Oceanological and Hydrobiological Studies
International Journal of Oceanography and Hydrobiology
Vol. XXXVIII, No.2

Institute of Oceanography (51-61) University of Gdańsk
ISSN 1730-413X 2009 eISSN 1897-3191

DOI 10.2478/v10009-009-0021-9
Original research paper

Received: *July 03, 2008*
Accepted: *February 24, 2009*

Distribution of heavy metals in the Mała Wełna River system (western Poland)

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Key words: heavy metals, surface water, suspension, bottom sediment, Mała Wełna river

Abstract

This paper reports the results of measurements of heavy metal concentrations in water, suspension, and bottom sediment samples collected at eight sites along the Mała Wełna River (western Poland). The samples were collected once a month from May to August 2006. The highest variations in the water of the Mała Wełna River were noted in the concentrations of Zn, Pb, and Cu. The results indicate that the suspension plays an important role in the transportation of pollutants contaminating the water and later in the accumulation of pollutants in the bottom sediments. The concentration of heavy metals in the bottom sediments were determined

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individually in grain size fractions: >2, 2-1, 1-0.5, 0.5-0.25, 0.25-0.1, 0.1-0.063, <0.063 mm. Concentrations of them were the lowest in the 0.5-0.25 and 0.25-0.1 mm fractions, and were the highest in the 0.1-0.063 and <0.063 fractions.

INTRODUCTION

Heavy metals are one of the main pollutants in the aquatic environment. They enter the surface waters in dissolved form and as associates with substances washed off the ground. They can migrate over long distances in forms adsorbed on suspension, as colloids, and as ionic species. The metals dissolved in the aquatic phase can undergo precipitation as a result of changes in physicochemical conditions (pH, oxidation, redox potential, salination) and be adsorbed on solids suspended in water (Jha et al. 2002, Sobczyński et al. 2004). Therefore, the analysis of suspension provides reliable information on the accumulation and transportation of different components entering aquatic ecosystems (Adamiec 2004). The concentration, reactivity, and bioavailability of metals in the water-suspension-bottom sediment system are strongly related to processes taking place in aquatic ecosystems and anthropogenic pressure (Sobczyński et al. 2004). Recently, problems related to the mobility of heavy metals have become of great significance and their analysis requires knowledge of particular species bound to solid particles in the suspension and bottom sediments (Okonkowo et al. 2005).

The bottom sediments are particularly stable analytical materials and analysis of their composition provides information on the history of physical and chemical changes in the entire catchment area (Jha et al. 2002). On the other hand, the metals immobilized in the bottom sediments can become mobile and bioavailable, thus posing a threat to living organisms (Głosińska et al. 2005, Samir et al. 2006). The bottom sediments are not only carriers of heavy metals but can also become a source in rivers (Gűmgűm et al. 2001, Frankowski et al. 2005).

The objectives of the study were: (1) to establish the spatial and temporal variability in concentrations of heavy metals (Cd, Cu, Cr, Ni, Pb, Zn,) in water, suspension (heavy metals adsorbed on suspensions), and bottom sediments in the Mała Wełna River system; (2) to estimate the potential avability of metals contained in grain size fractions of the bottom sediments.

MATERIALS AND METHODS

Study area

The Mała Wełna River catchment area lies in the middle of the Wielkopolsko-Kujawska Lowland (Kondracki 2000). The river is 83.8 km long

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and its catchment area is 688 km^2. Up to the profile Kiszkowo at the end of the catchment fragment studied, the Mała Wełna River flows through eight lakes with a total water surface area of 392.8 ha and a complex of fish ponds with a surface area of 235.1 ha (Fig. 1). The catchment area of the river is mostly agricultural (arable land 82.7%), forests (6.0%), orchards (0.3%) and idle land (9.0%). The area of the catchment fragment studied is 342 km^2, and the length of the river in this fragment is 45.3 km, with a mean slope of 0.58‰.

