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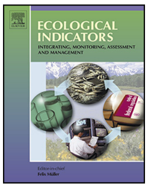

Review

Dissolved reactive manganese as a new index determining the trophic status of limnic waters

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ABSTRACT

Dissolved reactive manganese seems to be one of the parameters which determines the trophic status of limnic waters, as suggested by its strong correlations with total phosphorus, chlorophyll *a*, and water pH. The determination of the trophic status involved the application of reactive manganese due to its bioavailability, providing information on the actual, not just the potential (as in the case of total phosphorus or total organic carbon), threat of water eutrophication.

The calculation of trophic states index (TSI) based on the reactive manganese concentration, as determined by $\mathrm{TSI_{DRMn}} = 20.61\ \ln(\mathrm{DRMn}) - 35.03$, permits the rational assessment of the trophic status of lakes. Oligotrophic lakes are distinguished by concentrations of DRMn < 25 μg/L, mesotrophic by 25–60 μg/L, eutrophic by 60–150 μg/L, and hypertrophic by >150 μg/L.

The trophic status of 25 lakes located in central Europe in north-eastern Poland was determined based on the proposed “manganese index” and verified by commonly applied indices proposed by Carlson, Kratzer and Brezonik, and Dunalska.

Contents

1. Introduction

Manganese is a trace element which is necessary for life in both plants and animals. It has very important functions in a variety of metabolic processes, particularly photosynthesis. It also participates in the biosynthesis of chlorophyll, which is necessary for the proper functioning of photosystem PSII (Mousavi et al., 2011; Nusrat and Rafiq, 2011). Manganese is an essential element for the proper conduction of redox processes in plant cells. It acts as a carrier of oxygen by participating in electron transport during photosynthesis (Cheniae and Martin, 1970; Babcock, 1987). It is also recognized as a “special operations” element. It accumulates in enzymes such as acidic superoxide dismutase or glycoside phosphatase. Manganese contributes to the reduction of nitrate (V) ions in plants and the hydrolysis of peptides, amides (peptidases) and urea (arginases) (Fraústo da Silva and Williams, 1991). Moreover, manganese is an essential element for the development of lower plants, e.g., algae. Its deficiency causes the growth inhibition of *Chlorella vulgaris* (Tanner et al., 1960) and disorders of the electron transport chain lead to the inhibition of photosynthesis (Kessler et al., 1957; Kessler, 1970; Sauer, 1980). Increasing the concentration of manganese in the environment reslts in the stimulation of RNA polymerase activity (Mousavi et al., 2011), which may cause an increase in the protein

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concentration in algal cells. Earlier studies have shown that reactive manganese also causes an increase in the concentration of monosaccharides in algal cells (Cudowski and Pietryczuk, 2014).

This element commonly occurs in surface waters. Its concentration largely depends on the degree of its elution from bottom sediments and plant remains. To a lesser degree, it also comes from industrial wastewater. Manganese occurs in natural waters in the form of mineral compounds and, to a lesser extent, organic compounds. Its forms particularly depend on the intensity of the microbiological processes which occur in water ecosystems. The microorganisms influencing its form are inter alia aquatic fungi which participate in the process of organic matter decomposition (Kuznetsov, 1970; Yagi, 1993). By producing manganese peroxidase, mycoplankton catalyze the oxidation of manganese(II) ions to manganese(III) (Wurzbacher et al., 2010), which is stabilized by organic acids (Vincent and Christou, 1987; Lis 1980). Due to the reactivity of manganese(III) ions, they are included in the process of the decomposition of the phenol structures of lignin and humic substances (Wurzbacher et al., 2010). Particular fractions of manganese in reservoir are subject to multiple transformations. Such transformations depend on a number of factors, including water movement, its chemical composition, and the presence of macrophytes. In stratified lakes, the oxidation of manganese(II) ions in the surface layer is performed by microorganisms from genera *Metallogenium* and *Siderocapsa*. This process causes the formation of manganese(IV) oxide, which migrates to the bottom of the reservoir. In the near-bottom layer, its main reductor is organic matter, which in the result of oxidation migrates to the bottom of the reservoir. The resulting manganese(II) ions can migrate to the metalimnion and then the epilimnion (Wetzel, 2001). Moreover, the oxidized form of manganese, i.e., Mn(IV), can co-precipitate with iron, developing so-called iron-manganese concretions, in which manganese occurs in the form of birnessite or todorokite (Wehrli et al., 1995). The co-precipitation of both metals is particularly possible during spring and autumn water mixing, and the precipitated concretions migrate to the bottom sediment. These mechanisms are very important from the point of view of water hydrochemistry and functioning of lentic ecosystems. Multiple circumstances suggest that it restricts the water eutrophication process.

