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THE EVALUATION OF THE CONCENTRATION OF CHLORIDES AND SULPHATES IN SURFACE WATER OF THE NATIONAL NATURE RESERVE ČIČOV OXBOW

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In the years 2013–2014 we evaluated changes in concentrations of chlorides and sulphates in waters of the National Nature Reserve Čičov oxbow depending on the time and place of sampling. Collections of samples were realized regularly at monthly intervals, always in the half of a month. Sampling sites were determined in order to assess the impact of natural and anthropogenic source of surface water quality. In order to evaluate the quality of surface water in the sampling sites by individual indicators, we used the values of the 90th percentile (P90), which was calculated from the measured values and then compared with their matching set of limit values referred to the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. According to that Regulation, the recommended value for chlorides is 200 mg dm^{-3} and for sulphates 250 mg dm^{-3}. Based on the calculated values of 90th percentile (P90) of these indicators, we found out that the calculated characteristic values are lower.

Keywords: chlorides, sulphates, national nature reserve, surface water, oxbow

Chlorides are readily soluble in water and are present almost in all natural waters (Rao, 2008). In terms of quantitative representation of anions in natural waters they generally occur in the third and fourth place (Pitter, 2009). Their natural resources may be precipitation or geologic bedrock containing chlorides (Mashmburn, 2004). Anthropogenic sources are agricultural waste from livestock production, applied potassium fertilizers in form of KCl, road salt used in winter for maintenance of roads and some kinds of waste waters (Twort, 2001, Nollet et al., 2013). Sulphates are normal parts of natural waters where they occur mainly as anion SO_4^{2-} (Weiner, 2012). However, in anaerobic environment they are vulnerable to biochemical reduction to the form of hydrogen sulfide (Orolínová, 2009). These processes occur in waters with anaerobic conditions, such as wetlands (Weiner, 2012). Natural resources of sulphates are minerals containing sulfur and anthropogenic resources are mine water from lignite mining, waste water from industry, where sulfates or sulfuric acids were used in production process, urban and industrial air pollutants containing SO_2 and SO_3 emissions resulting from the combustion of fossil fuels and penetrating atmospheric waters (Pitter, 2009, Ratnayaka et al., 2009). Subsequently, they can reach watercourses in the form of precipitation (Sprague et al., 2007). Their concentrations in surface waters are generally in tens to hundred mg dm^{-3} (Pitter, 2009).

Material and methods

The National Nature Reserve Čičov oxbow (47° 46´ N 17° 43´ E) is a left-side oxbow of the Danube river, which is separated from the main stream by a dam. It is located in the Danube Lowland in the most wooded part of the protected landscape area, 30 km from Komárno in direction to Bratislava. It is located in the cadastral area of Čičov and Kľúčovec at an altitude of 110 m, it belongs to the river-basin of the Danube. It was announced s national nature reserve in 1964 on the area of 79.8715 ha, the water area is 79.87 ha, and the protective zone is 55.25 ha. The Čičov oxbow is considered to be the largest lake in the oxbow of the river in Slovakia. After the break Danube dyke in 1899 was created. The average water depth is about 3 m, the maximum measured depth was 7.5 m. The bank is divided by small peninsulas and bays. It is an important habitat for aquatic and wetland communities, which are characteristic for the meadow forests along the Danube River with 24 kinds of fish, over 100 species of birds and several other rare species of animals and plants (Hanušin, 2009). The area is particularly influenced by the flow of Danube, from which the oxbow water is fed by subsurface seepage (Szabóová, 1989). Depending on the water level, the surrounding area is waterlogged and flooded. From mid-summer, the groundwater is declining because the evaporation dominates over precipitation. By the Rye Island, the channel Vrbina – Medveďov and the Čiližský stream open into the oxbow. The area is rain-snow runoff type, with the accumulation of water in December – January, with high water levels in February – April (Varga et al., 2006).

