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Original Research

Analysis of Heavy Metals in Particular Granulometric Fractions of Bottom Sediments in the Mała Wełna River (Poland)

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Abstract

The paper presents the results of determinations of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in 24 samples of bottom sediments collected in six gauging cross-sections along the course of the Mała Wełna river (western Poland). The samples were collected once a month from May to August 2006. The determinations were made separately in the following granulometric fractions: >2.0, 2.0-1.0, 1.0-0.5, 0.5-0.25, 0.25-0.1, 0.1-0.063, and <0.063 mm, using 3M HCl as the extraction agent. The concentrations of the heavy metals studied were lowest in the 0.5-0.25 and 0.25-0.1 mm fractions, and the highest in the 0.1-0.063 and <0.063 mm fractions, and also in the larger fraction. The determinations were made using atomic absorption spectrometry with flame atomization (F-AAS).

Keywords: heavy metals, bottom sediment, grain size, Mała Wełna river

Introduction

The content of heavy metals in river bottom sediments is often used as an indicator of their anthropogenic pollution [1]. In stable flow conditions, bottom sediments provide information about the history of physico-chemical changes in the whole of the catchment area studied [2]. The metals deposited in bottom sediments can become mobile, so they can be a real threat to living organisms. Therefore, river bottom sediments are not only sinks for heavy metals but also their sources [3]. Because of differences in the analytical procedures used at different centres, the results often cannot be compared or prevent an actual evaluation of the conditions in a given water course, especially in ecological terms. As follows from a survey of the literature, the Polish Geological Institute uses extractions from the 0.2 mm fraction obtained by dry sieving [4, 5]. According to the Polish ISO 11466 Standard, measurements should be performed after extraction of the 0.15 mm grain-size fraction obtained by dry sieving [6], while according to Länder-Arbeitsgemeinschaft Wasser "LAWA," extraction should be made of the 0.02 mm fraction obtained by wet sieving [7].

Different authors have used samples of a variety of grain sizes and different methods of sieving: Korfali and Davies used the 0.075 mm fraction and dry sieving [8], Boszke et al. used the <0.2, 0.2-0.5, 0.5-1.0, and 1.0-2.0 mm fractions and wet sieving through a nylon sieve [9], while Adamiec and Helios-Rybicka [10] and Helios Rybicka et al. [11] used the <0.02 mm fraction and wet sieving. Huang and Lin [12] and Lu et al. [13] determined heavy metals in the <0.063 mm fraction, while Takalioglu et al. [14] and Singh et al. [15], the 0.270 mm fraction;

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Feng et al. [16], the <1.0 mm fraction; and Cuong and Obbard [17], the <0.063 mm fraction.

This study was undertaken to find out which grain-size fraction of river bottom sediment contained the highest and the lowest concentrations of HCl-labile species of the heavy metals studied. The material came from the bottom of the Mała Wełna river in the Wielkopolska Lowland.

Experimental Procedures

Study Area

The Mała Wełna river catchment lies in the middle of the Wielkopolska-Kujawy Lowland. The total length of the river is 83.8 km, and its catchment area is 688 km^2. The catchment is predominantly agricultural in character (82.7% arable land), while other uses include forests (8.0%), orchards (0.3%), and fallow land (9.0%). The Mała Wełna river flows through 8 lakes with a total area of 392.8 ha and a complex of fish ponds occupying an area of 235.1 ha (Fig. 1). The catchment area down to this cross-section is 342 km^2, the length of this section of the river is 45.3 km, and the longitudinal slope of land reaches 0.58‰ [18].