Eutrophication is a process which causes an increase in the productivity of waters. It results from an increase in the nitrogen and phosphorus concentrations, causing the mass development of aquatic vegetation, which in turn leads to an increase in the concentration of organic matter. The trophic status of stagnant waters is usually estimated based on observations of the availability of substrates and the level of primary production during the vegetation season. In the first stage of eutrophication, the intensive development of algal biomass occurs. The resulting mass algal "blooms" lead to the restriction of photosynthesis and further to the deterioration of oxygen conditions in water. The control of manganese concentrations, particularly reactive manganese, during the process of water eutrophication is of the utmost importance because this element facilitates the growth of algae (Cudowski and Pietryczuk, 2014). Eutrophication has become a global problem. This process has been recorded in lakes, seas, and rivers throughout the world (Imai et al., 2006; Selaman et al., 2008). Therefore, numerous authors have attempted to estimate the trophic status by applying water quality indices (Kratzer and Brezonik, 1981; Canfield et al., 1983; Vollenweider, 1989; Nixon, 1995; Lean, 1998 Eloranta, 1999; Håkanson and Boulion, 2001, 2002) and developing methodologies aimed at impeding or even reversing eutrophication processes. The primary and secondary products of photosynthesis which accumulate within an ecosystem and are not subject to decomposition due to oxygen deficits in the water depths cause eutrophication. This process contributes to a decrease in the volume of a lake and therefore to the loss of its utility values. Therefore, lakes should be continuously monitored by controlling easy-to-analyze indices (Galvez-Cloutier and Sanchez, 2007). Carlson (1977) and Walker (1979) proposed the assessment of the eutrophication progress based on trophic state indices (TSI), dependent on the mean chlorophyll *a* concentration, mean total phosphorus (TP) concentration, and Secchi disk visibility. According to later papers by Forsberg and Ryding (1980) and Nürnberg (2001), the changes in the trophic status of water ecosystems can be estimated using not only the chlorophyll *a* and total phosphorus concentrations but also the total nitrogen concentration. Moreover, indices exist which determine the relationship between the trophic status and the kinetic balance of organic matter decomposition. The index of trophic state (ITS) could be determined by the changes in the quantitative relationship between oxygen and carbon(IV) oxygen concentrations based on disturbances in the balance between the processes of the production and decomposition of organic substances in an ecosystem. The biotic balance of surface waters could be also expressed by the function of the values of pH and oxygen saturation in water (Neverova-Dziopak, 2006). Moreover, as Dunalska (2011) proposed, water trophic status index could be determined by total organic carbon (TOC) concentration.

The aim of the study was to develop such a trophic indicator of waters which has a simple designation, does not cause any analytical problems for the researcher and does not require (as in the case of currently used indicators) sample preparation for analysis, e.g., by mineralization. In addition, the next goal of this manuscript was to identify an index which could provide information on the actual, not just the potential (as in the case of TP or TOC), threat of water eutrophication. Therefore, a model describing the ecological state of limnic waters with the application of manganese as a trophic index was elaborated.

2. Materials and methods

The hydrochemical monitoring of the limnic waters of north-eastern Poland, aimed at the determination of their trophic status, was performed in the years 2005–2013. Samples were taken in the summer season (July) from the epilimnion during the occurrence of favorable meteorological conditions which permitted the acquisition of credible results. Over the study period, samples were taken from the open water zone three times from each lake. The study involved a group of 25 lakes in north-eastern Poland (Fig. 1) with varied hydrological conditions and mictic and morphological types. Using a multi-parameter Hydrolab sonde, the following parameters were measured in the field: water temperature, pH, electrolytic conductivity (EC), oxygen saturation and oxygen concentration. Moreover, visibility (SD) was measured by the use of Secchi disk.

