# CONCENTRATIONS OF Zn, Pb, Cu, Cd AND Ni IN THE WATERS OF THE NAREW RIVER AND SOME OF ITS TRIBUTARIES

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#### Abstract

In the paper, the effects of differences in land use of a catchment and settlements on the variability of heavy metals concentrations (Zn, Pb, Cu, Cd, Ni) in the Narew River and some of its tributaries such as the Biebrza, upper Narew, Pisa, Omulew and Rozoga rivers were studied. The investigations continued from 1997 to 2002. The areas dewatered by the water-cources differ considerably in terms of environmental features (forests, wetlands, bogs and water reservoirs), land use (arable lands, grasslands) and population (man-made areas). The total catchment of the Narew River at the cross-section in Zamski Kościelne was also taken into account

The urban areas make up from 0.5% of the Rozoga River to 2.5% of the upper Narew catchment. Water samples were collected quarterly (April, July, October and January) from four study sites located near the river mouth and were analyzed for Zn, Pb, Cu, Cd and Ni by the AAS method. The results showed that concentrations of Pb, Cu, Cd and Ni increased along the Narew River due to the accumulation of the elements in water. A significant influence on high heavy metal concentrations in water was produced by the town of Białystok, a source of large amounts of municipal pollutants discharged into the river. This mainly affected the content of Zn, as the highest pollution with this element was detected in the upper Narew River. The lowest Zn concentrations were observed in the Omulew River water, where forests dominated in the area, covering more than 48% of the catchment. The research showed that wetlands and lakes significantly decreased Pb, Cu, Cd and Ni concentrations in flowing water, but the presence of large inhabited areas with dense population and municipal pollution increased concentrations of heavy metals in river water.

Key words: haevy metals, Narew River, tributaries, land use.

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# STĘŻENIE Zn, Pb, Cu, Cd I Ni W WODACH NARWI I WYBRANYCH JEJ DOPŁYWÓW

#### Abstrakt

W pracy badano wpływ zróżnicowanego użytkowania obszaru zlewni oraz osadnictwa na zmienność stężenia metali ciężkich (Zn, Pb, Cu, Cd, Ni) w wodach Narwi i wybranych jej dopływów: Biebrzy, górnej Narwi, Pisy, Omulwi i Rozogi. Odprowadzają one wody z obszarów (zlewnie cząstkowe) znacząco zróżnicowanych pod względem warunków przyrodniczych (lasy, obszary podmokłe, bagna, zbiorniki wodne), sposobu użytkowania (grunty orne, użytki zielone) i zaludnienia terenu (tereny zantropogenizowane). Uwzględniono również zlewnie całkowitą Narwi po punkt pomiarowy w Zambskach Kościelnych. Na obszarze badań tereny zurbanizowane zajmują od 0,5% powierzchni w zlewni Rozogi do 2,5% w zlewni górnej Narwi. Badania obejmowały lata 1997–2002. Próbki wody pobierano z nurtu rzeki w punktach przyujściowych cztery razy w roku: wiosną (kwiecień), latem (lipiec), jesienią (październik) i zimą (styczeń). Oznaczenia Zn, Pb, Cu, Cd i Ni wykonano metoda absorpcyjnej spektrometrii atomowej. Wykazano, że wraz z biegiem rzeki Narwi, w wyniku kumulacji pierwiastków w wodzie, wzrastało stężenie Pb, Cu, Cd i Ni. Na wzrost stężenia metali ciężkich znaczący wpływ wywarła obecność w zlewni dużej jednostki osadniczej – miasta Białystok. Było to związane z dopływem większej ilości zanieczyszczeń bytowych powodujących wzrost stężenia Zn w górnej Narwi. Najniższe stężenie Zn stwierdzono w wodach odpływających Omulwią, w której zlewni dominowały lasy - ponad 48% powierzchni. Wykazano również, że występowanie terenów bagiennych, torfowych i zbiorników w zlewni wpływa na zmniejszenie stężenia Pb, Cu, Cd i Ni w wodach rzecznych, ale obecność dużych jednostek osadniczych i związany z tym dopływ zanieczyszczeń bytowych powoduje zwiększenie stężenia badanych metali ciężkich w wodzie rzecznej.

