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The relationship between the content of zinc and major elements in lake sediments in Poland

Zależność między stężeniem cynku i pierwiastków głównych w osadach jezior w Polsce

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Abstract
A total of 409 sediment samples were collected from lake deeps of 260 lakes in the Greater Poland, Pomerania and Masuria Lakelands. All samples (fraction <0.2 mm) were analysed for the concentration of zinc (Zn), Al, Ca, Mg, Fe, K, Mn, Na, P, S and TOC. The Zn concentration in the lake sediments varied from <6 to 1006 mg/kg, the average concentration was 93 mg/kg and the geometric mean 74 mg/kg. In most of the samples, the Zn concentration was less than 200 mg/kg (except in 19 samples). The Zn concentration shows significant correlation with the contents of Al, K, S and $C_{org.}$, and poor or no correlation with the contents of Mn, Na and Ca. Scatter plots show a clear relationship between the Zn content and the contents of Al and K, indicating that a significant part of Zn is associated in the sediments with clay minerals. There is also a correlation between the Zn content and the concentrations of $C_{org.}$ and S, suggesting that a part of Zn is bound by organic matter. A relatively poor relationship between the Zn concentration and the concentrations of Fe and P has also been found, indicating that a part of Zn may also be associated with iron minerals. Factor analysis has shown that in lake sediments of the Masuria and Greater Poland Lakelands Zn is primarily bound by organic matter, whereas in lake sediments of the Pomeranian Lakeland by clay minerals.

Streszczenie
Z głęboczków jezior Pojezierzy: Wielkopolskiego, Pomorskiego i Mazurskiego pobrano 409 próbek osadów. We wszystkich próbkach określono zawartość cynku oraz Ca, Mg, Fe, K, Mn, Na, P, S i OWO. W osadach zawartość Zn zmieniała się w zakresie od <6 do 1006 mg/kg, średnie stężenie wynosiło 93 mg/kg, a średnia geometryczna – 74 mg/kg. W większości zbadanych próbek zawartość cynku była niższa od 200 mg/kg (za wyjątkiem 19 próbek). Stwierdzono, że stężenie Zn wykazuje średnią korelację z zawartością Al, K, S i $C_{org.}$ oraz słabą lub brak korelacji z zawartością Mn, Na i Ca. Wykresy rozrzutu wykazały wyraźną zależność między zawartością Zn, a zawartością Al i K, co wskazuje, że w osadach znaczna część cynku związana jest z minerałami ilastymi. Widoczna jest także korelacja między zawartością Zn i stężeniem $C_{org.}$ oraz S, co interpretować można, że część cynku została związana przez materię organiczną. Stwierdzono także zależność między stężeniem Zn a stężeniem P oraz Fe (korelacje są stosunkowo słabe) co sugeruje, że cynk po części może być związany także przez minerały żelaza. Analiza czynnikowa wykazała, że w osadach pobranych z jezior Pojezierza Mazurskiego i Wielkopolskiego cynk jest przede wszystkim związany przez materię organiczną, a w osadach jezior Pojezierza Pomorskiego przez minerały ilaste.

1. INTRODUCTION

Zinc is an essential element for animals, plants and microorganisms, and is involved in basic metabolic processes. It is present in more than 100 enzymes (e.g. anhydrases, dehydrogenases, peptidases, phosphatases). A bigger problem for organisms is the scarcity of zinc than its excess. In mammals, its deficiency causes anaemia, slow growth rates and poor glucose tolerance, and the excess of zinc inhibits the activity of many calcium-binding proteins and affects the metabolism of copper and iron, as well as leads to the accumulation of zinc in tissues, especially in the kidney and liver. For plants, zinc is necessary for the synthesis of compounds regulating their growth and development, and the deficiency of zinc causes chlorosis and dwarfism of leaves. Although zinc is an essential element for plants, most plants show metabolic disorders at zinc concentrations exceeding 100 mg/kg; however, there are plant species called metallophytes which contain more than 10,000 mg/kg of zinc. In the aqueous environment, zinc is subject to accumulation and biomagnification in the trophic chain, sometimes to a dangerous level, e.g. when accumulated by the fish's gills it can cause their permanent damage (Gale et al. 2004; Dean et al. 2007; Murugan et al. 2008).

