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THE QUALITY OF WATER OF THE MANTOVO RESERVOIR (REPUBLIC OF MACEDONIA)

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Abstract — The aim of the paper is to evaluate the quality of water of the Mantovo Reservoir (Southeast Macedonia) based on physico-chemical parameters and the macrozoobenthos. Monthly sampling was performed during 2003 and 2004. Temperature and DO depth profile data indicate that the Mantovo Reservoir is a dimictic lake. Based on mean nutrient concentrations, the Mantovo Reservoir can be considered as being phosphorus-deficient. During the summer stratification, very high concentrations of Mn (2,819 μg/l) and Cu (147.6 μg/l) were detected in the lower profundal. Limnodrilus hoffmeisteri was the dominant species, which indicates the presence of organic pollution. Dominance of Chaoborus crystallinus and decline in abundance of L. hoffmeisteri in the lower profundal indicate a deterioration of environmental status in the deepest part of the lake.

Key words: Water quality, physical and chemical parameters, macrozoobenthos, Mantovo Reservoir, , Macedonia

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INTRODUCTION

Reservoirs are essential resources of water for human use. They are usually constructed in areas of water scarcity or excess, or where there are agricultural and technological reasons to have a controlled water facility. In modern times, they have also contributed to industrial development by providing cheap sources of hydroelectric power (Thornton et al., 1990).

Reservoirs are managed water bodies and there is therefore a particular need for the managers to understand their physical, chemical, and biological features. This knowledge is acquired through assessment of water quality data gathered during routine monitoring programs. The quality of water in the reservoir can be maintained within desired quality limits only by effective monitoring of selected water quality parameters (World Lake Vision Committee, 2003), which provides a base for design of short- and long-term management plans.

In many cases, reservoirs receive a large influx of nutrients and suspended matter from the watershed area, and intensive sedimentation could occur. An allochthonous nutrient load (primarily phosphorus and nitrogen) usually leads to increased biological production (Ivanc and Miljanović, 2003). Decomposers break down organic matter originating both from the watershed and the lake itself. Increased decomposition is accompanied by enhanced oxygen consumption by microorganisms, which can result in oxygen depletion, particularly in the hypolimnion of lakes. This indirect effect of eutrophication on oxygen condition causes changes in the structure of oxygen dependent benthic communities, especially in the profundal region (Palmer, 1968). In general, the profundal is less complex than most benthic lake habitats, and the macroinvertebrate fauna is correspondingly less diverse. Oxygen concentration and the supply of organic food material from the photic zones above are both directly related to lake productivity (Brinkhurst, 1974). This means that profundal invertebrate communities are strongly influenced by the trophic state of a lake and can be used in assess-

ing the ecological conditions of a given lake. In other words, they are a more conservative measure of the average environmental conditions than chemical data alone (Rosenberg and Resh, 1993).

Contamination of water and sediments from toxic and hazardous substances can also reduce the quality of lake water (World Lake Vision Committee, 2003).

The effects of trace metal pollution on aquatic systems have been studied extensively as a result of widespread contamination by inorganic and organo-metallic species from industrial processes. In attempting to quantify metal pollutant effects, studies are often hampered by the presence of more than one metallic element and the variable toxicity of most metals caused by changes in molecular form (chemical speciation) with variation of environmental conditions (e.g., temperature, oxygen conditions, pH, alkalinity, and organic compounds) (Salomons and Förstner, 1984), and simple relationships between water or sediment levels and concentrations of aquatic organisms (including aquatic macroinvertebrates) are seldom shown in field studies (Luoma, 1989). Moreover, macroinvertebrate sensitivity to trace metal pollution may vary depending on life history and behavior (Johnson et al., 1992).

In matters of water supply, the Republic of Macedonia mostly relies on surface water resources, and 19 larger and more than 100 small reservoirs have been constructed. They are used for water supply, hydro energy production, irrigation, fishing, and tourism (Slavevska-Stamenković et al., 2008). However, little attention was given to quality of the water of Macedonian reservoirs. Only a few reservoirs have been subjected to complex physical-chemical and biological investigation (Stojkovski, 1960; Smiljkov, 1996; Miljanović et al., 2004), and adequate routine monitoring, ecological protection, and management are missing.

The main objective of this study was to evaluate the quality of water of the Mantovo Reservoir (southeastern part of the Republic of Macedonia) based on physical and chemical parameters and the macrozoobenthos as a contribution to knowledge of the reservoirs in Macedonia. Possible sources of pollution are also discussed.

STUDY AREA AND MATERIAL AND METHODS

The Mantovo Reservoir is located in a northern temperate area in the southeastern part of the Republic of Macedonia at an altitude of 402.5 m. The reservoir was built in 1978 by damming the Kriva Lakavica River, which belongs to temporal waters (Gelev, 2001). The main purpose is irrigation, as well as fishing. Its surface area is about 4.94 km^2. 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 the water level are 3-5 m. Geologically, the bottom is primarily composed of igneous rocks rich in copper, iron, and manganese (Mijalov, 1991).

