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Speciation of Heavy Metals in Bottom Sediments of Lakes in the Area of Wielkopolski National Park

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Abstract

This paper reports results of speciation analysis of selected heavy metals (Fe, Mn, Zn, Ni, Cu, Pb, Cd) in bottom sediment samples collected from 11 lakes in the area of Wielkopolski National Park, which is a protected area subjected to limited anthropogenic factors. The main aim of the study was determination of the distribution of the metals among five speciaiton forms defined by Tessier: exchangeable, bound to carbonates, bound to hydrated oxides of iron and manganese, bound to organic matter and others. The particular forms were isolated by sequential extraction.

Keywords: heavy metals, bottom sediments, lakes, sequential extraction, speciation.

Introduction

Speciation study of heavy metals in bottom sediments of surface water reservoirs are usually conducted in the areas subjected to enhanced anthropogenic factors since an increased level of heavy metal presence is a consequence of man's activity. The paper reports results of a speciation study of heavy metals found in bottom sediments of the lakes lying within the legally protected natural area of Wielkopolski National Park (WNP), subjected to limited anthropogenic factors [1]. Chemical composition of the sediments has been described in separate reports [2-4]. The first stage of the study included investigation of only one Góreckie Lake and the results have been presented in [5]. In this paper results of a speciation study of sediments from 11 lakes within the WNP, Góreckie Lake included, are reported and analysed jointly.

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Material and Methods

Wielkopolski National Park occupies an area of 7620 ha in the Wielkopolski Lake District, about 15 km south of the city of Poznan. This area can be approximated by a triangle spanned by the towns Lubon, Mosina and Steszew, with a small enclave called Trzcielinskie Swamps near Tomice. The borders of the Park were changed in 1996 and its present area is 7620 ha, of which forests occupy 4379 ha (57.4%), farmland - 2313 ha (30.4%), water reservoirs - 447 ha (5.9%), and wasteland - 115 ha (1.5%). The remaining area of 366 ha (4.8%) is taken by villages or towns, roads and others. The sculpture of the area is a result of the Scandinavian glacier activity during the last Baltic glaciation.

This study was performed on bottom sediment samples from 11 lakes: Budzyńskie, Chomęcickie, Góreckie, Jarosławieckie, Kociołek, Lipno, Łódzko-Dymaczewskie, Rosnowskie Duże, Rosnowskie Małe, Skrzynka, and Witobelskie. The earlier monitoring tests did not reveal significantly increased pollution of the lake

waters with heavy metals. Although the metal concentrations were higher than the geochemical background levels given in literature usually for river waters, in particular those of lead, cadmium, zinc and nickel, but were within the limits demanded of first class purity waters [1]. 43 samples were collected for the study. The method of their collection and initial processing were presented in an earlier paper on speciation of metals in bottom sediments of Goreckie Lake [5]. Distinction, isolation and quantitative determination of the speciation forms of metals was conducted according to a modified scheme proposed by Tessiera, for exchangeable metals (fraction I), metals bound with carbonates (fraction II), hydrated oxides of iron and manganese (fraction III), organic matter (fraction IV) and permanently immobilised metals (fraction V) and others described in detail in [9]. The methods employed and a full scheme of the sequential extraction applied have been presented in [5]. In solutions metals have been determined by atomic absorption spectrometry with flame atomisation, on an AAnalyst 300 made by Perkin Elmer.

Results and Discussion

The mean contents of metals in the bottom sediments of Wielkopolski National Park lakes were: Fe - 8800 mg/kg dry matter (in Goreckie Lake - GL- 9150 mg/kg), Mn - 538 mg/kg dry matter (GL - 350 mg/kg), Zn - 86.2 mg/kg dry matter (GL - 64 mg/kg), Ni - 17.1 mg/kg dry matter (GL - 13.0 mg/kg), Cu - 15.2 mg/kg dry matter (GL - 12.0 mg/kg), Pb - 52.3 mg/kg dry matter (GL - 47.5 mg/kg), Cd - 4.5 mg/kg dry matter (GL - 3.4 mg/kg), Cr - 11.3 mg/kg dry matter (GL - 9.7 mg/kg) and were slightly higher than the values determined within the programme of monitoring of sediments in water reservoirs in Poland [2, 3, 5, 10-14]. This little enhanced level might be the result of different procedures of sample mineralisation and processing and does not indicate an alarming increase in pollution with these metals [15]. Only an increased content of cadmium is probably related to a higher level of geochemical background in the area [16]. Close values to those determined for bottom sediments from Wielkopolski National Park lakes were reported by Solecki and Chibowski in samples of bottom sediments from lakes Piaseczno and Masluchowskie, in the area of relatively unpolluted Łęczyńsko--Włodawskie Lake District [17]. In bottom sediment samples from Długie Lake in Olsztyn, which has been for a long time a receiver of wastes and sewage from nearby streets, high contents of copper, lead, and zinc were determined [18]. Also, in the samples of bottom sediments from the much polluted Swarzedzkie Lake near Poznan, the contents of copper, zinc, lead, chromium and cadmium were high [19]. The level of heavy metal concentration in the sediment samples from these lakes was much higher than in the lakes from the Wielkopolski National Park, which was a consequence of strong anthropogenic factors. The bottom sediments from the Goczałkowice dam, one of the main sources of drinking water for Upper Silesia, were found to contain highly elevated levels of cadmium as a result of pollution from nearby industries [20].

More than in the total content of heavy metals in sediment samples we were interested in contributions of their particular speciation forms. Figs. 1-7 present mean percent contribution of particular speciation forms and for each form such statistical parameters as mean values, medians, maximum and minimum values, upper and lower quartiles illustrating accumulation of results about the median. The data have been obtained taking into account all samples collected from 11 lakes in the WNP area, treating them as one community.

