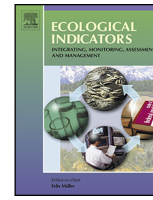
Ecological Indicators 48 (2015) 721–727

Contents lists available at ScienceDirect

Ecological Indicators

journal homepage: www.elsevier.com/locate/ecolind



Review

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

A. Cudowski *

University of Białystok, Institute of Biology, Department of Hydrobiology, Świerkowa 20B, 15-950 Białystok, Poland

ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form 19 September 2014
Accepted 22 September 2014

Keywords:
Trophic states index
Dissolved reactive manganese
Eutrophication
Lake

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 $TSI_{DRMn} = 20.61\ \ln(DRMn) - 35.03$, 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

* Tel.: +48 857457388.
E-mail address: cudad@uwb.edu.pl (A. Cudowski).

http://dx.doi.org/10.1016/j.ecolind.2014.09.035

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