The Mantovo Reservoir exhibits a number of 'unfavorable' characteristics. Before filling of the reservoir, vegetation was not removed, so the newly formed reservoir contained a large quantity of undecomposed organic matter. In relation to the initial plan, the lake's volume has undergone significant reduction due to increased consumption and strong erosion on the steep shores (Gorgievski, 1999). Further, a spillway for outflow from the reservoir in the dam area has not been constructed, and the water level is regulated via an artificial channel (the Vrastica was built in the foothills of Mt. Smrdeš and is 8.26 km long). This contributes to more intensive siltation (Gelev, 2001), accelerated aging, and eutrophication of the reservoir, all of which has shortened the period of its exploitation.

Monthly sampling of surface and bottom water and the bottom fauna from four stations situated on the depth profile across the reservoir was performed during the period from May 2003 to April 2004.

Surface (0.5 m below the surface) and bottom (0.5 m above the bottom) water samples were taken with a Rutner bottom sampler and stored in 1.5-l polyethylene bottles. Before sampling, the bottles were rinsed twice with reservoir water. Samples in ~100 ml Winkler bottles were also collected for

further dissolved oxygen (DO) analysis. After field testing of water samples – which included measurements of temperature (with a centigrade thermometer), pH (with a Hanna pHep pocket pH meter), and transparency (with 20-cm-dia. Secchi disks) – samples were transported to the laboratory in portable coolers.

In the laboratory, water samples were filtered through glass fiber filters (Whatman GF/C 0.45 μm) and divided into two parts: one bottle (0.5 l) was acidified with 1 ml of HNO_3 and stored at 4°C for metal analyses (iron, manganese, copper, and lead) with a Varian Spectra AA 640Z atomic absorption spectrometer.

The other bottle (1 l) was stored at 4°C without the addition of preservatives. A titration procedure was used for dissolved oxygen (Winkler method), chloride (0.0141 N mercuric nitrate), and calcium and magnesium (0.01 M EDTA); and a UV-Vis spectrophotometer was employed for ammonia (direct nesslerization), nitrites (diazotization), nitrates (cadmium reduction), sulfates (turbidimetric method), and total phosphorus (molybdenum blue procedure). The dissolved organic matter was expressed as consumption of $KMnO_4$.

Standard analytical methods recommended by APHA (1992) were used. The Macedonian water quality standard (Water Classification, Official Gazette, 1999) was applied for status evaluation.

Bottom fauna samples were collected at four stations situated on the profile of different depths across the reservoir (Fig. 1): in the littoral (depth of 2.8 m), in the sublittoral (depth of 6.8 m), and in the profundal (depths of 10.2 m – upper profundal and 20.3 m – lower profundal). Due to the steep shores, a littoral area is located only near the mouth of the Kriva Lakavica River. The bed material in the littoral area is composed mainly of fine sediment (silt and fine sand). Coarse sand and gravel are present with participation of no more than 10%. Woody debris and detritus cover the bottom in particular areas (about 5% of the bottom in the littoral zone). The character and structure of littoral sediments influence the formation of sublittoral habitats. Thus, the bed in the sublittoral contains a higher percentage of sand and decomposing vegetation than in the littoral. The upper profundal is situated in the center of the lake in a zone thought to be less subject to environmental variation caused by mass water movement. The bed is composed of silt. The lower profundal is located near the dam. Its bed is composed of fine black sediment with an unpleasant odor (Smiljkov et al., 2008), which indicates the presence of toxic sulfides (Prat, 1978).

Biological examinations were carried out according to standard methodology for sampling (Rosenberg et al., 1997). Two benthic samples were taken with an Ekman's grab at each sampling station and fixed with 4% formaldehyde. Further processing of the material was conducted in the Laboratory of Invertebrates and Animal Ecology, Institute of Biology, Faculty of Science, Skopje, Macedonia.

Brodgar software (Version 2.5.2, 2006) was used for statistical analyses.

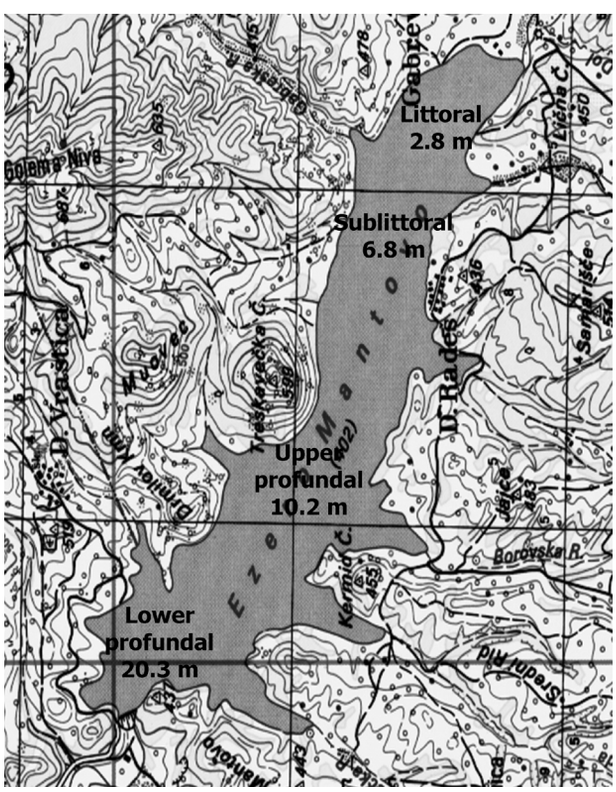

Fig. 1. Map of the Mantovo Reservoir, including sampling stations.

