DISTRIBUTION OF TRACE ELEMENTS IN MEROMICTIC PIT LAKE

EWA SZAREK-GWIAZDA* and ROMAN ŻUREK
Institute of Nature Conservation, Polish Academy of Sciences, Mickiewicza 33, Kraków, Poland
*(*author for correspondence, e-mail: szarek@iop.krakow.pl)*

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Abstract. Studies were conducted at the deepest location of the meromictic Piaseczno pit lake, southern Poland, which was created in abandoned sulphur opencast. Pearson correlation and PCA were used to established the relationship between the elements and physico-chemical parameters of the water, whereas discriminant test to study vertical and time differentiation of Cd, Pb, Sr, Cu, Zn, Mn, and Fe concentrations. The results indicated both vertical (except Cu and Zn) and time differentiations of studied elements in the lake water. The highest concentrations of Cd, Pb, and Sr were found in the monimolimnion, that of Mn and Fe in the anoxic water. Depth profiles of Cu and Zn did not show any pronounced trend. Pb and Sr distributions in the water were related to alkalinity, Cl^- and COD, Cd to alkalinity and Cl^-, Mn and Fe to the redox conditions, Mn to water pH, and Fe to the alkalinity. The upper (0–15 cm) layer of the sediment consisted mainly of S (24.2 Atom%), Fe (21.62%), Ca (18.4%), Si (14.3%), and (Al 6.3%) and reflected mainly processes proceeded in the anoxic water-sediment interface. Calculated accumulation coefficients (K_d) of the elements in the sediment are discussed.

Keywords: pit lake, trace elements, water, sediment

1. Introduction

The distributions of trace elements in water and sediment of meromictic lakes were studied rather intensively (Fevert, 1987; Balistrieri *et al.*, 1994; Hongve, 1997; Lienemann *et al.*, 1997; Taillefert *et al.*, 2000a,b; Taillefert and Gaillard, 2002). However, such studies were not conducted till now in meromictic lake created in sulphur opencast. Many of meromictic lakes have salty water like: Paul Lake, USA (MacGregor *et al.*, 1998; Taillefert *et al.*, 2000a), hypersaline Mono Lake, USA (Hoeft *et al.*, 2002, 2003). Some of them have alkaline water (Iwanoff, 1998).

Each of the meromictic lakes has its own special character due to the origin and geochemical background of the catchment basin. To describe the processes regulating the trace elements distributions in the water column of meromictic lake the theoretical thermodynamic calculations and laboratory models with synthetic phases were performed (Taillefert and Gaillard, 2002; Taillefert *et al.*, 2000a,b). However, the results indicate on high difficulties to predict the fate of trace elements in natural ecosystems for parameters obtained from lab experiments. Numerous works indicate an important role of organic ligands (DOM) (Albéric *et al.*, 2000), organo-sulfide ligands (Taillefert *et al.*, 2000a), carbonate (Anderson *et al.*, 1985),

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bacteria and algae (LaKind and Stone, 1989; Deng and Stumm, 1994; Mac Gregor *et al.*, 1998) in metals cycling in the water column. However, geochemical pathway of trace metals in various meromictic lakes can be different. Therefore, in order to better recognise the trace element distributions in lake water and sediment it is necessary to investigate each type of meromictic lake.

The aim of the study was to investigate the distributions of trace elements in water and their accumulations in sediment of meromictic Piaseczno pit lake (southern Poland) created in an old sulphur opencast. The parameters which might influence the distributions of trace elements in the water were also recognised.

2. Study Area

Piaseczno lake is situated in the Tarnobrzeg Sulphur Region (21°35′ E, 50°35′ N) in southern Poland. At present the surface area of the lake is 63 ha, water volume 3.5 mln m^3 and maximum depth 21 m. It originated in an old sulphur mine which was working in the years 1956–1971. The mining uncovered surrounding bedrock i.e. mud, sand, gravels clayey deposits, sulphur-bearing limestone, gypsum, and sands (Pawowski *et al.*, 1985). The opencast was naturally filling with highly mineralised Tertiary and Quaternary waters. Because ground-water seepage is dominant source, geochemical properties of surrounding bedrocks strongly influence water chemistry of Piaseczno lake. In ground water considerable amounts of calcium and sulphate leaching from the gypsum-rich rocks were found (Frankiewicz and Pucek, 2006). For technical purposes the level of water table is artificially kept at ordinate 122 m a.s.l.. Everyday 15 000 m^3 of lake water is pumped off to Vistula River. In the future it will rise to natural groundwater aquifer i.e. 245 m a.s.l..

2.1. GENERAL FEATURES OF THE WATER COLUMN

A detailed description of physico-chemical parameters of the water of Piaseczno lake in 2000 and 2001 was given by Żurek (2006). The author found lake temperature, oxygen, and density profiles. Temperature dependent stratification created hypolimnion below the depth of c. 10 m during summer. The size of epilimnion varied during the year from 2.5 to 6 m. Layer of oxycline varied in dependence on season and started between the depths 5–7.5 m, while finished between the depths 10–15 m. Monimolimnion was permanently anaerobic. In general, water pH was alkaline with increasing pH value in the epilimnion in summer (Table I). A neutral or slightly acidic water pH was periodically found at the depths of 10 and 15 m. Salt concentration (expressed as conductivity) was high with the highest values in the monimolimnion (mean 13792 μS cm^{-1}). Vertical profiles of water total hardness, alkalinity, and chlorides were similar. Their amounts were lower from the surface to the depth of 10 m, than increased reaching the maximum in the monimolimnion. Sulphates depth profile was different then those described above. They

TABLE I

Ranges and mean values of selected physico-chemical parameters in the water column of the Piaseczno lake in 2000–2001.

