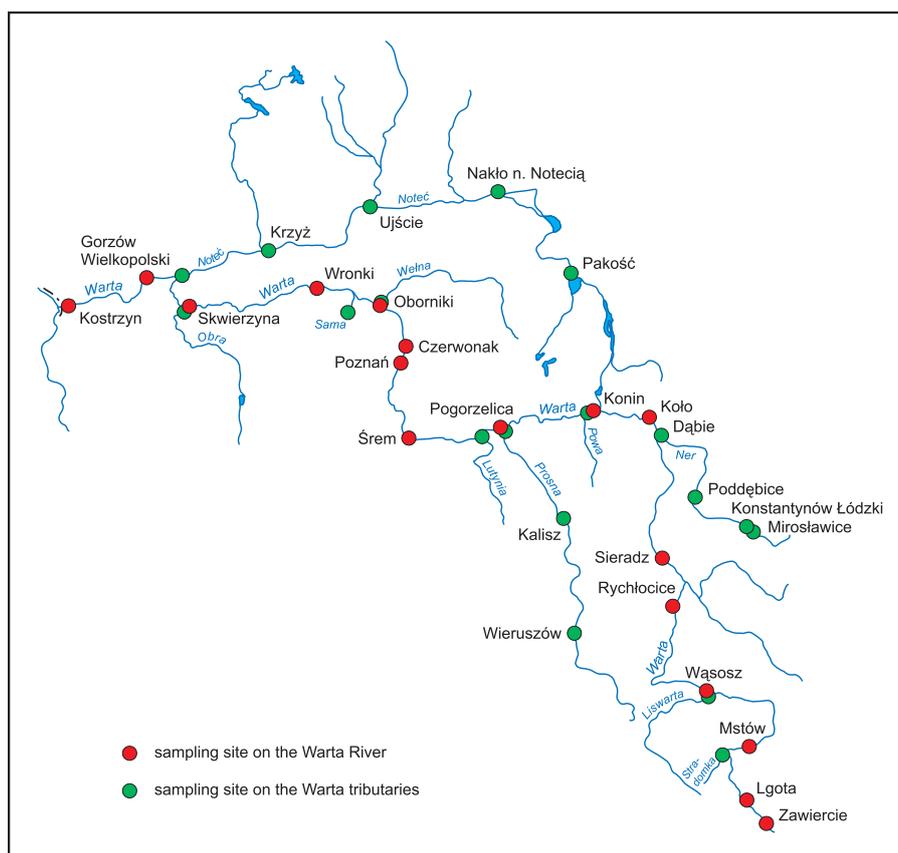


Fig. 1. Sampling sites of river sediments in the Warta River discharge basin

upper river course (Fig. 2). Similar high cadmium contents were detected in sediments of Ner and Stradomka rivers, where the average Cd value for the Ner at Mirosławice is 8.7 mg/kg, at Dąbie (river mouth) – 4.0 mg/kg, but for the Stradomka – 3.4 mg/kg. Concentrations of **cobalt** varied from <1 mg/kg to 85 mg/kg and its higher contents were noticed in sediments from the Warta River at Konin (average content – 17 mg/kg) and from the Stradomka (16 mg/kg) and from the Dobrzyńska River, side stream of the Ner River (11 mg/kg). **Chromium** contents in sediments varied from <1 mg/kg to 604 mg/kg and its slightly higher concentrations were observed in sediments from the upper part of Warta River comparing to its contents in sediments from the lower part of the river. Such increased Cr values in sediments were detected at Wąsosz, Wronki and Koło, with corresponding average contents of 68 mg/kg, 56 mg/kg and 56 mg/kg. Also high Cr concentrations were noticed in sediments of the Ner River, where the average chromium contents at Mirosławice is 337 mg/kg, at Dąbie – 115 mg/kg, and at Konstantynów – 109 mg/kg. **Copper** occurred in sediments changed from 1 mg/kg to 1042 mg/kg and its average concentrations above 100 mg/kg were found in samples taken from the Warta River at Konin (184 mg/kg) and from the Ner River at Mirosławice (126 mg/kg). Increased average contents of copper were observed also in sediments of the upper course Warta at Zawiercie (59 mg/kg), and in the rivers: Stradomka (58 mg/kg) and Dobrzyńska (60 mg/kg). Concentrations of **mercury** in analysed sediments varied from 0.001 mg/kg to 15.4 mg/kg, and its higher contents

