

BINDING FORM OF TRACE ELEMENTS IN SEDIMENT  
OF A MEROMICTIC LAKE

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al. A. Mickiewicza 33, 31-120 Kraków, Poland**Keywords:** Pit lake, trace elements, sediment, speciation.

**Abstract:** Speciation of trace elements in the sediment of a meromictic Piaseczno Lake (inundated opencast sulphur mine, southern Poland) with permanently anoxic monimolimnion was studied. A 6-step sequential extraction procedure was applied to determine operationally defined phases: exchangeable (F1), carbonate (F2), easily reducible (F3), moderately reducible (F4), organic/sulphides (F5), and residual (F6) in the sediment. The differences in trace elements (except Mn) speciation in the littoral sediment with the respect of lake depths were not found. Considerable difference in the trace elements speciation between the littoral sediment and permanently anoxic profundal one was found.

## INTRODUCTION

Sulphur mining was very intensive in the Tarnobrzeg Sulphur Region in southern Poland from the late 50's/early 90's of the 20<sup>th</sup> century. The sulphur ore was exploited by the open-pit method. When mining had ceased, the opencast was naturally filled with highly mineralized Tertiary and Quaternary waters and an artificial Piaseczno Lake was created. At present the lake has an area of 0.63 km<sup>2</sup> and maximum depth of 21.5 m [43, 44]. Piaseczno Lake is a meromictic water body owing to its basin morphology. Lake water is well oxygenated from the surface to the depth of 7.5–10 m, while monimolimnion is permanently anoxic [44]. Pit lakes or rivers from sulphide ore mining usually have acidic water due to oxidation of sulphide minerals [9, 22, 25]. Acidic mining lakes (pH < 3) represent a big environmental issue in former lignite mining [7, 16]. Inversely, Piaseczno Lake water is from neutral to alkaline (pH 6.9–8.5). It is very hard and rich in SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> anions, with the maximum amounts of Cl<sup>-</sup> anions, alkalinity, and organic matter (expressed as Chemical Oxygen Demand – COD) in the monimolimnion [44].

The chemical composition of Piaseczno Lake sediment is quite different in littoral and profundal parts. Littoral sediment consists mainly of silica (average 46.4%), sulphur (7.6%), calcium (5.6%), aluminum (4%), iron (2.4%), potassium (1.3%), and magnesium (1.1%) (in wt % dry mass). There, clay silty fraction (62–93%) dominates and the amount of organic matter is low (LOI) (1.6–12.6%) [34]. Upper (0–15 cm) layer of the profundal sediment is permanently anoxic and consisted mainly of Fe (32.4%), S (20.8%), Ca (19.8%), Si (10.8%), and Al (4.6%) [35].

Many authors [18, 19, 23, 30, 38, 40, 42] indicated changes of sediment-bound metals under changing redox conditions. The extent to which these changes control contaminant cycling is at present unclear [12]. Changes in both redox potential (Eh) and pH can accelerate desorption, partitioning of trace element, bacterial degradation and the oxidation of organic matter [11, 18, 39]. Studies of operationally defined phase-specific binding forms have the advantage of providing better insight into the mechanism of association of metals with mineralogical phases of the sediments as well as it is a good approach to show their real activity in aquatic environment. These methods were recently successfully applied to describe environmentally mobile and stable fractions of toxic metals [15, 20, 31, 33, 40, 41]. Differences in dissolved oxygen concentration with water depth of meromictic Piaseczno Lake undoubtedly affected the strength of element binding in the sediment, which influences metal availability to benthic organisms.

This study was conducted to recognize the phase-specific binding forms of trace elements in bottom sediment of meromictic pit Lake Piaseczno in southern Poland. Particular attention was paid to the influence of oxic and anoxic conditions on metal speciation.

## STUDY AREA

### *Catchment geology*

The Piaseczno area is composed of Holocene and Pleistocene mud, sands and gravel, the Sarmatian clayey deposits, sulphur-bearing limestone, gypsum, the Baranów sands, brown-coal clays, the Carboniferous siltstone and claystone [28]. The sulphur-bearing limestone is composed of calcite and sulphur, which makes up to 94% of the rock. The Sarmatian clayey deposits form a blanket of over 80% of the sulphur mine. The top soil and an under soil layer, which is 10 to 15 m in thickness are formed of the Holocene and Pleistocene mud, sands and gravel [21]. There are no roads or agricultural activities in the vicinity of the lake.

### *Sampling stations*

Because the littoral zone was narrow, especially on transects 2 and 3, samples of water were taken only from stations 1c, 2c, 3c (lake depth ~ 10 m; Fig. 1). The samples were collected at the depths of 9 m (i.e. 1 m above the bottom) in spring (3 April 2001) and summer (18 July 2001). In each sample the content of dissolved oxygen and pH were measured. The samples of water were not taken from station 4 (monimolimnion water). According to Żurek [44] monimolimnion water (lake depth of 21 m, ~ 1 m above the bottom) was anoxic and alkaline.