RESULTS AND DISCUSSION

Physical and *Chemical Analyses*

According to our results (Table 1), the Mantovo Reservoir is an alkaline (mean pH value of 8.13) hard-water lake (Ca^{2+} and Mg^{2+} concentrations reach up to 120.24 mg/l and 54.72 mg/l), which is typical of water bodies on carbonate rocks (Korfali and Davies, 2000). The prevalence of carbonate sedimentary rocks in the Mantovo Reservoir's drainage basin (Mijalov, 1991) is reflected in the water chemistry. The high pH values (Table 1) could be a consequence of overgrowth of cyanobacteria and other primary producers. The latter remove free carbon dioxide dissolved in the water by photosynthesis processes, leading to higher pH values (Rahman et al., 2005). However, further studies on the Mantovo Reservoir are needed to confirm this explanation. For example, it would be useful to determine chlorophyll *a* content in the water or perform a qualitative analysis of phytoplankton.

The analysis of temperature measurements presented in Fig. 2 confirmed that the Mantovo Reservoir is dimictic in its central and the deepest parts – the upper and lower profundal. From January to April, there was no variation in temperature, showing that the lake was well mixed. From May to October, stable summer stratification was recorded, as indicated by decrease in temperature in the upper and lower profundal regions. A short period of thermal stratification reversal was noticed in December.

The measurement of DO concentration presented in Fig. 3 shows that water was well oxygenated in winter, during spring and autumn mixing, and in the epilimnion (surface layer of water) during the summer months, which seems to be linked with high photosynthesis. During the summer stagnation period, however, oxygen depletion was observed in the near-bottom water. Our previous results (Slavevska-Stamenković et al., 2008) confirmed literature data (Wetzel, 2001) indicating that thermal stratification under conditions of considerable organic loading, low average water transparency (1.7 m), and high average concentration (19.99 mg/l) of dissolved organic matter (Table 1) is characterized by processes leading to pronounced oxygen deficits in the bottom water (Fig. 3). A possible explanation for the origin of organic loading is the fact that the soil and vegetation were not removed before filling of the reservoir. Also, considerable influence is exerted by the Kriva Lakavica River, which carries high content of sediments, silt, nutrients, and suspended matter into the Mantovo Reservoir.

Differences between the upper and lower profundal were recorded in regard to duration of the summer stratification period, and this affects chemistry of the bottom water.

In the upper profundal, DO values vary between

Table 1. Seasonal changes in pH, transparency, and concentration of ions and nutrients in the water column of the Mantovo Reservoir.

Parameter	Min	Max	Mean
pH	6.34	8.72	8.13
Transparency	1	2.3	1.7
Ca^{2+} (mg/l)	50.1	120.2	82.46
Mg^{2+} (mg/l)	6.08	54.72	25.53
NH_4^+ (mg/l)	0.02	1.03	0.42
Cl^- (mg/l)	16	25	20.7
SO_4^{2-} (mg/l)	20.62	48.11	37.23
NO_2^- (mg/l)	0.004	0.19	0.024
NO_3^- (mg/l)	0.13	2.54	0.68
TP (mg/l)	0.001	0.019	0.003
$KMnO_4$ cons. (mg/l)	16.89	24.70	19.99

1.2 and 5.7 mg/l O_2, while in the deepest parts of the lake they vary between 0.9 and 3.4 mg/l O_2 (Fig. 3). According to the Macedonian water quality standard (Water Classification, Official Gazette, 1999), the upper and lower profundals are evaluated as meso-eutrophic and hypereutrophic, respectively. A longer thermal stratification period (Fig. 2) causes more prolonged and pronounced oxygen deficits in the deepest parts of the lake, which belongs to the hypereutrophic category.

High mean Cl^- and SO_4^{2-} concentrations (20.7 mg/l and 37.23 mg/l) were measured (Table 1), which could be associated with arid conditions and lithological composition of the drainage basin. The