Zinc, which although forms a number of minerals of which the most common are sphalerite ZnS and smithsonite $ZnCO_3$, is primarily a widely distributed element in rock forming and accessory minerals: pyroxenes, amphiboles, micas garnets and magnetite. Its occurrence in sedimentary rocks and modern sediments is mainly due to the presence of detrital minerals – Fe–Mg silicates, magnetite and clay minerals, carbonates, organic matter, iron hydroxides and phosphates often of autochthonous origin (Chirinos et al. 2005; Webb et al. 2000; Lepane et al. 2007; Gale et al. 2004). The zinc concentration in soils that is the source of clastic material brought to the surface waters by surface runoff ranges from 10 to 300 mg/kg and depends primarily on its content in parent rocks, as well as on the content of organic matter and pH values. Carbonates (10–25 mg/kg) and sandstones (15–30 mg/kg) are poorer in zinc, compared with shales (80–120 mg/kg) (Kabata-Pendias, Mukherje 2007). Mobility of zinc in surface environments is controlled by its adsorption by clay minerals, Fe, Mn and Al hydroxides, and organic matter, as well as constrained by pH and Eh (Mäkinen, Pajunen 2005). The average zinc concentration in modern sediments of surface waters in Poland is 71 mg/kg, but in the central and northern parts of the country its concentrations are lower (<45 mg/kg) compared with southern Poland, in the Sudetes and Silesia, where magmatic rocks and ore mineralisation in Triassic dolomites are common (Lis, Pasieczna 1995, De Vos et al. 2006). The zinc concentration in sediments above which a negative impact on aquatic organisms is often observed has been found to be 459 mg/kg (MacDonald et al. 2000).

Zinc is introduced into the environment not only as a result of natural processes, but also due to human activities because the metal is important for the economy. It is primarily used to galvanise iron and steel against corrosion, and for the production of copper–zinc (brass) and zinc–aluminium (ZA) alloys. Moreover, zinc, due to its weight, replaces lead in various types of weights (in fishing or wheel balancing). Widely used are also zinc compounds such as zinc sulphate, which is used in electroplating, and in the textile industry as a mordant dye. Cadmium–zinc telluride is used in sensitive semiconductor devices, zinc oxide is used in the production of paints, varnishes, frit powders, in the glass industry (zinc regulates the melting of glass), in the enamelling industry (building and household products), and as a filler and an activator in the rubber industry. Zinc chloride is used as a wood impregnate in the textile industry, and as an additive for lubricants (retardant). Zinc sulphide is used in the production of lithopones (a component of white paints) and as a component of luminophores in watches and television sets, and zinc pyrithione is an antifungal component in paints, medicines and cosmetics. It is introduced into the environment from a number of sources among others as a result of coal burning, processing of zinc and lead ores, zinc metallurgy, transport, agriculture (microfertiliser, pesticides, animal feed additive), and due to weather-induced destruction of buildings (flaking paints, corrosion of galvanised metal sheets and pipes), means of transport during operation (e.g. tire wear) and, obviously, as a result of discharge of wastewater into surface waters and the use of sewage sediments in agriculture.

The aim of the study was find out which components of the sediments zinc are related to, since the form of its occurrence in the sediments, as well as of other trace elements, is very important because of its potential mobility and availability to the biosphere.

2. SCOPE AND METHODS

Studies of water sediments in Poland have been carried out within the subsystem of State Environmental Monitoring: Monitoring of the quality of inland surface waters, and include determination of concentrations of heavy metals and selected persistent organic pollutants in modern sediments of rivers and lakes in the country. The tests have been performed by the Polish Geological Institute – National Research Institute since 1990. Direct supervision of the implementation of the research programme is performed by the Monitoring Department at the Chief Inspectorate for Environmental Protection.