Geological structure consists mostly of Neogene clays – Pannonia sediments of the lake, covered by quaternary Holocene alluvial sediments of gravel, sand, loess and flood waters. The basic quaternary elements are: fluvial – wetland sediments with organic additives and fluvial –

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alluvial sediments in the lowlands. In terms of soil conditions in the western part of the area, clayey soil types are dominant, and the eastern part is dominated by clay-loam soil. The main soil types are: black soils carbonate, local peat soils on the carbonate alluvial sediments, and alluvial gley soils on the carbonate and non-carbonate sediments, mollic gley, mollic fluvisols and gley on the carbonate and noncarbonate alluvial sediments. Hydrogeological basis of the area consists of quaternary sands and gravels of alluvial. The National nature reserve Čičov oxbow is located in dry to moderately dry areas with the average annual temperature of 9.9 °C. The coldest month is January, with average monthly temperature -2.1 °C and the warmest month is July, with average monthly temperature 20.5 °C. Territory is not only our warmest zone, but it is also one of the driest areas of the Slovak Republic. Average annual rainfall is 550–600 mm, the most precipitation falls in the months of May, June and July (average monthly rainfall 59.3 mm). The area is located in one of the windiest areas of Slovakia. The maximum speed of the wind and the windiest days occur in winter and spring. The predominant wind direction is NW (Varga et al., 2006).

The collections of samples were realized regularly at monthly intervals, always in the half of a month during the years 2013 and 2014. The sampling sites were determined in order to assess the impact of natural and anthropogenic source of surface water quality. Specifically, we identified eight sampling points (Figure 1):

1. Sampling point – 47° 46′ 7.17″ north latitude and 17° 43′ 7.56″ east longitude, 110 m above sea level, located about 150 m from the mouth of the Číližský stream into the reserve. The average depth of the sampling point is 0.31 m.
2. Sampling point – -47° 46′ 6.51″ north latitude and 17° 43′ 7.81″ east longitude, 104 m above sea level, is located 20 m near the mouth of Čiližský stream. Its average depth is 0.37 m.
3. Sampling point – 47° 46′ 5.88″ north latitude and 17° 44′ 0.40″ east longitude, 107 m above sea level, located in the northeastern part of the national nature reserve. The average depth of the sampler is 0.43 m.
4. Sampling point – 47° 46′ 4.04″ north latitude and 17° 44′ 1.87″ east longitude, 111 m above sea level, located in the northeastern part, with an average depth of 0.43 m.
5. Sampling point – 47° 46′ 2.09″ north latitude and 17° 44′ 0.32″ east longitude, 111 m above sea level, the average depth of the sampling point is 0.50 m.
6. Sampling point – 47° 46′ 0.02″ north latitude and 17° 43′ 8.26″ east longitude, 111 m above sea level, similar to the 5. sampling site is located on the first side distributary. The average depth is 0.37 m.
7. Sampling point – 47° 46′ 2.23″ north latitude and 17° 43′ 4.45″ east longitude, 117 m above sea level, located on the second side distributary of the reservation, the average depth 0.39 m.
8. Sampling point – 47° 46′ 3.77″ north latitude and 17° 43′ 5.91″ east longitude, 117 m above sea level, located in the second side distributary of reserve with an average depth 0.39 m.