occurred in the upper part of Warta River and below Poznań; the average Hg contents at Poznań is 0.43 mg/kg and at Wronki – 0.29 mg/kg (Fig. 3). High mercury concentrations were detected in sediments from the Ner River, where the average contents are: at Konstantynów Łódzki – 1.74 mg/kg Hg, at Mirosławice – 1.43 mg/kg and at Dąbie – 0.63 mg/kg. Similar increased Hg values were observed also in sediments of Stradomka River (average content – 0.46 mg/kg). The highest mercury concentration – the average content of 10.1 mg/kg – was found in sediments of the Ner tributary – the Dobrzyńska River. Contents of **nickel** fluctuated from 1 mg/kg to 230 mg/kg and its higher concentrations were noticed in the Warta River at Porajów below the Stradomka mouth (average contents – 26 mg/kg) and at Poznań (25 mg/kg). Sediments of the upper course of Warta have higher nickel contents than deposits of the middle and the its lower course. Also the Ner deposits at Mirosławice show increased nickel concentration – average contents of 37 mg/kg.

**Lead** occurred in river sediments in limits from <5 mg/kg to 2410 mg/kg and its increased contents were detected in the upper course of Warta River (at Lgota, at Zawiercie) and at Konin (Fig. 4). Comparable higher Pb values were observed in sediments of the Ner River at Mirosławice (average contents – 104 mg/kg), from the middle course of the Noteć River at Ujście (72 mg/kg) and from the Stradomka River (108 mg/kg). Concentrations of **strontium** in analysed sediments varied from 2 mg/kg do 206 mg/kg and its higher contents were found in samples from the Noteć River, in which the average Sr con-

tents values are: at Ujście – 96 mg/kg, at Nakło – 85 mg/kg and at Pakość – 77 mg/kg. Inflow of Noteć waters into the Warta River produced the increase of strontium concentration in Warta sediments at Kostrzyń. **Vanadium** concentration in river sediments fluctuated from 1 mg/kg to 146 mg/kg and its increased concentrations were detected in the Warta deposits at Konin and in the Stradomka sediments, in which its average contents were 35 mg/kg and 20 mg/kg respectively. **Zinc** contents in sampled deposits varied from 6 mg/kg to 3420 mg/kg and its average concentrations above 200 mg/kg were detected

in the Ner sediments at Konstantynów (354 mg/kg), at Mirosławice (711 mg/kg), at Poddębice (345 mg/kg) and at Dąbie (284 mg/kg), as well as in deposits of the rivers: Stradomka (1148 mg/kg), Prosna at Kalisz (229 mg/kg) and Dobrzyńka at Ksawerów (290 mg/kg). In the Warta sediments the highest Zn concentrations were noticed in the upper river part at Lgota (1503 mg/kg), at Zawiercie (835 mg/kg), at Mstów (398 mg/kg) and in the middle river at Konin (624 mg/kg) and at Wronki (208 mg/kg) (Fig. 5).

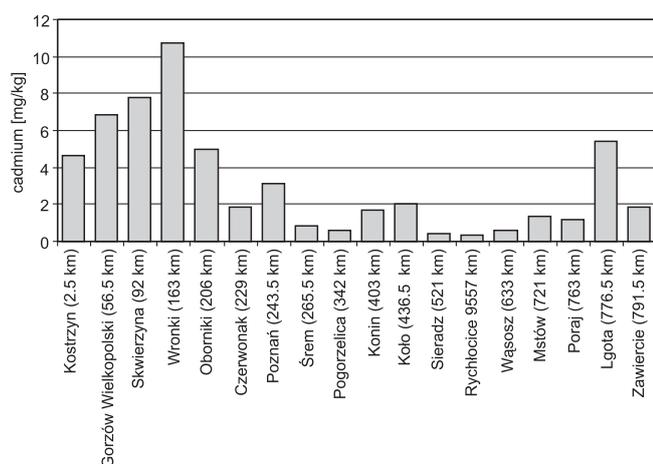


Fig. 2. Average cadmium contents in the Warta River sediments (1991–2005)

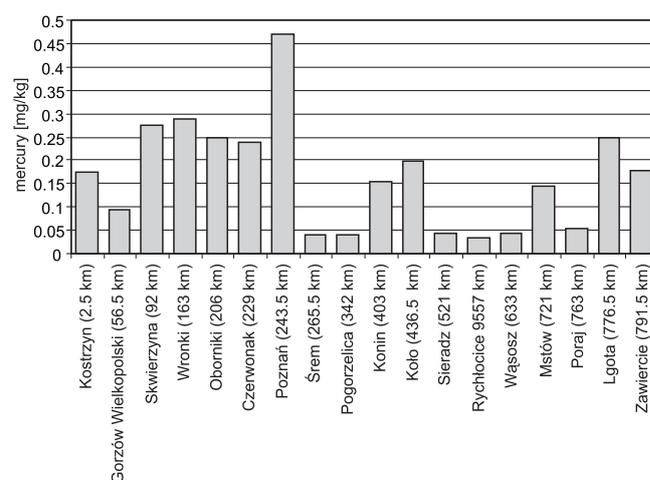


Fig. 3. Average mercury contents in the Warta River sediments (1991–2005)

