Differentiation of Iron and Manganese Concentrations in Waters of Suwałki Landscape Park

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Abstract

Iron and manganese differentiation were analyzed in the lakes, rivers, springs, and groundwaters the Suwałki Landscape Park (SLP) in July 2009. The major aim of this study was to evaluate the relationship between manganese and iron concentrations and other physical and chemical water parameters. The waters of SLP differed in terms of fractional composition of manganese and iron. Higher concentrations of total iron and manganese were observed in groundwaters (1645 μgFe/dm^3, 949 μgMn/dm^3). The fractional composition of iron and manganese depends on the amount of dissolved organic carbon (DOC) related to the development of metaloorganic complexes. Manganese compounds are more volatile in an aquatic environment than iron compounds, as manifested in the variable fractional composition of manganese in the lakes of SLP.

Keywords: manganese, iron, surface waters, shallow groundwaters, ecotones

Introduction

Manganese and iron are elements commonly found in surface waters. The main sources of these metals are natural processes of leaching from the ground, secretion of aquatic organisms, and sewage supply. Manganese and iron can be present in various oxidation states: Mn (+I, +II, +III, +IV, +V, +VI, +VII), Fe (+II, +III, +IV, +V, +IV), and in a soluble or colloidal form in surface waters [1]. Biogeochemical and physical transformations of iron and manganese involve processes such as: co-precipitation, adsorption, redox reactions, complexation reactions, and photochemical reactions. The presence of manganese and iron determines a number of processes in aquatic ecosystems. The metals are components of enzymes and proteins. Iron is responsible for transporting oxygen, and strengthens the immune system in animals. Iron is essential in the process of photosynthesis and electron transport in the respiratory chain in plants. Manganese participates in the synthesis of nucleic acids and corticosteroids. It is also an important component of glycoside phosphatase, and affects the synthesis of peptides, amides, and urea in plants [2]. Increasing attention has been paid to the negative effects of the presence of manganese and iron in surface waters. Elevated levels of iron and manganese are known to contribute to bacterial growth. The multiplication of bacterial colonies results in the deterioration of water properties, making it turbid, with unpleasant taste and

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smell. It directly affects the functioning of the drinking water supply. Water purification measures become necessary, involving the removal of manganese and iron from water.

Manganese and iron fractions have not been analyzed in the surface waters of Suwałki Landscape Park so far. The only data available concern the concentrations of these metals in groundwaters, namely the quaternary groundwater aquifer of a bicarbonate-calcium-magnesium type. According to data from the Polish Geological Institute, the mean total iron and manganese fraction concentrations in the Lithuanian Lakeland amounted to 1300 µgFe/dm^3 and 600 µgMn/dm^3 in 2002 and 2004, respectively [3].

The primary objective of this study was to determine the concentrations of manganese and iron fractions in the waters of lakes, rivers, and springs, as well as groundwaters collected from the ecotones of Suwałki Landscape Park. The relationship between manganese and iron concentrations and other physical and chemical water parameters was also analysed.

Study Area and Methods

Suwalki Landscape Park is located in a region known as the Polish Green Lungs, in the northern part of Podlasie province. It was established in 1976 and protects a unique landscape developed during the glacial period. The park's area amounts to 6,284 ha, 60% of which constitutes agricultural land, 24% forests and woodlands, 10% water, and 6% other land. SLP is located in the catchment areas of two rivers: Czarna Hańcza and Szeszupa, within the Niemen River basin. SLP includes a number of natural lakes and groundwater outflows [4]. The lakes of SLP have been fairly thoroughly studied in hydrochemical and environmental terms [5-9]. The majority of lakes of SLP are eutrophic [10], with the exception of the deepest lake in Poland, namely Lake Hańcza (108.5 m depth), as well as Lakes Perty and Jaczno and the Turtul pond, which are mesotrophic [6].