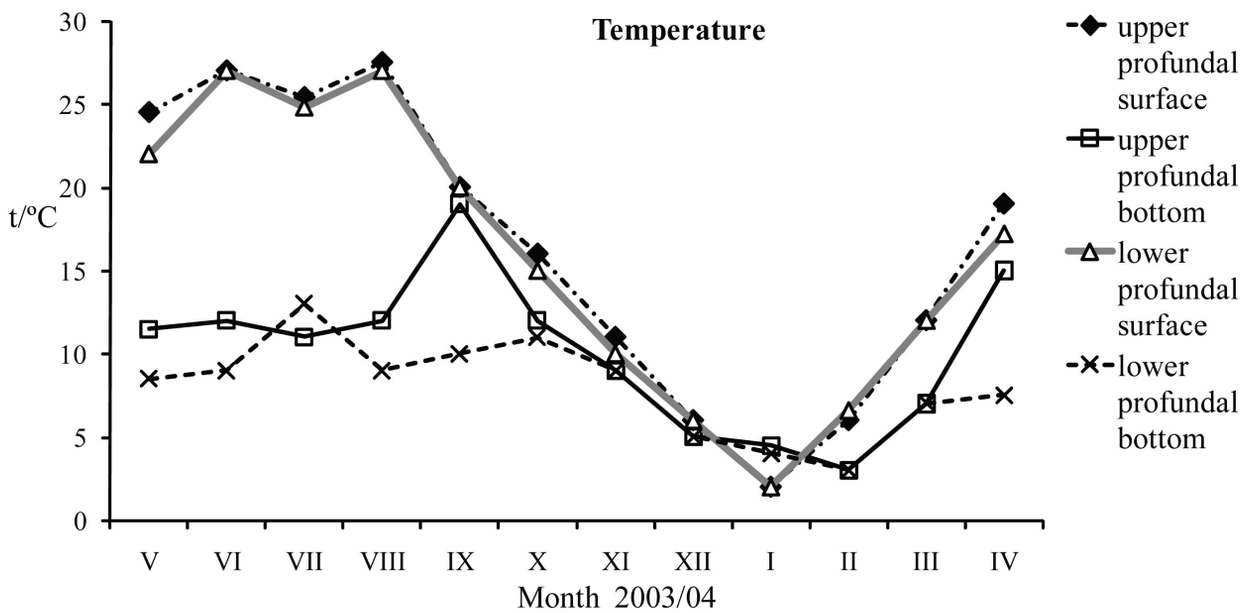

Fig. 2. Seasonal changes of temperature (°C) in the water column of the Mantovo Reservoir.

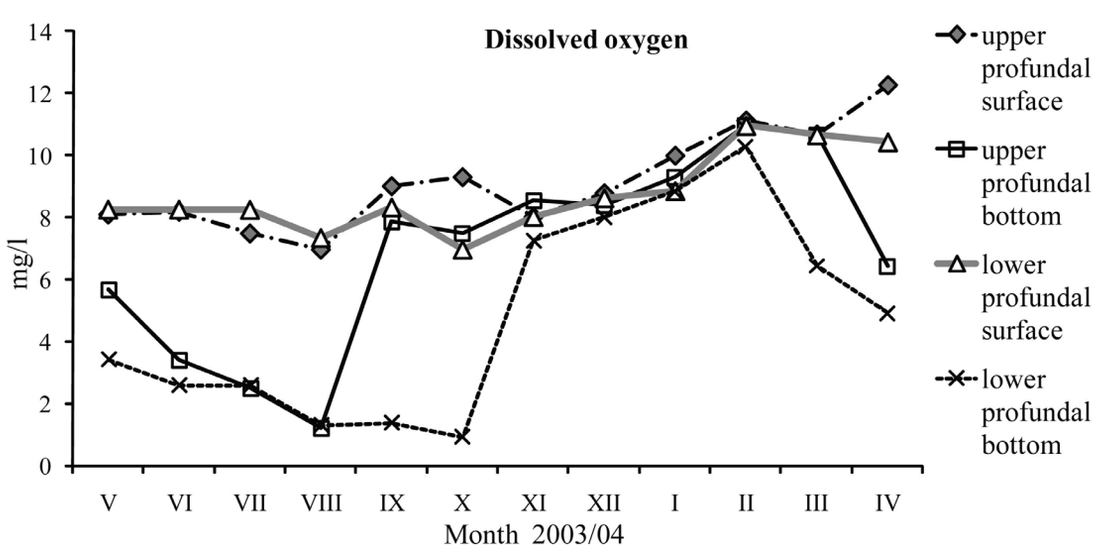

Fig. 3. Seasonal variation in dissolved oxygen concentration (mg/l) in the water column of the Mantovo Reservoir.

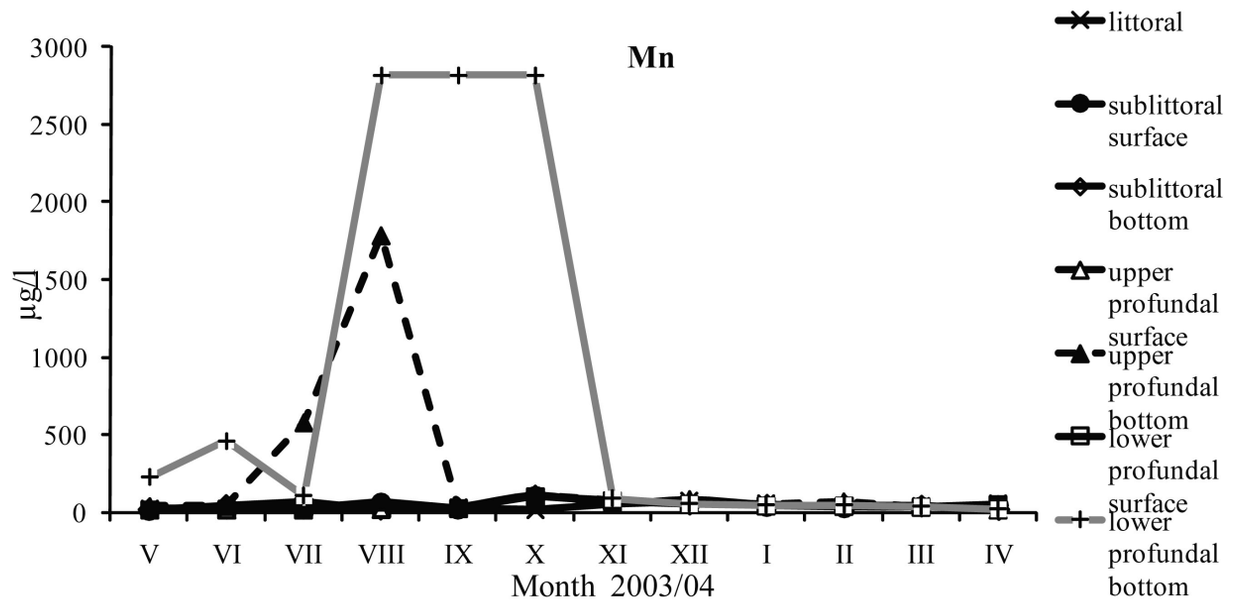

Fig. 4. Seasonal changes in concentration of Mn in the water column of the Mantovo Reservoir.