Iron. Analysis of the contribution of particular fractions of iron present in the sediment samples from Goreckie Lake has shown the predominant contribution of fraction V - 46% and the fraction bound to organic matter (fraction IV - 40%). The contribution of the fraction in the form of oxides was much smaller (fraction III - 14%) and those of fractions I (exchangeable) and II (bound to carbonates) were very small [5]. The contribution of different fractions in the samples from the other lakes was similar. In all samples from the lakes studied, the mean contribution of fraction HI (bound to hydrated oxides of iron and manganese) was a bit higher (17%) than in the sample from the Goreckie Lake, and the contribution of fraction V a bit lower (43%). The distribution among the other three fractions was the same. A similar distribution of iron among the fractions distinguished was noted for the sediment samples from the artificial water reservoir Goczałkowice, on the Vistula river. Kwapuliński and Wichuła [20] reported that the iron occurred predominantly in fraction V, but the fraction of oxides bound twice as much iron as that bound with organic matter. Welte et al. [21] studied sediment samples taken at two different locations from the drinking water reservoir in Orly on the river Seine and reported even greater prevalence of the fraction of iron bound to hydrated oxides of iron and manganese over the fraction bound to organic matter. Dominant in one sample was iron in fraction V, while in the other in the fraction of hydrated iron and manganese oxides. Tessier et al. [8] studied bottom sediment samples from the rivers Yamaska and Saint-Francois in Canada, and reported that similarly as in the samples from WNP, the fraction of hydrated iron and manganese oxides contained 13-14% of the total amount of iron. The difference was that the dominant amount of iron was present in fraction V, and the amount in the fraction bound to organic matter was marginal. These results can be explained by a smaller content of organic matter in river sediments. The total content of iron and most of the other heavy metals determined was much higher than in samples from the Goreckie Lake and other lakes from the WNP area.

Manganese. In bottom sediments from Goreckie Lake, manganese occurred mainly in the fraction bound to carbonates (fraction II - 41%) and hydrated oxides (fraction III - 31%). The amount of manganese in the exchangeable fraction (fraction I- 11%) and in fraction V (9.9%) was much smaller. The fraction in which it was bound to organic matter contained only 6.1% of its total content [5]. In the other lakes from the area of WNP this distribution was different. In all samples from the WNP

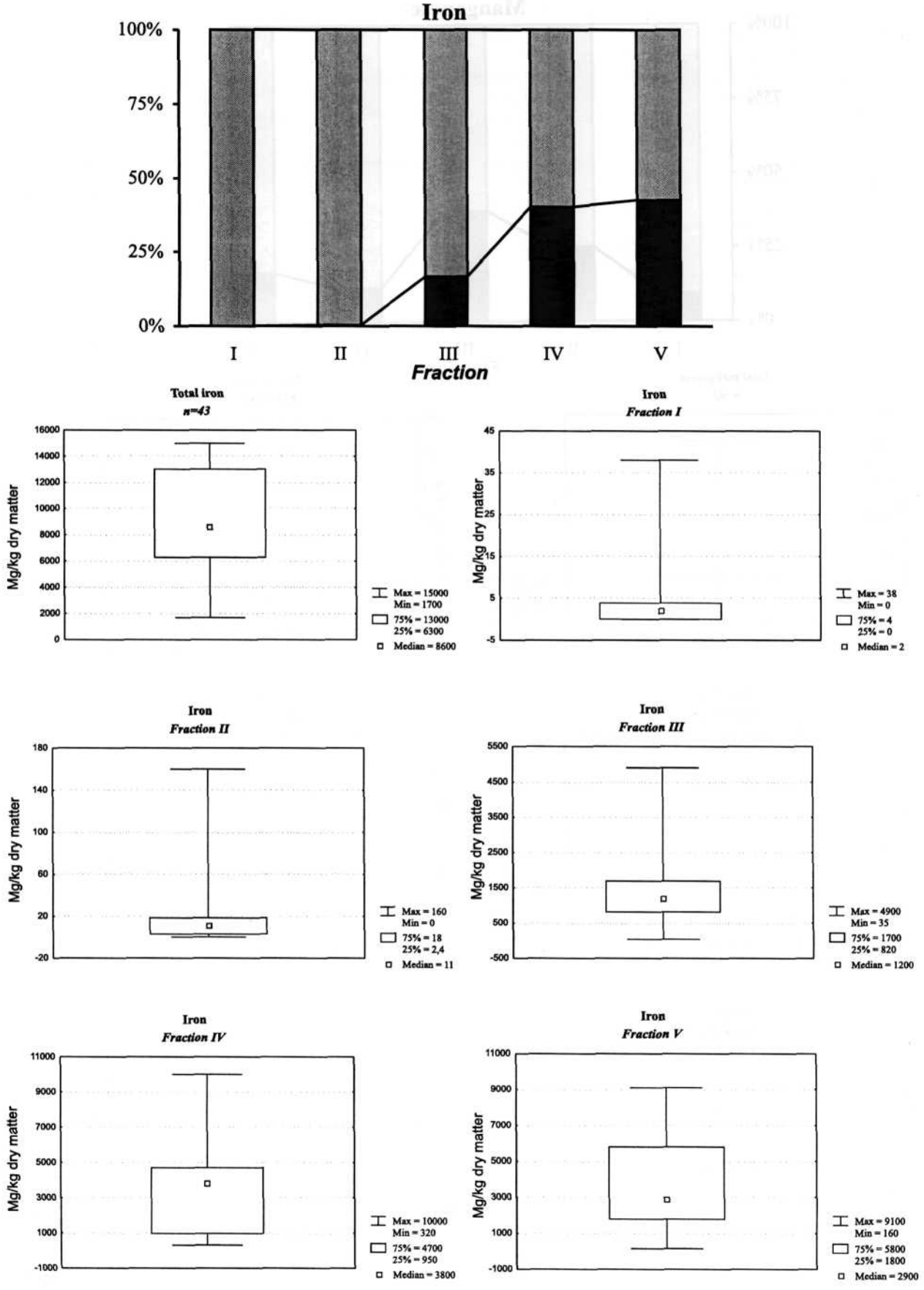

Fig. 1. Percent contribution of iron in particular fractions in the total content of this metal, in samples from 11 lakes in Wielkopolski National Park (mean values); graphical presentation of statistical parameters for each group of variables.