Water samples were collected in July 2009. The observed high water level resulted directly from heavy rainfall in May and June. July is also a month with particularly evident negative impact of tourism and agriculture on the water quality in SLP. This is manifested in increased concentrations of organic matter and phosphorus in surface waters [8, 10]. The study was carried out on 24 lakes, 10 rivers, 8 springs, and 8 groundwaters (Fig. 1). It collected 15 samples of river waters including 3 water samples from the course of the Czarna Hańcza and 4 from Szeszupa, and the other samples from small streams and drainage lakes. From the lakes we collected a total of 50 water samples. In large-area lakes the study
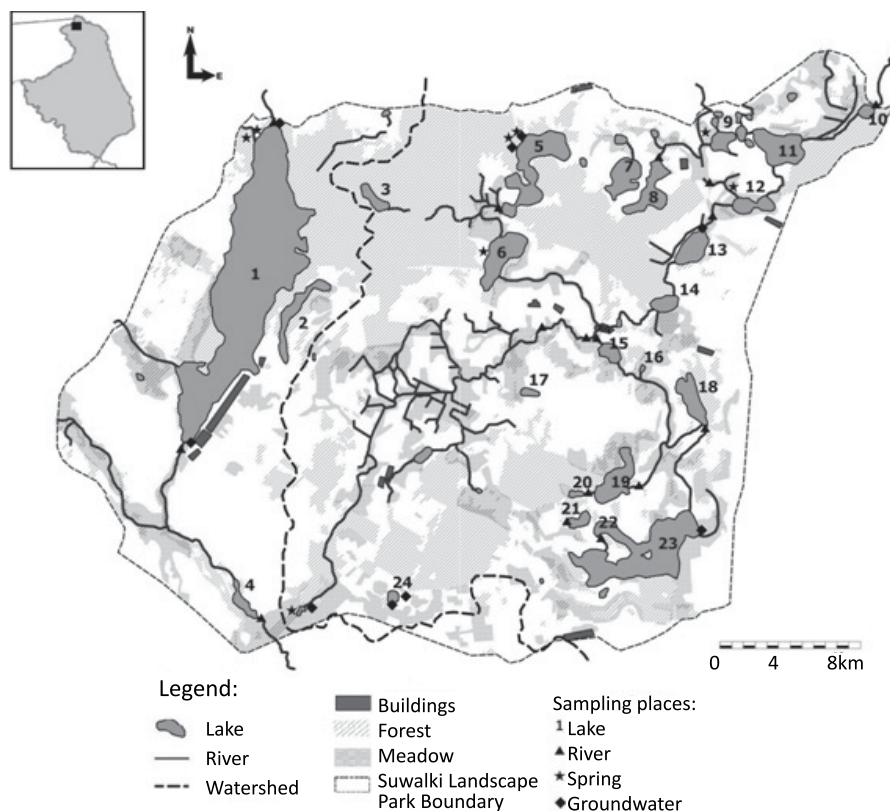

Fig. 1. Map of Suwałki Landscape Park (northeastern Poland) with studied type of waters. Lakes: 1. Hańcza, 2. Boczniel, 3. Pogorzałek, 4. Turtul Staw, 5. Jaczno, 6. Kameduł, 7. Kojle, 8. Perty, 9. Czarne Kleszczowieckie, 10. Postawelek, 11. Przechodnie, 12. Krajwelek, 13. Okrągłe, 14. Gulbin, 15. Udziejek, 16. Smouda, 17. Błędne, 18. Kopane, 19. Jeglówek, 20. Jegłóweczek, 21. Kluczysko, 22. Szurpiły Jodel, 23. Szurpiły, and 24. Linówek.

was carried out on water from different depths. For example, Lake Hańcza water was collected from 0 m, 2 m, 7 m, and 30 m depths, and further from the northern and southern parts of the lake. The water samples from Lake Szurpiły were collected from 0 m, 6 m, and 20 m depths, and 2 additional sampling sites. Moreover, stratified water was collected from Pogorzałek (0 m, 4 m, 7 m), Przechodnie (0 m, 4 m), Linówek (0 m, 4 m), Jeglówek (0 m, 6 m, 20 m), Udziejek (0 m, 5 m), Okrągłe (0 m, 6 m), Krajwelek (0 m, 6 m), and Kameduł (0 m, 6 m, 26 m). Examined groundwaters samples were collected with installed piezometers from 0.3-0.5 m depth. In total, we collected 81 water samples from different types of water in SLP and stored in 5-liter polyethylene containers. Chemical analysis was carried out in the Department of Hydrobiology laboratory on the next day.