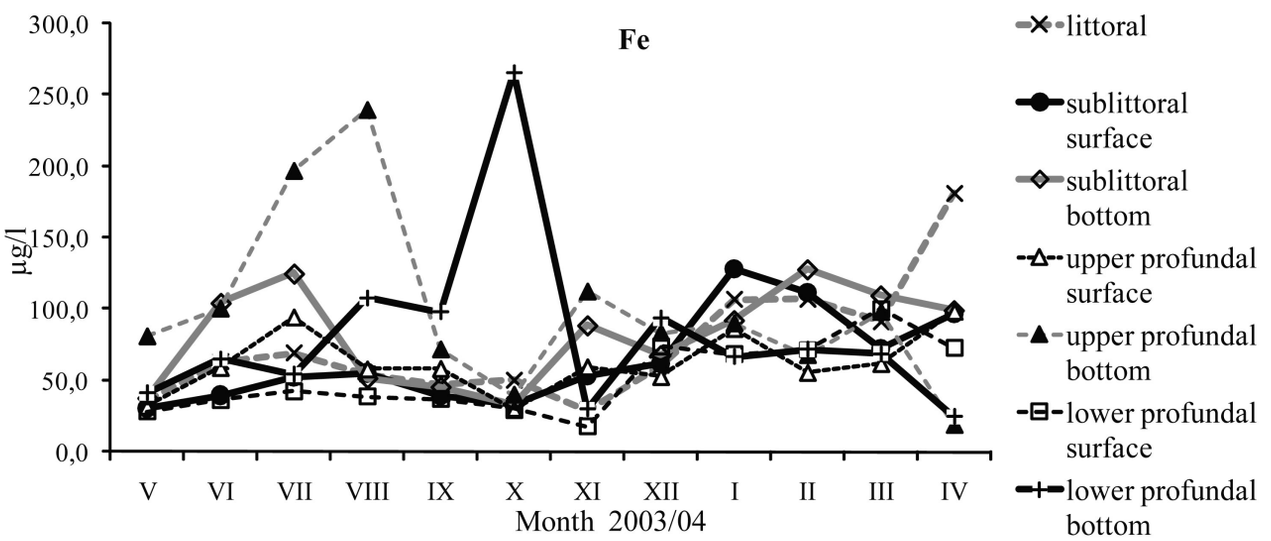

Fig. 5. Seasonal changes in concentration of Fe in the water column of the Mantovo Reservoir.

slight variation of Cl^- and SO_4^{2-} observed during the investigated period indicates lower ion inputs from the watershed.

Based on mean values of TP (0.003 mg/l) and NO_3^- (0.68 mg/l), the reservoir can be considered as being nutrient-deficient, which is a consequence of non-intensive agricultural activities in the Mantovo Reservoir's surroundings. It seems that an additional factor influencing the level of phosphorus was ionic balance. According to Wetzel (2001), if oxygen is present near the bottom (higher pH), phosphate will quickly precipitate in the sediment. If, however, oxygen becomes depleted (lower pH due to exces-

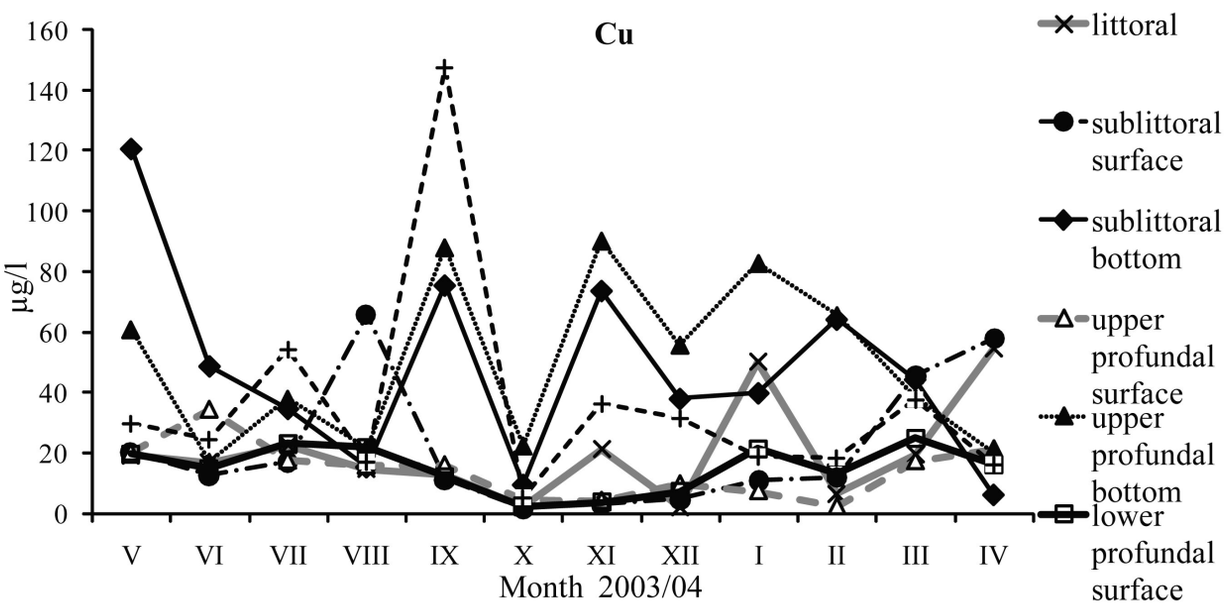

Fig. 6. Seasonal changes in concentration of Cu in the water column of the Mantovo Reservoir.