Depth [m]	Dissolved oxygen mg O_2 dm^{-3}	pH	Conductivity $\mu S\ cm^{-1}$	Total hardness mg $CaCO_3$ dm^{-3}	Alkalinity °N	Chloride mg dm^{-3}	Sulphate mg dm^{-3}	CO_2 mg dm^{-3}	BOD_5 mg O_2 dm^{-3}	COD mg O_2 dm^{-3}
0–10	1.1–13.8	6.9–8.2	1255–2564	553–1382	4.8–25.2	125–254	339–1027	0–163	0.2–4.2	11.8–49.6
	9.4	7.6	2161	1088	13.3	191	872	23.1	1.6	35.2
15	0.0–0.7	7.0–7.3	2729–3080	1285–1739	12.5–35.0	295–373	961–1024	120–295	0.0–0.3	38.0–92.0
	0.3	7.1	2865	1436	29.4	326	1005	101.2	0.2	64.1
20	0.6–1.6	7.2–7.7	11058–16912	1490–1873	25.5–84.0	3950–5325	215–474	101–208	0.1–0.8	638.8–1302
	1.0	7.5	13792	1690	69.8	4448	374	150	0.4	892.8

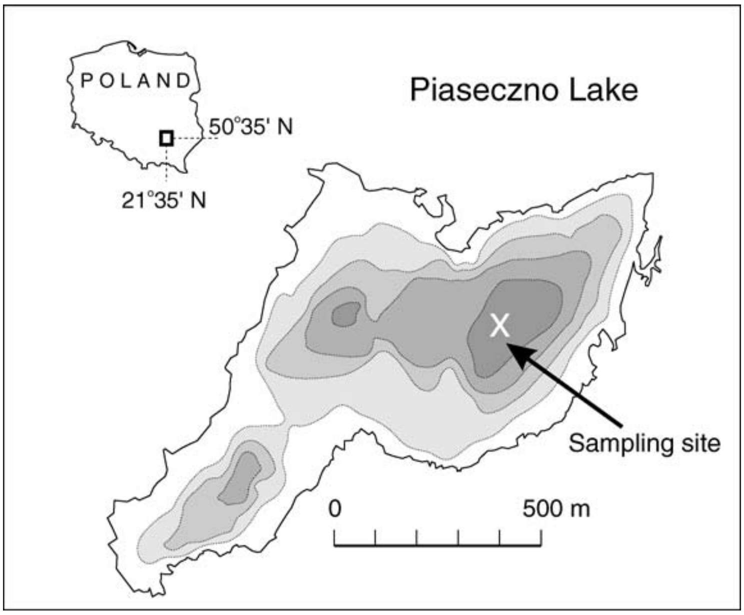

Figure 1. Map of the study area (Piaseczno lake) with the location of sampling point.

attained maximum value (c. 1000 mg dm^{-3}) between the depths 10–15 m, while in the upper and lower layers sulphate amounts were lower. The amount of CO_2 was lower in deeper waters. The amount of organic matter (expressed as BOD_5) in the water column was low. In the monimolimnion a considerable amount of organic matter (expressed as COD) was found. Due to the salts accumulation the density of water in the monimolimnion was the biggest. Density gradient slows down the transport of dissolved species from the monimolimnion to the epilimnion. The thermal, oxygen and density stratification of the lake was similiar to those observed in meromictic lake: Lake Cadagno (Alps, Switzerland) (Tonolla *et al.*, 1998; Deldon *et al.*, 2001).

3. Material and Methods

3.1. SAMPLE COLLECTION

Samples of water were taken using bathometer at the deepest location of the lake (depth c. 21 m) from the depths of 0, 2.5, 5, 7.5, 10, 15, and 20 m (monimolimnion) in following dates: 28.II, 4.V, 27.VI, 26.VIII, 24.X, 28.XI 2000 and 3.I, 30.I, 26.II, 3.IV 2001 (70 samples, in total) (Figure 1). In those samples total trace element concentrations were measured. From the same locality samples of the upper (0–15 cm) layer of the sediment were taken using a polyethylene corer (diameter 4 cm) and placed into plastic containers in four season: spring (4.V 2000), summer (26.VIII 2000), autumn (28.XI 2000), and winter (30.I 2001). One sediment sample contained three subsamples. This layer of the sediment was of loosely consistence and had a black colour. In all samples total Cd, Pb, Cu, Zn, Mn, Fe, and Sr concentrations, pH and amount of organic matter were determined. In the samples collected in the summer the analysis of major elements (Na, Mg, K, Si, S, Al, Ca, Fe) and minerals were conducted.