In 2010–2012, 409 water sediment samples were collected from profundal zone of 260 lakes in the Greater Poland, Pomerania and Masuria Lakelands (Fig. 1) (one sample was taken from each <250 ha lake, two samples from each 250–500 ha lake, three samples from each 500–1,000 ha lake, four samples from each 1,000–5,000 ha lake, five samples from each lake over 5,000 ha in size). The samples were taken from the near-surface 5 cm layer of sediments from lake deeps. All the samples (fraction <0.2 mm) were analysed for the content of zinc and elements forming the sediment components (clay minerals, organic matter, iron hydroxides, sulphides, phosphorous) that can retain zinc in sediments, including calcium, magnesium, iron, potassium, manganese, sodium, phosphorus, sulphur and organic carbon. The contents of Al,

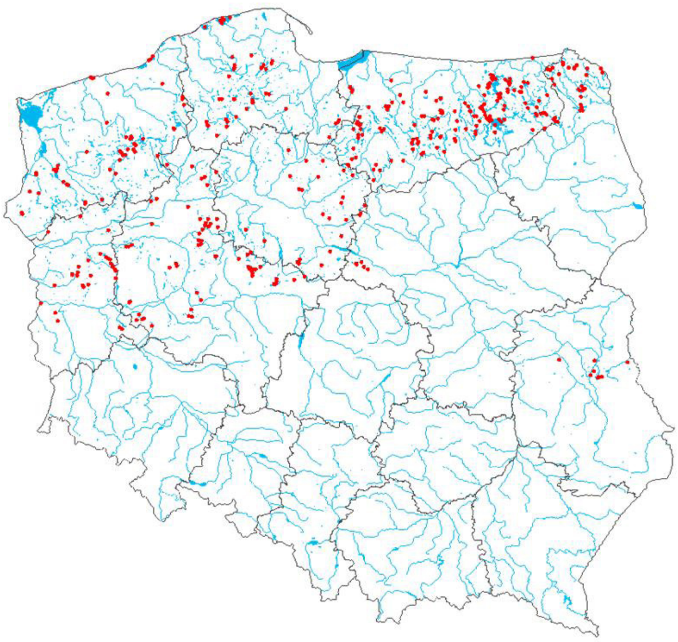

Fig 1. Map of lakes sampled

Ca, Mg, Fe, K, Mn, Na, P, S and zinc were determined by atomic emission spectrometry with inductively coupled plasma ICP-OES (Thermo Scientific iCAP6500) from the solutions obtained after digesting sediment samples with the aqua regia. The organic carbon content (TOC) was determined by coulometric titration from the solid sample (Ströhlein Coulomat 702 CS/LI). In order to assess the quality of the studies, reference material (WQB-3 lake sediment) was also analysed.

To determine the statistical parameters, make histograms and perform the factor analysis, the SATISTICA program was used.

3. RESULTS AND DISCUSSION

The zinc concentration in the sediments varied from 6 to 1006 mg/kg, average concentration was 93 mg/kg, geometric mean 74 mg/kg and median 78 mg/kg. In most of the samples, the zinc concentration was lower than 200 mg/kg (Fig. 2).

The zinc concentration was higher than 200 mg/kg only in 19 samples; among others in those collected from the following lakes: Karczemne, Klasztorne, Człuchowskie, Ełckie, Łagowskie, Zamkowe near Wałcz and Chodzieskie. The villages located by the lakes produced large amounts of sewage, which were discharged in the past to these lakes. Currently, the sources of pollutants are the street dusts and eroded urban soils enter the lakes with surface runoff. Because the histogram of zinc concentration in sediments shows the distribution close to normal for sediment samples with a zinc content up to 200 mg/kg, and due to the occurrence of other forms of zinc in the unpolluted or slightly contaminated sediment than in sediments heavily polluted by sewage sludge, samples with a zinc content greater than 200 mg/kg were excluded from considerations in the analysis of the correlation between the zinc concentration in the sediments and the contents of some major elements (scatter plots, correlation coefficients, factor analysis), as well as in determining the statistical parameters for lake sediments from different lakelands.