Iron was determined by means of the spectropho-tometric method involving the measurement of the intensity of the orange colour derived from the complex formed by the reaction of ferrous iron from 1.10-phenanthroline in the pH range from 2.9 to 3.5 as described by Hermanowicz et al. [11]. Manganese was determined by means of the spectrophotometric method involving the reduction of manganese ions in a higher oxidation state to manganese (II). This reaction occurs in alkaline conditions (pH 9.5-10.5) in the presence of formaldoxime. The resulting complex is oxidized by atmospheric oxygen to a compound in which manganese is in oxidation state +IV and has typical brown colour [12]. Standard addition methods were used in the case of low concentrations of iron at values $<50 \mu gFe/dm^3$, and manganese at values $<20 \mu gFe/dm^3$.

The methods were applied for the purpose of the determination of iron and manganese fractions. The fractionation is based on the classification of the analyte or groups of the analytes described by physical and chemical properties [13]. Five iron and manganese fractions are generally distinguished: total fraction (TFe, TMn), dissolved fraction (DFe, DMn), reactive fraction (DRFe, DRMn), dissolved organic fraction (DOFe, DOMn), and insoluble fraction (PFe, PMn). The total fraction was determined in non-filtered water after prior digestion with concentrated sulphuric acid (VI) and 30% hydrogen peroxide. The soluble fraction was determined in water filtered through a filter GF/F with a pore diameter of 0.45 μm and subject to digestion with concentrated sulphuric acid (VI) and 30% hydrogen peroxide. The reactive fraction was determined in water filtered through a filter GF/F without prior mineralization.

Chemical water analyses were performed in accordance with ISO standards, by means of methods described by Hermanowicz et al. [11]. The concentration of dissolved organic carbon (DOC) was determined with the application of a Shimadzu TOC analyzer 5050 of the IR detector, and following methods described by Zieliński and Górniak [14]. Water electrolytic conductivity (EC), water temperature, oxygen concentration, and water pH were determined by means of a HachLange multiparameter probe.

Statistical analysis was conducted with the application of STATISTICA 10 software. Calculations of ionic composition and water saturation index (SI) of inorganic compounds were determined using the PHREEQC Interactive 2.15. The saturation index (SI), also called the index of stability of the inorganic compound, describes the relationship:

$$SI = \log \frac{\Pi [A_i]^{\alpha i}}{K_M}$$

A_i – ith ion concentration [mol·dm^{-3}]
K_M – ion solubility

The compound is precipitated from the water when SI>0, and dissolved when SI<0. The chemical equilibrium between the precipitated substance and water occurs when SI is in the range from -0.5 to 0.5 [15, 16].

Results and Discussion

The waters of SLP are of bicarbonate-calcium hydrochemical type. Their composition was dominated by calcium cations, constituting more than 75% of all cations. Magnesium ions reached a contribution of 15.8-19.9%. The content of bicarbonate exceeded 90% of total anions. The low contribution of sulphate and chloride confirms the natural character of the environment of SLP. Chemical and biological indicators show a relatively low trophic status of the lakes [6-9, 17]. Ionic forms were the basic form of occurrence of dissolved compounds of the waters of lakes, rivers, and springs, as well as shallow groundwaters of SLP.