3.2. ANALYTICAL METHODS

For trace elements analysis the water samples were stored in 100 mL polyethylene bottles. In lab 100 mL of the not filtered water was acidified to pH 2 with HNO_3 and concentrated by evaporation within a few hours after sampling. The residue was placed in a 50 mL volumetric quartz flask and filled with double-distilled water. All water samples were analysed in duplicate. All polyethylene bottles and plastic cups, used in this study, were cleaned and soaked in 30% HNO_3 for 48hrs and then rinsed twice with double distilled-water.

The pH of sediment was measured with an Orion pH meter (Expandable ion Analyser EA 940). Organic matter concentration was estimated by loss on ignition (LOI) at 550 °C for 2 hrs.

Sediment sample used for Cd determination was homogenized using Planetary Mill "Pulverisette 5" with teflon balls. Three subsamples of sediment (c. 0.5 g dry wt.) were then digested with 15 mL conc. HNO_3 in tubes on a heated block of a Tecator Digestion System 12 in conjunction with an Autostep 2000 controller set to 120 °C for 2 hrs. After digestion the concentration of tubes was filtered through a 0.45 μm filter into a 50 mL volumetric flask and filled to the mark with double-distilled water. The measurements were made using a Perkin-Elmer 403 atomic absorption spectrophotometer equipped with a Graphite Furnace (HGA–74) and determined according to the manual recommendations.

The sediment samples used for total Pb, Cu, Zn, Mn, Fe, and Sr determination were grinding with a mixture of 3 g of the material and 0.3 g of paraffin (MERCK Hoechst wax C micropowder) in a planetary mill (Pulverisette 7 Fritsch) at 500 rpm for 5 min. Then 2.7 g of the powder was used for preparation of tablets (31 mm in diameter) in a pallet die (Graseby-Specac). The tablets were produced by application of a pressure of 25 t for about 5 seconds. The measurements were made using an energy-dispersive X-ray spectrometer (ED 2000, Oxford Instruments, UK) under vacuum. This spectrometer is equipped with a silver anode X-ray tube and had a Si (Li) detector (area 30 mm^2, thickness 3 mm) with an 8 μm thick beryllium window (FWHM at 5.9 keV = 145 eV). Following working conditions were applied: tube voltage 40 kV, current 20 μA (thin Ag filter in front of the tube), lifetime 360 s. The calculations of elemental concentrations were based on standard sediments IAEA-SL1 and IAEA-SL3 from the International Atomic Energy Agency.

Field emission electron scanning microscope Hitachi S-4700 equipped in microanalyser system – EDS X-Ray detector and VANTAGE software of NORAN® was used to analyse of major elements (Na, Ca, Mg, Al, Si, S, Cl, K, and Fe). Minerals were deteremined with Philips PW 1830 X-ray diffractometer equipped in system X'Pert ADP.

3.3. STATISTICS

The data were analysed using the SYSTAT® statistical package. PCA and Pearson's correlation coefficient were used to examine the relationships between the elements as well between the elements and other physico-chemical parameters of the water. The loading in PC analyses were rotated by varimax method and sorted. The orthogonal varimax rotation method minimises the number of variables that had a high loading on each factor what simplified the interpretation of results. Chi-square test and Wilks λ test, in which all eigenvalues were equal, constituted basic tests for estimation significance of PC analyses. Discriminant analysis was carried out to establish the differences in vertical and time distribution of trace element in the lake water. To determine time differentiation the data set including separate water depth was used. Different thresholds of introducing or removing the variables were tested. Time-spatial drawings were made in Surfer® and Grapher® programs. The physico-chemical parameters of the water used in the statistical calculations were given by R. Żurek. The accumulation coefficient (K_d) of trace element in the sediment was calculated as a ratio of the trace element concentration in the sediment to that in the water at the depths of 20 m. The K_d values obtained on 4.V 2000, 26.VIII 2000, 28.XI 2000, and 30.I 2001 were used to calculate the mean accumulation coefficient.

4. Results

4.1. WATER

The concentration of Cd in the water column ranged: 0.21–43.0 μg L^{-1}, Pb 0.5–183.3 μg L^{-1}, Cu 0.5–59.5 μg L^{-1}, Zn 2.5–40.2 μg L^{-1}, Mn 0.27–8.35 mg L^{-1}, Fe 0.05–57.4 mg L^{-1}, and Sr 1.2–29.5 mg L^{-1}. In general, the concentrations of Zn in the water was low, that of Cd, Pb, Cu, Mn, and Fe ranged from relatively low to very high, whereas that of Sr was very high compared with unpolluted region.