The average zinc concentrations determined in the lake sediments of the Greater Poland, Pomerania and Masuria Lakelands are similar: 68, 60 and 75 mg/kg, respectively (Table 1).

Among the tested samples, those with the zinc concentration in the range of 60–80 mg/kg are dominant (Fig. 2). The average concentrations of zinc in the investigated lakes are higher than the average value determined in the sediments of the littoral zone of 993 Polish lakes, which is 29 mg/kg (Lis, Pasieczna 1995). It has been found that there are differences in the occurrence of the correlation of the zinc content with the contents of major elements in sediments taken from lakes in different lakelands (Table 2).

The zinc content in lake sediments of the Greater Poland Lakeland shows significant correlations ($r > 0.50$) with the contents of sulphur, organic carbon and aluminium, and poor correlations ($r > 0.30$) with the contents of potassium, iron, phosphorus and magnesium. In sediments from the Pomeranian Lakeland, the zinc concentration shows significant correlations ($r > 0.5$) with the contents of

Table 1. Statistical parameters of Zn, Al, Ca, Fe, Hg, Mn, K, Mg, Mn, Na, P, S and TOC in the lake sediments

	Total (n=409)			Greater Poland Lakeland (n = 102)			Pomerania Lakeland (n = 79)			Masuria Lakeland (n = 207)		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Zn (mg/kg)	74	6	1,006	68	8	174	60	6	200	75	11	194
Al (%)	0.373	0.04	2.23	0.30	0.04	1.45	0.32	0.05	2.18	0.42	0.06	1.97
Ca (%)	8.91	0.05	30.63	11.51	0.05	30.27	7.25	0.09	29.41	9.14	0.20	30.63
Fe (%)	1.26	0.10	10.91	1.02	0.10	6.43	1.10	0.15	4.96	1.46	0.10	10.91
K (%)	0.081	0.005	0.510	0.059	0.005	0.302	0.069	0.005	0.330	0.098	0.011	0.510
Mg (%)	0.26	0.01	1.25	0.20	0.01	0.59	0.21	0.02	0.69	0.33	0.01	1.25
Mn (mg/kg)	644	32	11,770	613	32	4,193	589	56	4,999	679	33	11,770
Na (%)	0.020	0.006	0.536	0.021	0.006	0.049	0.025	0.009	0.536	0.018	0.007	0.036
P (%)	0.087	0.005	1.925	0.073	0.005	0.437	0.077	0.010	0.510	0.096	0.016	0.595
S (%)	0.825	0.023	4.629	0.852	0.023	4.629	0.788	0.031	3.757	0.814	0.049	4.229
TOC (%)	5.93	0.19	22.90	5.16	0.19	15.50	5.02	0.19	21.00	6.51	0.48	22.90

Table 2. Correlation coefficients between the zinc concentration and the concentrations of Al, Ca, Fe, K, Mg, Mn, Na, P, S and TOC

Element	Greater Poland Lakeland (p = 0,05, n = 102)	Pomerania Lakeland (p = 0,05, n = 79)	Masuria Lakeland (p = 0,05, n = 207)
Al	0.50	0.63	0.49
Ca	0.03	-0.25	-0.37
Fe	0.33	0.53	0.28
K	0.36	0.54	0.43
Mg	0.30	0.31	0.20
Mn	0.09	0.26	0.00
Na	0.25	0.09	0.33
P	0.30	0.38	0.25
S	0.52	0.51	0.35
TOC	0.53	0.55	0.40