The highest average concentration of the total fraction of iron was observed in groundwaters (TFe>900 μgFe/dm^3) and rivers (TFe>750 μgFe/dm^3) (Fig. 2). The
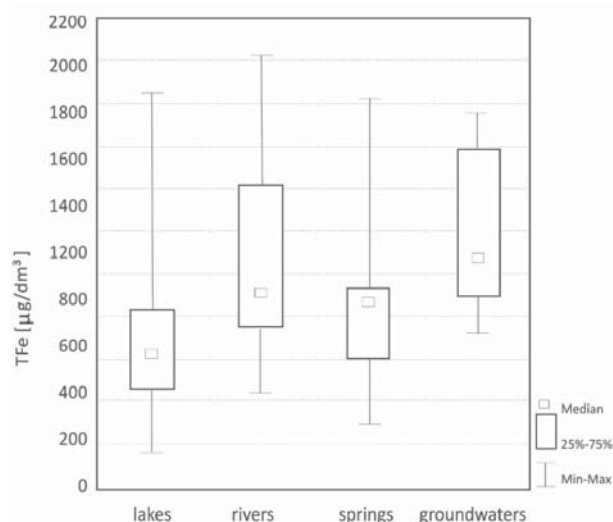
Fig. 2. The concentration of the total fraction of iron (TFe) in the waters of SLP (July 2009).

Table 1. Average concentrations of the total fraction of iron (TFe) and manganese (TMn) (±standard deviation), and the ratio of Fe:Mn in all the types of SLP waters (July 2009).

	TFe [μg Fe/dm³] ±SD	TMn [μg Mn/dm³] ±SD	Fe:Mn
Lakes	881±659	642±362	1,34
Rivers	1081±496	640±428	3,21
Springs	862±484	959 ±565	0,90
Groundwaters	1645±1476	649±242	2,53

Szeszupa River below Lake Okrągłe (7044 μgFe/dm³), a stream flowing out of Lake Jeglówek (8680 μgFe/dm³), and a spring near Lake Kameduł (5060 μgFe/dm³) showed the highest TFe values. This suggests high oxygenation of river waters, affecting the precipitation of insoluble iron (III) hydroxide [18]. The lowest concentration of the TFe was observed in springs and lakes. Manganese ions were present in higher concentrations in groundwaters (TMn>900 μgMn /dm³) than in surface waters of SLP. The concentration of the total fraction of manganese in lakes, rivers, and shallow groundwaters was found to be similar and reached a mean value of 640 μgMn /dm³ (Table 1).

In the structure of iron and manganese in groundwaters, the lowest concentration was observed in the case of the DOFe and DOMn (<25%), and the highest, more than 50%, for PFe and PMn (Fig. 3a,b). Plants play an important role in the biogeochemical cycle of metals in shallow groundwaters. These waters are located directly in the root zone of plants able to absorb and accumulate

metals. The manganese absorption process is stimulated by the presence of nitrates (V) and potassium [19]. The concentration of nitrates (V) was found to be twice higher in shallow groundwaters than in lake waters. The highest potassium concentration was observed in shallow groundwaters (3.3 mg/dm³). Another factor influencing the form of iron and manganese is the oxidation-reduction potential. The lowest mean redox potential value (196.7 mV) was recorded in shallow groundwaters. This suggests a low concentration of oxidizing factors.

The springs of SLP have the lowest concentrations of DOFe and DOMn in comparison to the other types of water bodies (Fig. 3a, b). Springs, as natural groundwater outflows, have the lowest mean concentration of DOC (8.1 mg/dm³) in comparison to rivers (13.7 mg/dm³), lakes (13.4 mg/dm³), and shallow groundwaters (17.7 mg/dm³). Metals develop organometallic complexes in the presence of dissolved organic carbon (DOC). This results in reduced development of metaloorganic complexes. DOC consists of low molecular weight compounds such as organic acids, amino acids, proteins, and carbohydrates, constituting the dissolved organic fraction combined with iron and manganese ions [14]. Springs are a kind of transition zone between groundwaters and surface waters. The minerals are retained while the organic compounds are being carried in the water column in river and lake systems [20]. This is reflected in the highest concentration of the insoluble fraction in comparison to the other types of water bodies. This demonstrates the processes of metal precipitation in the niches of springs, particularly in the form of oxides and carbonates.