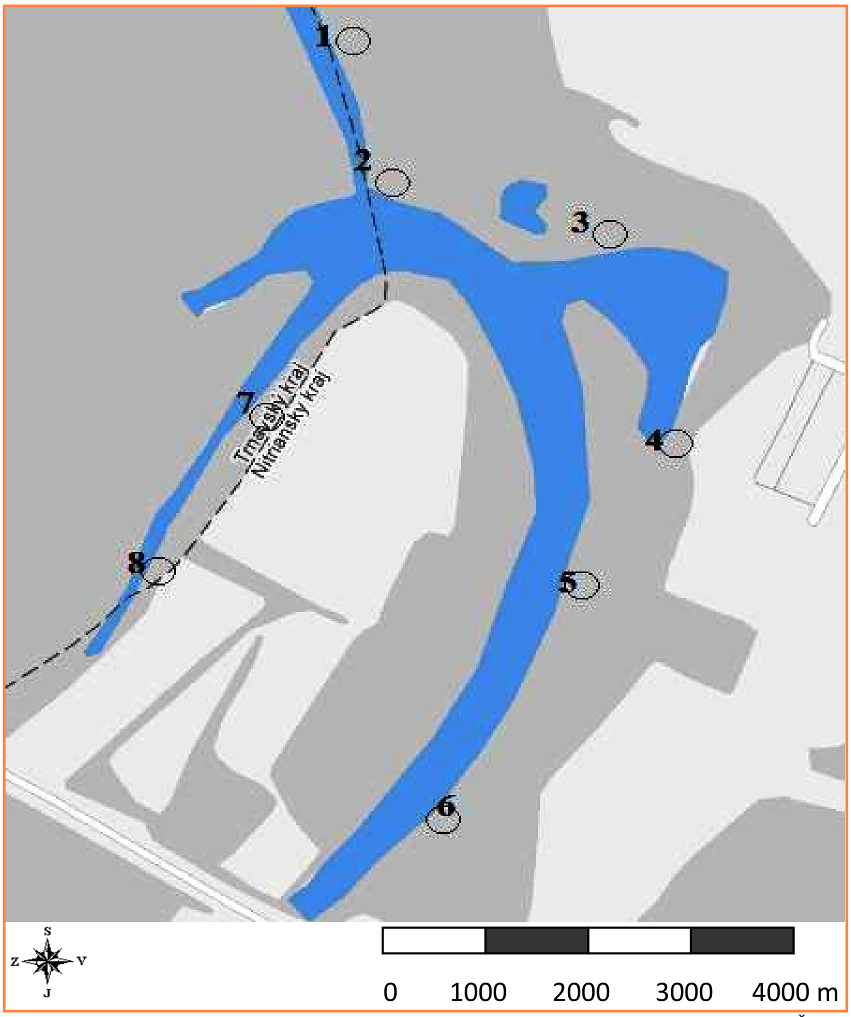

Figure 1 Map of individual sampling places in the National Nature Reserve Čičov oxbow

In the collected water samples we determined the concentration of chlorides by the Mohr titration method and sulphates by the titration method by lead nitrate. To the evaluation of the quality of surface water in the sampling sites by individual indicators we used the values of the 90th percentile (P90), which was calculated from the measured values and then compared with their matching set of limit values referred to the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. Statistical analyzes were performed using Statistica, the analysis of variance, and to evaluate the interrelations between indicators we used the Pearson correlation coefficient.

Results and discussion

Average concentrations of chlorides in waters of the National Nature Reserve Čičov oxbow in the monitored years varied from 29.5 mg dm^{-3} (year 2013) to 41.75 mg dm^{-3} (year 2014) and average concentration for the whole monitored period represented 35.62 mg dm^{-3} (Figure 2). It agrees with the statement of Dimkic et al. (2008) and Hunt et al. (2012), who report that their average concentrations in surface waters ranging, from 10–100 mg dm^{-3}. Kvetanová (2012) in the Čaradice stream in the years 2005–2010 states their average concentration of 20.54 mg dm^{-3}. Higher average concentration of Cl- (65.38 mg dm^{-3}) in the years 2006–2008 in waters of the Nature Reserve Alúvium Žitavy was found by Noskovič, Palatická (2009).