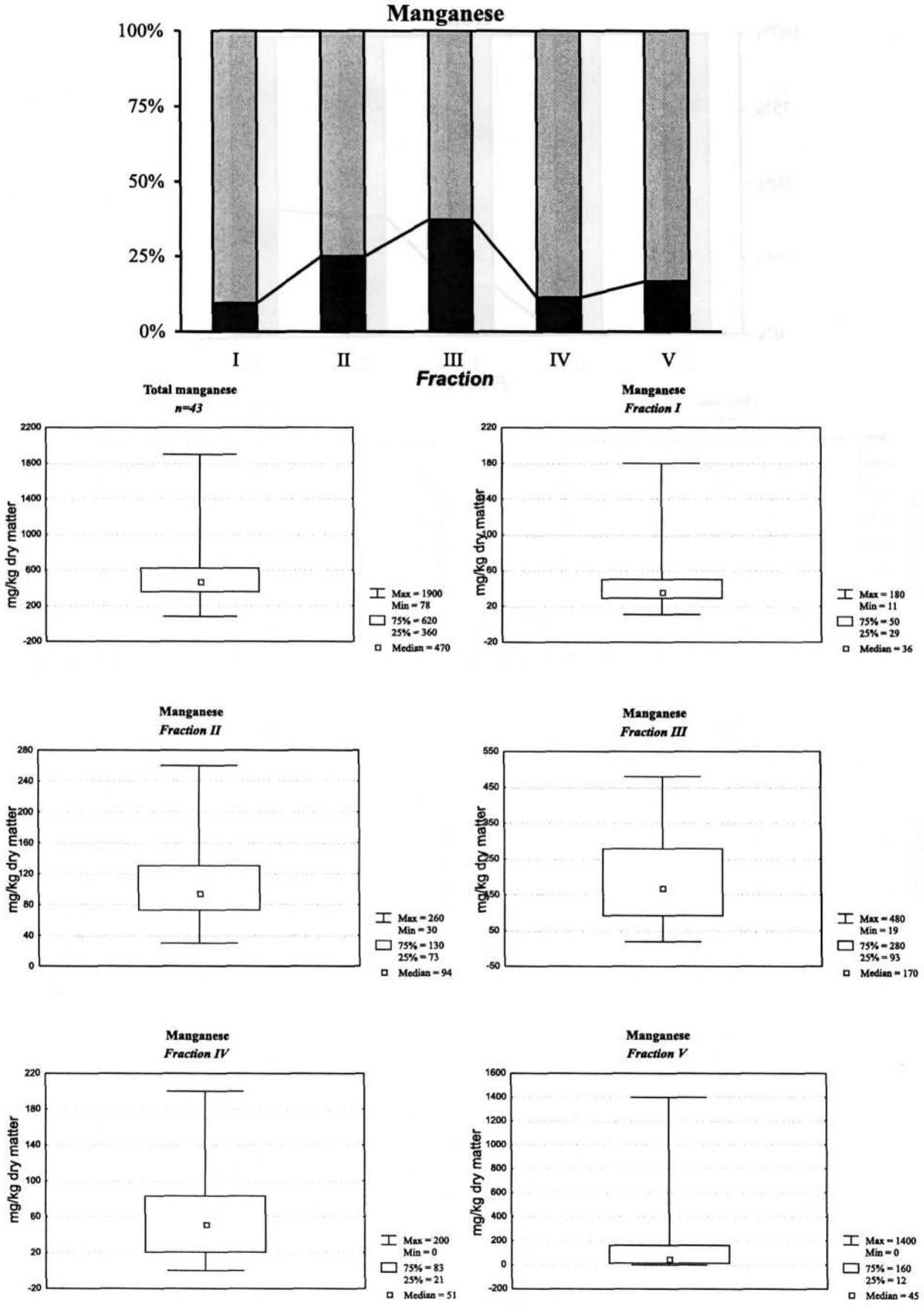

Fig. 2. Percent contribution of manganese in particular fractions in the total amount of this metal, in samples from 11 lakes in WNP (mean values), and graphical presentation of statistical parameters for each group of variables.