The rivers of SLP have the highest concentration of DOFe and DOMn in comparison to lakes, springs, and shallow groundwaters of SLP (Fig. 3a, b). The majority
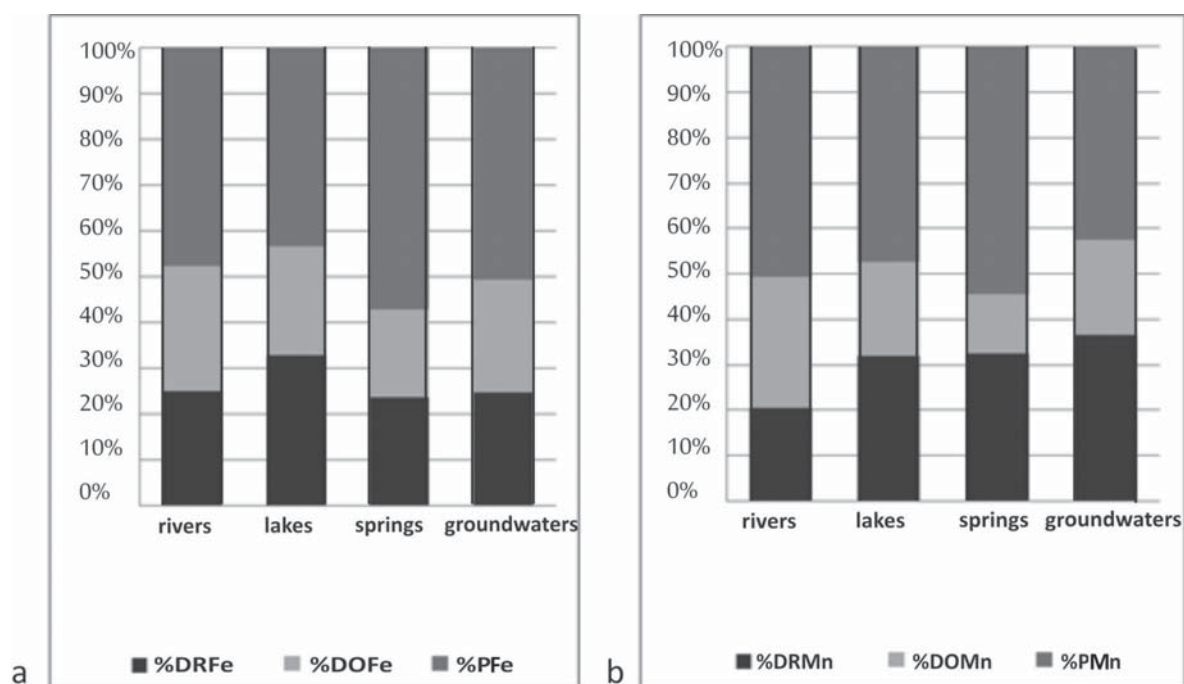