Depending on the time of sampling, higher average concentrations for the whole monitored period were recorded mainly in summer and autumn, with the maximum average concentration in the month of September (46.73 mg dm^{-3}) (Figure 3). Similar results in different climate area were provided by Ahuj (2013), who found the maximum average concentration (41.0 mg dm^{-3}) during the years 2010 and 2011 in autumn in lake Salt Creek, Indiana. Hunt et al. (2012) state that in natural conditions, the peak in concentration of chlorides can be especially during summer when there is reduction in the water level due to prevailing evaporation over precipitation. It was also confirmed by us through positive correlation between the chlorides and temperature (r = 0.52) (Figure 4). The lowest average concentration for the whole monitored period was recorded in January (25.26 mg dm^{-3}). Simultaneously, in January and February 2013, we found their minimum average concentration (14.73 mg dm^{-3}). Noskovič et al. (2010) found the minimum average concentration in waters of the National Reserve Žitavský luh in the years 2003–2005 in March (26.76 mg dm^{-3}). We assume that the cause of low concentrations of chlorides in these months was the increased water level in the National Nature Reserve Čičov oxbow. It can be stated that during the monitored period, seasonal regularity in dynamics of their concentrations was reflected.

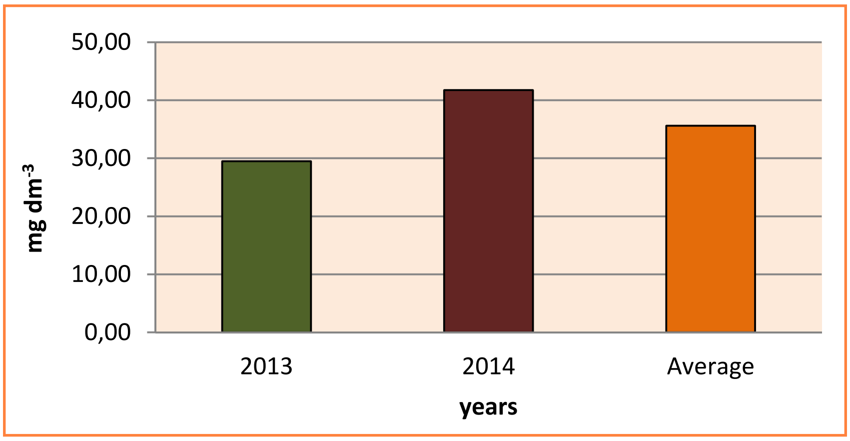

Figure 2 Average concentrations of chlorides in the years 2013–2014

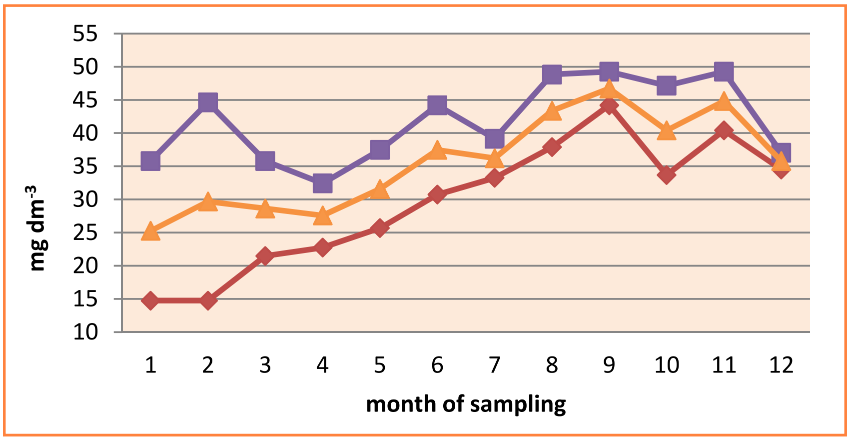

Figure 3 Average concentrations of chlorides depending on the month of sampling in the years 2013–2014