In the laboratory, the total organic carbon concentration (TOC) was determined using the high-temperature catalytic method of incineration in a TOC-5050A analyzer by Shimadzu. Total nitrogen (TN) was determined using the Kjeldahl method (PN-EN 25663:2001), the chlorophyll *a* concentration was determined using the spectrophotometric method (PN-86/C-05560/02), the total phosphorus (TP) concentration was determined using the molybdenian spectrophotometric method (APHA, 2012), and the concentration of the reactive manganese fraction (DRMn) was determined using the formaldehyde spectrophotometric method with own modifications (Górniak and Cudowski, 2006).

The collected physical and chemical data were subject to statistical analysis following the methodology proposed by Griffiths (2008). To analyze the existing differences among the lakes, a multi-dimensional analysis was applied, namely data clustering, in which Euclidean distance was assumed as the

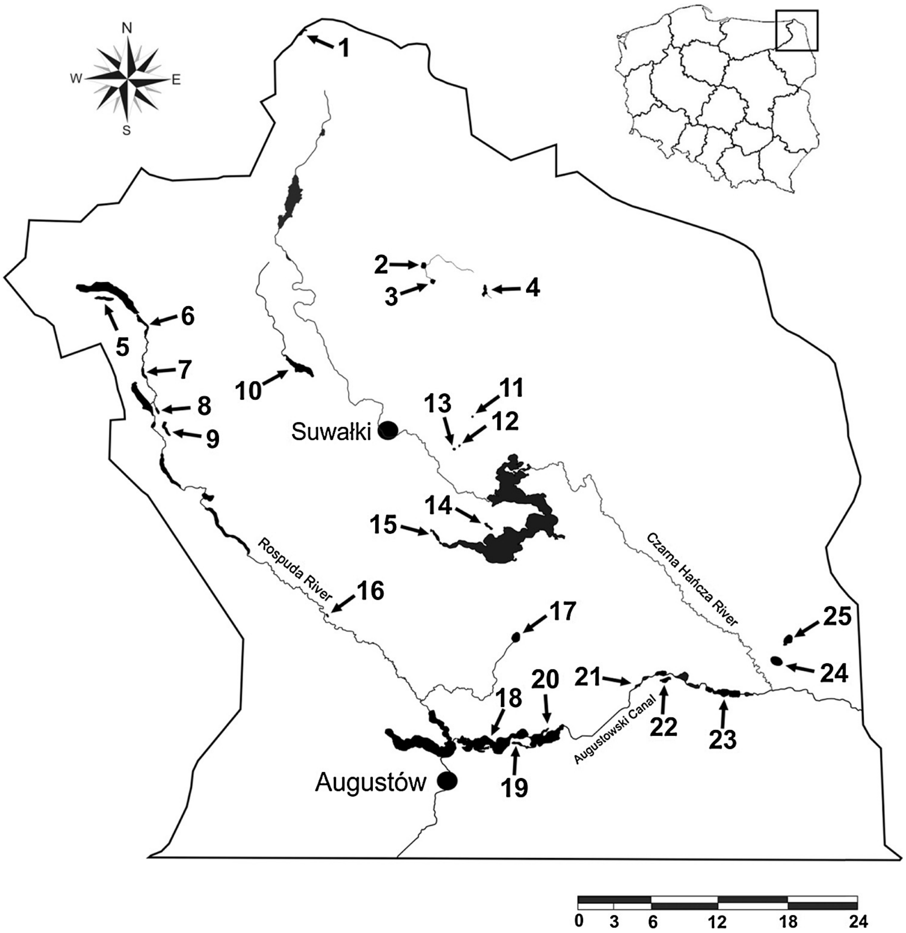

Fig. 1. The map showing the distribution of the investigated positions on the Polish territory in the northern part of the Podlasie region.

probability measure and Ward's method as the clustering procedure. Principal components analysis (PCA) determined the variables which best accounted for the differences among the studied objects. The absolute value of the component loadings of particular parameters permitted their identification. The DRMn concentration model was developed via backward stepwise regression. The differentiation of the distribution of a given parameter was described via the coefficient of variability (CV), defined as the ratio of the standard variation from a given sample to its arithmetic mean and expressed as a percent value (Nairy and Rao, 2003). All of the statistical calculations were performed using the Statistica 7 software. The provided map was developed using the ArcGIS software, version 9.3.1.