Depth profiles of Cd, Pb and Sr concentrations in Piaseczno lake were similar (Figure 2). The concentrations of those elements were lower from the surface to the depth of 10 m and then increased with depth reaching the highest values in the monimolimnion. Elevated trace element concentrations were periodically found in the surface water (e.g. Cd in October, January; Pb in January; Cu in January, Zn

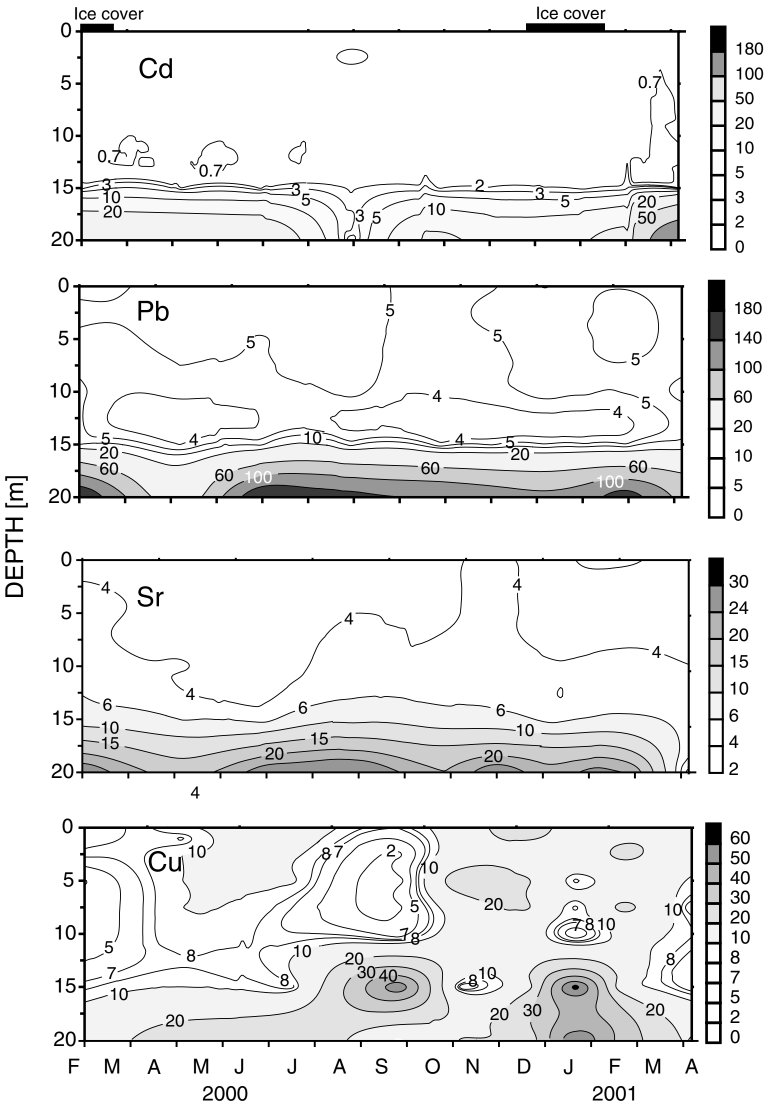

Figure 2. Annual variations of Cd, Pb, Cu ($\mu g \, L^{-1}$), and Sr ($mg \, L^{-1}$) in the Piaseczno lake in 2000 and 2001.

in August, October, November and Fe in June) indicating the importance of the atmospheric input.

The concentrations of Cu and Zn in the water column showed relatively low variability compared with above elements (Figures 2 and 3). The vertical profile of Cu was similar to those of Cd, Pb, and Sr from May to September. Its concentration was lower from the surface to the depth of 15 m and reached the highest value at the depth of 20 m. However, from November to April such a trend was not observed.