aluminium, iron, potassium, sulphur and organic carbon, and low correlations (r>0.3) with the concentrations of magnesium and phosphorus. In lake sediments collected from the Masuria Lakeland, the zinc concentration shows only a weak correlation (r>0.3) with the contents of aluminium, potassium, sodium, sulphur and organic carbon. In summary, all the examined sediments show significant or poor correlations between the zinc concentration and the concentrations of aluminium, potassium, sulphur and organic carbon. Strikingly, there is the lack of correlation or a very weak correlation between the contents of zinc and manganese, and no or negative correlation between the contents of zinc and calcium. Scatter plots have shown a clear relationship between the contents of zinc and the contents of aluminium and potassium, which indicates that a significant proportion of zinc is associated with clay minerals, likely with minerals from the illite-smectite group. The correlation between the content of zinc and the concentration of organic carbon and sulphur in the sediments is also apparent, indicating that part of zinc is bound by organic matter and sulphides. The role of iron sulphides in the retention of heavy metals in sediments has been presented in a number of publications. It has been experimentally proved, for example, that there is the possibility of immobilisation of mercury in contaminated sediments using iron sulphide nanoparticles (Xiong et al. 2009; Jeong et al. 2007). A poor correlation between the zinc concentration and the concentrations of phosphorus and iron shows that zinc may partly be also bound in iron minerals (pyrite, vivianite and goethite). The possibility of immobilisation of heavy metals by apatite (calcium phosphates) has been presented in many papers, and this apatite's ability is used to immobilise heavy metals in polluted environments (Corami et al. 2008; Arey 2001). The scatter plots illustrate the lack of correlation between the concentrations of zinc and the concentrations of sodium and manganese, and negative correlation between the contents of zinc and calcium (Fig. 3).

The factor analysis performed on sediment samples from the individual lakelands has shown the presence of two factors which explain nearly 50% of the variation. In lake sediments of the Greater Poland Lakeland, one factor combines zinc with sulphur and organic carbon, and the other factor groups aluminium, potassium and magnesium (Table 3). In lake sediments of the Pomeranian Lakeland, zinc is combined with aluminium and potassium, whereas in lake sediments of the Masuria Lakeland, like in the Greater Poland Lakeland, zinc is grouped with sulphur and organic carbon. Based on the results of factor analysis, it can be assumed that the occurrence of zinc in lake sediments collected from Masuria and Greater Poland is primarily related to organic matter, whereas in lake sediments of Pomerania with the presence of clay minerals. This is probably due to the fact that many of the tested lakes in the Pomeranian Lakeland are situated in the areas of till occurrence, while most of those in the Masuria and Greater Poland Lakelands, in which organic-rich sediments accumulated, are located in areas of sandy deposits.