The sediment samples were taken from ten stations in spring (3 April 2001) and summer (18 July 2001) (Fig. 1). They were collected using a polyethylene corer with an area of 12.56 cm<sup>2</sup> from the stations 1a, 1b, and 1c (lake depth of 1 m, littoral), stations 2a, 2b, and 2c (lake depth of 5 m, littoral), stations 3a, 3b, and 3c (lake depth of 10 m, littoral) and station 4 (lake depth of 21 m; permanently anoxic profundal sediment). One sediment sample contained several subsamples. Stations were located on three transects, which differed in the slope of the lake basin and the degree of shelter from the wind (Fig. 1). Transect 1 was situated in open part of the lake and was exposed to wave action. It had a forested shore reducing soil erosion; it resulted in a thin layer of sediment. On transect 1 more stones and gravel than on transects 2 and 3 was found. Transects 2 and 3 had very steep slopes resulted from the excavation of sulphur-bearing limestone, compared to tran-

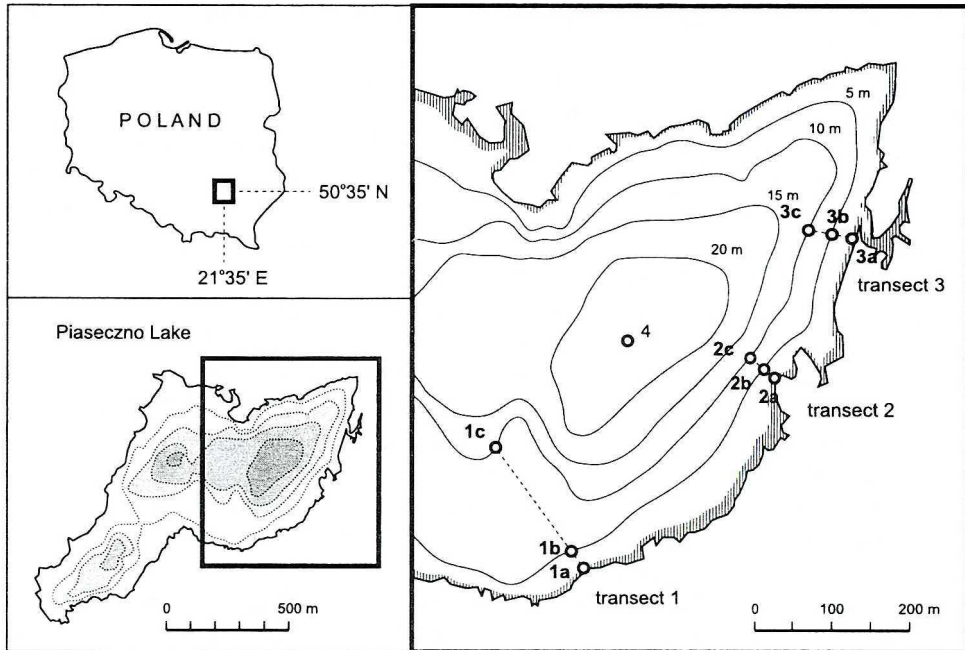


Fig. 1. Map of the study area (Piaseczno Lake) with location of sampling points

sect 1. They were situated in a protected part of the lake, not exposed to wave action, so they had thicker layer of sediment. For each sediment sample pH, total and phase-specific binding forms of trace elements were determined.

## MATERIAL AND METHODS

### *Analytical methods*

pH of the water and wet sediment were measured with the Orion pH-meter (Expandable Ion Analyser EA 940). The concentration of dissolved oxygen was determined using the Winkler method [1].

Samples of sediments used for total trace element analysis were dried at 105°C for  $\geq 24$  h. The samples for Pb, Cu, Mn, and Fe determination were then ground (3 g of the sediment and 0.3 g of paraffin, MERCK *Hoechst wax C micropowder*) in a planetary mill (Pulverisette 7, Fritsch) at 500 rpm for 5 min. Tablets (2.7 g, 31 mm in diameter) were prepared in a pallet die (Graseby-Specac), under a pressure of 25 Mg for about 5 seconds. The measurements were carried out using an energy-dispersive X-ray spectrometer (ED 2000, Oxford Instruments). The element concentrations were based on standard sediments IAEA-SL1 obtained from the International Atomic Energy Agency. The detection limits (DL) were calculated from the relationship  $DL = 3 \cdot \sqrt{BACKGROUND}$ . The DL values for studied elements were  $\sim 1$  ppm.