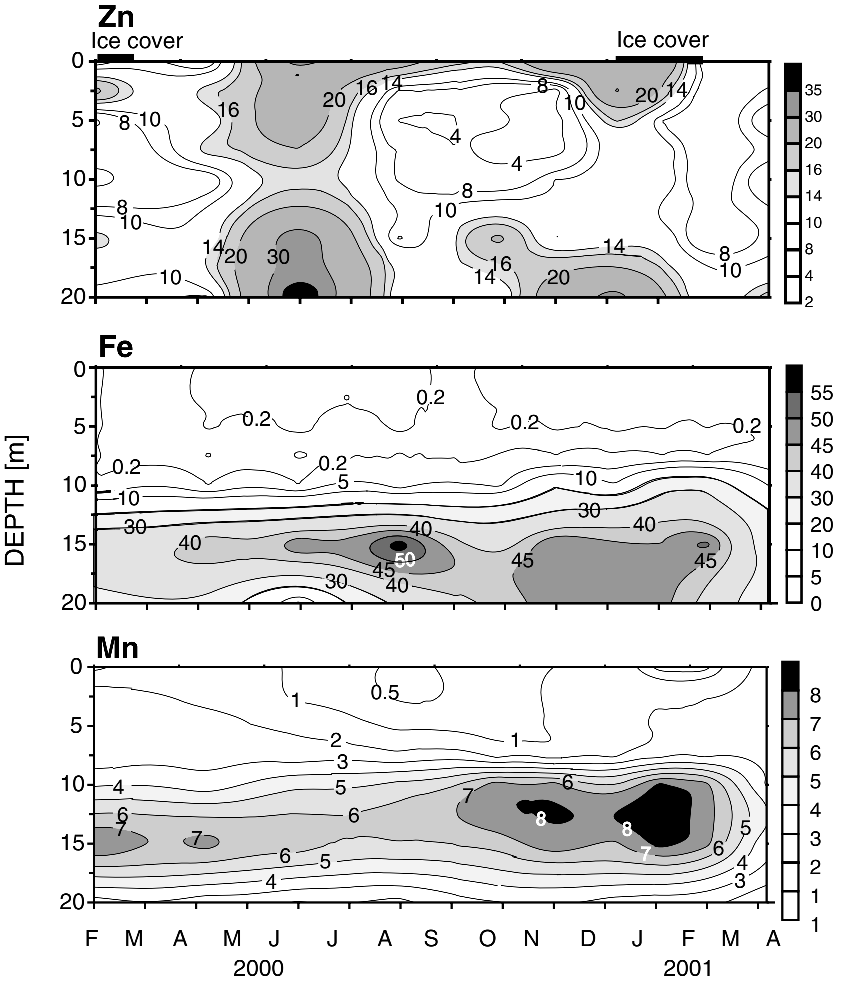

Figure 3. Annual variations of Zn (μg L^{-1}), Mn (mg L^{-1}), and Fe (mg L^{-1}) in the Piaseczno lake in 2000 and 2001.

The concentration of Zn in the water was relatively low, and did not show any pronounced seasonal or vertical trend.

The pattern of Mn and Fe migrations in the water column was different than those described above (Figure 3). Concentrations of Mn and Fe were generally lower in the oxic zone (depths: 0–7.5 m) and higher in anoxic one. The peak of Mn and Fe concentrations occurred below oxic-anoxic transition. Manganese reached the maximum value between depths 10–15 m, and then its concentration dropped at the depth of 20 m. Elevated concentration of Fe was found between depths 10–20 m, but periodically its decrease at the depth of 20 m was found. Over the year vertical movement of maximum Mn and Fe concentrations was found. In May after

TABLE II

Pearson correlation coefficients between trace elements and chemical parameters of the water of the Piaseczno lake in 2000–2001

	Cd	Pb	Cu	Zn	Mn	Fe	Sr
pH	0.00	0.05	−0.05	0.19	**−0.77**	−0.49	−0.04
O_2	−0.28	−0.45	−0.22	−0.07	**−0.68**	**−0.81**	−0.56
Alkalinity	**0.57**	**0.86**	0.42	0.24	0.08	0.59	**0.81**
CO_2	0.25	0.41	0.27	**0.99**	**0.62**	**0.83**	0.50
Cl^-	**0.57**	**0.94**	0.40	0.26	−0.11	0.46	**0.91**
SO_4^{2-}	−0.47	−0.80	−0.35	−0.26	0.43	−0.16	−0.70
COD	0.49	**0.93**	0.39	0.28	−0.11	0.43	**0.91**
Cd	1.00	0.46	0.13	0.13	−0.12	0.20	0.23
Pb		1.00	0.38	0.27	−0.13	0.40	**0.91**
Cu			1.00	0.21	0.08	0.35	0.43
Zn				1.00	−0.90	0.13	0.23
Mn					1.00	**0.64**	0.02
Fe						1.00	**0.54**
Sr							1.00

Bold – significant correlations.

the spring mixing of water, when the layer of oxic water was wide, the maximum concentrations of Mn and Fe were found in the deeper part of lake (15 m). Towards the end of the winter when the oxic layer of the water was thin, the maximum concentrations of Mn and Fe were already found at the depth of 10 m. In the oxic water the highest Mn and Fe concentrations were found during spring mixing (April). In this time the water of rude colour was observed.

4.2. STATISTICS

To establish parameters which governed the trace element distribution in the water of Piaseczno lake some statistical techniques were used. The result of Pearson correlation showed that the Pb and Sr were significantly correlated to alkalinity, Cl^- and COD (Table II). Cadmium showed positive correlation with alkalinity and Cl^-. However, those relationships were not so strong as in the case of Pb and Sr. Copper did not show any pronounced relationship with the studied parameters, whereas zinc showed the significant one with CO_2. Manganese and iron migrations in water column were related to the redox conditions and that of Mn with water pH. The positive correlation between the Fe concentration and alkalinity was also found.

The results of the Principal Component Analysis (PCA) are shown in Table III. Only those chemical variables with values >0.7 were taken into consideration.

TABLE III

Principal component analysis (PCA) of physico-chemical parameters and trace elements in the Piaseczno lake water in 2000–2001

Parameter	PC1	PC2	PC3	PC4	PC5	PC6
pH	0.09	**−0.82**	−0.25	−0.01	−0.00	0.31
O_2	−0.34	**−0.88**	0.04	−0.08	−0.07	0.04
Conductivity	**0.84**	0.22	0.00	−0.27	−0.26	0.15
Alkalinity	**0.80**	0.37	0.06	0.17	0.28	0.13
CO_2	0.32	**0.83**	0.11	0.11	0.17	0.18
SO_4^{2-}	−0.84	0.30	−0.18	−0.11	−0.20	−0.13
Cl^-	**0.96**	0.14	0.01	0.14	0.17	0.06
COD	**0.96**	0.13	−0.01	0.22	0.10	0.04
Cd	0.46	0.08	−0.02	0.05	**0.79**	0.00
Pb	**0.92**	0.08	0.06	0.23	0.08	0.01
Sr	**0.90**	0.24	0.01	0.15	−0.26	0.07
Mn	−0.19	**0.90**	0.11	0.03	−0.17	−0.12
Fe	0.34	**0.82**	0.10	−0.07	−0.04	0.28
Cu	0.22	0.17	0.46	0.11	−0.16	0.31
Zn	0.21	−0.08	0.02	**0.70**	−0.03	0.38

Bold – significant values.