Sample Collection and Preparation

Bottom sediment samples were collected once a month from May to August 2006, at six gauging cross-sections along the course of the Mała Wełna river (Fig. 1). The samples of 10-15 cm in depth were collected by a Czapla-1 core sampler (Mera-Błonie, Gdańsk, Poland) into polyethylene (PE) containers and subjected to granulometric analysis. The sediment sample was air-dried and dry-divided into seven grain-size fractions in a mechanical LAB-11-200/UP shaker (Brzesko, Poland) with a series of stainless steel sieves. The aim of the study was to determined content of HCl-labile heavy metals for the grain-size fractions of >2.0; 2.0-1.0; 1.0-0.5; 0.5-0.25; 0.25-0.1; 0.1-0.063; and <0.063 mm. Each fraction was subjected to extraction with a water solution of hydrochloric acid (Merck, Pro Analysis, Darmstadt, Germany) at a ratio of 1:4 (3M HCl). A portion of 1.5 g was heated for 1 h in a water bath at 95°C.

Reagents

The reagents used were of analytical grade, while water was deionized in a Milli Q-RG (Millipore, France) and had a resistivity of >18MΩ. The standard solutions were made from commercially available standards for AAS analysis (Merck, Darmstadt, Germany). A solution of HCl made by Merck (Merck, Pro Analysis, Darmstadt, Germany) was made by dissolving the acid of a density d=1.19 g mL^{-1} with deionized water at a ratio of 1:4 (3M HCl).

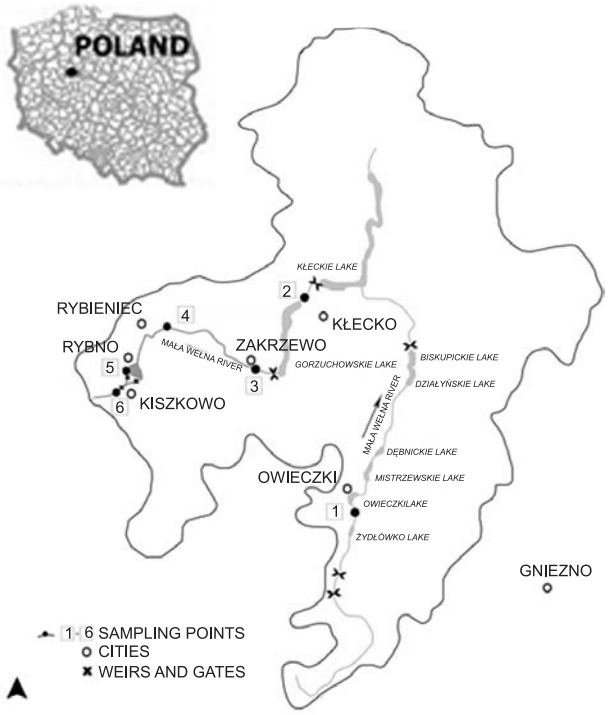

Fig. 1. Location of the sampling sites.

Apparatus

The metals Cd, Cr, Cu, Ni, Pb and Zn were determined by atomic absorption spectrometry with flame atomization (F-AAS) on a two-beam Perkin Elmer instrument, AAnalyst 300 model (Perkin Elmer, Norwalk, Connecticut, USA). The instrument was equipped with a Perkin Elmer AS 90 autosampler (Perkin Elmer, Norwalk, Connecticut, USA). The hollow cathode lamps (HCL) employed were made by the same producer (Perkin Elmer, Norwalk, Connecticut, USA). The optimized instrument parameters are given in Table 1.

Results and Discussion

Quality Control

The results of the analyses performed were verified against the results for the certified reference material SRM 2709. The certified values of recovery for particular heavy metals determined by the EPA 3050 method, recommended for SRM 2709 by the National Institute of Standards and Technology, were in the range of 54.8%-118% [19].

The SRM 2709-certified material was analyzed in six replicates by the F-AAS technique, and the median, standard deviation and relative standard deviation [%] were calculated. The results obtained for the certified material and the recovery values obtained for the heavy metals upon extraction with an HCl water solution at a ratio of 1:4 (3M HCl) are given in Table 2.

Table 1. Conditions of Cd, Cr, Cu, Ni, Pb and Zn determinations by the F-AAS technique.

