Оригинален научен труд
Original Scientific Article

INFLUENCE OF THE SUMMER STRATIFICATION ON THE PRESENCE OF MANGANESE, IRON AND COPPER IN MANTOVO RESERVOIR

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ABSTRACT

Slavevska-Stamenković V., Smiljkov S. & Stafilov T. (2008): Influence of the summer stratification on the presence of manganese, iron and copper in Mantovo reservoir. Proceedings of the III Congress of Ecologists of the Republic of Macedonia with International Participation, 06-09.10.2007, Struga. Special issues of Macedonian Ecological Society, Vol. 8, Skopje.

The objective of this study was to provide more detailed information about seasonally vertical distributions of dissolved oxygen (DO), temperature and dissolved iron, manganese and copper in the water column of Mantovo reservoir (South-Eastern part of the Republic of Macedonia), during the period from May 2003 to April 2004. Monthly sampling on the surface and bottom water from central and the deepest part of the lake was performed. Temperature was measured directly on the field. DO was determined by Winkler method while the concentration of dissolved iron, manganese and copper by atomic absorption spectrometry. The results of temperature and dissolved oxygen measurement show that Mantovo reservoir presents dimictic lake. From January to April there was no variation trend for temperature and DO, showing that the lake was well mixed. From May to October, stable summer stratification developed, as indicated by the decrease in DO and temperature at the lowest level of water. Under hypoxic condition iron, manganese and copper release from the sediment and accumulate in the hypolimnion of Mantovo reservoir.

Key words: Mantovo reservoir, DO, temperature, iron, manganese, copper

ИЗВОД

Славевска-Стаменковиќ В., Смиљков, С. и Стафилов Т. (2008): Влијанието на летната стратификација на присуството на манган, железо и бакар во акумулацијата Мантово. Зборник на трудови од III Конгрес на еколозите на Македонија со меѓународно учество, 06-09.10.2007, Струга. Посебни изданија на Македонското еколошко друштво, Кн. 8, Скопје.

Целта на оваа студија е да обезбеди подетални информации за сезонската вертикална дистрибуција на температурата, концентрацијата на растворениот кислород и на раствореното железо, манган и бакар во водниот столб на акумулацијата Мантово (југоисточен дел на Република Македонија), во периодот од мај 2003 до април 2004. Извршено е месечно колекционирање на површинска и длабинска вода од централниот и најдлабокиот дел на езерото. Температурата е мерена директно на терен. Концентрацијата на растворениот кислород е определена со помош на Winkler-овиот метод додека концентрацијата на раствореното железо, манган и бакар со примена на атомската апсорпциона спектрометрија. Резултатите од мерењата на температурата и растворениот кислород покажаа дека акумулацијата Мантово претставува димиктичко езеро. Во периодот од јануари до април нема варирања на температурата и концентрацијата на растворениот кислород, што укажува на миксија. Од мај до октомври, пак, се развива стабилна летна стратификација, на што укажува опаѓањето на концентрацијата на растворениот кислород и температурата на длабинската вода. Во услови на хипооксија, железото, манганот и бакарот се ослободуваат од седиментот и се акумулираат во хиполимнионот на акумулацијата Мантово.

Клучни зборови: Акумулација Мантово, растворен кислород, температура, железо, манган, бакар

Introduction

Throughout the history humans have constructed artificial lakes, also called reservoirs, impoundments or dams in different regions of the world, primarily for addressing problems of water scarcity, or alternatively for providing flood protection. In modern times, they also are used for such purposes as hydropower generation, sports and commercial fisheries and water-based recreation (World Lake Vision Committee, 2003).

Water quality is one of the main characteristics of a water storage reservoir, even when its purpose is other than human water supply. Already in the planning stages water quality has to be simulated and predicted (water treatment processes depend on future reservoir water quality). If predicted quality is not satisfying some changes or precaution measures must be implemented (such as increasing or decreasing normal water level, eliminating shallow areas, controlling nutrient inflow, protecting the catchments). Excessive nutrient loads (primarily phosphorus and nitrogen) can cause accelerated eutrophication (Ivanc and Miljanović, 2003). Additionally, contamination of water and sediments from toxic and hazardous substances can also degrade lake water quality (World Lake Vision Committee, 2003). Those of greatest concern to human and ecosystem health are some heavy metals (e.g., mercury, arsenic, cadmium, lead, chromium, iron, copper and manganese).