Fig. 3. Structure of iron (a) and manganese (b) in all the types of SLP waters (July 2009).
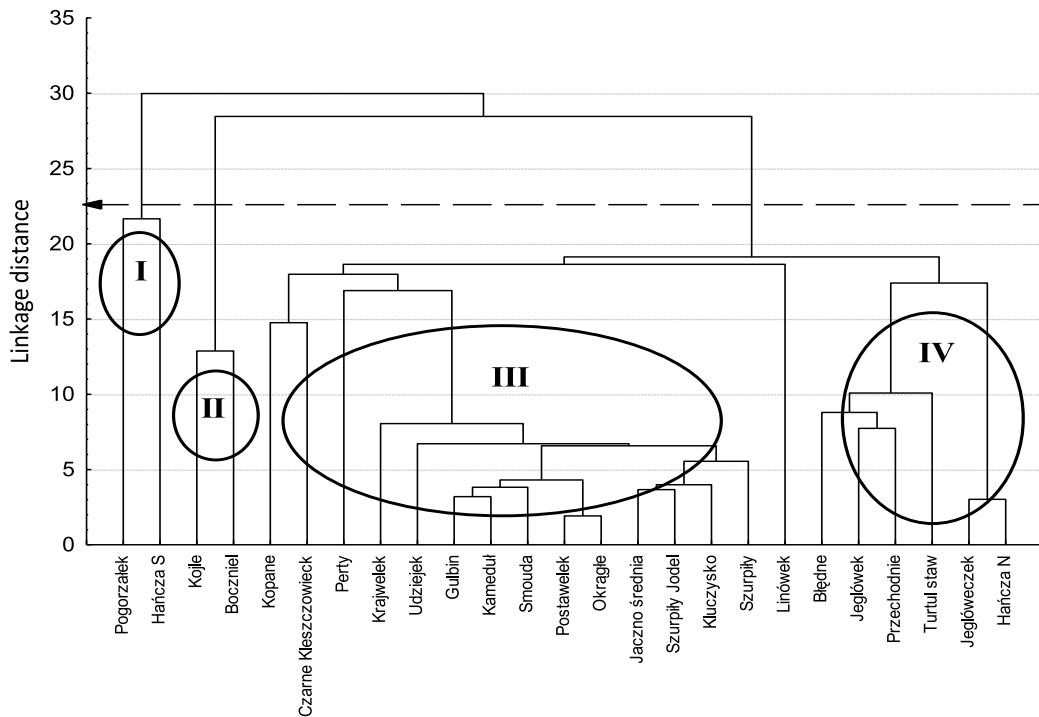
Fig. 4. Groups of lakes of varying concentrations of manganese separated from the cluster analysis (July 2009).

of iron and manganese ions are connected to fulvic and humic acids [21, 22]. The most durable compounds of organic iron are developed at pH close to neutral, whereas at alkaline pH, iron hardly reacts with DOC [23]. The pH value of river waters was the lowest (pH<8) in comparison to lakes, springs, and shallow groundwaters. This seems to confirm our hypothesis. The lowest concentration of the reactive fractions of manganese (DRMn) was recorded in rivers (Fig. 3b). The percentage of reactive manganese was 20% in fractional composition. The oxidized form of manganese with iron developed iron-manganese concretions. Due to a high load of iron, manganese ions are immobilized, making manganese biologically unavailable in river waters.

Table 2. Physical and chemical parameters selected in groups of the SLP lakes (July 2009) (Statistical difference – test rang, Duncan method).

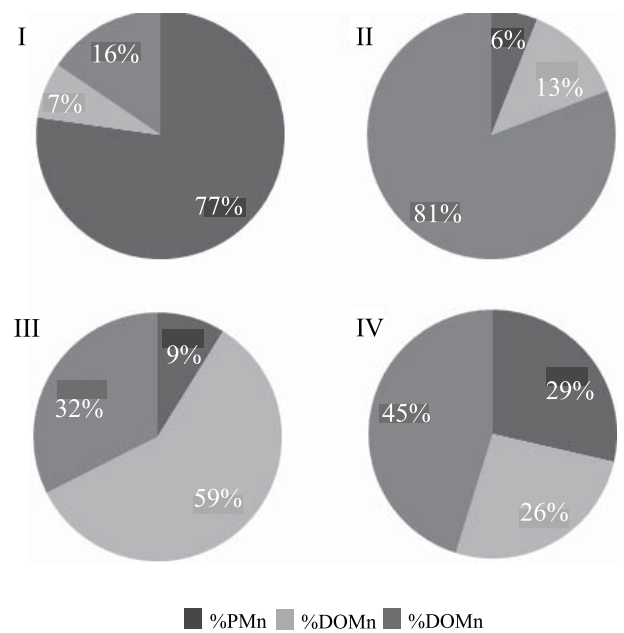| Parameters	I (a)	II (b)	III (c)	IV (d)	Statistical difference
number of samples	4	4	29	29	
pH	8.4	7.7	8.7	8.0	a-b, a-d, b-c, b-d
EC [μS/cm]	391.0	255.6	209.3	311.6	a-c
Eh [mV]	275.3	200.7	136.3	197.8	a-c
DOC [mgC/dm³]	11.4	13.7	17.0	16.3	
Cl [mg/dm³]	7.3	6.5	8.3	9.1	b-d, c-d
HCO$_3^-$ [mgC/dm³]	61.0	41.7	35.7	45.9	a-c
N-mineral [μgN/dm³]	327	226	135	151	a-c, c-d
N-NH$_4^+$ [μgN/dm³]	265	173	91	105	a-c, c-d
DRFe [μgFe/dm³]	177	462	457	211	