Parameter		Cd	Cr	Cu	Pb	Zn	Ni
Wavelength	[nm]	228.8	357.9	324.8	217.0	213.9	232.0
Slit width	[nm]	0.7	0.7	0.7	0.7	0.7	0.2
Lamp current	[mA]	4	5	5	10	10	10
Oxid flow	[L min^{-1}]	10	8.6	10	10	10	10
Fuel flow	[L min^{-1}]	2	3.1	2	2	2	2
Sample flow rate	[mL min^{-1}]	4	4	4	4	4	4
Flame type		Air/Acetylene					

Table 2. Determination results of the certified reference material SRM 2709 by means of the F-AAS technique.

		Cu	Cr	Pb	Ni	Zn	Cd
Certified value	[mg kg^{-1}]	34.6±0.7	130±4	18.9±0.5	88.0±5.0	106±3	0.38±0.01
Analyzed value*	[mg kg^{-1}]	33.5±0.6	71.2±0.7	19.6±0.5	70.4±1.8	85.8±1.4	0.45±0.01
Analyzed value**	[mg kg^{-1}]	24.0±2.0	38.1±1.6	11.5±0.8	55.3±2.3	74.8 ± 2.0	0.39±0.01
Recovery*	[%]	97.8 ± 1.9	54.8±1.0	103.9±2.7	81.4±2.4	80.9±1.6	118±0.9
Recovery**	[%]	69.4±5.8	29.3±1.2	60.8±4.2	62.8±2.6	70.5±3.5	102.5±2.5

*- EPA 3050 method; **- 3M HCl method

The recovery values obtained were lower than the certified ones (NIST, 2002), which can be due to the use of a 1:4 HCl water solution (3M HCl) to isolate the HCl-labile fractions of the metals. An interesting result was the recovery obtained for chromium, 29.3 ± 1.2%. Such a low recovery can be a consequence of a stronger bonding of this element by the material studied.

Grain Size Distributions

Samples of the bottom sediment from the Mała Wełna river were dried at room temperature and subjected to granulometric analysis to separate seven grain-size fractions. The results of the sieving of 100 g bottom sediment samples are shown in Fig. 2.

The granulometric analysis showed a considerable contribution of the grain-size fractions 0.5-0.25, 0.25-0.1 and 1.0-0.5 mm (Fig. 2). Fractions smaller than 0.1 mm made up less than 10% of the total sample mass, while the 2.0-1.0 and >2.0 mm fractions constituted from 0 to 30%, depending on the location of the collecting site (Fig. 2).

Factor analysis was performed on all the samples of bottom sediments subjected to granulometric analysis, which made it possible to distinguish three groups of grain-size distribution (Fig. 3).

The first group (A) included samples denoted by the numbers: 1A, 1J1, 2A, 2J1, 3J1, 4M, 5J, and 6J; their

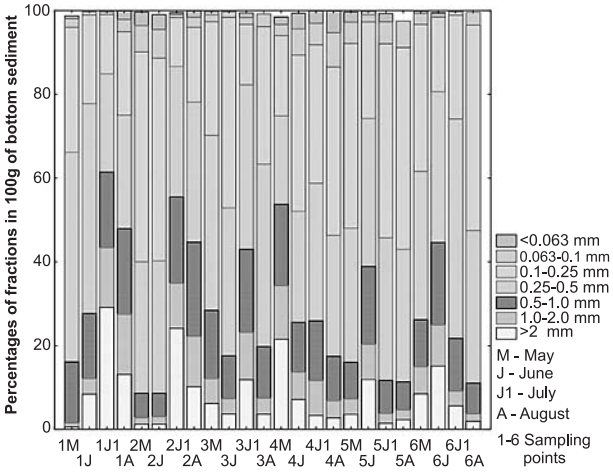

Fig. 2. Percentages of particular granulometric fractions in the samples of bottom sediments collected at all measuring sites in the study period (sampling sites 1-6).

grain-size fractions were 1.0-0.5, 2.0-1.0 and >2.0 mm. The second group (B) contained samples 1J, 1M, 3M, 3J, 3A, 6M, 6J1, and 6A with grain-size fractions of 0.5-0.25 and 0.25-0.1 mm. The third group (C) comprised samples 2M, 2J, 4A, 4J, 4J1, 5M, 5J1, and 5A with 0.1-0.063 and <0.063 mm fractions. It can be observed in Fig. 3 that the sediment samples collected from sites 4 and 5 display a low variability of the grain-size