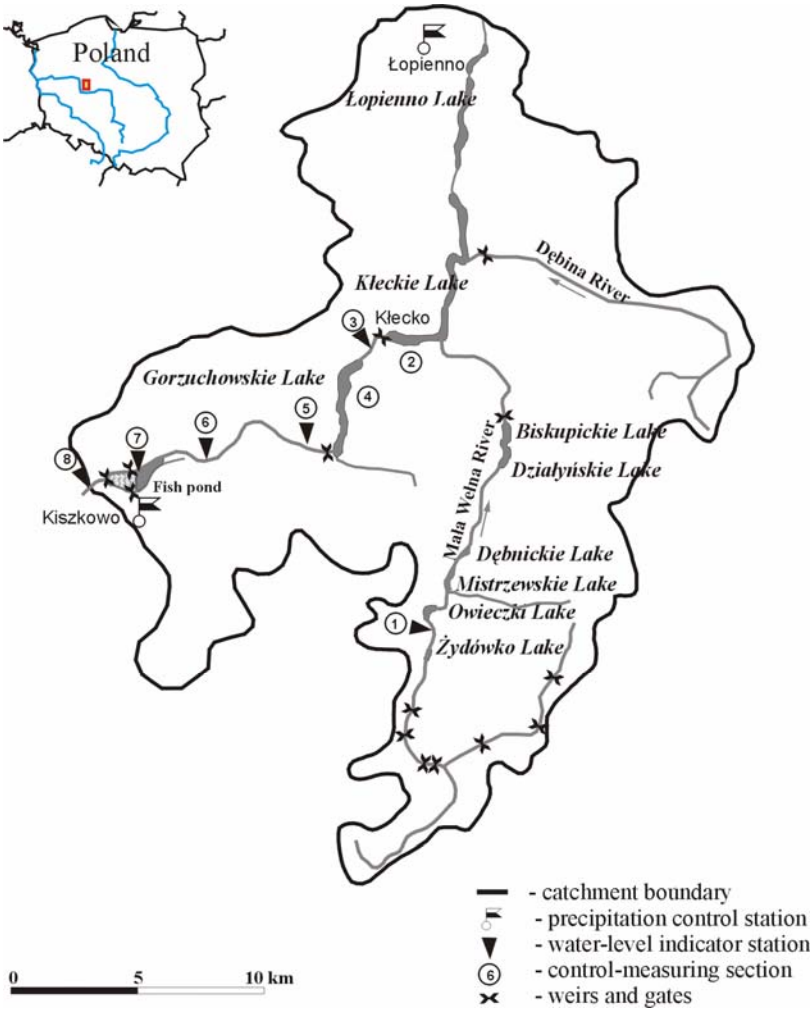


Fig. 1. Catchment of the Mała Wełna River down to the Kiszkowo cross-section.

Sample collection and preparation

Once a month from May to August 2006, samples of water, suspension, and bottom sediments were collected at eight sites along the course of the Mała Wełna River (Fig. 1). The samples were taken with a Toń 2 sampler and placed into polyethylene (PE) bottles. The samples were filtered through a membrane filter with a pore size of 0.45 μm and fixed with 65% HNO_3 (Merck, Darmstadt, Germany). To determine the heavy metal contents adsorbed on suspension, one litre of water was collected, filtered through a membrane filter with a pore size of 0.45 μm, then the suspension was extracted with hydrochloric acid (Merck, Darmstadt, Germany) at a 1:4 ratio. The bottom sediment samples were collected with a Czapla-1 core-sampler (Mera-Błonie, Gdańsk, Poland) and placed into PE containers. The sediment sample was dry-divided into seven-grain size fractions through a LAB-11-200/UP mechanical shaker (Brzesko, Poland) with a series of stainless steel sieves. The content of the metals was determined in grain size fractions: >2 mm, 2-1 mm, 1-0.5 mm, 0.5-0.25 mm, 0.25-0.1 mm, 0.1-0.063 mm, <0.063 mm after extraction with hydrochloric acid (Merck, Darmstadt, Germany) at a 1:4 ratio (Lis and Pasieczna 1995). The sample was heated for 1 hour in a water bath at 95°C.

Chemical analysis

Determinations of Cd, Cr, Cu, Ni, Pb and Zn were performed with atomic absorption spectrometry with flame atomization (F-AAS) on a two-beam Perkin Elmer instrument, model AAnalyst 300 (Perkin Elmer, Norwalk, Connecticut, USA). This instrument is equipped with an autosampler made by Perkin Elmer, model AS 90 (Perkin Elmer, Norwalk, Connecticut, USA). Hollow Cathode Lamps (HCL) were used for the determinations (Perkin Elmer, Norwalk, Connecticut, USA).

Reagents

All the reagents used were of analytical grade, and the water was deionized with a resistivity >18MΩ in a Milli Q-RG apparatus (Milipore, France). The reference standard solutions were made of commercial standards for AAS analysis by Merck (Merck, Darmstadt, Germany). The water solutions of HCl (Merck, Pro Analysis, Darmstadt, Germany) was made by diluting the acid of a density of $d = 1.19$ g ml^{-1} at 1:4 with deionised water.