Metals enter reservoir from a variety of sources, such as: (1) rocks and soils directly exposed to surface waters which is the largest natural source, (2) dead and decomposing vegetation and animal matter, (3) wet and dry fallout of atmospheric particulate matter, and (4) from anthropogenetic activities, including the discharge of various treated and untreated solid and liquid wastes into the water body (Lasheen, 1987). Among trace metals, manganese, iron and copper play a biochemical role in the life processes of aquatic plants and animals, and their presence in the aquatic environment is essential (Cover and Wilhm, 1982). However, at high concentrations, these trace metals become toxic (Nurnberg, 1982). A further special feature of toxic metals is that they are not biodegradable. Instead they undergo a biogeochemical cycle with substantially different residence times in the various spheres and compartments of the environment. Within this cycle they will be taken up also by man, predominantly from food and drinking water. In this respect toxic metals constitute a particular risk, because, although a certain fraction of the ingested amount is again excreted, they have a tendency to accumulate in vital organs (Nurnberg, 1982).

Furthermore, because of the ecological significance and the pollution potential of trace metals, it is important to understand processes responsible for mobilization of trace metals in water column. A number of studies confirmed that thermal stratification, as well as the content of organic matter has significant effects on trace metal accumulation and distribution in reservoir, notably to iron, manganese and copper (Fisher and Wente, 1993; Hudson and Morel, 1993; Vasconcelos et al., 2002; Morel and Price, 2003).

There are 19 larger and more than 100 small reservoirs in R. Macedonia. Most of them are being used for water supplying and for hydro energy while few of them are being used for irrigation, fishing and tourism etc. However, to date, there have been no detailed studies about thermal regime of Macedonian reservoir, as well as its influence on presence on iron, manganese and cooper in water column.

The specific objectives of the present study, conducted in Mantovo reservoir (South-East part of the Republic of Macedonia) are:

1. To provide more detailed information about seasonally vertical distributions of temperature and dissolved oxygen (DO);
2. To determine the level of dissolved iron, manganese and copper in the water column of Mantovo reservoir;
3. To determine major processes affecting the distribution of iron, manganese and copper in the water column of Mantovo reservoir.

Study area

The Mantovo reservoir is located in the northern temperate area, in the South-Eastern part of the Republic of Macedonia at an altitude of 402.5 m. The reservoir was built in 1978, by damming the River Kriva Lakavica which belongs to temporal waters (Гелев, 2001). The main purpose is irrigation on Strumica and Radovis fields, as well as fishing (Стојмилов, 2003). Its surface area is about 4.94 km². The length of the reservoir is approximately 5.5 km and average width is about 0.80 km. The maximal depth is about 20 m, and fluctuations of water level are 3-5 m. Geological structure of bottom is primary of igneous rocks rich with copper, iron, manganese (Мијалов, 1991). Before filling the reservoir vegetation wasn't remove, so it is obvious that newly formed reservoir contained a large quantity of undecomposed organic matter. From the period of construction, the volume of the lake has undergone significant reduction due to increased consumption and strong erosion on steep shores (Ѓорѓиевски и др., 1998). Also, water was never released at the dam because there isn't outflow from the reservoir (Гелев, 2001).