Fig. 5. Structure of manganese in four groups of the SLP lakes (July 2009).

Table 3. The main forms of iron (μgFe/dm³) and manganese (μgMn/dm³) in SLP waters (July 2009).

Speciation	Lakes	Rivers	Springs	Groundwaters
number of samples	50	15	8	8
Fe^{2+}	17	17	15	681
$Fe(OH)_3$	726	1363	1705	173
$Fe(OH)^{2+}$	77	186	126	67
$Fe(OH)^{4-}$	59	134	132	4
Mn^{2+}	283	279	345	567
$MnCO_3$	278	275	345	190
$MnHCO_3$	78	85	78	199

SLP lakes were found to have completely different chemical compositions in terms of iron and manganese contents. The total iron concentrations were mostly below 1000 μgFe/dm³, and manganese below 800 μgMn/dm³ in lakes. The only exception was Lake Kameduł (1,384 μgFe/dm³). This can be indirectly associated with the spring (5,190 μgFe/dm³) and the Jaczniówka River supplying the lake (770 μgFe/dm³). The spring water was calculated to account for only 0.01% of the lake water supply per day, and 4.6% per year. The Jaczniówka River accounts for 2.7% of the lake water supply per day. Therefore, the river plays a larger role in supplying Lake Kameduł than the spring.

Some of the lakes of SLP showed similarities in terms of the fractional composition of manganese. They were divided into four groups, each distinguished by a different manganese structure (Fig. 4). Iron fraction showed no such similarity. Lakes belonging to the first group were dominated by the PMn (77%) (Fig. 5). The highest concentrations were reached by mineral nitrogen, bicarbonate, ammonia nitrogen, and total phosphorus fractions. The lakes are distinguished by the highest values of electrolytic conductivity and redox potential. The concentration of DOC was the lowest in comparison to other groups of lakes, resulting in a low proportion of the DOMn (7%) (Table 2, Fig. 5). High concentrations of the PMn can be explained by the precipitation of colloids in water under high oxygenation (SWWT= 110%). Phosphorus is an important parameter, causing precipitation of high concentrations of iron (III) and manganese (II). Moreover, manganese and iron act synergistically, and are subject to co-precipitation to the bottom sediments in the processes of sedimentation.

The second group of lakes includes two eutrophic lakes: Lakes Boczniel (TSI=57 [6]), and Kojle (TSI=54 [4]). The highest concentration in the fractional composition of manganese was reached by the DRMn (Fig. 5). Cudowski and Zieliński reported that high concentrations of DOC in water determine high concentrations of the DRMn [1]. The processes of release of metals from sediments occurring in the hypolimnion in low-oxygen water are the primary source of DRMn [18]. The third group of lakes includes Lake Pogorzałek and the southern part of Lake Hańcza (Fig. 4). Hańcza Lake is the biggest lake in SLP and the structure of manganese differs in various parts of the lake. The dominant fraction was the DOMn (Fig. 5). The lakes are distinguished by high concentrations of organic matter. The DOC load in Lake Pogorzałek was estimated at 2,224 kg in 2009-10 [17]. The concentration of DOC was positively correlated with the concentration of DOMn (p = 0.0006). Moreover, these two lakes had more alkaline water pH than the others. Higher pH determines high concentrations of the organic-manganese complexes in waters. The fourth group includes lakes with an even distribution of fractional composition of manganese, with a slight predominance of the DRMn. These lakes are distinguished by low concentrations of oxygen and DOC. The processes of precipitation are balanced with the process of release of the reactive forms of metals.