RESULTS AND DISCUSSION

The concentrations of heavy metals detected in the river water were in the

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following ranges: Cd <0.001–0.003 mg l^{-1}; Cr <0.004–0.009 mg l^{-1}; Cu <0.004–0.089 mg l^{-1}; Ni <0.006–0.015 mg l^{-1}; Pb <0.010–0.040 mg l^{-1} and Zn 0.005-0.115 mg l^{-1}. The statistical parameters of the metal concentrations in the water samples are shown in Table 1.

Table 1

Results of determination of heavy metals in the Mała Wełna River water and adsorbed on the suspension samples (mg l^{-1}), n=32.

Parameters	Minimum	Maximum	Median	S_d
	Water			
Cd	<0.001	0.003	0.002	0.001
Cr	<0.004	0.009	0.004	0.004
Cu	<0.004	0.089	0.004	0.015
Ni	<0.006	0.015	0.006	0.006
Pb	<0.010	0.040	0.022	0.010
Zn	0.005	0.115	0.017	0.023
	Suspension			
Cd	<0.001	0.072	0.001	0.013
Cr	<0.004	0.077	0.004	0.013
Cu	<0.004	0.947	0.056	0.170
Ni	<0.006	0.221	0.006	0.048
Pb	<0.010	0.170	0.010	0.032
Zn	0.052	1.763	0.140	0.320

No significant differences in the concentrations of Cd, Cr, or Ni were observed in the water at particular measuring sites, as confirmed by variance analysis (ANOVA). The highest concentrations of Pb were found in the samples collected at site 1, whereas the highest concentration of Cu was detected at site 3 (Fig. 2A), which suggests local pollution with this element. The level of Zn was also elevated at sites 5 and 8 (Fig. 2A), which was interpreted as a result of pollution from the neighboring sewage treatment plant.

Analysis of the seasonal changes of the heavy metal concentrations in water revealed that the level of Cd was low with a small increase in July and August. Chromium was found in generally higher concentrations than Cd, and its highest concentration was determined in August. In comparison to that in the other months, an anomalous concentration of Cu was detected in May (Fig. 2A). The concentration of Pb was the lowest in June and the highest in May and August. The highest concentration of Zn was observed in June, while the highest level of Ni in July (Fig. 2A).

The literature provides data on the concentrations of heavy metals in the water of many rivers in Poland. The current results were compared with those for the Oder River, where Cd 0.0011 mg l^{-1}, Cr 0.0371 mg l^{-1}, Cu 0.0235 mg l^{-1}, Ni 0.0272 mg l^{-1}, Pb 0.0109 mg l^{-1}, Zn 0.202 mg l^{-1} (Helios Rybicka et

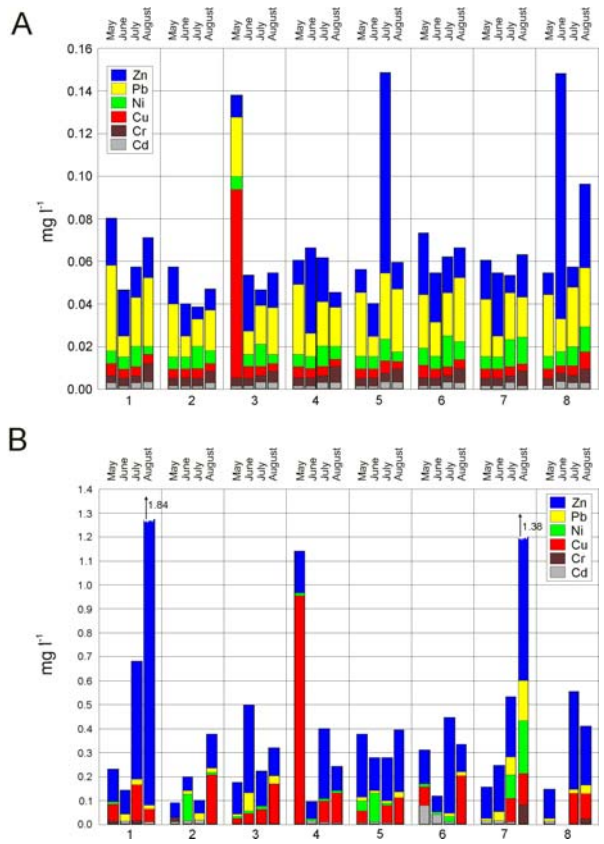


Fig. 2. Variation in the heavy metal concentration in water samples (A) and adsorbed on suspension (B) at different measuring sites (sampling sites 1-8).

al. 2005), for the Warta River near Poznań, where Cd <0.001 mg l^{-1}, Cr <0.003 mg l^{-1}, Cu 0.004 mg l^{-1}, Ni <0.005 mg l^{-1}, Pb <0.010 mg l^{-1} and Zn 0.052 mg l^{-1} (Lis and Pasieczna 2005), and for the Warta River near Mosina, where Cr 0.006 mg l^{-1}, Cd <0.001 mg l^{-1}, Cu 0.007 mg l^{-1}, Ni 0.013 mg l^{-1}, Pb 0.026 mg l^{-1} and Zn 0.023 mg l^{-1} (Sobczyński et al. 2004). According to this comparison, the concentration of heavy metals in the Mała Wełna River was comparable to the levels of these metals in the two main Polish rivers.