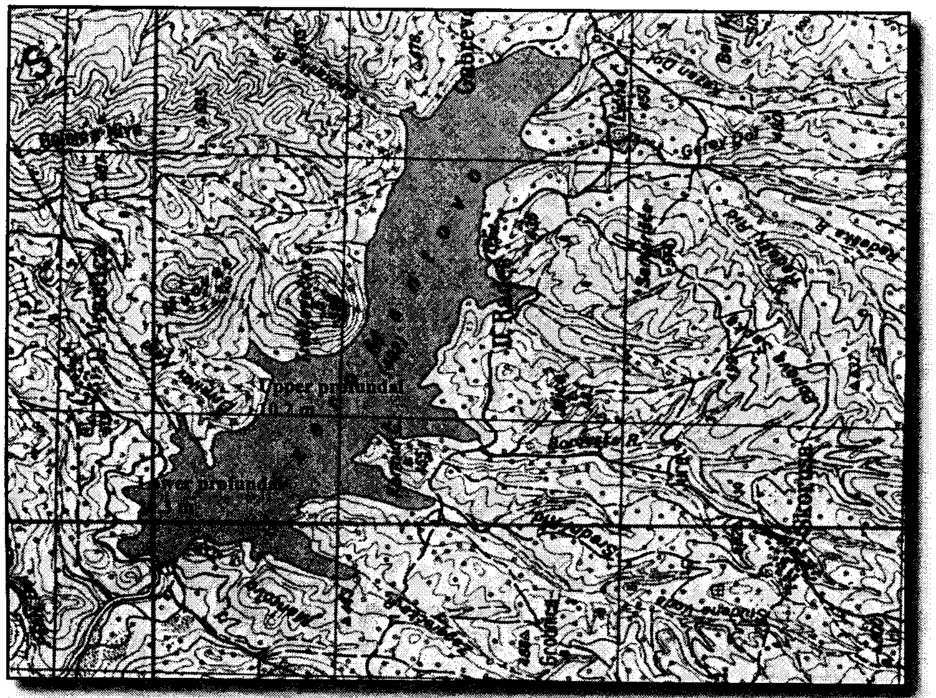

Fig. 1. Investigated localities in the Mantovo reservoir (upper and lower profundal region)
Сл. 1. Истражувани локалитети на акумулацијата Мантово (горен и долен профундал)

Materials and methods

Monthly sampling from the Mantovo reservoir was performed during the period from May 2003 to April 2004. Because the most part of the lake is shallow and well mixed (Славевска-Стаменковиќ, 2007), only profundal region was included in this study. Accordingly, surface (0.5 m under surface) and bottom (0.5 m above the bottom) water samples were taken only from the central (10.2 m) and the deepest part close to the dam (20.3 m), which belong to the upper and lower profundal region, respectively (Fig. 1).

Temperature was measured directly on the field. In order to calculate the concentration of DO, standard Winkler bottles were used, while for the analyses of the concentration of dissolved iron, manganese and copper, water samples were stored in 0.5 l polyethylene bottles and conserved with HNO_3 of high quality (1 ml acid per 0.5 l of water).

The concentration of dissolved iron, manganese and copper was determined by Varian Spectra AA 640Z atomic absorption spectrometer after filtering water samples through glass fiber filters (Whatman GF/C 0.45 μm). DO was measured by Winkler titration method. All analytical methods used are

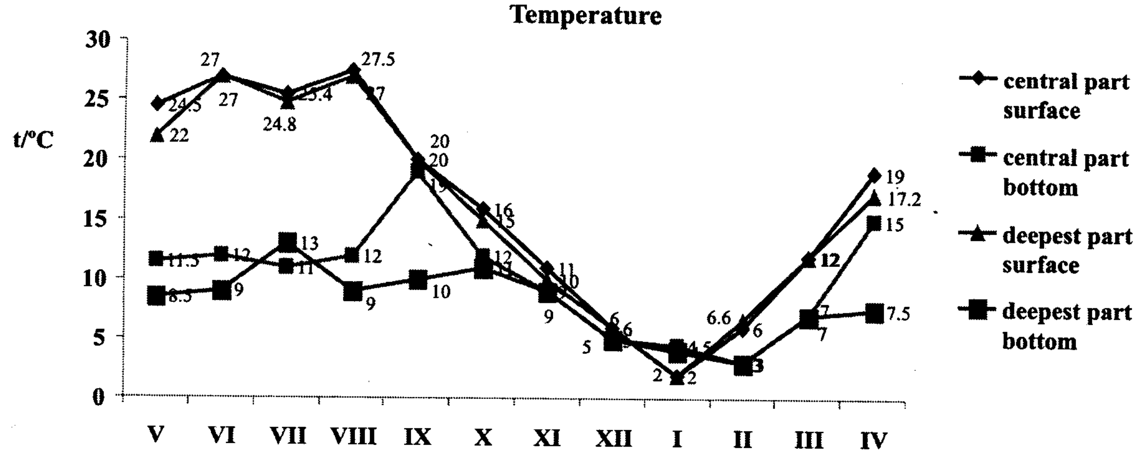

Fig. 2. Seasonal changes in temperature (°C) in the water column of Mantovo reservoir.
Сл. 2. Сезонски промени на температурата (°C) во водениот столб на акумулацијата Мантово.

standard ones, recommended by APHA (1992).