Sediment samples used to determine the total Cd concentration were homogenized using the planetary mill (Pulverisette 5) with Teflon grinding balls. Triplicates of approximately 0.5 g of dry sediment were digested with 15 cm<sup>3</sup> conc. HNO<sub>3</sub> in tubes on the heated block of a Tecator Digestion System 12, in conjunction with an Autostep

2000 controller set to 120°C for 2 h. After digestion, the concentration of each tube was filtered through a 0.45 µm filter into a calibrated 50 cm<sup>3</sup> volumetric flask. The remaining sediment in each tube was rinsed with double distilled water to remove all of the acid solution. Then the flask was filled with double-distilled water. The reference material NCS DC 73308 (stream sediment) was digested in the same way. Cadmium concentration in reference material was 1.18 µg g<sup>-1</sup> (certified value 1.12 ± 0.08 µg g<sup>-1</sup>).

Analyses of an operationally defined phase-specific binding form of elements in the sediment were carried out according to the method of Förstner and Calmano [13]. The obtained six fractions are described below.

F1: exchangeable cations. Includes the elements adsorbed to exchange sites on the surface of sediment particles – the most mobile and available fraction. Trace elements can be released from this fraction under changing water conditions [14].

F2: carbonate phase. This fraction is influenced by pH changes and is considered as moderately mobile and available to organisms [5, 6].

F3: easily reducible phase, i.e. Mn oxide, amorphous Fe oxide. Amorphous ferromanganese oxyhydrates with their associated elements will be dissolved under reductive conditions in the sediment [2, 4]. Similarly to F2, this phase is regarded as moderately mobile and bioavailable.

F4: moderately reducible phase (poorly crystalline Fe/Mn-oxyhydroxides). Fe/Mn oxides exist as nodules, concretions, cement between particles or as a coating on particles and are very good trace element scavengers. It is a relatively stable bound metal phase [8].

F5: organic matter and sulphide phase. This fraction represents trace elements bound to insoluble organic matter i.e. living organisms, detritus, and coating on mineral particles. Organic matter degradation under aerobic and anaerobic conditions influenced trace elements releasing from this phase. Considerable amounts of trace elements are usually bound to sulphides under anaerobic conditions [18, 19, 42]. This fraction is susceptible to pH and Eh conditions.

F6: residual phase. The residual phase represents metals largely embedded in the crystal lattice of the sediment fraction and is relatively stable in a natural sediment environment.

About 0.5 g of fresh sediment (wet wt) was used for the extraction. For extracting trace element from each fraction the following methods were used:

F1. The sediment sample (0.5 g wet wt) was extracted for 2 h shaking time with 1 M ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>), pH 7.0, at room temperature, at solid/solution ratio of 1:20.

F2. The residue from fraction 1 was leached for 5 h shaking time with 1 M sodium acetate (CH<sub>3</sub>COONa) adjusted to pH 5.0 with acetic acid, at room temperature, at solid/solution ratio of 1:20.

F3. The residue from fraction 2 was leached for 12 h shaking time with 0.1 M hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) adjusted to pH 2.0 with HCl, at solid/solution ratio of 1:100, at room temperature.

F4. The residue from fraction 3 was extracted for 24 h shaking time with 0.2 M ammonium oxalate (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and 0.2 M oxalic acid H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; adjusted to pH 3.0 with nitric acid, at solid/solution ratio of 1:100, at room temperature.

During extractions 1–4 the samples remain in the centrifuges vessels. These analyses were conducted in a chamber under oxygen-free conditions. After extraction the solutions were centrifuged with 3500 rpm and then filtered through a 0.45  $\mu\text{m}$  mesh.

F5. The residue obtained after step 4 was transferred into a 100  $\text{cm}^3$  beaker; 30%  $\text{H}_2\text{O}_2$  was added and digested at 85°C. The procedure (addition of  $\text{H}_2\text{O}_2$ ) was repeated three times until the solution finished to bubble. Then the solution was evaporated until nearly dry. Then 1 M ammonium acetate  $\text{CH}_3\text{COONH}_4$  was added and shaken for 2 h. After shaking the solution was centrifuged with 3500 rpm.

F6. The residue from fraction 5 was digested with 65% nitric acid ( $\text{HNO}_3$ ) for 2 h, at 120°C, at solid/solution ratio of 1:100.