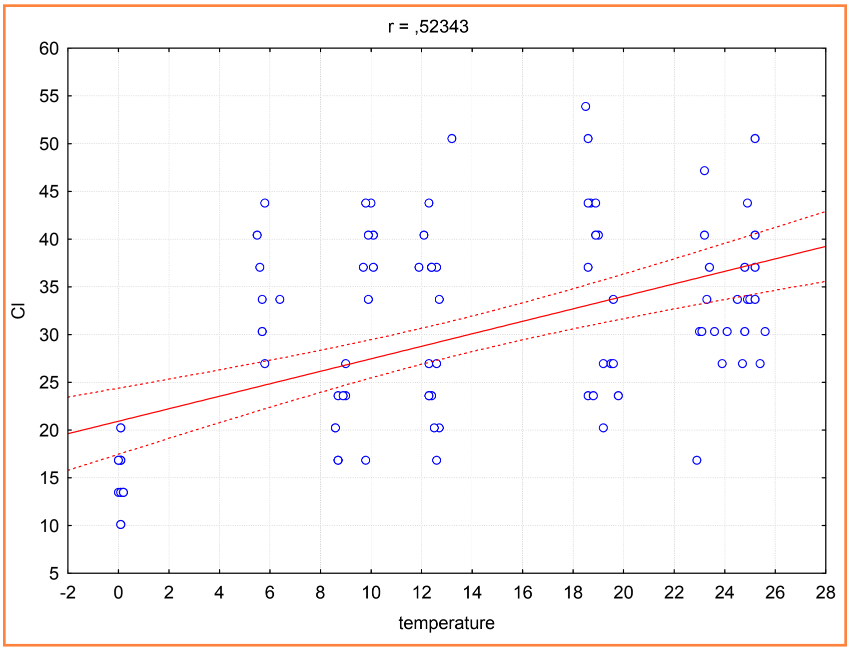

Figure 4 Interdependence between chlorides and water temperature

Concentrations of chlorides in waters of the National Nature Reserve Čičov oxbow was changing depending

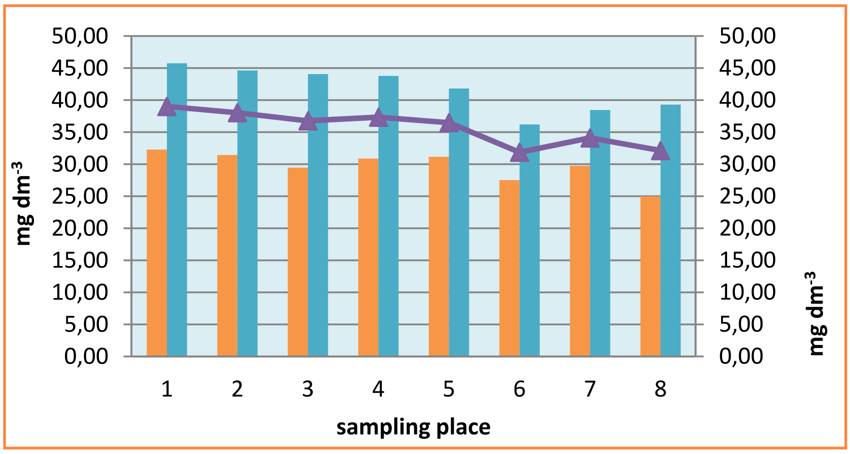

Figure 5 Average concentrations of chlorides depending on the place of sampling in the years 2013–2014