Table 4. Values of the saturation index (SI) relative to the minerals in SLP waters (July 2009).

Mineral		Lakes	Rivers	Springs	Ecotone zone
Goethite	FeOOH	8,85	9,14	9,22	8,21
Hematite	Fe_2O_3	19,67	20,27	20,40	18,40
Syderite	$Fe CO_3$	-0,55	-0,60	-0,47	0,56
Jarozite K	$KFe_3(SO_4)_2(OH)_6$	-4,27	-3,25	-3,55	-4,03
Melanteryte	$Fe SO_4 \cdot 7H_2O$	-8,78	-8,93	-8,83	-7,06
Wiwianite	$Fe_3(PO_4)_2 \cdot 8H_2O$	-5,48	-5,52	-5,57	-2,36
Iron (III) hydroxide	$Fe(OH)_3$	3,19	3,38	3,71	2,54
Husmanite	Mn_3O_4	-7,12	-6,18	-6,74	-11,75
Manganite	$MnO_2 \cdot Mn(OH)_2$	-2,87	-2,70	-2,27	-4,81
Pyrochroite	$Mn(OH)_2$	-4,57	-4,72	-4,40	-5,42
Pyrolusite	MnO_2	-8,15	-7,16	-7,75	-11,10
Rodochrozite	$MnCO_3$	0,91	0,92	0,99	0,75

The SLP lakes represent trophic status from mesotrophy to eutrophy [6], which suggests diverse factors affecting water quality. A similar concentration of iron and manganese in lakes and the other types of water emphasize its natural character. The higher concentrations of DOC may be a problem in lakes, resulting in iron complexation, which affects the elevated levels of reactive fraction of manganese [1]. Such conditions are conducive to eutrophication. The studies have a significant role in water reservoir protection. Analysis of the structure of iron and manganese can be indirectly used to assess water quality.

The lakes, rivers, springs, and shallow groundwaters of SLP differed in terms of manganese and iron concentrations. The highest values of the iron-to-manganese concentration ratio were found in rivers and groundwaters, and the lowest in springs (Table 1). The ratio values in groundwaters depend on the rocks building their basin, and the intensity of mechanical denudation [18]. Concentrations of both of the metals were fairly in springs (850-950 $\mu g/dm^3$), with a slight predominance of manganese (Table 1). Iron concentrations depend on iron hydroxide. Manganese concentrations are determined by cation Mn^{2+} and chemical compound $MnCO_3$ (Table 3). The saturation index values for minerals containing iron and manganese were similar in all of the water types studied (Table 4). A higher possibility of dissolving hausmanite and pyrolusite in shallow groundwaters was determined. The springs have the highest values of the water saturation index, resulting in precipitation hematite, goethite, and iron (III) hydroxide.

Conclusions

1. The concentration ranges of TFe and TMn were from 300 to 8,680 $\mu gFe/dm^3$ and from 57 to 1,728 $\mu gMn/dm^3$ in SLP waters.
2. The groundwaters, springs, rivers, and lakes of SLP are different in terms of fractional composition of both metals with predominance of insoluble fractions. The highest concentrations of organic fractions of both metals were found in rivers. The highest concentration of DRFe was observed in groundwaters and DRMn in lakes.
3. Iron shows higher stability in an aquatic environment, while manganese compounds are more volatile, as manifested in the variable fractional composition of manganese in lakes.
4. The fractional composition of iron and manganese depends on the content of organic matter related to the development of metaloorganic complexes.
5. The concentration of reactive manganese fraction indirectly suggests the lakes' trophic status.

Acknowledgements

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