Słowa kluczowe: metale ciężkie, Narew i jej dopływy, użytkowanie zlewni.

## INTRODUCTION

It is commonly believed that the main causes of increasing surface water pollution are intensive agricultural production, increased urbanisation and industralisation and transport (Koc 1994, Pistelok, Galas 1999, Vink et al. 1999, Lääne et al. 2005).

Among the many threats that water ecosystems are exposed to, heavy metals are a serious risk factor. Although they play an important physiological role in living organisms, once they exceed a certain threshold level, they become dangerous. Excessive amounts of heavy metals inhibit biological processes involved in the self-cleaning of river waters, and may also threaten health of aqueous organisms (Lin, Chen 1998, Hermanowicz et al. 1999). The concentration of heavy metals in the Narew River is associated with the agricultural use of the rivers catchment and with some urbanized areas near the river. Heavy metals are found in artificial fertilizers and chemical pest control preparations; they are also present in certain waste products used in farming (Falencka-Jablośnka 1991, Grabińska et al. 2005b, Koc 1994). Wastewater and sewage discharged from villages or towns as well as from food processing industry plants

located in the Narew River catchment are another essential factor adding to the water pollution (SkorbiŁowicz 2005).

The present study dealt with the diversified utilization and urbanization of the river's catchment and the effect of these factors on the content of heavy metals in the waters of the Narew and some of its tributaries. Another reason for undertaking such analyses was the fact that the waters carried by the Narew supply the Warsaw agglomeration (the Zegrzyń water reservoir).

### AREA OF THE STUDY

Determination of heavy metals (Zn, Pb, Cu, Cd and Ni) was carried out for five partial catchments, i.e. the Biebrza (7 057 km²), the upper Narew (6 077 km²), the Omulew (2 053 km²) and the Rozoga (493 km²) as well as for the complete catchment of the Narew river to the measuring point at Zambski Kościelne (27 782 km²). All these catchments are highly diversified in terms of land use and population density (Table 1).

Table 1
Land use in the catchments (%)

Land use	Omulew	Rozoga	Pisa	Biebrza	Upper Narew	Narew
Man-made areas	1.25	0.52	0.90	1.13	2.70	1.51
Arable lands	18.10	24.27	32.38	37.88	31.5	34.68
Meadows and pastures	29.40	41.98	20.52	28.54	29.3	28.18
Forest	48.17	32.91	37.72	25.15	34.78	31.58
Wetland zones	0.86	_	0.48	5.08	1.26	1.79
Water bodies	2.22	0.32	8.00	2.22	0.46	2.26

The land cover of the Narew catchment, which lies in the extra-glacial zone, is composed predominantly of old-glacial land cover and some young post-glacial land. The whole of the upper Narew catchment lies in old post-glacial landscape, while the rivers of Omulew, Rozoga, Pisa and Biebrza drain catchments in transition zone between old and young post-glacial landscape.

The morphogenesis of the latter catchments comprise high plains without lakes, sandurs and high plains with lakes. As regards the type of use, the Narew River catchment is an agricultural and forested catch-

ment. The diversity of farming conditions within the river catchment has several causes: varied geomorphological parameters, different soil and climatic conditions, various land cover and differences in the sozologic infrastructure. One thing that is characteristic of this area is the low level of urbanization and industrialization. The share of the urbanized land in the partial catchments investigated ranged from 2.7% in the upper Narew catchment to 0.5% in the Rozogi River catchment (Grabinska et al. 2005a).

## **METHODS**

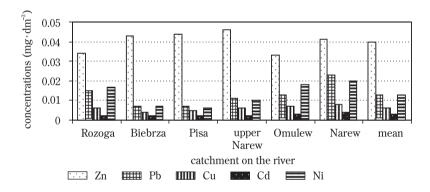
The research period covered years 1997–2002. Water samples were collected from the river current four times a year: in April (spring), July (summer), October (autumn) and January (winter). In the tributary rivers, water samples were taken from sites located at the river inflows. Two sampling sites were established on the Narew: at Strękowa Góra (262 km of the river flow), which was a site representative for the partial Narew catchment, and at the measuring point in Zambski Kościelne, which closed the area selected for the investigations. Determinations of Zn, Pb, Cu, Cd and Ni were conducted by atomic absorption spectrophotometry (Hermanowicz et al. 1999). Volumes of the annual load of metals flowing away from the area under study (kg · ha<sup>-1</sup>) were worked out as the sum of products of mean water flows in the watercourses and corresponding mean concentrations of a given element. The results of the determinations were processed statistically using analysis of variance.