3. Results and discussion

The studied lakes showed largely varied pH, ranging from strongly acidic to alkaline. The pH values varied from 3.07 to 8.98. The lowest pH values were recorded for dystrophic lakes. Alkaline pH values were observed for the remaining lakes. Electrolytic conductivity, which is an indicator of water pollution, varied from 11 µS/cm to 897 µS/cm. Its minimum values were recorded in dystrophic lakes (Suchar Wielki), and the maximum values were recorded in Pejcze and Staw Gielucha Lakes. All of the studied lakes showed good oxygenation of the epilimnion. The concentration of dissolved oxygen in the water varied from 7.55 mg/L to 10.5 mg/L. The lowest values of this parameter were obviously recorded for the most polluted lakes, i.e., Pejcze and Staw Gielucha Lakes, and the highest values were recorded for Płaskie, Brożane, and Busznica Lakes.

The Secchi disk visibility in all of the lakes throughout the study period varied from 0.1 m to 7.6 m. Busznica Lake had the highest Secchi disk visibility, but Staw Gielucha Lake had the lowest, similar to the chlorophyll *a* concentrations, which varied from 1.57 µg/L to 430.6 µg/L. The analyzed group of lakes showed total nitrogen concentrations ranging from 0.2 mgN/L to 19.8 mgN/L. The minimum values were recorded for Brożane Lake, and the maximum were recorded for Pejcze Lake. These findings corresponded with the total organic carbon concentrations, which varied from 1.13 mgC/L to 39.1 mgC/L. Total phosphorus concentrations varied from 16.8 µgP/L to 3887 µgP/L, reaching the minimum values in Busznica Lake and maximum in Pejcze Lake. The distribution of the reactive manganese concentrations was identical, with values ranging from 25.7 µgMn/L to 969.5 µgMn/L.

The calculated trophic state indices for the 25 selected lakes in north-eastern Poland showed that 7 of the lakes were mesotrophic, 2 were hypertrophic, 12 were eutrophic, and the remaining 4 were dystrophic. Certain partial indices, e.g., TSI_{CHL}, have lower values than the remaining ones (Table 1), particularly those calculated for Długie Filipowskie and Staw Lakes. The determined manganese index permits the estimation of the trophic status of lakes. Combined with the Carlson index, it enables a more accurate description of the trophic status of lakes. This accuracy is currently very important due to the systematic deterioration of the

Table 1
The average values of selected indicators of the trophic status of lakes in north-eastern Poland calculated on the basis of our own analysis. The lakes are numbered as in Fig. 1. No coefficient of variability calculated for the individual indicators of trophic for any of the studied lakes was higher than 8%, supporting the temporal stability of the analysed group of lakes.

Lake [number]	Trophic state					
	Carlson (1977)			Kratzer and Brezonik (1981)	Dunalska (2011)	This study
	TSI_{SD}	TSI_{CHL}	TSI_{TP}	TSI_{TN}	TSI_{TOC}	TSI_{SRMn}
Wysokie [15]	54.2	49.8	76.6	63.7	51.0	67.1
Siekierowo [9]	57.7	53.3	73.7	62.0	67.0	65.7
Grauże [4]	57.8	43.4	80.1	63.3	52.3	62.7
Kamienne [6]	50.1	50.9	80.4	57.7	47.7	55.8
Gatno [8]	51.3	47.6	70.6	55.2	60.4	61.5
Długie Filipowskie [7]	49.8	36.7	74.7	46.5	65.6	51.2
Ślepe [16]	49.3	49.7	56.1	40.1	55.4	47.9
Pejcze [3]	91.6	89.1	123.3	97.5	78.2	106.7
Staw Gielucha [2]	94.2	90.1	105.5	90.9	71.3	102.3
Mikaszewo [23]	61.1	54.4	82.6	60.3	57.2	58.5
Pobojno [22]	63.7	71.6	76.7	59.2	67.2	68.1
Wojciech [19]	53.2	43.4	61.3	50.4	58.6	59.7
Gorczyckie [21]	56.3	58.0	80.3	57.3	67.7	51.7
Brożane [25]	33.2	41.0	58.1	31.5	40.6	47.1
Płaskie [24]	36.8	39.8	60.7	40.2	45.6	46.7
Busznica [17]	30.7	35.0	44.8	39.1	43.1	31.9
Studzieniczne [20]	40.4	53.2	70.1	41.3	60.0	32.6
Białe Augustowskie [18]	43.7	44.5	60.4	33.4	55.5	32.2
Dunajewo [1]	50.4	55.3	66.3	63.4	51.1	60.3
Okmin [10]	35.7	46.8	66.9	41.2	43.2	39.0
Staw [15]	55.4	38.9	69.3	60.3	60.6	64.6
Suchar IV [12]	68.6	71.6	68.1	74.2	83.9	99.2
Suchar II [13]	61.3	71.4	71.6	75.5	79.1	85.6
Wądołek [11]	57.2	51.1	65.5	76.1	82.1	91.8
Suchar Wielki [14]	66.7	44.4	60.6	77.9	77.8	93.3