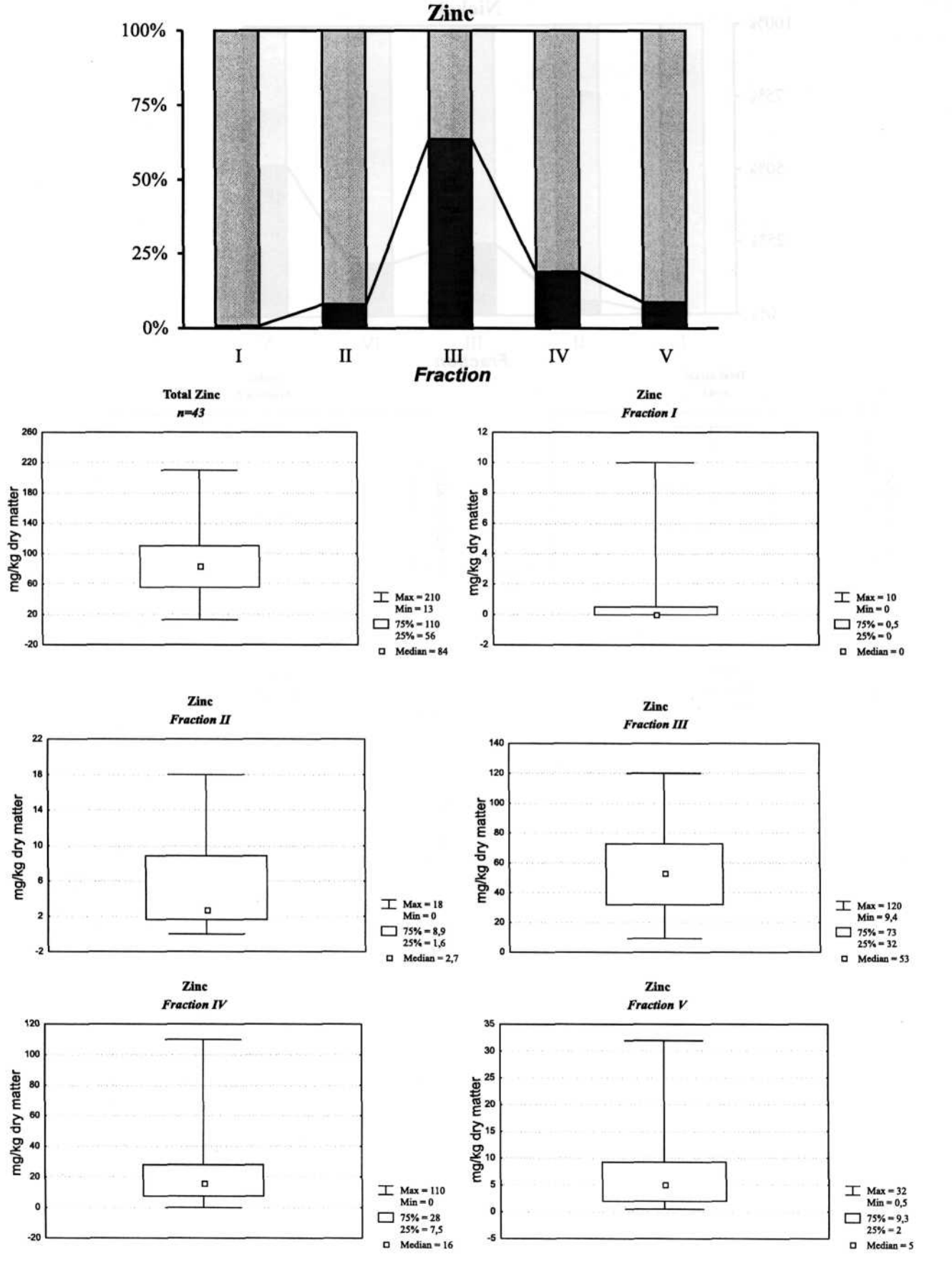

Fig. 3. Percent contribution of zinc in particular fractions in the total amount of this metal, in samples from 11 lakes in WNP (mean values), and graphical presentation of statistical parameters for each group of variables.

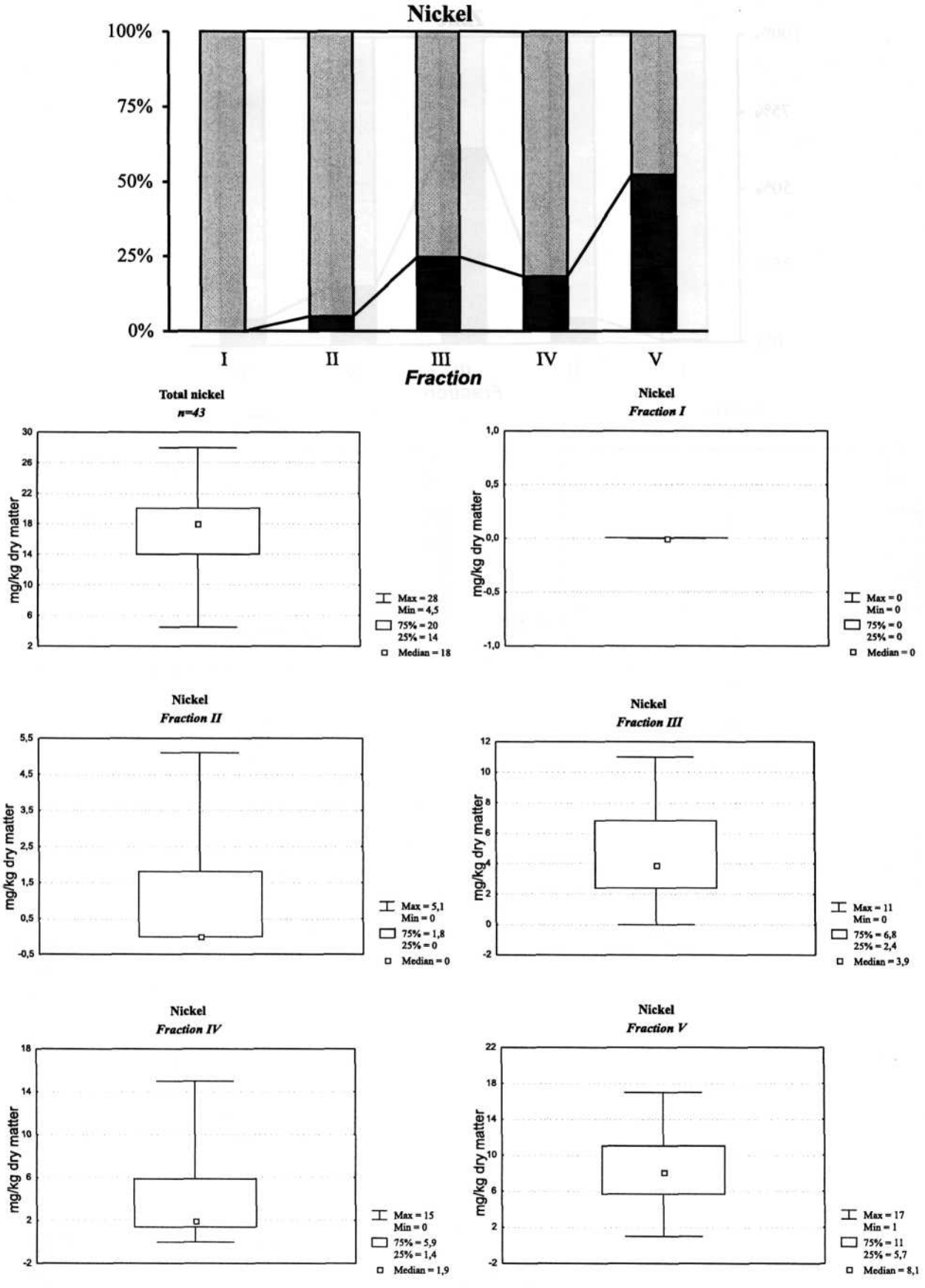

Fig. 4. Percent contribution of nickel in particular fractions in the total amount of this metal, in samples from 11 lakes in WNP (mean values), and graphical presentation of statistical parameters for each group of variables.