The total Cd concentration as well as Cd, Pb, Cu, Mn, and Fe concentrations in the extracts were determined with Perkin-Elmer 403 atomic absorption spectrophotometer using technique of graphite furnace atomic absorption (GFAAS), while some extracts of Mn and Fe by direct flame aspiration with an acetylene-air flame (FAAS). Calibration solutions of trace elements were prepared immediately before analysis from the 1000  $\text{mg dm}^{-3}$  metal stock solution purchased from the Central Office of Measures, Warsaw. The calibration curve was checked with replicate analyses of calibration solutions at the start and subsequently at every tenth sample analyzed. Analysis of blank was conducted to check the purity of reagents and all results were corrected for blanks. The percentage coefficient of variation of total Cd in triplicate sediment sample analyses ranged from 4.8 to 9.6%. The sum of the concentrations obtained with the six-step selective leaching method was compared with those obtained with the total acid-soluble procedure and a good agreement (Cd 92–102%, Pb 89–103%, Cu 95–112%, Mn 82–105%, Fe 95–111%) was found. The detection limits for studied elements (in  $\mu\text{g dm}^{-3}$ ) determined using GFAAS technique were following: Cd – 0.01, Pb – 0.3, Cu – 0.3, Mn – 0.03, and Fe – 0.06, while using FAAS technique were following: Mn – 2 and Fe – 6.

To convert the results obtained from sequential extraction expressed as  $\mu\text{g g}^{-1}$  wet weight to dry weight the percentage of water in the sediment samples was determined. About 1 g of each sediment samples was dried in an oven at 120°C for 4 h. All results are expressed as  $\mu\text{g g}^{-1}$  dry weight.

## RESULTS AND DISCUSSION

### *Oxygen and pH conditions in the littoral water*

In April, after water mixing, the water at the depth of 9 m was well oxygenated at stations 1c and 3c, while poorly at the station 2c (Tab. 1). In July the water at those stations was poorly oxygenated. The monimolimnion was anoxic both in April and July. Water pH

Table 1. The amounts of dissolved oxygen and pH in the water at studied depths in Piaseczno Lake in 2001; the data regarding the deepest point (20 m) are given according to Żurek [44]

Stations	Depth [m]	Dissolved oxygen [ $\text{mg O}_2 \text{ dm}^{-3}$ ]		pH	
		April	July	April	July
Station 1c	9	9.60	1.92	7.4	7.3
Station 2c	9	0.96	0.96	7.7	7.8
Station 3c	9	9.90	0.96	7.4	7.2
Station 4	20	0	0	7.4	8.4

was from neutral to alkaline both at the depth of 9 m and in the monimolimnion. It is well known that changes in redox and pH conditions induce geochemical cycling most of trace elements [10, 36, 37].

### ***Total concentrations and speciation of the trace elements***

Total concentrations of trace elements in the bottom sediment at different depths of the lake in 2001 are given in Table 2. In general, the trace element concentrations in profundal sediment (except Fe) were among those found in the littoral one. Only Fe concentrations in the profundal sediment were about 3 times higher compared to those in the littoral one. Similarly Hongve [19] found higher Fe concentration in deeper anoxic sediment in comparison to oxic one and similar Mn concentration in these stations in meromictic Lake Nordbytjernet (SE Norway). Ciglencčki *et al.* [10] found about 50% higher Mn and Fe accumulation in the permanently anoxic sediment in comparison to the oxic one of meromictic Rogoznica Lake.

Table 2. Trace element concentrations (N = 6; minimum, maximum, mean, standard deviation, and coefficient of variance) on studied depths in the sediment of Piaseczno Lake in 2001: lake depths of 1 m included data from stations 1a, 2a, 3a; 5 m – stations 1b, 2b, 3b; 10 m – stations 1c, 2c, 3c

Lake depth		Elements				
		Cd [ $\mu\text{g g}^{-1}$ ]	Pb [ $\mu\text{g g}^{-1}$ ]	Cu [ $\mu\text{g g}^{-1}$ ]	Mn [%]	Fe [%]
1 m (N = 6)	Minimum	0.1	13.0	22.0	0.11	1.49
	Maximum	1.9	29.0	60.0	0.63	2.41
	Mean	1.0	20.7	40.8	0.35	1.97
	SD	0.9	6.6	12.8	0.2	0.4
	CV (%)	89	32	31	62	20
5 m (N = 6)	Minimum	0.1	18.0	42.0	0.2	1.8
	Maximum	3.7	31.0	62.0	2.6	3.4
	Mean	1.3	25.2	50.7	0.7	2.5
	SD	1.4	5.0	8.2	0.9	0.5
	CV (%)	106	20	16	134	22
10 m (N = 6)	Minimum	0.2	10.0	30.0	0.1	1.7
	Maximum	5.6	29.0	62.0	1.1	4.2
	Mean	1.6	22.5	44.5	0.4	2.5
	SD	2.0	7.0	12.4	0.4	0.9
	CV (%)	124	31	28	87	37
21 m (N = 6)	Minimum	0.4	3.0	28.0	0.1	3.2
	Maximum	2.3	22.0	39.0	0.3	12.0
	Mean	1.1	12.5	33.5	0.2	7.6
	SD	0.8	13.4	7.8	0.1	6.2
	CV (%)	73.2	107.5	23.2	79.8	82.0

The coefficient of variances (CV) indicated higher variability of Cd and Mn concentrations than those of Pb, Cu, and Fe (except the depth of 10 m) in the littoral sediment of Piaseczno Lake. The variability of Pb and Fe concentrations at station 4, i.e. under anoxic conditions, were higher than in the littoral sediment. pH of wet sediment was from neutral to alkaline and ranged from 6.9 to 8.1.