ecological state of lakes. The cluster analysis provided on the basis of the obtained results separated 5 groups of lakes (Fig. 2). The lakes can be divided into 4 groups in terms of trophic status, with group I including dystrophic lakes, group II including hypertrophic lakes, groups III and IV including eutrophic lakes, and group V including mesotrophic lakes. Moreover, the eutrophic lakes were divided into two groups by the mictic type. Group III includes polymictic lakes, and group IV includes dimictic lakes.

The comparison of particular trophic status indices shows that in all harmonious lakes, the TSI_{TP} values, and therefore the total phosphorus concentrations, were higher than the values of the remaining indices based on Secchi disk visibility, chlorophyll *a*, total nitrogen, and total carbon concentrations (Table 1). Theoretically, all of these indices should have similar values and identify the same trophic type of water. This result would suggest the harmonious development of the lakes, undisturbed by anthropopressure (Matthews et al., 2002). The comparison of the trophic status of the discussed lakes with those of lakes from other regions of Poland shows a number of similarities. In many lakes of the Masurian Lakeland (Pyka et al., 2007) or Lubuskie Lakeland (Pełechata et al., 2006), strong differentiation is observed among particular trophic status indices, i.e., their imbalance. The role of phosphorus and the index calculated based on its concentration in the surface water layer is still emphasized by many authors as a basic indicator of the trophic status. This indicator has usually higher values than the remaining ones,

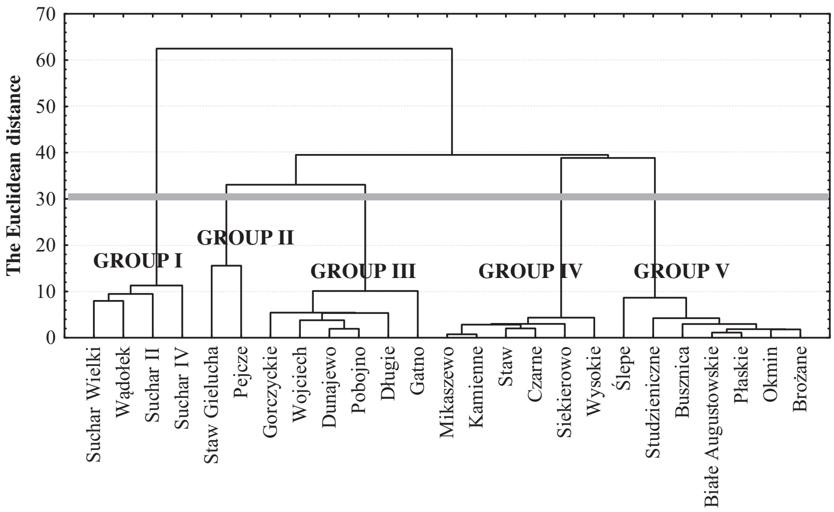

Fig. 2. The results of the cluster analysis of the selected lakes in north-eastern Poland.