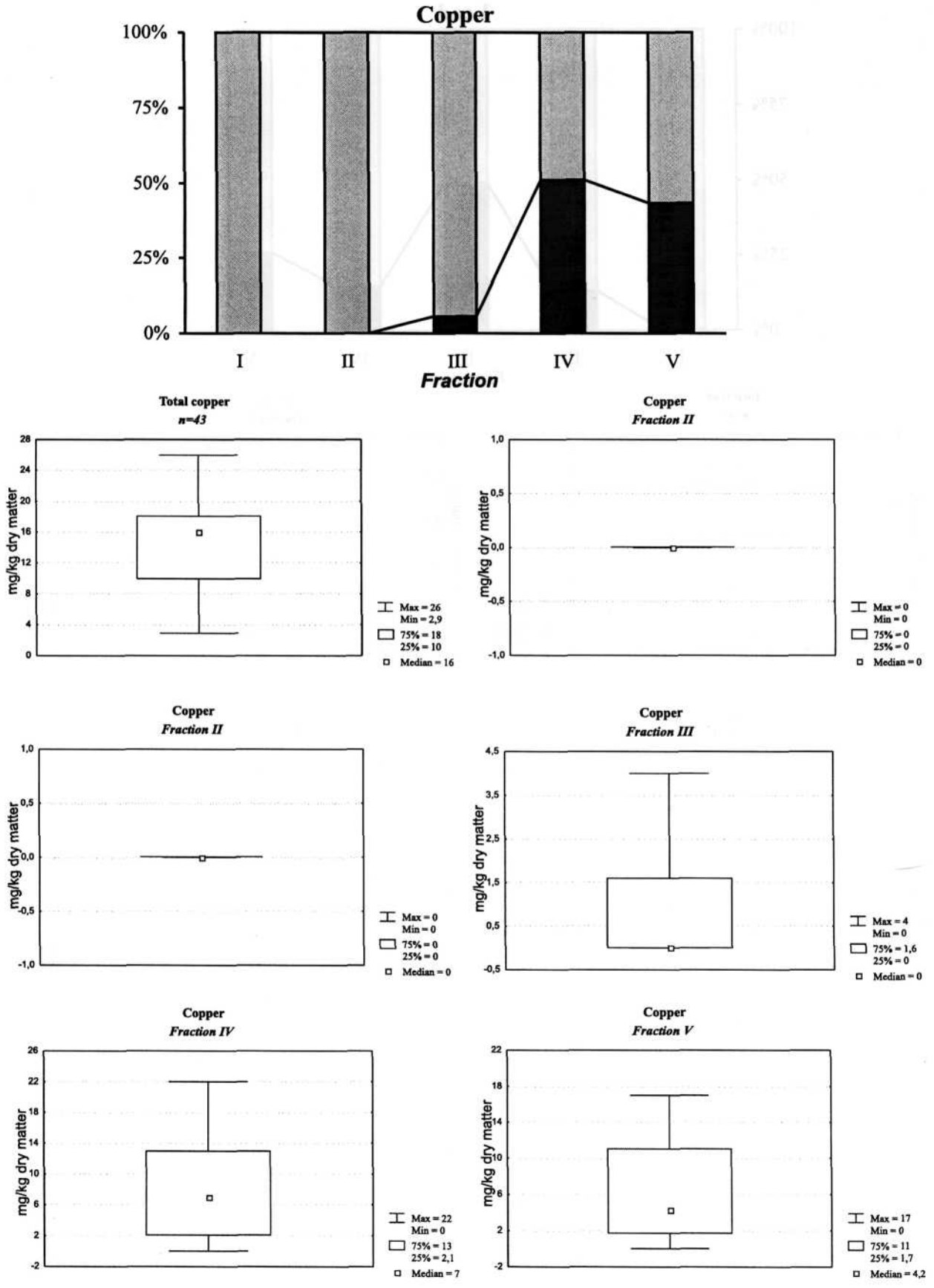

Fig. 5. Percent contribution of copper in particular fractions in the total amount of this metal, in samples from 11 lakes in WNP (mean values), and graphical presentation of statistical parameters for each group of variables.