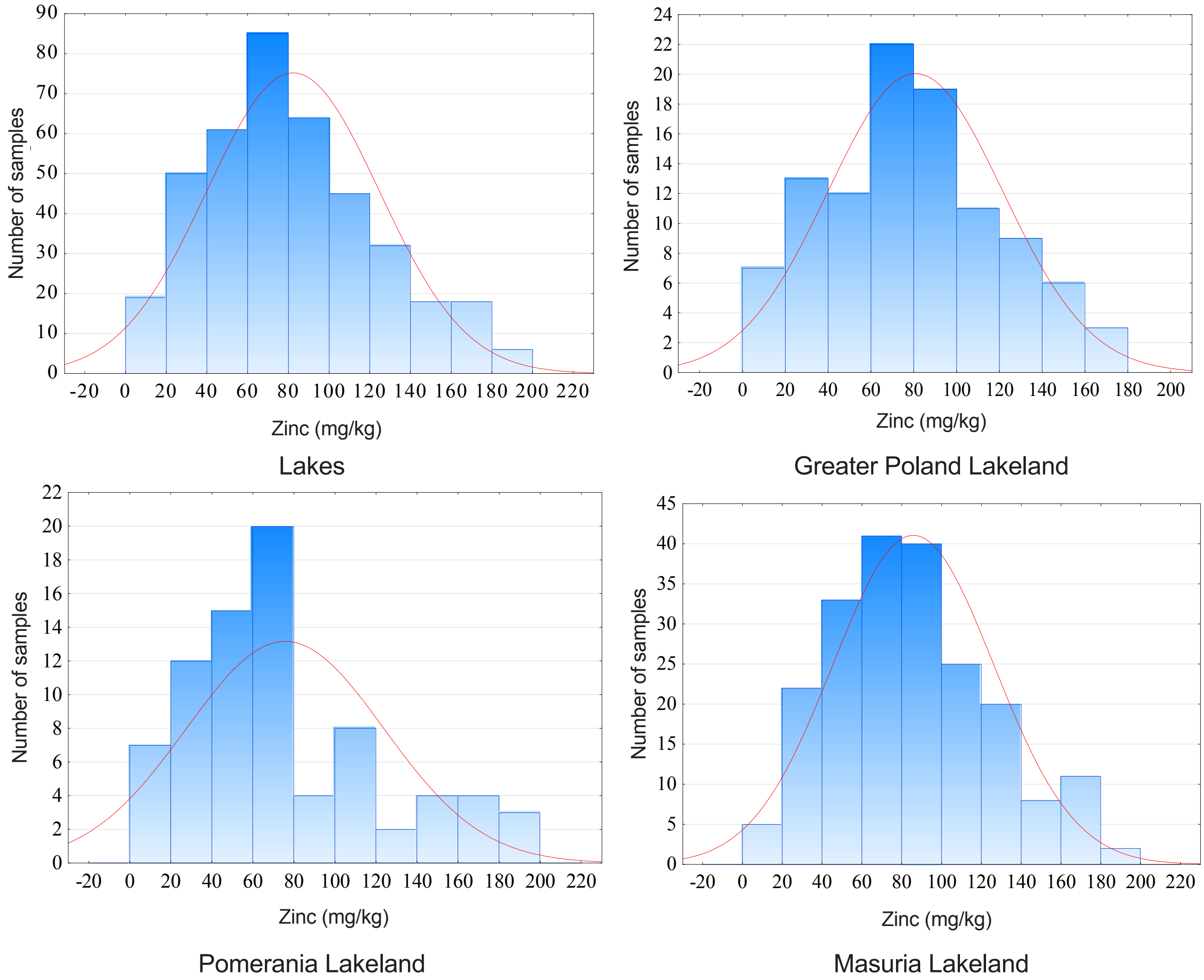

Fig. 2. Histograms of the zinc concentration in the lake sediments

4. CONCLUSIONS

1. The zinc concentration in sediments taken from lake deeps in most cases did not exceed 200 mg/kg, and the average concentration was 93 mg/kg, which was significantly higher than the average concentration in littoral lake sediments in Poland.
2. The zinc concentration shows a clear correlation with the levels of Al, K, S and $C_{org.}$, and a very poor or no correlation with the contents of Mn, Na and Ca.
3. Analyses have shown a clear relationship between the content of zinc and the contents of Al and K, as well as a correlation between the content of zinc and the concentration of $C_{org.}$ and S.
4. Factor analysis has revealed that in lake sediments of the Masuria and Greater Poland Lakelands, the presence of zinc is related to sulphur and organic carbon, and in the Pomeranian Lakeland to aluminium and potassium.

Table 3. Factor analysis

Parameter	Greater Poland Lakeland			Pomerania Lakeland			Masuria Lakeland		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Al	0.945	0.231	0.116	0.900	-0.194	-0.062	0.970	0.067	-0.005
Ca	-0.486	0.065	-0.576	-0.435	0.631	-0.322	-0.712	-0.306	0.386
Fe	0.252	0.562	0.323	0.543	0.122	0.637	0.422	0.051	0.473
K	0.948	0.006	0.010	0.798	-0.217	0.108	0.965	-0.015	0.034
Mg	0.739	-0.110	-0.383	0.431	0.050	0.221	0.831	-0.314	0.072
Mn	-0.155	0.217	-0.057	0.006	0.671	0.405	-0.082	-0.172	0.630
Na	0.026	0.047	-0.712	0.081	-0.207	0.813	0.121	0.227	0.339
P	0.089	0.309	-0.167	0.162	0.642	0.296	0.020	0.083	0.653
S	0.008	0.844	0.099	0.477	0.083	0.595	-0.222	0.648	0.242
Zn	0.412	0.750	-0.389	0.863	0.356	0.120	0.470	0.729	0.330
TOC	0.189	0.722	0.025	0.529	0.118	0.184	-0.033	0.777	-0.205
Var.Fact.	7.474	7.221	4.510	10.756	3.600	3.506	8.733	6.151	3.438
Share	0.234	0.226	0.141	0.336	0.113	0.110	0.273	0.192	0.107