### *Differences between studied depths*

The binding form of trace elements in the littoral sediment is showed in Figures 2 and 3. In general, Cd was a mobile element in the littoral sediment. Most of Cd was bound to carbonates at the depths of 1 and 10 m (up to 58.2% and 43.6%, respectively) (Fig. 2). Considerable amount of Cd there was also bound to F6 (on average about 26% of the total amount), F5 (16 and 19%, respectively), and F3 (19%). Slightly different pattern of Cd association with sediment particles was found at the stations located at the depth of 5 m. Most of Cd there was bound to F6 (up to 53% of the total amount), but also to F2, F3 (~ 22%), and F5 (~ 15%). Slightly different pattern of Cd binding form in sediments in a small degree polluted lakes was found by Zerbe *et al.* [41], Sobczyński and Siepak [31], and Fytianos and Lourantou [15]. In the sediment of Góreckie Lake [41] Cd was mainly associated with organic matter (43%), and in lesser amount bound to iron and manganese oxides (28%) and carbonates (18%). In the sediments of other 11 lakes in the area of Wielkopolski National Park (WNP) Cd was mainly bound to hydrated iron and manganese oxides (42%), in smaller amounts bound to organic matter (28%), residual (15%), and carbonates (10%) [31]. Cadmium dominated in organic/sulphidic phase (40%) also in the sediment of Lake Volvi, whereas in carbonates (35%) in sediment of Koronia Lake in Greece [15].

The pattern of Pb binding form in the sediment on all the stations located at the littoral sediment of Piaseczno Lake was similar. Great part of Pb was bound to immobile F6 (~ 50% of the total amount), higher amounts of Pb were also bound to F2 (about 14%), F3 (about 18, 15, and 18% at the depths of 1, 5, and 10 m, respectively), and F4 (about 17%) (Fig. 2). Lead dominated in hydrated iron and manganese oxides forms and residual also in sediments of other little polluted lakes [15, 31, 41]. Higher amount of Pb was also associated with carbonates or organic/sulphidic fraction in those lakes.

Cu was mainly associated with immobile F4 and F6 at the littoral sediment of Piaseczno Lake (Fig. 2). The amounts of Cu associated with F4 and F6 (about 38%) were similar at the depth of 1 m, while Cu dominated in residual phase (F6) at the depths of 5 and 10 m (about 54 and 47%, respectively). Only about 10% of the total amount of Cu was associated with F5 and less than 1.5% with the most mobile F1 at all littoral stations. Considerable amount of Cu bound to residual fraction (83%), but also bound to organic matter (16%) in the sediment of Góreckie Lake was found by Zerbe *et al.* [41]. Great part of Cu associated with organic matter (51%), but also with residual fraction in lakes in Wielkopolski National Park was found by Sobczyński and Siepak [31]. Cu dominated in the forms of stable organic complexes and metal sulfides (40%) also in sediments of Koronia and Volvi Lakes in Greece [15]. Small amount of Cu (and other metals) associated with the organic/sulphides fraction in the littoral sediment of Piaseczno Lake can be explained by oligotrophic character of the lake and small amount of organic matter in the sediment [34].

Manganese was associated mainly with F2, F3 and F4 in the sediment of the Piaseczno Lake (Fig. 3). Much smaller amounts of Mn were associated with exchangeable