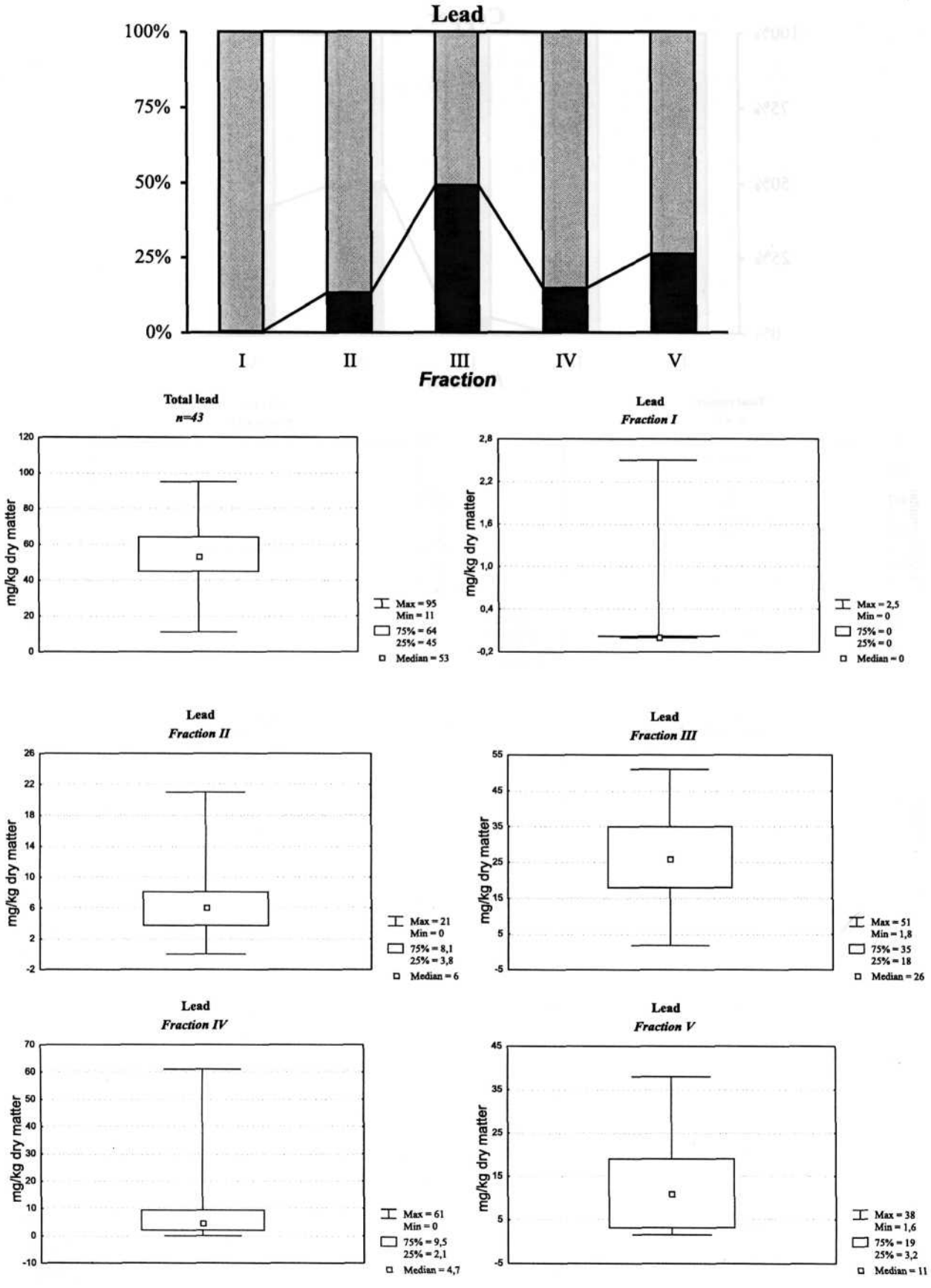

Fig. 6. Percent contribution of lead in particular fractions in the total amount of this metal, in samples from 11 lakes in WNP (mean values), and graphical presentation of statistical parameters for each group of variables.

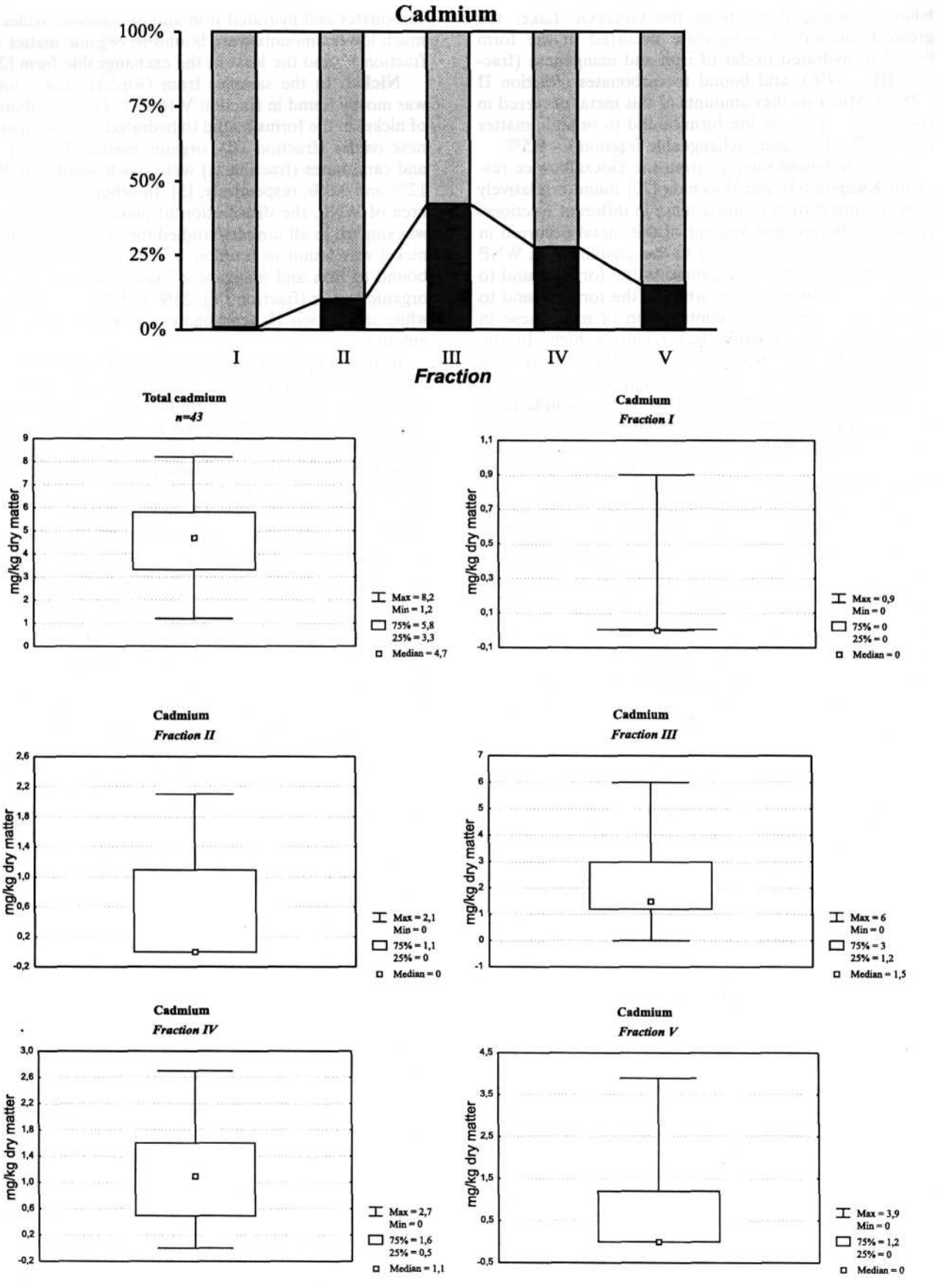

Fig. 7. Percent contribution of cadmium in particular fractions in the total amount of this metal, in samples from 11 lakes in WNP (mean values), and graphical presentation of statistical parameters for each group of variables.

lakes, including those from the Goreckie Lake, the greatest amount of manganese occurred in the form bound to hydrated oxides of iron and manganese (fraction III - 37%), and bound to carbonates (fraction II - 25%). Much smaller amounts of this metal occurred in fraction V - 17%, in the form bound to organic matter fraction IV- 11% and exchangeable fraction I - 9.5%.