The concentrations of heavy metals adsorbed on the suspension varied within the ranges: Cd <0.001–0.072 mg l^{-1}; Cr <0.004–0.077 mg l^{-1}; Cu <0.004–0.947 mg l^{-1}; Ni <0.006–0.221 mg l^{-1}; Pb <0.010–0.170 mg l^{-1} and Zn 0.052–1.763 mg l^{-1} (Table 1).

No significant variations in the level of Cr and Pb adsorbed on the

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suspension at particular sites was observed (Fig. 2B). An increased level of Cd was detected at sites 6, whereas an elevated level of Ni was found at sites 2, 5, and 7. The concentration of Zn was the lowest at sites 2 and 4 (Kłeckie and Gorzuchowskie Lake), while it was the highest at sites 1 and 7 (Fig. 2B). An important observation is the highest level of Cu (Fig. 3A) in the suspension collected from Gorzuchowskie Lake in May, which is near site 3, Kłeckie Lake, where the anomalous concentration of this element was noted in the water. This anomalous concentration of copper adsorbed on suspension was reflected by an increase in its concentration in the bottom sediment at the next station (site 4, Fig. 3B).

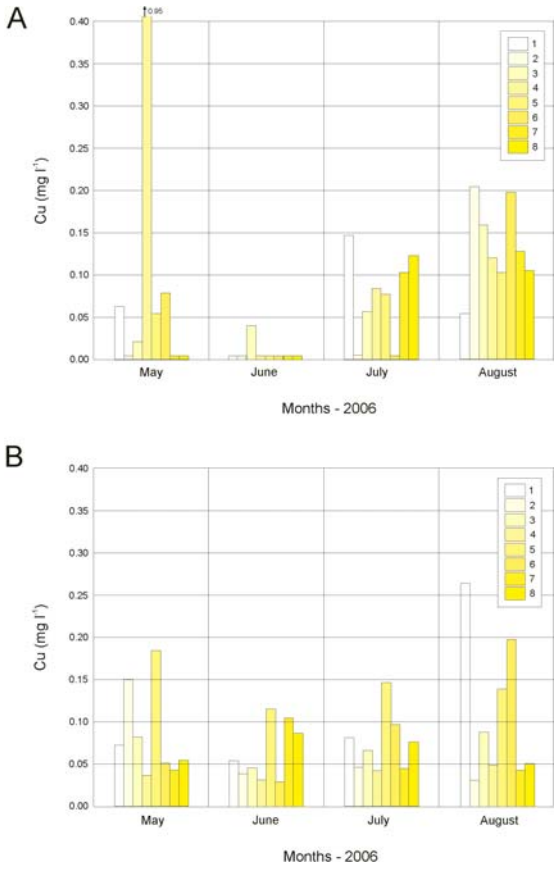


Fig. 3. Time variations in the concentration of copper adsorbed on the suspension (A) and bottom sediments in the fraction 0.1 mm (B); (sampling sites 1-8).

Analysis of the seasonal variation revealed a decrease of the concentrations of the heavy metals adsorbed on suspension studied in June. This result is illustrated for Cu in Fig. 3A. The increase of the concentration of the heavy metals adsorbed on the suspension is reflected by their increased level in the bottom sediment in May, July, and August with respect to the level in June (Fig. 3A, 3B).

The lowest contents of heavy metals in grain size fractions of the bottom sediments were found in the fractions 0.5-0.25 and 0.25-0.1 mm, while the highest in the fractions 0.1-0.063 and <0.063 mm (Table 2). This tendency was found for all analyzed heavy metals and is illustrated on the example of Cu in Fig. 4A. The percentage contribution of the granulometric fractions with the highest contents of the analyzed metals 0.1-0.063 and <0.063 mm, was 1.6 and 0.8% in 100 g d.m. of the bottom sediment, respectively, and was the lowest of all fractions (Fig. 4B).

Table 2

Results of determination of heavy metals in grain size fractions of the Mała Wełna River bottom sediment.