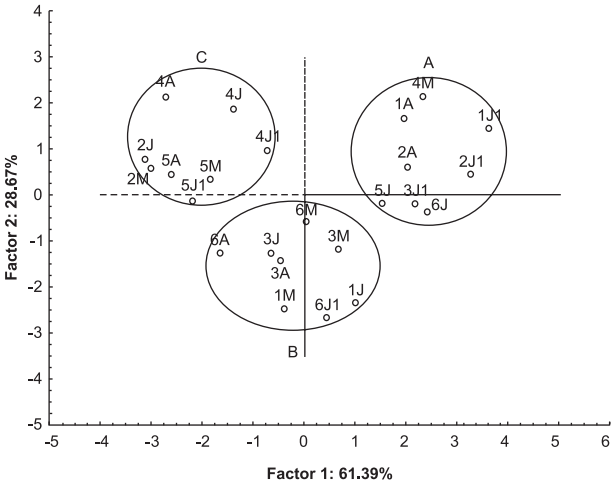

Fig. 3. Factor analysis of the distribution of grain-size fractions at all collecting sites and in all months of the study period.

distribution and a higher proportion of the finer fractions, 0.1-0.063 and <0.063 mm, than the remaining samples. Such a distribution is caused by low water discharge at sampling sites 4 and 5.

Metal Concentrations in Sediment

As follows from the analysis of the levels of the selected heavy metals in the particular granulometric fractions, the content of their HCl-labile species increases as grain size decreases (Fig. 4).

This effect is mainly due to the porosity and surface area of the particular sample fractions. Fractions of a small grain size have a larger surface area, hence they contain a higher amount of HCl-labile species of heavy metals (Fig. 4). The 1.0-0.5, 2.0-1.0 and >2.0 mm fractions were observed to have higher levels of HCl-labile species of heavy metals than the 0.5-0.25 and 0.25-0.1 mm fractions, which is connected with growth in the porosity of grains as their specific surface decreases [24].

As Zhu et al. [20] and Zou et al. [21] report, the predominant fraction in lacustrine deposits is that of <0.063 mm grain-size; it makes up >50% of all the fractions obtained from bottom sediment samples. Hence it seems justified to analyze this fraction as one representative of lakes. In the bottom sediments of the Mała Wełna river the highest concentrations of the HCl-labile species of heavy metals were found in the fraction of the smallest grain size (0.1-0.063, <0.063), whose percent contribution to the total mass of the samples was very small. It should be noted that other authors, e.g. Lin et al. [22], Jain and Sharma [23], Frankowski et al. [24] obtained similar results of heavy metals for the finest fractions. Kowalski et al. [25] also obtained similar results of mercury in samples of sedimentary rock in finest fractions.

In the 0.25-0.1 and 0.5-0.25 mm fractions, the concentration of the HCl-labile heavy metal species was lower (Fig. 4). However, because of their percent contribution to the sample mass (100 g), these fractions contained the highest amounts of this type of heavy metal species (Fig. 5). In the 1.0-0.5 to >2.0 mm fraction, the levels of the HCl-labile heavy metal species were higher than in those of the grain sizes of 0.25-0.1 and 0.5-0.25 mm (Fig. 4), but the proportion of the former showed variations (Fig.5). Therefore, depending on the aim of the study, to get reliable results for river bottom sediment samples it seems justified to analyze selected granulometric fractions. If the aim of a study is to determine the content of the HCl-labile heavy metal species in the samples, it is recommended to analyze the fractions from >2.0 to <0.063 mm.