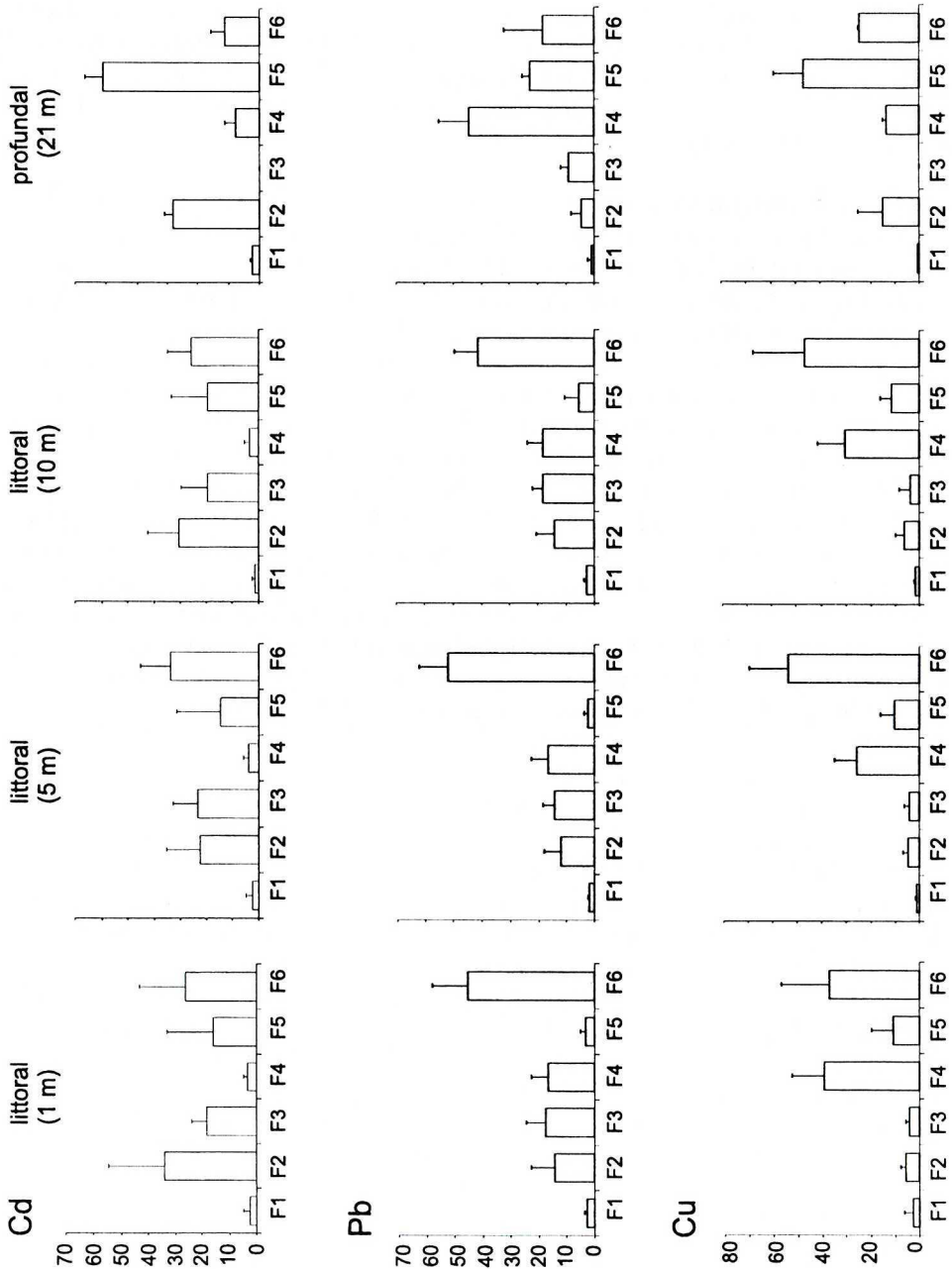


Fig. 2. Mean percentages and standard deviations of binding forms of Cd, Pb, and Cu in the bottom sediment of Piaseczno Lake in 2001 (for each depth: N = 6, i.e. three sampling stations and two months); fractions: F1 – exchangeable, F2 – carbonate, F3 – easily reducible, F4 – moderately reducible, F5 – organic/sulphides, F6 – residual