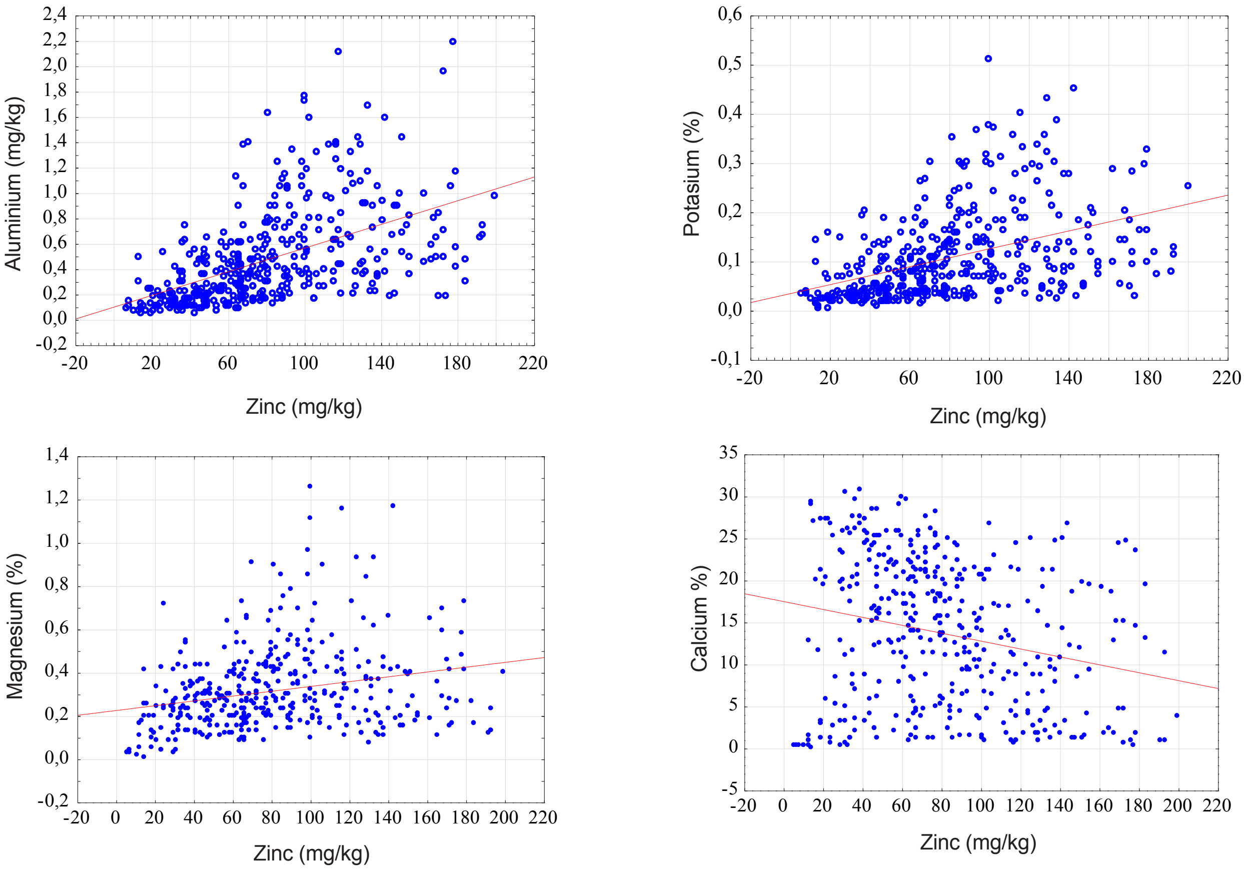

Fig. 3. Scatter plots of the zinc concentration versus the concentrations of selected elements