The monitored parameters were interpreted according to Macedonian water quality standard (The regulation on Water Classification, Official Gazette 18/99).

Results and discussion

The results of temperature measurement show that Mantovo reservoir presents dimictic lake (Fig. 2). From January to April there was no variation trend for temperature, showing that the lake was well mixed. From May to October, stable summer stratification developed, as indicated by the decrease in temperature in the upper and lower profundal region. Short period of the reversal thermal stratification was noticed in December.

The amount of oxygen in the water is an important indicator of overall lake health. Water temperature and thermal stratification, as well as content of organic mater in the water column play an important role in determining the amount of oxygen found in the lakes and reservoirs (Wetzel, 1975). In the case of Mantovo reservoir, Славевска-Стаменковиќ (2007) detected high average concentration on dissolved organic matter as consumption on $KMnO_4$ (19.99 mg/l) which correspond to the category of eutrophic water. This parameter indicates presence on considerable organic loading in the given reservoir, which wasn't surprisingly because before filling the reservoir vegetation wasn't removed. The measurement of the concentration of DO in Mantovo reservoir show that water was well oxygenated in winter, during spring and autumn mixing, and in epilimnion (surface layer of water) during summer stagnation.

In the near-bottom water, during the summer stratification period oxygen depletion was observed (Fig. 3). Namely, DO is cut-off from all sources of oxygen, while organisms continue to respire and consume oxygen in the hypolimnion. Concerning to duration on stratification period there were noticed some differences between upper and lower profundal which affects the chemistry on the bottom water (Fig. 3). According to Macedonian water quality standard (the regulation on Water Classification, Official Gazette 18/99) values of DO in the upper profundal fluctuated in the region of meso-eutrophy (1.2-5.7 mg/l O_2). Longer presence and permanence of thermal stratification cause more prolonged and pronounced oxygen deficits in the deepest parts of the lake which corresponds to the category of hyper-eutrophy (0.9-3.4 mg/l O_2). Under hypoxic, almost anoxic condition, it is possible that large amounts of toxic sulfides were also produced in this region, which, according to the suggestion of Prat (1978), was confirmed with black color on the mud and unpleasant odor (personal observation directly on the field).

According to Cover and Wilhm (1982), Wu et al. (2001), Brian et al. (2003) and Alagarsamy et al. (2005), redox sensitive elements such as iron, manganese and copper, will be reduced under condition of low oxygen and redox potential (E_h). The latter exhibit seasonal changes resulting from changes in oxidizing and reducing conditions in lake that stratifies in summer (Cover & Wilhm, 1982).

It is evident that this phenomenon plays an important role in the cycling of iron, manganese and copper in Mantovo Reservoir. It can be seen from the seasonal changes in concentration on manganese, iron and copper in the surface and bottom water from central (upper profundal) and the deepest part (lower profundal) of Mantovo reservoir presented on Figs. 4-6.

It is clear that small variation existed between the concentration of iron, manganese and copper in the water column in spring and fall, which is due to well oxygenated water. The range of concentra-

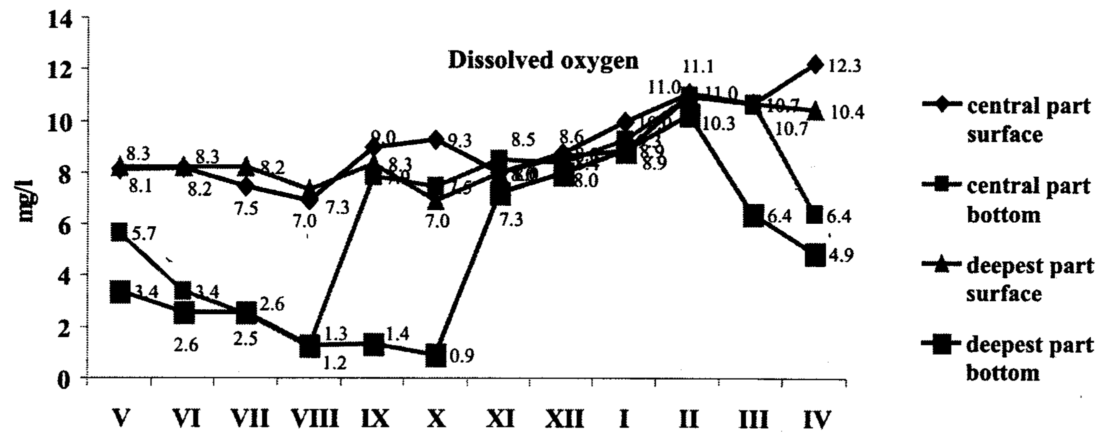

Fig. 3. Seasonal variation in oxygen concentration (mg/l) in the water column of Mantovo Reservoir.
Сл. 3. Сезонски варирања на концентрацијата на кислород (мг/л) во водениот столб на акумулацијата Мантово.