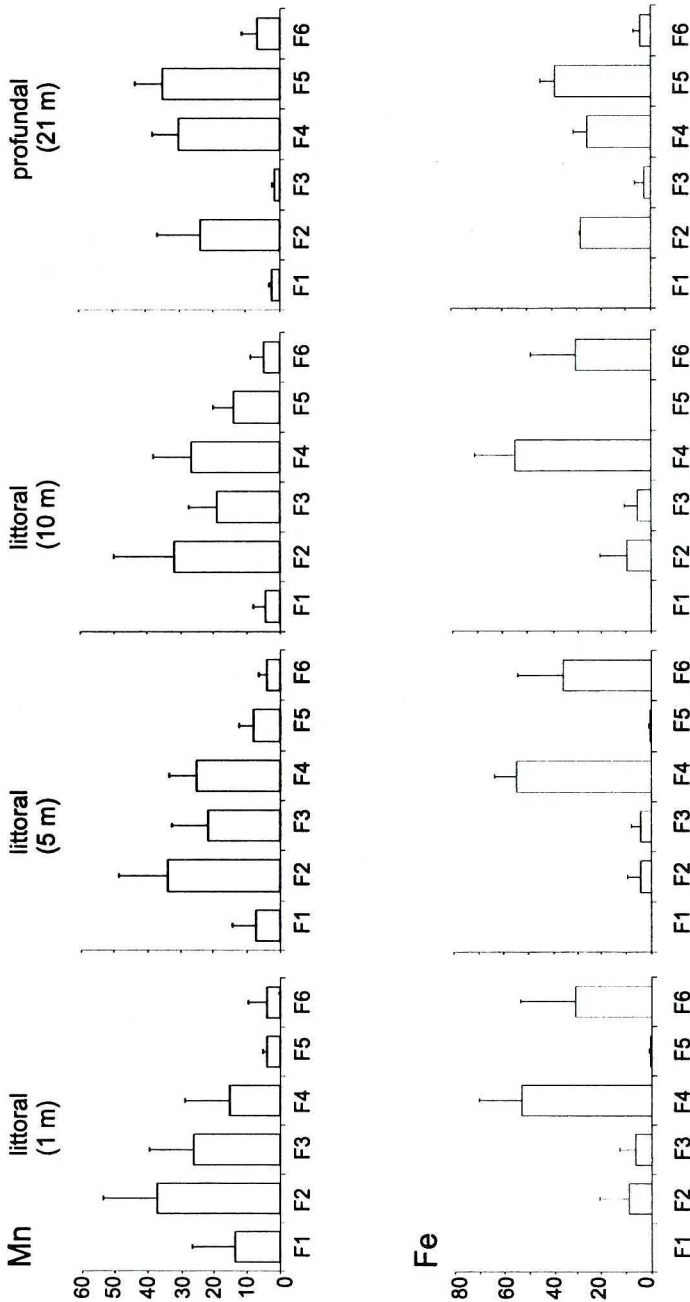


Fig. 3. Mean percentages and standard deviations of binding forms of Mn and Fe in the bottom sediment of Piaseczno Lake in 2001 (for each depth: N = 6, i.e. three sampling stations and two months); fractions: F1 – exchangeable, F2 – carbonate, F3 – easily reducible, F4 – moderately reducible, F5 – organic/sulphides, F6 – residual

fraction, organic/sulphidic fraction and residual. Similar pattern of Mn occurrence, i.e. its predominance in carbonates and hydrated oxides of iron and manganese, in Góreckie Lake (41% and 31%, respectively) was found by Zerbe [41] and in 11 lakes in Wielkopolski National Park (37% and 25%, respectively) was found by Sobczyński and Siepak [31].

The mobility of Mn changed together with depth of the Piaseczno Lake. Mn was the most mobile at the stations located at the depth of 1 m and its mobility lowered with lake depth. In total, to F1 (the most mobile phase), F2, and F3 (moderately mobile phases) were bound ~ 77% of Mn at the stations located at the depth of 1 m, while 63% and 55% of Mn at the depth of 5 and 10 m. An increase in Mn associated with organic/sulphide phase (F5) and with an increase in lake depth was found. It was a result of enhanced reductive condition of the bottom water at the lake depth of 10 m (Tab. 1). Manganese was probably mainly bound to sulphides because the amount of organic matter in the littoral sediment in May and July was similar [34]. It is well known that under reductive condition in the water-sediment interface sulphide compounds are created [2, 4, 10, 18, 19].

Fe was rather immobile element in the littoral sediment of Piaseczno Lake. Most of Fe was bound to F4 (~ 54%) and F6 (~ 31–37%) at all littoral stations (Fig. 3). Less than 10% of Fe was bound to F2, while less than 0.1% of Fe was bound to the most mobile F1. Great amount of Fe associated with residual and organic matter fraction in bottom sediment from 11 lakes in WNP was found by Sobczyński and Siepak [31] and in sediment of Góreckie Lake by Zerbe *et al.* [41]. Fe dominated in residual, the reducible fractions and to a lesser extent the organic/sulphidic fraction in Koronia and Volvi lakes (Greece) [15].

High values of standard deviations (Fig. 2) reflected differences in the amount of trace element bound to selected phase both between studied dates and also between stations located at the studied depths. The obtained results did not show any changes in binding form of trace elements (except Mn) in the littoral sediment with respect to the lake depths.

Considerable differences in the phase specific binding form of the trace elements between littoral sediment (stations 1a, 1b, 1c, 2a, 2b, 2c, 3a, 3b, 3c; the depth of 1, 5, and 10 m) and the anoxic profundal one (station 4, the depth of 21 m) were found (Fig. 2). In the anoxic sediment most of Cd was associated with phases F5 (~ 51%) and F2 (~ 28%). Pb was mainly bound to F4 (~ 44%), F5 (~ 23%), and F6 (~ 18%). Considerable amount of Cu was bound to F5 (~ 46%), F6 (~ 24%), and F2 (~ 15%). The pattern of Mn and Fe binding form in profundal sediment were similar. Those elements were mainly bound to F5, F4, and F2.