Considering the fact that most authors separate the granulometric fraction with a grain size of <0.063 mm and that this is the fraction they analyze for heavy metals, it might be assumed to be representative. However, as Fig. 2 and Table 3 show, it is not always possible to separate and analyze this fraction, and hence to compare the research results. Thus, for example, the Geochemical Atlas of Poland at a scale of 1:2,500,000 gives heavy metal determinations for the <0.2 mm fraction obtained by extraction with hydrochloric acid 1:4 (3M HCl) [4]. The Geochemical Atlas of Poznań and its Environs at a scale of 1:100,000 also cites heavy metal figures for the <0.2 mm fraction from extraction with aqua regia [5]. In turn, the Geochemical Atlas of Europe reports heavy metal results derived from the <0.15 mm fraction [26]. The geochemical studies of bottom sediments in Poland made within the monitoring network give the grain size taken for chemical analysis as <0.2 mm [27].

The results of determination of the heavy metals (Cu, Cr, Pb, Ni, Zn and Cd) in individual fractions of the river bottom sediment samples studied are presented in Table 3.

Conclusions

On the basis of the study of bottom sediments from the Mała Wełna river carried out between May and August 2006, the following conclusions can be formed:

1. The granulometric analysis of the bottom sediment samples by dry method has revealed high proportions of 0.5-0.25, 0.25-0.1 and 0.5-0.25 mm fractions. Those with grain sizes of 0.1-0.063 mm and <0.063 mm make up less than 10% of total sediment mass, while the coarser fractions, 1.0-2.0 and >2.0 mm, from 0% to 30% depending on the sampling site.
2. The lowest concentrations of heavy metals extracted with 3M HCl were found to occur in the 0.5-0.25 and 0.25-0.1 mm fractions, and the highest in the 0.1-0.063 and <0.063 mm fractions. Their elevated levels were also observed in the >2.0 mm fraction. Hence, in the granulometric analysis of river bottom sediments by dry method it may be crucial to determine heavy metals not only in the finest grain-size fraction, which may not always be separable in the samples, but also in the larger fraction.