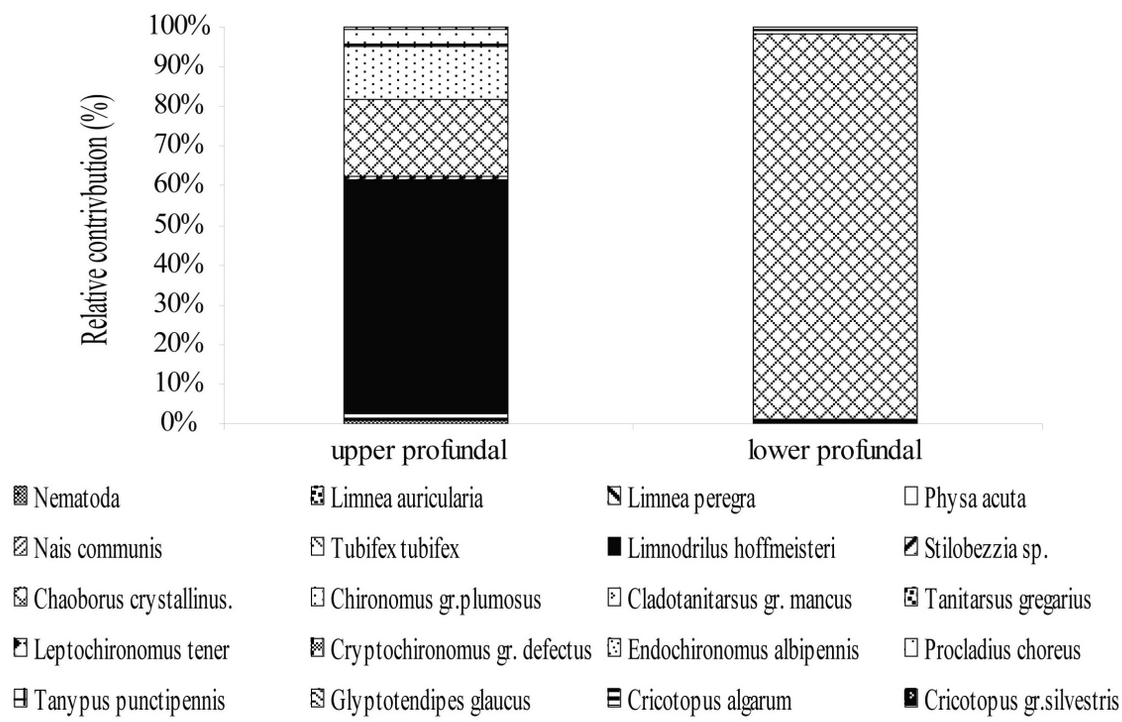

Fig. 7. Relative contribution (%) of macrozoobenthos taxa from the upper and lower parts of the Mantovo Reservoir.

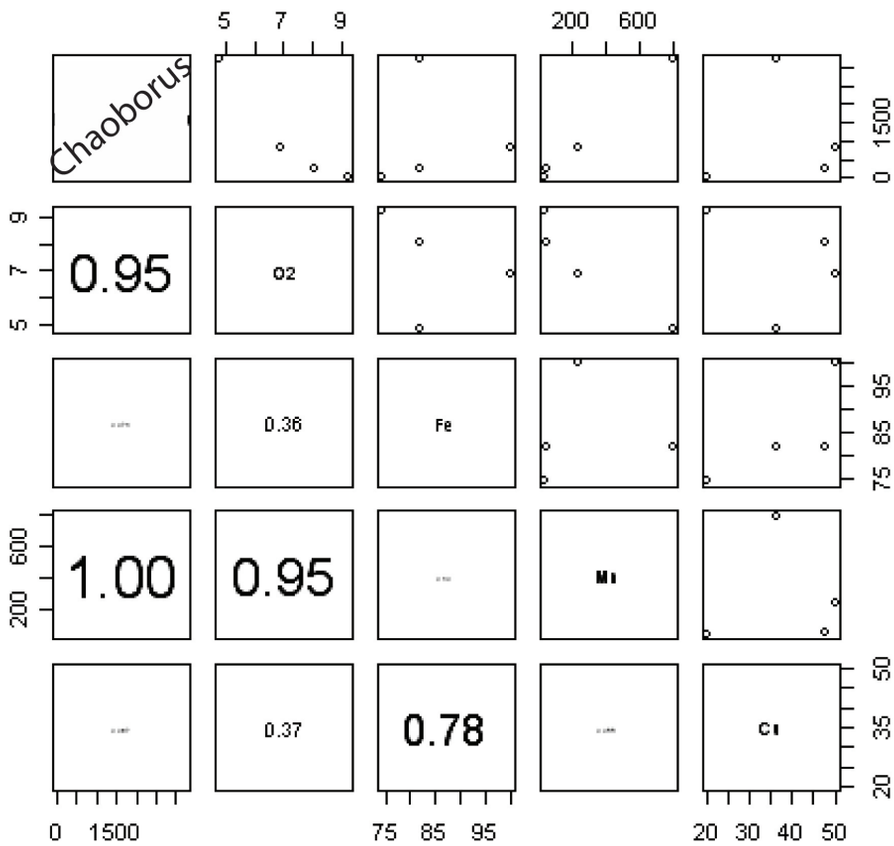

Fig. 8. Correlation between *C. crystallinus* density and some variables.