In the sediment samples from the Goczalkowice reservoir Kwapulinski and Wiechula [20] found a relatively uniform distribution of manganese in different fractions. However, the greatest amount of this metal occurred in the fraction of oxides, similar to the samples from WNP lakes. The amount of manganese in the forms bound to organic matter was greater, while in the forms bound to carbonates - lower. The contribution of manganese in the exchangeable fraction was relatively high. In the samples of the river Seine reservoirs sediments taken at two different locations - the most manganese occurred in the form bound to carbonates (like in the sample from Goreckie Lake) or in the form bound to hydrated iron and manganese oxides. Much smaller amounts of this metal occurred in the form of fraction V and I [21]. In typical river sediments, Tessier et al. [8] reported the greatest amount of manganese in fraction V, and a relatively great amount of this metal in the form bound to carbonates. In almost all cases the smallest amount of manganese was in the form bound to organic matter.

Zinc. In the samples of sediments from Goreckie Lake, the most amount of zinc occurred in the form bound to hydrated iron and manganese oxides (fraction III - 58%). In much smaller amounts it occurred in the form bound to carbonates (fraction II - 16%) and bound to organic matter (fraction IV - 16%). The amounts found in fraction V and I were 8.6% and 1.9%, respectively [5]. In the sediments from the other WNP lakes, the distribution of zinc forms was similar. In all samples from all the lakes in the WNP area the greatest amount of zinc occurred in the form bound to hydrated iron and manganese oxides (fraction III - 63%), much less in the fraction bound to organic matter (fraction IV - 9.2%), fraction V (8.9%) and fraction II (7.8%). The amount of zinc in the exchangeable fraction was very low (0.7%).

In the bottom sediment samples from Dlugie Lake in Olsztyn, zinc occurred mainly in the form bound to hydrated iron and manganese oxides, its amount in fraction V was also relatively great and smaller in the form bound to organic matter [18]. In the samples from Goczatkowice the greatest amount of zinc was in the form bound to iron and manganese oxides, smaller in fraction V and in the form bound to organic matter, and very small in the form bound to carbonates [20]. Welte et al. [21] reported the greatest amount of zinc in the form bound to organic matter in the samples from the river Seine sediments. The contribution of the form bound to hydrated iron and manganese oxides was smaller, and that of fraction V and the form bound to carbonates was very small. In the sediment from the Canadian rivers, the largest amount of zinc occurred in fraction V, smaller in the form bound to iron and manganese oxides, and small in the form bound to organic matter [8]. In the samples from bottom sediments from the rivers in the area of Rybnicki Okreg Weglowy [Rybnicki Coal Mines District] (ROW), zinc was found mainly in the form bound to carbonates and hydrated iron and manganese oxides. Its much lower amounts were bound to organic matter and fraction V, and the least in the exchangeable form [22].

Nickel. In the samples from Goreckie Lake, nickel was mostly found in fraction V (66%). The contributions of nickel in the forms bound to hydrated iron and manganese oxides (fraction **III),** organic matter (fraction IV) and carbonates (fraction II) were much smaller at 20%, 12% and 3.8%, respectively, [5]. In other lakes from the area of WNP, the distribution of nickel in the fractions was similar. In all samples studied the greatest amount of nickel was found in fraction V (52%), smaller in form bound to iron and manganese oxides (fraction **III)** and organic matter (fraction IV): 25% and 18%, respectively, while in fraction II, (carbonates) only 5% of the total amount.

In the samples of sediments from Vegoritis Lake in Greece, Ure et al. [23] determined the greatest amount of nickel occurring in the form bound to organic matter, and smaller in fraction V. Nickel in other fractions occurred in very small amounts. In the river Seine sediments, Tessier et al. [8] the contribution of nickel in fraction V was the greatest, like in the samples from the WNP lakes, and that of the forms bound to hydrated iron and manganese oxides was significant. In the samples from Goczalkowice reservoir, the greatest amount of nickel was found in fraction V, and relatively great in the form bound to organic matter [20]. Also Welte et al. [21] reported the greatest amount of nickel in fraction V. In the sample from one locality the second greatest amount of nickel occurred in the form bound to organic matter (as in the sample from Goczalkowice reservoir) [20], while in the sample from the other locality, in the form bound to hydrated iron and manganese oxides (like in the samples from the WNP lakes). In both samples studied in [21] the contribution of nickel in the form bound to carbonates was also significant. In the samples of bottom sediments from the rivers in the ROW area, Wardas [22] reported the greatest amount of nickel in fraction V, and its large amounts in the form bound to carbonates and hydrated iron and manganese oxides. Much smaller amounts of nickel were found in the exchangeable fraction and to a great surprise it was not determined in the fraction bound to organic matter.

Copper. In the samples from Goreckie Lake, the most amount of copper occurred fraction V (83%). Its much smaller amounts were bound to organic matter (fraction IV - 16%) and hydrated iron and manganese oxides (fraction **III** - 2.9%) [5]. In the samples of sediments from the other WNP lakes, dominant were the forms of copper bound to organic matter. Consequently, taking into account all samples from all WNP lakes, the amount of copper in the form bound to organic matter was the greatest (51%). Its amount in fraction V was not much smaller (43%), and in fraction III - forms bound to hydrated iron and manganese oxides - made only 5.8% of the total amount of this metal. Copper was not determined in fraction I (exchangeable forms) and fraction II (carbonates).