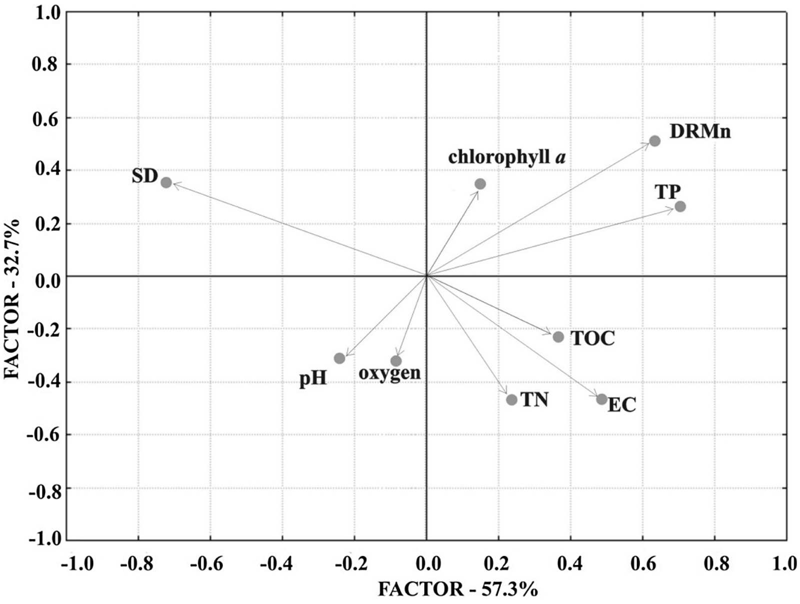

Fig. 3. Diagram of the component loadings, presenting the first two principal components jointly accounting for 90% of the variance of the original variables for the studied lakes, based on parameters determining the water trophic status.

because it includes entire pool of phosphorus which cannot be used by living organisms. Therefore, in my opinion, it is not a completely credible index of the water trophic status. Knowledge of the total concentration of this element in water only provides information on a potential threat of water eutrophication. The phosphorus can be very quickly precipitated with calcium, in view of the high concentration of these elements in the water and very high solubility product of calcium phosphate(V) ($pK_{so} = 26.0$). The result of this process is a change of phosphorus form in the inaccessible for autotrophs, and limiting the precipitation of this element with manganese. The above consideration is confirmed by the existence of a directly proportional correlation between total phosphorus and reactive manganese concentrations ($r^2 = 0.93$, $p < 0.001$). In turn, the manganese which is present in the solution in the form of Mn^{2+} has theoretically a higher capacity (in comparison with calcium) for precipitation with carbonates in the form of manganese(II) carbonate ($pK_{so} = 9.3$), which are common in the analyzed waters belonging to the triple ion type of waters (HCO_3^-–Ca^{2+}–Mg^{2+}) according to the hydrochemical classification of surface waters by Altowski and Szwiec (1956). In stagnant freshwater, however, concentrations of calcium ions is about 4 orders of magnitude higher compared with manganese. Therefore, the reaction of calcium carbonate precipitation ($pK_{so} = 8.4$) is privileged compared to reaction of manganese(II) carbonate precipitation, which has higher solubility product. This reaction leads to the development of limnic chalk, resulting from the biochemical precipitation of calcium carbonate. Due to such precipitation, no precipitation of manganese(II) with carbonates occurs, what results in an increase in the concentrations of the reactive fraction of manganese in lakes and, therefore, an increase in water eutrophication. Growing reactive manganese concentrations cause growth in the number of cells of algae *C. vulgaris* (Cudowski and Pietryczuk, 2014). Moreover, reactive manganese has been demonstrated to stimulate an increase in the concentrations of monosaccharides, proteins, and chlorophylls *a* and *b* in the cells of algae *C. vulgaris* as well as an increase in the activity of enzymes such as superoxide dismutase and glutathione reductase (Cudowski and Pietryczuk, 2014). Next to reactive manganese, phosphorus (Wu et al., 2006; Higgins et al., 2011) and pH (Weisse and Stadler, 2006; Shi et al., 2009) are obvious factors causing intensive phytoplankton growth. All of these parameters are found in the equation of multi-factor regression. The equation of multi-factor regression accounts for 90% of cases at a Durbin–Watson index of 1.95, showing the relationship among the concentration of total phosphorus, the primary factor leading to water eutrophication, and other parameters, including reactive manganese:

$$\mathrm{TP}(\mu\gamma/\mathrm{L}) = 5.32\,\mathrm{pH} - 0.30\ \mathrm{chl.}\,a(\mu\mathrm{g/L}) + 2.35\ \mathrm{DRMn}(\mu\mathrm{g/L})$$

After transforming the equation, a correlation was obtained indicating a considerable effect of the reactive fraction of manganese on the trophic status of limnic waters.