The obtained result indicated that carbonates played an important role in the accumulation of Cd, Cu, Mn, and Fe in anoxic sediment (station 4) of Piaseczno Lake. The relationship of trace element and carbonates resulted from high alkalinity of the monimolimnion water (max. 84°N) [44]. Positive relations between carbonates and Cd, Mn, and Fe in anoxic sediment were also found by Guo *et al.* [18] and Hongve [19]. Mean amount of Cd bound to carbonates in littoral and profundal sediment of Piaseczno Lake was similar. Inversely Zuomis *et al.* [42] determined a decrease in the Cd content in carbonate fraction from 12% in anoxic sediment to 3% in oxic one.

The obtained result indicated important role of organic/sulphide phase in Cd, Cu, Mn, and Fe binding in the sediment of Piaseczno Lake. Considerable amount of trace element associated with organic/sulphidic phase in anoxic sediment were also found by Guo *et al.* [18], van Rysen *et al.* [30], Loska *et al.* [23], Loska and Wiechula [24], Zuomis

*et al.* [42], and Hongve [19]. Up to 40–45% of Cd associated with sulphides in anoxic sediment of Rybnik Reservoir was determined by Loska and Wiechula [24]. An increase in the amount of Cd associated with sulphide phase from 5% in oxic sediment to 35% in anoxic one in the Mulde Reservoir (Saxony, Germany) was found by Zuomis *et al.* [42]. In anoxic sediment metals are present predominately as metal sulphides ( $MS_{(s)}$ ), they may be adsorbed to metal sulphide surfaces (metal sulphide- $Me^{+2}$ ), or they may be adsorbed to organic matter (OM- $M^{+2}$ ) [26, 32]. Considerable amount of metal in organic/sulphide phase may exist as acid volatile sulfide (AVS). AVS is considered to control metal bioavailability in anoxic sediment [3, 27, 29]. AVS can be transformed to more stable reduced sulphide phases, but may also persist for long time in sediment. Peng *et al.* [29] determined about 81% of Cd, 76% of Pb, while only 1.1% of Cu associated with AVS in anoxic sediment. Ngiam and Lim [27] found ~ 70% of Cd and Pb associated with acid volatile sulfides, while most of Cu was bound to organic matter in organic/sulphidic fraction in anoxic sediment. The formation of insoluble Cu complexes with large molecular humic compounds under reducing conditions was found by Griffin *et al.* [17].

As mentioned above, a great part of Pb, Mn and Fe in the anoxic sediment of Piaseczno Lake was found in moderately reducible phase. It was probably caused by the extremely high Fe content both in the monimolimnion water (up to 45 mg dm<sup>-3</sup>) and in the upper (0–15 cm) layer of the profundal sediment (32.4% dry wt) [35]. Tallefert *et al.* [36] found that below oxic-anoxic transition in meromictic Paul Lake hydrous Fe oxides form complex aggregates with exocellular polymeric substances and they contain high amount of Pb. These particles can sink to the bottom. Inversely, predominant fractions of Pb were carbonates, but also sulphides and residual in anoxic sediment of Rybnik Reservoir [40].

## CONCLUSION

The operationally defined binding forms of trace elements in bottom sediment of meromictic Piaseczno Lake (inundated opencast sulphur mine, southern Poland) with permanently anoxic monimolimnion were studied. Particular attention was paid to the influence of oxic and anoxic conditions on metal speciation.

The changes in binding form of trace elements (except Mn) in the littoral sediment with the respect of lake depths were not high. An increase in the reductive conditions of water at the depth of 9 m did not cause a drastic change in the phase-specific binding form of trace elements in the sediment at the depth of 10 m, as it was found in the profundal sediment under permanently anoxic conditions (station 4).

The significant differences in the trace elements speciation between the littoral sediment and permanently anoxic profundal sediment (station 4, the depth of 21 m) were found. In the permanently anoxic sediment the elements were mainly associated with carbonates (Cd, Cu, Mn, and Fe), moderately reducible phase (Pb, Mn, and Fe) and organic/sulphide phase (Cd, Cu, Mn, and Fe).

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#### FORMY WYSTĘPOWANIA METALI CIĘŻKICH W OSADZIE MEROMIKTYCZNEGO JEZIORA

Badano specjację metali ciężkich w osadzie meromiktycznego jeziora Piaseczno (zatopiona kopalnia siarki, południowa Polska) ze stałe beztlenowym hypolimnionem. Wykorzystano sześciostopniową ekstrakcję sekwencyjną w celu oznaczenia operacyjnie zdefiniowanych faz: jonowymienną (F1), węglanową (F2), łatwo redukowalną (F3), średnio redukowalną (F4), organiczno-siarczkową (F5) i pozostałą (F6). Nie stwierdzono różnic w specjacji metali ciężkich (z wyjątkiem Mn) w osadzie litoralu wraz ze zwiększającą się głębokością jeziora. Stwierdzono istotne różnice w specjacji metali ciężkich pomiędzy osadem litoralu, a stałe beztlenowym osadem profundalu.