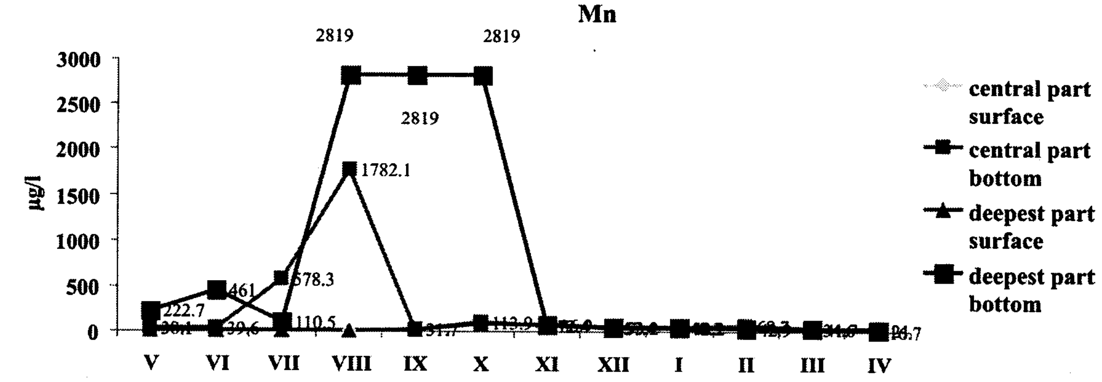

Fig. 4. Seasonal changes in concentration on manganese (μg/l) in the water column of Mantovo reservoir.
Сл. 4. Сезонски промени во концентрацијата на манган (μg/l) во водниот столб на акумулацијата Мантово.

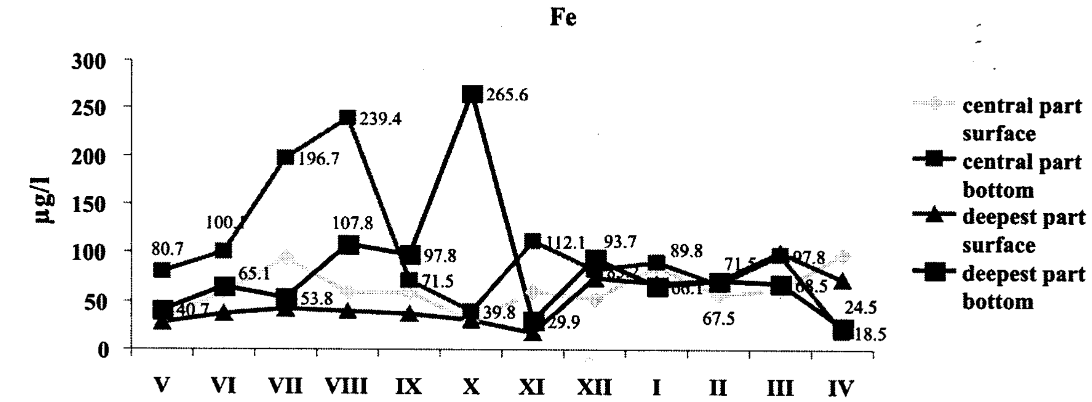

Fig. 5. Seasonal changes in concentration on iron (μg/l) in the water column of Mantovo reservoir.
Сл. 5. Сезонски промени во концентрацијата на железо (μg/l) во водниот столб на акумулацијата Мантово.