$$\mathrm{DRMn}(\mu\gamma/\mathrm{L}) = 0.425\,\mathrm{TP}(\mu\gamma/\mathrm{L}) + 0.128\ \mathrm{chl.}\,a(\mu\gamma/\mathrm{L}) - 2.26\,\mathrm{pH}$$

According to the principal components analysis (Fig. 3), dissolved reactive manganese is strongly positively correlated with parameters such as total phosphorus and chlorophyll *a* and negatively correlated with pH. The remaining parameters, i.e., Secchi disk visibility, total organic carbon, and total nitrogen, are

Table 2
The values of selected parameters determining the trophic status of the lakes according to Carlson (1977) and the proposed manganese index (DRMn).

SD (m)	Chlorophyll *a* (μg/L)	TP (μg/L)	DRMn (μg/L)	TSI value	Trophic state
>8	<2	<10	<25	<30	Oligotrophy
2–8	2–15	10–30	25–60	30–50	Mezotrophy
0.5–2	15–500	30–300	60–150	50–70	Eutrophy
<0.5	>500	>300	>150	>70	Hypertrophy

not significantly correlated with reactive manganese. In addition, PCA analysis shows that the reactive manganese is negatively correlated with the concentration of oxygen in the water, while electrolytic conductivity has no influence on DRMn (Fig. 3). Both of these parameters do not directly affect on the eutrophication process, hence they were not included in the equation of multi-factor regression analysis.

Based on Carlson's trophic state indices (Carlson, 1977), a trophic state index with the application of the reactive manganese fraction was also calculated.

$$\mathrm{TSI}_{\mathrm{DRMn}} = 20.61\ln(\mathrm{DRMn}) - 35.03$$

The calculated trophic state indices for the studied lakes (Table 1) and the resulting identification of the trophic statuses of the lakes showed that the proposed "manganese index" (Table 2) corresponds with the trophic statuses of waters according to Carlson. In terms of numerical values, the proposed "manganese trophic index" has the strongest correlation ($r^2 = 0.87$, $p < 0.001$) with the Kratzer and Brezonik index (Kratzer and Brezonik, 1981). This correlation is likely due to the occurrence of nitrogen in the environment in dissolved forms available for autotrophs, similar to reactive manganese. The phosphorus (Carlson, 1977) or carbon (Dunalska, 2011) indices show the total concentrations of both these elements. However, not all of their forms are biologically available to living organisms. Therefore, their values may vary from the actual trophic status of the lake, what was not recorded in the case of manganese index. However, it should be emphasized that the proposed manganese index also has limitations as to its use. It should not be used only in the case of saline lakes. Increased salinity favors shifting the equilibrium of the complexation reaction of heavy metal ions with anions, such as chloride, contained in the saline water. The consequence of this condition is a decrease in the concentration of the most bioavailable forms of ionic elements, including reactive manganese (Pitter, 1999; Wetzel, 2001). The last two indices, i.e., Secchi disk visibility and chlorophyll *a* concentration, have similar numerical values and they are strongly correlated ($r^2 = 0.76$, $p < 0.005$), because intensive algal growth restricts disk visibility. $\mathrm{TSI}_{\mathrm{SD}} > \mathrm{TSI}_{\mathrm{CHL}}$ suggests the prevalence of small algae restricting visibility, while $\mathrm{TSI}_{\mathrm{CHL}} > \mathrm{TSI}_{\mathrm{SD}}$ suggests the predominance in water of large algae, e.g., *Aphanizomenon*.

The overall conclusion is that the proposed "indicator of manganese", in contrast to other commonly used indicators, takes into account the bioavailable form of this element. This indicator is ideally suited to assess the trophic status of almost any type of water in lakes with the exception of saline lakes. The use of a manganese indicator to assess the trophic status of lakes appears to be the simplest method, because determination of the reactive manganese concentration in the water does not require preliminary procedures for sample preparation (e.g., mineralization of the sample), as is the case for phosphorus, nitrogen and carbon. High values of this manganese indicator provide information about eutrophication, which may be limited (and/or undone) through numerous treatments, including the oxygenation of the bottom water layers. The increased concentration of oxygen in the water results in the oxidation of manganese(II) to manganese(IV), precipitating it from the water column with the compounds of phosphorus and carbon and thereby slowing the eutrophication process.

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