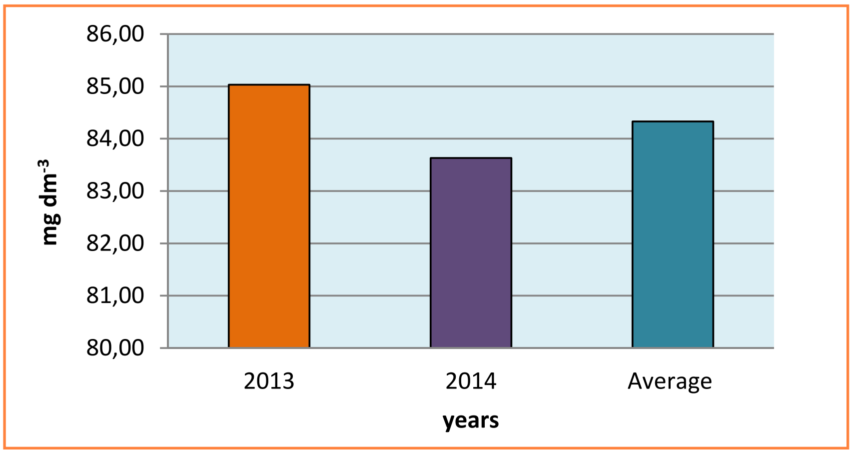

Figure 6 Average concentrations of sulphates in the years 2013–2014

on the place of sampling. From the graph of average values (Figure 5) it is clear that the highest average concentration (45.75 mg dm^{-3}) was measured in the year 2014 in sampling place no. 1. In this sampling place we found the maximum average concentration (39.01 mg dm^{-3}) for the whole monitored period. We assume that increasing concentration of chlorides in sampling place no. 1, which is located in the mouth of the Čiližsky creek into the Čičov oxbow is related with the fact that its catchment area is largely made up by intensively cultivated arable land from which the chlorides get into the water of this creek, especially from applied potassium fertilizers. The use of potassium fertilizers in form of KCl is considered an important anthropogenic source of water pollution by several authors (Pitter, 2009; Noskovič a Palatická, 2009; Kvetanová, 2012). We expect that other source of chlorides in waters of the Čičov oxbow can be subsurface seepage of water from the river Danube, Szabóová (1989) reports that the water level in the oxbow is influenced by this seepage. The minimum average concentration (31.85 mg dm^{-3}) was found in the first side arm (sampling place no. 6).

From the analysis of variance for chlorides it is clear that the impact of the year, month and sampling place was statistically significantly important (Table 1). The Government Regulation no. 269/2010 Coll. provides recommended values for chlorides 200 mg dm^{-3}. Based on the calculated values of 90th percentile (P 90) of this indicator, we found out that the calculated characteristic values are lower.

Sulphates have been quantitatively more represented in waters of the National nature reserve Čičov oxbow than chlorides. Their average concentration in the monitored years ranged from 83.63 mg dm^{-3} (2014) to 85.03 mg dm^{-3} (2013). Lower average concentration (58.37 mg dm^{-3}) for the period 2003–2005 in the water of Nature reserve Alúvium Žitavy was found by Noskovič et al., (2010). Average concentration for the whole monitored period represented 84.33 mg dm^{-3} (Figure 6). Higher average concentration of sulphates in lake Prexy, Iowa (204.8 mg dm^{-3}) was reported by Hsieh, Lantz (2012). In Illinois, their concentrations in water flows ranged from 30–150 mg dm^{-3} based on the data obtained in monitoring running in the years 2000–2007, (Iowa Department of Natural Resources, 2009).

Changes in average concentrations of sulphates during the monitored years depending on the time of sampling are shown in figure 7. From the above mentioned figure it is clear that average concentrations of SO_4^{2-} ranged from 58.50 (July, 2013) to 102.75 mg dm^{-3} (January, 2014). We can conclude that their higher average concentration in the years 2013–2014 were found in winter period, with maximum average concentration in February (91.56 mg dm^{-3}) and minimum average concentration in July (61.56 mg dm^{-3}). The decrease in concentration of SO_4^{2-} in waters of the National nature reservation Čičov oxbow in summer

Table 1 Analysis of variance for chlorides concentration

	Analysis of variance for Cl				
	sum of Squares	**Df**	**mean Square**	**F-ratio**	***p*-value**
Year	6991.8	1	6991.8	230.493	0.000000
Month	9169.2	11	833.6	27.479	0.000000
Sampling place	1219.8	7	174.3	5.745	0.000023

Table 2 Analysis of variance for sulphates concentration

	Analysis of variance for sulphate				
	sum of squares	Df	mean Square	F-ratio	*p*-value
Year	95	1	95	0.35	0.555626
Month	15380	11	1398	5.516	0.000005
Sampling place	2234	7	319	1.178	0.325168