In the samples from Dtugie Lake in Olsztyn dominant was the amount of copper bound to organic matter, while the rest of the metal present in the sediment occurred in the form bound to hydrated oxides of iron and manga-

nese. Surprisingly, no copper in fraction V was determined, although the contribution of this fraction in the other samples was significant [18]. The distribution of copper in particular fractions was similar to samples from WNP lakes and Goczalkowice reservoir: the dominant form was that bound to organic matter and slightly less amount of copper occurred in fraction V [20]. In one of the samples studied by Welte et al. [21], the amounts of copper in fraction V and the fraction bound to organic matter were the greatest and comparable, while in the other sample dominant was the fraction of copper bound to hydrated iron and manganese oxides, while the contribution of the other two fractions was much smaller. Tessier et al. [8], in the sediments from the Canadian rivers Yamaska and Saint-Francois, found the greatest amount of copper in fraction V, smaller in the forms bound to organic matter and hydrated iron and manganese oxides. In the samples of bottom sediments from the rivers in the ROW area, the most amount of copper was found in fraction V, somewhat smaller in the form bound to hydrated oxides and smaller in the form bound to organic matter. Very small amounts of copper were determined in the exchangeable fraction and in the form bound to carbonates [22].

Lead. In the samples from Goreckie Lake the largest amounts of lead occurred in the form bound to hydrated oxides of iron and manganese (fraction III - 34%), in fraction V (34%) and in the form bound to carbonates (fraction II - 21%). Its smaller amounts were determined in the form bound to organic matter (fraction IV - 10%) and exchangeable forms (fraction I - 0.8%) [5]. In the samples from the other lakes in the WNP area, the largest amount of lead occurred in the form bound to hydrated iron and manganese oxides (fraction HI). Taking into account all samples from all the lakes in the area, his fraction was dominant (49%). The contribution of fraction V was smaller (26%), and that of the forms bound to organic matter and carbonates was similar and equal 15% and 13%, respectively.

In sediment from Dlugie Lake in Olsztyn the greatest amount of lead occurred in the forms bound to iron and manganese oxides, and the contribution of fraction V was a bit smaller. The amount of lead bound to organic matter was much smaller [18]. In the samples from Goczalkowice reservoir lead occurred mainly in fraction V, in a considerable amount in the forms bound to hydrated iron and manganese oxides and organic matter [20]. In the bottom sediment from the drinking water reservoirs in Orly on the river Seine, Welte et al. [21] found lead mostly in the forms bound to hydrated iron and manganese oxides, but in one sample the contribution of fraction V was dominant. The distribution of lead in particular forms was similar in the samples studied by [8]. In the samples from rivers in the ROW area, Wardas [22] determined the greatest amounts of lead in the forms bound to hydrated iron and manganese oxides, smaller in fraction V. Much smaller was the amount of lead in the forms bound to organic matter, and it practically did not occur in the exchangeable fraction.

Cadmium. In the sediment samples from Goreckie Lake, cadmium was mainly found in the form bound to organic matter (43%) and in smaller amounts in the forms bound to hydrated oxides of iron and manganese (28%) and carbonates (18%) and in fraction V (5.9%) [5]. In samples from the other lakes in the area of WNP it occurred mainly in forms bound to hydrated iron and manganese oxides and fraction V. In all samples from all the lakes in the area of WNP, cadmium was found mainly in the forms bound to hydrated iron and manganese oxides (42%), in smaller amounts in the forms bound to organic matter (28%), in fraction V (15%) and in the forms bound to carbonates (10%).

In the samples from Goczalkowice reservoir the greatest amount of cadmium occurred in the forms bound to organic matter and in fraction V. In fractions I, II and III cadmium was found in rather small amounts [20]. In the sample from the reservoir Orly on the river Seine cadmium was only determined in the fraction bound to organic matter [21]. Tessier et al. [8] reported only small amounts of this metal in the forms bound to hydrated oxides of iron and manganese, while its amounts in the other fractions were beyond the level of determinability. In the two samples of sediments from the rivers in the ROW area, Wardas [22] determined cadmium only in fraction V. In the other samples the contribution of this fraction was much smaller, and the greatest amount of cadmium was found in the forms bound to organic matter and hydrated oxides of iron and manganese. No presence of cadmium in the exchangeable fraction was determined.

Conclusion

As follows from analysis of speciation forms of occurrence of the metals studied, manganese occurred mainly in the exchangeable forms (fraction I) and in the forms bound to carbonates (fraction II). These fractions are the most easily released to bulk water and thus the most bioavailable. Such metals as lead, cadmium, zinc and nickel were found in much smaller amounts in fraction II and practically not at all in fraction I. Iron and copper practically did not occur in any of these fractions. The metals occurring in fractions I and II can be released to bulk water as a result of change in the ionic composition of water or a decrease in water pH. Zinc, lead, cadmium and manganese were found in dominant amounts in the forms bound to hydrated iron and manganese - fraction **III.** Much less was the contribution of this fraction in the presence of nickel and surprisingly small amounts of iron occurred in this speciation form. The amount of copper in fraction III made only a few percent of its total content. The metals occurring in fraction **III** in bottom sediments are less mobile than those in fractions I and II and can be released to bulk water in the situation of strongly reducing conditions in the near bottom layer. In the forms bound to organic matter (fraction IV), mostly copper and iron were found. The contribution of nickel, cadmium, lead, zinc and manganese in this fraction was smaller. The metals occurring in fraction IV are even less mobile and can be released to bulk water as a result of mineralisation of organic matter. However, mineralisation may be accompanied by transition of the metals to one of the other speciation forms and thus they can stay in the sediment. Fraction V is permanently immobilised and it was the main form of occurrence of nickel and

iron, and bound significant amounts of copper and lead. Its contribution was smaller for cadmium, manganese and zinc. The metals occurring in this fraction in natural conditions cannot be released to bulk water so they are practically unavailable for living organisms and excluded from biocirculation.

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