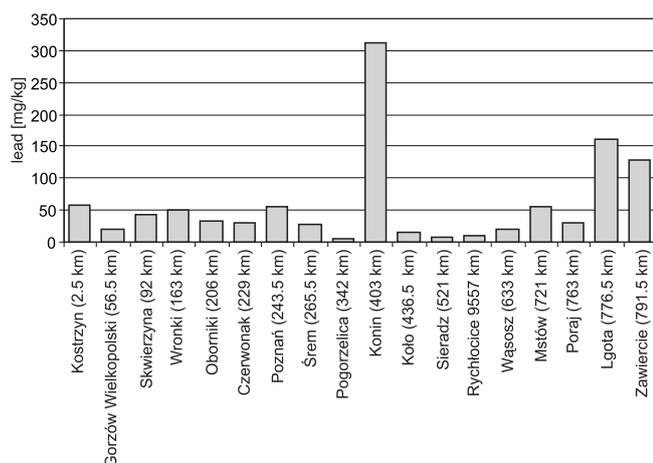


Fig. 4. Average lead contents in the Warta River sediments (1991–2005)

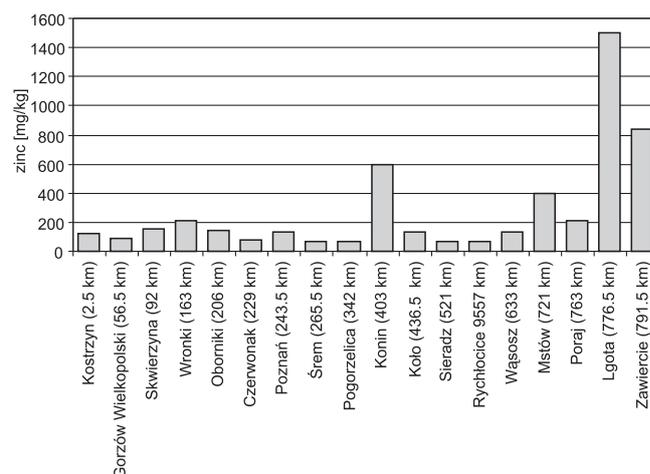


Fig. 5. Average zinc contents in the Warta River sediments (1991–2005)

## CONCLUSIONS

Continued during dozen or so years monitoring observations in the area of Warta discharge basin evidenced the distinctly increased contents of such elements as: Ag, Cd, Cr, Cu, Hg, Pb and Zn in Warta sediments between Konin to the Warta mouth into the Odra River and in sediments of the upper Warta River comparing to concentrations of these elements to its geochemical background values (Lis, Pasieczna 1995). Higher elements contents in sediments are anthropogenic origin and resulted from supply of communal and industrial sewages from cities located along the river, first of all from Poznań, Konin and Częstochowa. Increased concentrations of silver, cadmium, lead and zinc noticed in sediments of the upper Warta River may origin from wastewater delivered from factories located in Zawiercie and Myszków and could be in part of natural provenience, connected with exposures of Triassic dolomites, locally mineralised with zinc and lead sulphides. Higher stron-

tium contents in the Noteć sediments cause increase of strontium concentration in the Warta sediments below the Noteć mouth. Among 11 studied tributaries of the Warta River the higher concentrations of trace elements are observed in sediments of Ner, Stradomka, Noteć and Prosna rivers. High contents of Cd, Cr, Cu, Hg, Pb and Zn in the Ner sediments resulted from sewages delivered by the Łódź agglomeration. High concentrations of Cd, Hg, Ni, Pb and Zn in the Stradomka deposits are caused by sewages supplied by Częstochowa. Occurrence of increased amounts of Cu, Pb and Zn in the middle part of Noteć River and of Cu and Pb in the middle part of Prosna River are also the effect of delivered sewages from communal-industrial centres. Observations of last 15 years indicated the significant decrease of some harmful elements in sediments of the Warta River and of its most polluted tributaries – Ner and Stradomka.

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