Factors 1 and 2 were the most significant and accounted c. 64% of the total variance. The relationships were highly significant (Chi-square test, $n = 60$, $\mathrm{df} = 253$, $p < 0.00001$). First factor indicates a strong positive association with Cl^-, alkalinity, COD, Pb, and Sr i.e. the ions related to the meromictic character of the lake. Factor 2 shows a strong positive association with Fe and Mn and a negative one with dissolved oxygen and pH (the most important parameters governed their distribution in the water column). The remaining factors did not provide information about the studied elements.

The differences in vertical and time distribution of trace element in the lake water were tested by discriminant analysis. Discriminant model with seven variables describing vertical distributions of trace elements was highly significant (Wilks $\lambda = 0.002$, $F = 39.394$, $p < 0.00001$ for df = 24, 186) (Table IV). Overlaying the observations from neighbouring sampling sites diminish total correctness in the internal jackknife test to 60%. Factor 1 separated variables in three depths groups. Group (1) included the variables between the depths: 0–10 m, group (2) those at the depth of 15 m, and group (3) at the depths of 20 m. This distribution pattern reflected depth profiles of Cd, Pb, and Sr (the most significant components). The distribution pattern of chemical variables separated in Factor 2 was partly similar to those separated in Factor 1. The variables were separated in two depth groups. Group (1) included the elements between the depths: 0–7.5 m and 20 m, group (2) those at the depth of 10–15 m. The transitional character of the depths of 7.5 m

TABLE IV

Canonical scores of group means calculated for Cd, Pb, Cu, Zn, Mn, Fe, and Sr data set in water column in Piaseczno lake. Wilk's lambda = 0.002, approx. $F = 39.394$ for df = 24, 186

Depth [m]	1	2	3	4
0	−3.298	1.698	−0.764	0.0290
2.5	−3.051	1.475	−0.347	−0.0027
5	−3.108	1.286	−0.113	−0.0154
7.5	−3.161	0.947	0.318	−0.0189
10	−2.878	−2.091	1.989	0.0105
15	0.597	−4.227	−1.323	−0.0033
20	14.899	0.913	0.241	0.0008

TABLE V

Chemical composition of the upper 0–15 cm layer of the sediment of the Piaseczno lake.

	Si %	S %	Cl %	K %	Ca %	Al %	Cd μg g^{-1}	Pb μg g^{-1}	Cu μg g^{-1}	Zn μg g^{-1}	Mn %	Fe %	Sr μg g^{-1}
Min	9.0	27.9	4.6	0.4	3.8	0.9	1.12	3.0	11.0	38.0	0.1	3.2	666.0
Max	37.0	35.9	21.8	1.2	5.8	3.7	2.28	24.0	39.0	83.0	0.3	12.0	1112.0
Mean	18.4	32.2	15.6	0.7	4.9	1.8	1.6	16.3	26.0	54.7	0.2	8.5	817.0
SD	16.1	4.0	9.5	0.4	1.0	1.6	0.6	11.6	14.1	24.7	0.1	4.7	255.5

and 20 m was visible. It was connected with the migration and transformation of Mn and Fe compounds (i.e. the most significant components of the Factor 2) in the water column and in the water – sediment interface. Remaining Factors (3 and 4) were not significant.

The result of discriminant analysis of the time distribution of trace element in the lake water calculated for the whole set of data did not show any significant differences. It was caused by strong vertical differentations in trace element concentrations. Therefore the discriminant analysis was conducted separately for each studied water depth. Results for discriminant analysis at selected depths in time had a single contrast with one degree of freedom. First canonical variable accounts near 100% of the dispersion in all studied water depths. The result showed that the concentrations of studied trace metals at the depths of 0, 10 and 15 m were similar (Wilks λ from 0.06 to 0.298, F from 0.3 to 2.2, and df = 7,1), whereas at the depths of 2.5 m (Wilks $\lambda = 0$, F = 10198, df = 7,1), 5 m (Wilks $\lambda = 0$, F = 725, df = 7,1), and 20 m (Wilks $\lambda = 0$, F = 935, and df = 7,1) significantly differed during the year. In general the concentration of trace elements differ the most from the remaining at the depth of 2.5 in August and October, at the depth of 5 m in winter months (January, February, April) and in the monimolimnion in April.