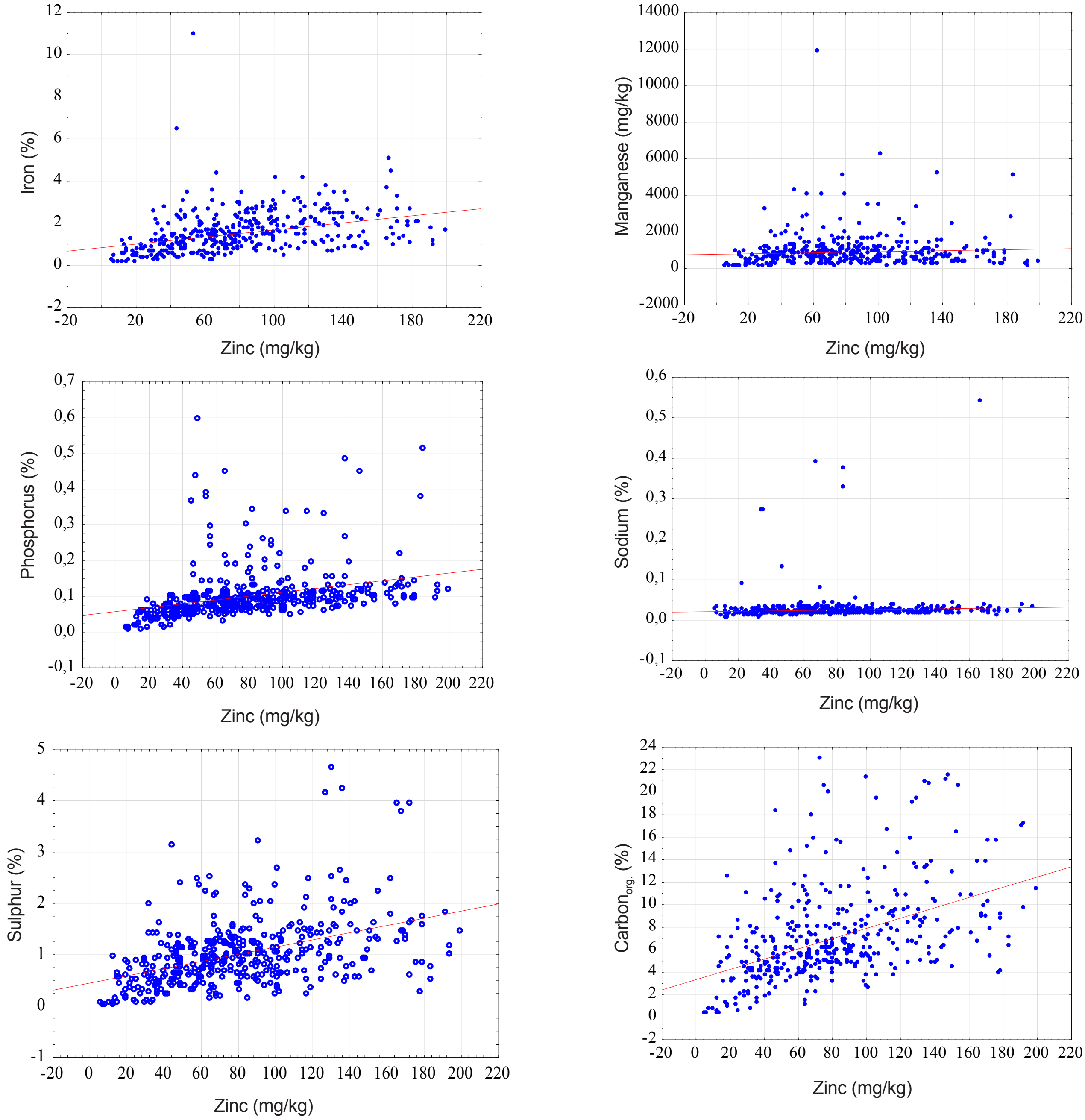

Fig. 3. Scatter plots of the zinc concentration versus the concentrations of selected elements (cont.)

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