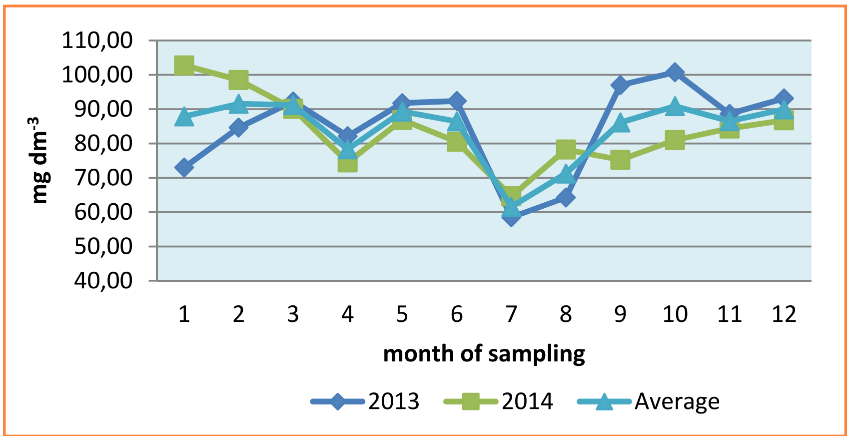

Figure 7 Average concentrations of sulphates depending on the month of sampling in the years 2013–2014

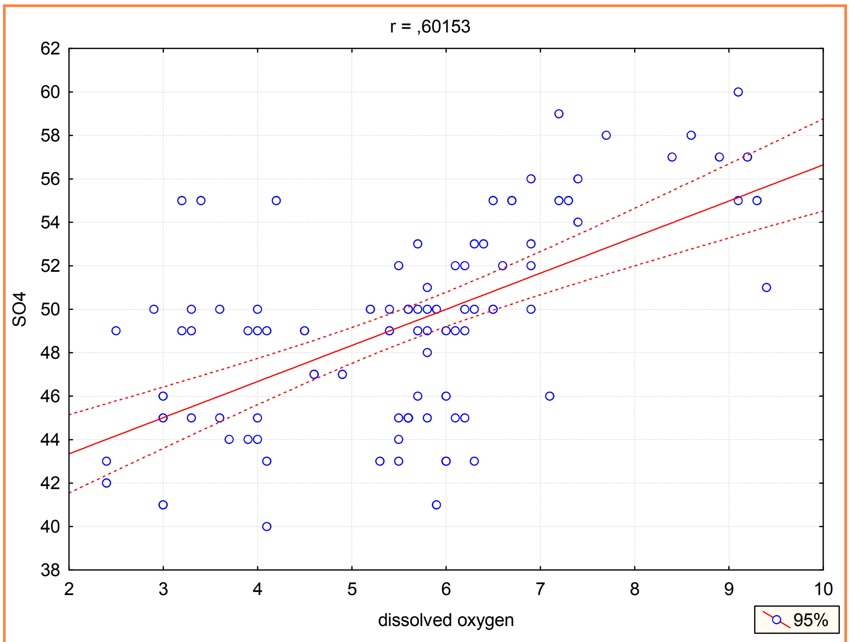

Figure 8 Interdependence between sulphates and concentration of dissolved oxygen

period is likely caused by low dissolved oxygen concentration. It also confirms positive correlation between indicator dissolved oxygen and sulphates (r = 0.60) (Figure 8). According to Kadlec and Wallac (2009) under anaerobic conditions, heterotrophic bacteria present biochemically reduced sulphate to hydrogen sulphide in the water. Wetzel (2001) and Weiner (2012) state that sulphates are largely released into water as hydrogen sulphide in anaerobic decomposition of sulfur-containing organic matter. During the monitored period the regularity in their seasonal dynamics was not reflected. Impact of month of sampling on changes in sulphates concentrations were confirmed statistically (Table 2).