sive decomposition, etc.), phosphates dissociate in soluble form and migrate from the sediment into the overlying waters. It is likely that the water's alkalinity (Table 1) caused the precipitation of phosphorus with Ca^{2+} and other cations (e.g., Fe^{2+}) into the sediment of the investigated reservoir. The highest value (0.019 mg/l), recorded at a depth of 10.2 m in June 2004, has to be regarded as an isolated occurrence, probably caused by the release of phosphorus from the sediment following the decomposition of organic material accumulating on the bottom.

According to the results of nitrogen compound measurements (mean conc. of 0.024 mg/l NO_2^-), the reservoir could be assessed as belonging to class III-IV (Water Classification, Official Gazette, 1999). These data suggest that oxygen deficit may be partly responsible for the lack of ammonia oxidation to nitrite and subsequently nitrate. Additionally, high nitrite concentrations are often associated with unsatisfactory microbiological quality of water (Chapman and Kimstach, 1997).

Seasonal changes in concentrations of Fe, Mn, and Cu in the surface and bottom water from four stations situated on the depth profile across the reservoir are presented in Figs. 4-6. It is clear that small variation existed between the concentrations of iron, manganese and copper in the water column in spring and fall, which according to Alagarsamy et al. (2005) is due to well-oxygenated water. The range of concentration during these seasons varied 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. The concentration of manganese and iron in most cases was greater in bottom water than in surface water. In contrast to concentrations of manganese and iron, higher concentration of copper was measured

in bottom water than in surface water. Bearing in mind that heavy metals bound with sulfide could be released into well-oxidized water (Shen et al., 2007), it is possible that cooper in the Mantovo Reservoir exists in sulfide form, which was not covered in our investigation.

A recent survey of the influence of summer stratification on the presence of manganese, iron, and copper in the Mantovo Reservoir (Slavevska-Stamenković et al., 2008) showed higher concentrations of metals above the bottom than those in the surface water, confirming that their reduction and dissolution occurred. According to Wu et al. (2001), redox-sensitive elements such as iron, manganese, and copper will be reduced under conditions of low oxygen and redox potential (E_h). In addition, under conditions of more prolonged and pronounced oxygen deficits in the deepest parts of the lake (Fig. 3) during summer stratification, higher concentrations on Mn (2819 μg/l), Fe (265.6 μg/l), and Cu (147.6 μg/l) were found in the lower profundal (Figs. 4-6), which is in agreement with results reported in the literature (Wu et al., 2001).

It should be stressed that the concentrations of manganese and copper detected in the deepest part of the lake are very high (toxic levels) and belong to class V (Water Classification, Official Gazette, 1999).

Manganese and cooper in the Mantovo Reservoir could be a consequence of geological structure of the region, since the substrate is mainly composed of igneous rocks rich in manganese, iron, and copper (Mijalov, 1991). Additionally, as a result of strong erosion on its steep shores (Gorgievski, 1999), the Mantovo Reservoir receives a large influx of sediments from the surrounding watershed that might contain sediment-bound toxic metals.

Bottom Fauna Analyses

The results of biological analyses (fully discussed by Smiljkov et al., 2008) show that *Limnodrilus hoffmeisteri*, *Chaoborus crystallinus*, *Procladius choreus*, *Cladotanytarsus* gr. *mancus*, and *Chironomus* gr. *plumosus* were dominant species, with 50.09, 15.55, 9.60, 7.45, and 7.33% contribution to the total benthic community, respectively. The great abundance of the latter was probably related to high concentrations of organic detritus deposited on the bottom and suspended in the water column, as is corroborated by the high average concentration (19.99 mg/l) of dissolved organic matter registered during the study period (see Table 1).

The assemblage of organisms living in the deeper zone provides an indication of past and current disturbances and can be used as a reliable indicator of lake productivity (Slavevska-Stamenković et al., 2008). Accordingly, this study is focused on the profundal fauna.

The results of this study show significant differences in structure of the bottom fauna from the upper and lower profundal (Fig. 7). To be specific, taxa highly tolerant of organic pollution and hypoxic conditions (Margaritora et al., 2003) – *L. hoffmeisteri* (58.92%), *C. crystallinus* (19.42%), and *C.* gr. *plumosus* (13.53%) – were the most abundant species in the central part of the reservoir (Fig. 7). Published data show that the mentioned species are present in the profundal of many other lakes and reservoirs (Bazzanti and Seminara, 1987), where they are probably adapted to hypolimnetic conditions of reduced oxygen content during summer stratification. Johnson et al. (1992) showed that they are also tolerant of metal pollution.