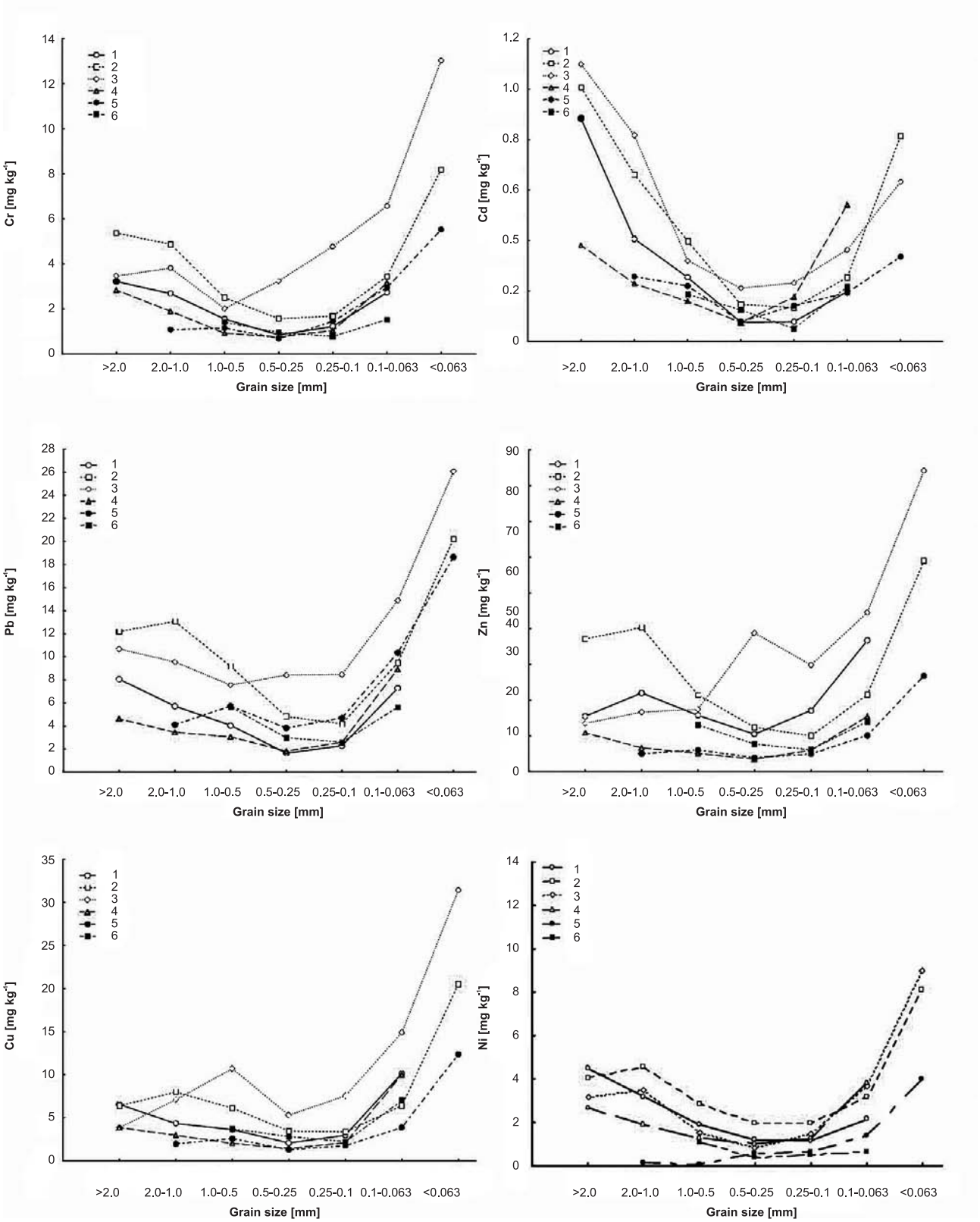

Fig. 4. The content of the HCl-labile species of the heavy metals studied in the particular granulometric fractions in samples collected in May 2006 at sampling sites 1-6.