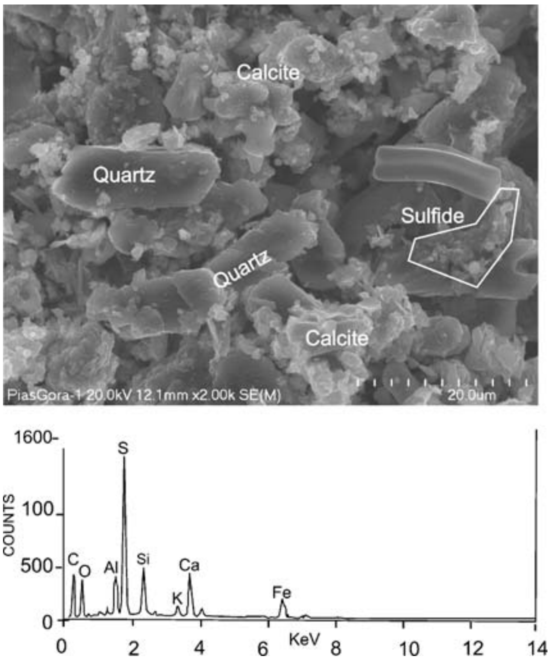

Figure 4. Typical analyses of major elements in upper layer of the sediment made by microanalyser system. Field emission electron scanning microscope was used. Identifications of some minerals were done with Philips PW 1830 X-ray diffractometer.

4.3. SEDIMENT

Chemical composition of the upper 0–15 cm layer of the sediment of the Piaseczno pit lake is given in Table V. It consisted mainly with S (24.2 Atom%), Fe (21.6%), Ca (18.4%), Si (14.3%), and Al (6.3%) (Figure 4). Amorphous sulphide gave wide background in crystallographic analysis. Crystalline minerals were identified as calcite, muscovite and quartz. Their sizes oscillate around 20 μm. This layer of sediment had an alkaline pH (7.2 –7.9) and small amount of organic matter (from 0.4 to 12.4%; expressed as LOI). The concentration of trace elements occurred there in the following ranges: Cd 1.1–2.3 μg g^{-1}, Pb 3–24 μg g^{-1}, Cu 11–39 μg g^{-1}, Zn 38–83 μg g^{-1}, Mn 0.1–0.3%, and Sr 666–1112 μg g^{-1}. Mean values and standard deviation of accumulation coefficients (K_d) of trace elements in the sediment of Piaseczno lake were following: Cd 522 ± 794, Pb 143 ± 113, Sr 428 ± 699, Cu 877 ± 633, Zn 3333 ± 1384, Mn 1163 ± 480, and Fe 2437 ± 892. They indicated that Zn and Fe were accumulated in the sediment in a highest degree, whereas Pb, Cd and Sr in a lower one. The accumulation of Fe in the sediment was c. 18 times higher than that of Pb.

5. Discussion

5.1. WATER

In general studied elements characterised a considerable vertical (except Cu and Zn) and time (except the depths of 10, 15 m) differentiation in the Piaseczno lake water. The vertical profiles of Cd, Pb, and Sr follow the distribution patterns observed in other meromictic lakes (Balistrieri *et al.*, 1994; Taillefert *et al.*, 2000a; Taillefert and Gaillard, 2002). Lead distribution in the water column of meromictic lake is often related to the cycling of Fe because Pb binds preferentially to oxides and other O-donor associated with the particles (Taillefert and Gaillard, 2002). Therefore, the peak of particular Pb occurs just below the oxic-anoxic transition. In Piaseczno lake such a Pb peak was not observed. Inversely to our results, some authors determined a decrease in the Cd or Pb concentrations in the anoxic bottom water of different water bodies. That decrease was caused by trace elements removal to sediment, by precipitation with sulphides (Fevert, 1987; Balistrieri *et al.*, 1994) or by adsorption onto FeS (Davison *et al.*, 1992; Morse and Arakaki, 1993).

Elevated concentrations of Cd, Pb and Sr in the monimolimnion of the Piaseczno lake resulted probably from its complexity with a strong ligand. Obtained results of Pearson's correlation indicated that geochemical pathway of Pb and Sr in the water was affected mainly by organic matter (expressed as COD) and inorganic (carbonates, Cl^-) ligands. They had to keep the elements in the solution in the monimolimnion. The complexity of trace elements with strong organic and inorganic ligands in meromictic lakes was described by other authors. Balistrieri *et al.* (1994) according to thermodynamic calculations for the anoxic region of the meromictic Hall Lake (USA) found that the reasonable concentration of dissolved forms of Cu, Ni, Pb, and Zn occurred in metal-inorganic sulphide complexes. Taillefert *et al.* (2000a) found that Pb was mainly complexed by sulphides and carbonates ($Pb\,(CO_3)_{2(aq)}$) as well by natural organic ligand in monimolimnion of meromictic Paul Lake (USA). Buffle (1988) pointed that complexes of Pb with carbonates were electrochemically labile. Taillefert *et al.* (2000a) indicated an important role of particulate organic matter in particulate Pb distribution in the water, what is in agreement with our results.

Obtained result indicated a relationship between the CO_2 and Zn contents. An increase in CO_2 amount occurred in deeper part of the lake water and was mainly caused by redissolution of $CaCO_3$ precipitated from the oxic layer. Therefore established relationship between Zn and CO_2 indicated that cycling of Zn was probably related to carbon cycling (CO_2–H_2CO_3–HCO_3^-) in the water column.