Average concentrations of sulphates in waters of the National nature reserve Čičov oxbow were also affected by the place of sampling (Figure 9). The highest average concentration for the whole monitored period was in the sampling place no. 3 (92.50 mg dm^{-3}), which was located in the northeastern part of the national nature reserve. In that sampling place in the year 2013 there was also detected the highest average concentration (101.50 mg dm^{-3}). The minimum average concentration for the whole monitored period was marked in the sampling place no. 5 (81.30 mg dm^{-3}), which was located in the first side arm. We assume that the source of sulphates in the water of sampling places was mainly decomposing organic matter. Weiner (2012) stated that the source of sulphates in surface waters can be emissions from industrial combustion of fuels containing sulfur, which release large amounts of sulphur oxides to the atmosphere, then get through rainfall into surface water, thus causing an increase in their concentrations. Similarly, another source of sulphates as well as chlorides in waters of the Čičov oxbow can be subsurface seepage from the river Danube.

The Government Regulation no. 269/2010 Coll. provides recommended value for sulphates – 250 mg dm^{-3}. Based on the calculated values of 90th percentile (P90) of this indicator, we found out that the calculated characteristic values are lower.

Conclusion

In waters of the National nature reserve Čičov oxbow we evaluated concentrations of chlorides and sulphates in the years 2013 and 2014. The average concentration of chlorides for the whole monitored period was 35.62 mg dm^{-3}. In terms of the time of sampling, the highest average

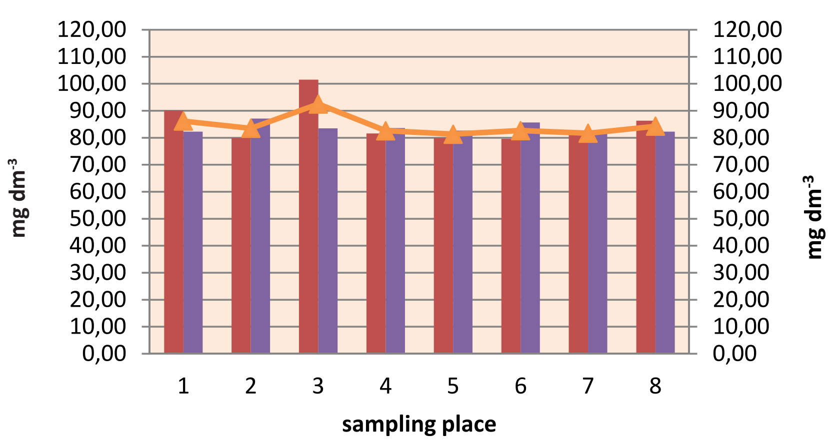

Figure 9 Average concentrations of sulphate depending on the place of sampling in the years 2013–2014

concentrations for the entire monitored period were reached in summer and autumn. The minimum average concentration was recorded in January (25.26 mg dm^{-3}) and the maximum in September (46.73 mg dm^{-3}). We expect that their higher concentrations in summer were caused by lower water levels due to prevailing evaporation over precipitation. Depending on the place of sampling, the highest average concentration (39.01 mg dm^{-3}) for the whole monitored period was in the mouth of the Čilížsky creek into the oxbow and the lowest (31.85 mg dm^{-3}) was found in the second side arm. Higher concentrations were probably related to the fact that its catchment area is largely made up by intensively cultivated arable land, from which chlorides get into waters of this creek, in particular from applied potassium fertilizers. From analysis of variance for chlorides it is clear that the impact of the year, month and sampling place was statistically significantly important. Average concentration of sulphates for the whole monitored period was 84.33 mg dm^{-3}. The highest average concentrations depending on the time of sampling were reached in winter period with the maximum value in February (91.56 mg dm^{-3}) and the lowest in July (61.56 mg dm^{-3}). Higher concentrations of sulphates in waters of the nature reserve in winter period were probably caused by higher concentrations of dissolved oxygen. Depending on the place of sampling, its maximum average concentration (92.50 mg dm^{-3}) for the whole monitored period was found in the northeastern part of reservation and the minimum value in the first side arm (81.30 mg dm^{-3}). We assume that the source of sulphate in waters of the sampling places was mainly decomposing organic matter. From the analysis of variance for sulphates it is clear that the impact of the month of sampling was statistically significantly important.

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