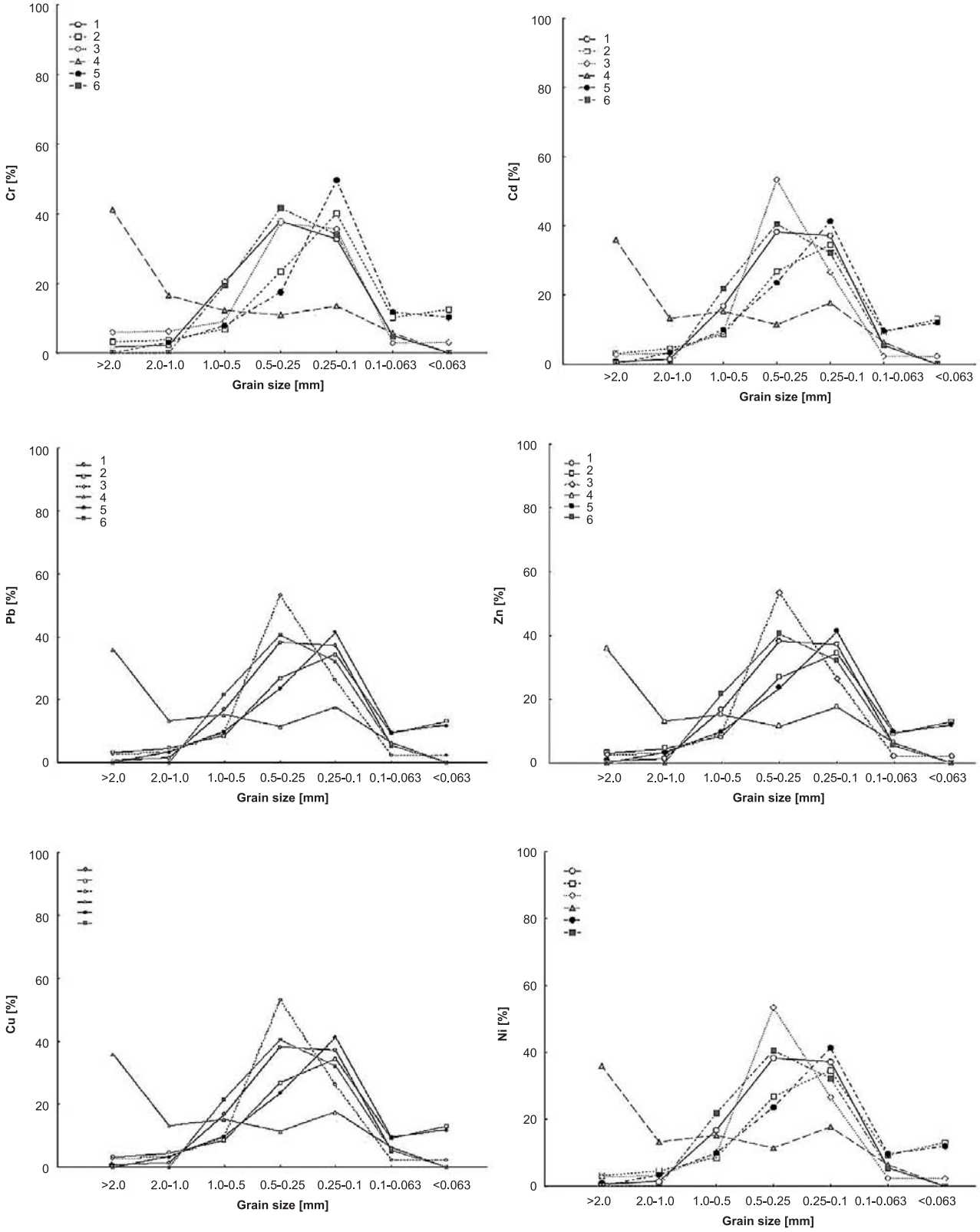

Fig. 5. The content of heavy metals (%) in 100 g of the bottom sediment in particular granulometric fractions at sampling sites 1-6.

Table 3. Mean and range concentrations of heavy metals in the bottom sediment samples collected from the Mała Wełna river (mg kg^{-1} d.m.).

Size fractions [mm]	Cu	Pb	Ni	Zn	Cd	Cr
>2.0 (n=24)	3.74 (1.29-9.68)	7.84 (2.15-25.2)	3.49 (1.04-19.2)	13.8 (3.79-83.7)	0.67 (0.02-2.2)	3.15 (0.36-10.5)
2.0-1.0 (n=24)	4.19 (1.99-31.8)	8.57 (3.22-52.9)	3.20 (0.16-5.12)	18.3 (5.02-146)	0.40 (0.13-0.93)	2.90 (1.08-9.16)
1.0-0.5 (n=24)	3.30 (1.69-14.6)	5.30 (1.65-28.9)	1.66 (0.07-5.96)	12.9 (4.40-63.3)	0.18 (0.03-0.81)	1.60 (0.73-5.65)
0.5-0.25 (n=24)	2.06 (1.21-8.61)	3.25 (1.16-12.6)	1.11 (0.26-4.82)	6.78 (3.15-38.8)	0.09 (BLD-0.51)	1.02 (0.28-3.25)
0.25-0.1 (n=24)	3.25 (1.21-10.8)	3.94 (0.69-11.8)	1.27 (0.50-4.70)	9.24 (2.80-37.2)	0.14 (BLD-0.58)	1.45 (0.34-4.78)
0.1-0.063 (n=19)	8.10 (3.45-25.3)	10.3 (3.40-24.1)	3.16 (0.61-13.8)	21.5 (8.71-79.4)	0.32 (0.03-1.6)	3.15 (1.38-6.57)
<0.063 (n=11)	18.2 (10.2-39.2)	23.6 (16.7-35.5)	8.10 (4.01-26.88)	63.2 (22.8-113)	0.70 (0.26-1.4)	7.04 (4.26-13.0)

BLD – below limit of detection

3. The use of one-step extraction using 3M HCl makes it possible to extract HCl-labile species of heavy metals from the bottom sediments. The advantages of this procedure are low cost of sample preparation for chemical analysis and ease of separating HCl-labile metal species from the sediments in comparison with multi-step extraction.

Acknowledgements

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