Depths profiles of Mn and Fe in Piaseczno lake, i.e. the occurrences of their highest concentrations below the oxic/anoxic interface, were similar to those from other meromictic lakes (Balistrieri *et al.*, 1994; Tonolla *et al.*, 1998; Taillefert *et al.*, 2000a; Perret *et al.*, 2000). Taillefert *et al.* (2000a) and Perret *et al.* (2000) found Fe peak just below the oxic-anoxic transition, iron dominated there mainly in particulate phase. Balistrieri *et al.* (1994), Tonolla *et al.* (1998) and Taillefert *et al.* (2000a) found an increase in dissolved Fe and Mn concentrations across the oxic-suboxic boundary and with depth in the anoxic layer. A decrease in Fe concentration in the near bottom water of the Piaseczno lake was probably influenced by ferrous sulphide precipitation. Balistrieri *et al.* (1994) determined a large increase in the concentration of particulate Fe below the sulphide maximum in the anoxic zone of the lake what explained Fe removal from the bottom water to the sediment.

The distributions of Mn and Fe in the Piaseczno lake were largely governed by redox conditions what is well known phenomenon in aquatic system. The occurrence of anoxic conditions causes a significant cycling of Fe and Mn in the oxic-anoxic interface, due to changes in their solubility related to the changes in oxidation state. Taillefert and Gaillard (2002) presented the transport model of Fe in the water column which includes oxidation of reduced Fe (II) to colloidal ferric iron Fe (III) in the oxic-anoxic transition, aggregation of colloidal iron to particulate iron Fe (III), and reduction of colloidal and particulate iron in the deep anoxic waters. The author pointed that many processes may regulate Fe cycling in the water column of meromictic lake. For instance Fe(II) can also react with other substances as sulphides, carbonate, phosphate and organic matter what may affect its transformation. The result indicated that in Piaseczno lake mainly carbonates influence Fe transformation.

Obtained result indicated that trace element contents varied considerable in time in the oxic and photic layer (depths of 2.5 and 5 m) i.e. in the layer, where the most intensive productive processes occurred. They influence the physico-chemical charcteristics of the water and in consequnce processes which govern the trace element speciations and distributions in the water (preciptation/dissolution, adsorption/desorption, biological uptake/release). Considerable variablity in the element contents found in monimolimnion was mostly connected with the processes undertaken in mixo- monimolimnion and water-sediment interface. There the concentration of some elements in April differ the most from those in the remaining months what was mainly influenced by water mixing.

5.2. SEDIMENT

The percentage share of chemical composition of the 0–15 cm upper layer of the sediment of Piaseczno lake (i.e. high amount of S and Fe) was mainly the effect of processes undertaken in the anoxic water-sediment interface. Under anoxic conditions the reduction of SO_4^{-2} to H_2S/HS^- following organic matter mineralization by bacteria, which leads to the formation of metal sulphides such as ZnS, Fe_2S, CdS, etc. Taillefert *et al.* (2000b) indicated a high reactivity of soluble Fe(III) with sulfide in natural porewaters. Soluble Fe (III) can be reducted by sulfide and aqueous FeS can be formed, if saturation is reached, and should facilitate the production of pyrite in natural sediments. According to LaKind and Stone (1989) and Deng and Stumm (1994) ferric iron can be also reducted by bacteria or nonreductively dissolved by organic compounds in the absence of micro-organisms. Dissolved Fe species can diffuse in and out of sediments (Taillefert *et al.*, 2000a). This may explain the differences in Fe concentration in the monimolimnion of Piaseczno lake. It is well known that a cycling of redox-sensitive elements like Fe and Mn play a fundamental role in the transport of trace element (Davison *et al.*, 1992; Perret *et al.*, 2000). The percentage share of chemical components of the lower layer of the sediment of Piaseczno lake was quite different. It consisted mainly of Si (48.2 Atom%), Ca (18%), Al (11.5%), S (9%), and Fe (7.5%) (E. Szarek-Gwiazda, R. Żurek unpubl. data) and reflected geochemical features of the catchment basin (Szarek-Gwiazda E. *et al.*, in press).

In general, the pH of the upper layer of sediment was alkaline what reflected geochemical peculiarities of the surrounding bedrocks (sulphur-bearing limestone, gypsum). The amount of organic matter was low what indicated oligotrophic character of the lake. The concentrations of Cd, Pb, Cu, Zn in the sediment was low, whereas those of Mn and Sr elevated in comparison with background levels given for shales by Turiekian and Wedephol (1961). Obtained results (mean values of accumulation coefficients K_d) indicated differences in accumulations of studied elements in the sediment of the Piaseczno lake. The elements might be divided into three groups according to their geochemical behaviour. First group included Cd, Pb, and Sr, which were in a smallest degree accumulated in the sediment. Their maximum concentrations occurred in the monimolimnion where they were strongly complexed by organic and inorganic ligands. Second group included Mn and Fe. Their cycling in the water column was associated mainly with redox conditions and pH, and that of Fe with carbonate. Anoxic conditions in the monimolimnion favour Fe precipitation to the sediment, therefore its accumulation in the sediment (K_d) was very high. Manganese was in a smaller degree accumulated in the sediment, what was caused by its considerable mobility (high values of standard deviations). Group 3 included Cu and Zn. Their behaviour in the water column was not clear. Zn in a considerable amount was accumulated in the sediment. High values of cumulation coefficients calculated for Zn and Fe indicate that the processes of their accumulation much predominance over their remobilization from the sediment.

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