Grain size fractions [mm]	Cd	Cr	Cu	Ni	Pb	Zn
	[mg kg^{-1} d.m.]					
>2	<0.5-2.2	0.5-40.6	0.8-9.7	<0.5-19.2	1.3-25.2	3.8-83.7
2-1	<0.5-0.9	1.1-9.2	1.1-31.8	<0.5-8.5	1.3-52.9	3.5-146.8
1-0.5	<0.5-0.8	0.5-11.3	1.0-14.6	<0.5-6.5	1.1-28.9	2.2-63.3
0.5-0.25	<0.5-0.5	<0.5-3.3	1.1-8.6	<0.5-4.8	0.6-12.6	1.6-38.8
0.25-0.1	<0.5-0.6	<0.5-4.8	1.2-10.8	<0.5-5.5	0.7-21.1	1.9-37.8
0.1-0.063	<0.5-1.2	1.2-6.6	2.3-25.3	0.6-16.0	2.7-24.1	7.4-79.4
<0.063	<0.5-1.4	3.8-13.0	10.2-39.2	2.6-26.9	8.4-35.5	22.8-113.4

The extraction of heavy metals in grain size fractions with hydrochloric acid at a 1:4 ratio permitted the determination of the available species of heavy metals in bottom sediment samples. This type of extraction can occur in real aquatic ecosystems in the case of increased environmental acidification. Heavy metals bounded with bottom sediment can easily be released in response to changes in physical and chemical conditions from sediments to suspension and bulk water, and become available. The increase of availability of the heavy metals from bottom sediment observed during the study, under real conditions may bring about the recontamination of the aquatic environment. The highest

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concentrations of heavy metals in the bottom sediment of grain size fraction <0.063 mm was also reported by Ciszewski (1997), Singh et al. (1999), Radke et al. (2004), Frankowski et al. (2005), and Zhu et al. (2006), Frankowski et al. (2008).

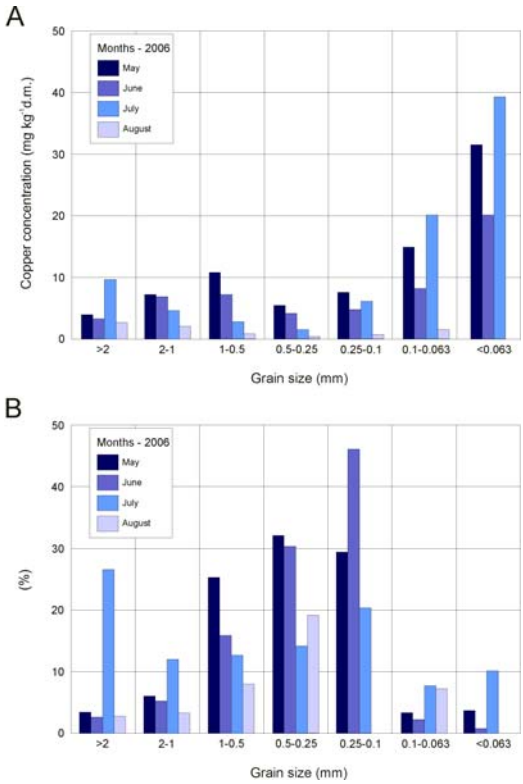


Fig. 4. Seasonal changes in the concentration of copper in the granulometric fractions of the bottom sediments for the cross-section Zakrzewo (A) and the percentage contribution of Cu in 100 g d.m. of bottom sediment (B).

CONCLUSIONS

The results of the heavy metals determination and analysis permit drawing the following conclusions:

1. In the samples collected at the series of sites along the course of the Mała Wełna River no significant variation in the concentrations of Cd, Cr, or Ni was found. On the other hand, the concentrations of Cu, Zn, and Pb showed variation, which could be related to the input of pollutants containing these

heavy metals into the river.
2. The seasonal variation of the concentrations in water of Pb, Zn, and Cu was noted.
3. The suspension was found to play an important role in accumulation and transport of pollutants released to the Mała Wełna River.
4. The analysis of the heavy metal concentrations in bottom sediments proved an accumulation of metals in this phase during the subsequent months.
5. Elevated concentrations of heavy metals adsorbed on suspension and in the bottom sediment were observed. Under particular conditions (e.g. increased acidity), the metals adsorbed in these phases can be released into the river water causing its secondary contamination.

ACKNOWLEDGEMENTS

This study was supported by the Agriculture Academy of Poznań and by the Adam Mickiewicz University of Poznań (Project number: 12/61/WI/06). Dr. M. Siepak is a scholar of the Foundation for Polish Science.

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