## **RESULTS**

The study demonstrated that the highest concentrations of lead, copper, cadmium and nickel occurred in the Narew river at the point closing the area selected for examinations (in Zambski Kościelne), which may be due to the progressing accumulation of elements in the river waters along its flow (Tab. 2, Fig. 1).

The highest zinc concentration along with elevated levels of the other metals were detected in the water of the upper Narew (sampling site at Strękowa Góra), where the Białystok agglomeration lies. Elevated levels of metals also occurred in the waters of the rivers Omulew and Rozoga, whose catchments differ in terms of use (agricultural and forested, respectively) but contain approximately the same share of rusty and pozolic soils, formed from sands and sandy gravel (Grabińska et al. 2005a).

Catchment of the river	Land use	Zn	Pb	Cu	Cd	Ni
Rozoga	agricultural	0.006-0.088	0.002-0.030	0.001-0.014	0.000-0.005	0.005-0.038
Biebrza	agricultural and forested	0.003-0.082	0.002-0.041	0.001-0.013	0.000-0.011	0.001-0.017
Pisa	£1	0.003-0.070	0.003-0.030	0.001-0.023	0.000-0.012	0.001-0.009
Upper Narew	forested and agricultural	0.003-0.070	0.003-0.044	0.003-0.021	0.001-0.009	0.001-0.057
Omulew	forested catchment	0.010-0.076	0.004-0.027	0.002-0.014	0.000-0.005	0.005-0.027
Narew	agricultural and forested	0.011-0.084	0.004-0.027	0.002-0.014	0.000-0.005	0.005-0.027



Land use catchments of the river: agricultural – Rozoga; agricultural and forested – Biebrza; agricultural and forested – Pisa; forested and agricultural – upper Narew; Forested catchment – Omulew; agricultural and forested – Narew

Fig. 1. Effect of land use on heavy metal concentrations in waters in each catchment

The lowest amounts of Pb, Cu, Cd and Ni were determined in the waters flowing out of the agricultural and forested catchments (the Biebrza and the Pisa rivers), with the highest share of wetland zones and lakes. The inflow of cleaner water with the Biebrza River current resulted in a local decrease in the unit outflow of heavy metals carried away with the Narew River. The lowest Zn concentration was determined in the waters flowing away in the Omulew River, whose catchment is characterized by a rather high percentage of semi-natural lands (61.3%) in the total surface area (Fig. 1).

The analysis enabled the authors to corroborate the opinion that presence of muddy, peat or wetlands in a river catchment depressed concentration of heavy metals in river waters. On the other hand, presence of large human settlements and consequent discharge of municipal wastewater and sewage increase concentrations of elements in river waters.

It was also found out that an increase in Cu corresponded to highly significant ( $\alpha$ <0.01) increase in the expected quantities of Pb and Ni as well as Cd and Pb and Ni in the water of the Narew River (sampling site in Zambski Koscielne). Very highly significant positive correlation was also discovered between the concentrations of Pb and Ni. Significant negative correlations were determined for Zn versus Cu, Pb and Ni.

The results seem to suggest that the concentration of heavy metals in the Narew and its tributary rivers examined is low, possible to term as natural (Świderska-Bróz 1987).

#### CONCLUSIONS

- 1. Although concentrations of Pb, Cu, Cd and Ni in the studied water are characteristic for non-polluted environment, the research showed increase along the Narew River due to the accumulation of the elements in water.
- 2. Significant influence on the Zn concentrations in water was produced by the town of Białystok, a source of considerable amounts of municipal pollutants discharged into the river.
- 3. Wetlands and lakes significantly decrease Pb, Cu, Cd and Ni concentrations in flowing water, but the presence of large inhabited areas with a dense population and consequent municipal pollution increased concentrations of the heavy metals in river water.

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