With respect to the profundal oligochaete assemblages (Milbrink et al., 2002) and the chironomid community (Sæther, 1979), dominance of *L. hoffmeisteri* and *C.* gr. *plumosus* in the upper profundal indicates a eutrophic condition in the Mantovo Reservoir.

However, *L. hoffmeisteri* (0.95%) and *C.* gr. *plumosus* (0.84%) were almost absent in the lower profundal (Fig. 7). To judge from the data of physico-chemical analyses performed on the Mantovo Reservoir, deterioration of conditions in the deepest part of the lake is the most likely explanation for the decline in their density and occasional disappearance. Benthic organisms in the bottom near the dam are exposed to oxygen deficits. In addition, it is possible that large amounts of toxic sulfides were

also produced in this region, and most organisms consequently disappear, as was observed in Lake Banyoles (Real et al., 2000). In this lake, only the phantom-midge *Chaoborus flavicans* was present at the end of the stratification period (i.e., after 5 months of anoxia), presumably because of the high sulphide content of water in the layer close to the sediment. These conditions are common to many southern Spanish reservoirs in summer, when no *Chironomus* sp. larvae or oligochaetes are found (Prat and Daroca, 1983).

At the same time, the significantly higher concentrations of Mn and Cu found in the lower profundal of the Mantovo Reservoir (Figs 4, 6) could have additional negative influence on the benthic community. Indeed, a combination of factors (such as toxic products of anaerobic respiration and the presence of high concentrations of trace metals) could result in mass mortality of benthic animals in the deepest part of the lake.

In such conditions, only *C. crystallinus* (97.21%) was present in considerable quantities in the bottom fauna of the deepest part of the lake (Fig. 7). Published data (Gosselin and Hare, 2003) indicate that this species can survive anoxic conditions accompanied by H_2S in concentrations five times higher than those known as lethal for other animals. While phantom-midge predation may control the abundance of tubificids and chironomids in the profundal, the abundance of the latter may exert little control over *C. crystallinus* larvae since they often prey heavily on zooplankton (Munger and Hare, 1997). Additionally, this species does not accumulate trace metals from overlying water because its exoskeleton is little permeable to dissolved contaminants (Munger and Hare, 1997). Statistical analysis (Fig. 8) shows that the density of *C. crystallinus* significantly correlates positively with Mn ($r = 1$) and negatively with oxygen ($r = -0.95$), which confirms that this species could survive anoxic conditions accompanied by high concentrations of Mn in the water.

Thus, the fauna from the lower profundal showed an impoverished community structure, clearly reflecting deteriorated conditions in the sediment and indicating dystrophic events in the deepest part of the lake. In regard to categories of lake quality (Wiederholm, 1980), the absence of chironomids and oligochaetes in the lower profundal indicate a bad ecological status of the Mantovo Reservoir.

CONCLUSIONS

This study represents the first detailed analysis of the quality of water of the Mantovo Reservoir (southeastern part of the Republic of Macedonia), based on physical and chemical parameters and the macrozoobenthos.

The results confirmed that thermal stratification, accompanied by high content of organic matter, leads to processes that cause pronounced oxygen deficits in the bottom water, as well as mobilization of manganese, iron, and copper from the sediment into the hypolimnion of the Mantovo Reservoir.

The low content of nutrients clearly indicates an oligotrophic status of the Mantovo Reservoir, while transparency and dissolved organic matter, as well as the community of profundal macroinvertebrates, suggest a higher trophic status. This contradiction can be attributed to the almost continuous movement of limnetic waters, which negatively affected phytoplankton production. On the other hand, the allochthonous organic input from the drainage basin and flooded vegetation decay allow high productivity of *L. hoffmeisteri* and *C.* gr. *plumosus*, which are tolerant of organic pollution.

The fauna of the upper and lower profundal region clearly indicated a eutrophic condition in the central part, passing over into a region of hypereutrophy in the deepest part of the lake.

In order to prevent further eutrophication processes, certain measures of lake ecosystem protection and conservation should be undertaken. Also, regular monitoring of water quality should be established.

Our study indicates that investigations of the Mantovo Reservoir should be continued in order to fully understand the dynamic nature of the reservoir and assess its environmental status. Some additional

parameters should be considered, for example the content of sulfides, as well characteristics of the sediment. In addition, other elements of biological quality relevant according to the Water Framework Directive (WFD, 2000) (phytoplankton, phytobenthos, aquatic macrophytes, and fish) should also be monitored.

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КВАЛИТЕТ ВОДЕ АКУМУЛАЦИЈЕ МАНТОВО, РЕПУБЛИКА МАКЕДОНИЈА

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Циљ рада је био да се процени квалитет воде акумулације Мантово (југоисточна Македонија) на основу физичко-хемијских параметара и водених макробескичмењака. Вршено је месечно прикупљање узорака током 2003. и 2004. Подаци о температури и растворeном кисеонику по профилима индиковали су да је Мантово димиктичка акумулација. На основу концентрације нутријената, Мантово се може окарактерисати као акумулација са дефицитом фосфора. Током летње стратификације, измерене су врло високе вредности мангана (2819 μg/l) и бакра (147.6 μg/l) у доњем профундалу. *Limnodrilus hoffmeisteri* је био доминантна врста, што указује на присуство органског загађења. Доминација врсте *Chaoborus crystallinus*, уз опадање абунданце *L. hoffmeisteri* у доњем профундалу, индикује погоршање статуса у најдубљем делу језера.