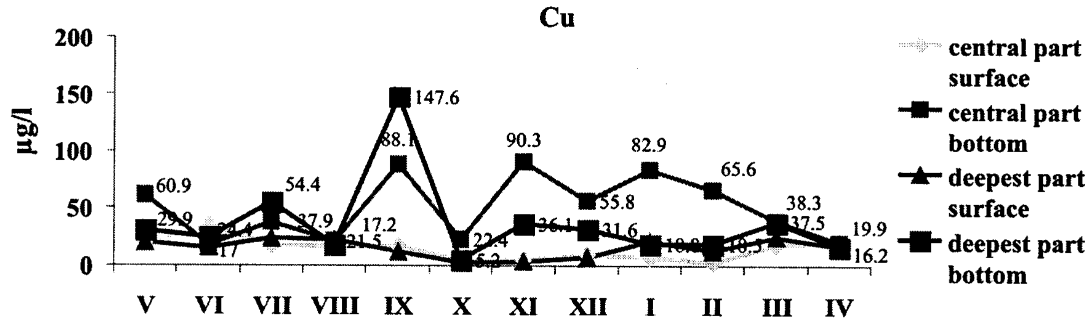

Fig. 6. Seasonal changes in concentration on copper (μg/l) in the water column of Mantovo reservoir.
Сл. 6. Сезонски промени во концентрацијата на бакар (μg/l) во водниот столб на акумулацијата Мантово.

tion during these seasons was from 16.7 to 86.9 μg/l for manganese, from 18.5 to 112.1 μg/l for iron and from 2.3 to 90.3 μg/l for copper. Although the concentration of manganese and iron in most cases was greater in bottom water than in surface, the differences were not significant. In opposit of the behaviour of manganese and iron, moderate high concentration of copper was measured in the bottom water under oxidizing condition. Having in mind that, heavy metals bound with sulfide could be released into the well oxidizing water (Shen et. al., 2007), it is possible that cooper in Mantovo Reservoir exists in sulfide form.

However, during summer stratification, dissolved manganese, iron and copper concentrations just above the sediment surface were significantly higher than those in the surface water, showing that their reduction and dissolution occurred. In addition, under condition of more prolonged and pronounced oxygen deficits in the deepest parts of the lake, higher concentrations on manganese (2819 μg/l), iron (265.6 μg/l) and copper (147.6 μg/l) were found in the lower profundal (Figs. 4-6) which is in agreement with the results reported in the literature (Cover and Wilhm, 1982; Wu et. al., 2001; Brian et. al., 2003).

It should be stressed that detected concentration on manganese and copper in the deepest part of the lake are very high (toxic level) and belong to V class (the regulation on Water Classification, Official Gazette of RM, 18/99).

Possible explanation for the origin of these metals in Mantovo reservoir is fact that geological structure of bottom is primary of igneous rocks rich with manganese, iron and copper. Additionally, as result of strong erosion on steep shores (Ѓорѓиевски и др., 1998) Mantovo reservoir receives a large influx of sediments, silt, nutrients and suspended matter from the surrounding watershed witch can contain sediment-bound toxic metals. Namely, it is well known that suspended solids can act as scavengers for trace metals in the water (Lasheen, 1987). Having in mind that contaminated sediments are a major source of pollution and represent a potential threat to all components of aquatic ecosystems (Sorensen et al. 1977; Landrum and Robbins 1990), investigation on Mantovo reservoir should continue in the future.

Conclusions

Investigation preformed in this study presents first detailed analyses on the presence of Mn, Fe and Cu in the water column of Mantovo reservoir.

The results confirmed that thermal stratification, accompanied with high content of organic matter, presents processes responsible for pronounced oxygen deficits in the bottom water, as well as for mobilization of manganese, iron and copper from sediment to the hypolimnion of Mantovo reservoir.

Further studies are needed to determine content of manganese, iron and copper in sediment of Mantovo reservoir.

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INFLUENCE OF THE SUMMER STRATIFICATION ON THE PRESENCE OF MANGANESE, IRON AND COPPER IN MANTOVO RESERVOIR

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Summary

This study demonstrates that Mantovo reservoir presents dimictic lake. In the near-bottom water, during the summer stratification period oxygen depletion was observed. Concerning to duration on stratification period there were noticed some differences between upper and lower profundal which affects the chemistry on the bottom water. Longer presence and permanence of thermal stratification caused more prolonged and pronounced oxygen deficits in the deepest parts of the lake. Consequently, higher concentrations on manganese (2819.0 μg/l), iron (265.6 μg/l) and copper (147.6 μg/l) were accumulated in the lower profundal.

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