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THE EVALUATION OF THE CONCENTRATION OF BIVALENT BASIC CATIONS IN SURFACE WATER OF THE NATIONAL NATURE RESERVE ČIČOV OXBOW

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During the years 2013–2014, the concentrations of bivalent basic cations Ca^{2+} and Mg^{2+} were evaluated in the water of the Čičov tributary, which belongs to the National Nature Reserve of the basin of the river Danube. On the basis of the results obtained, it can be stated that the average concentration of calcium for the whole reference period was 59.63 $mg.dm^{-3}$. Minimum average concentration depending on the time of sampling was found in November (48.42 $mg.dm^{-3}$) and maximum in July (70.73 $mg.dm^{-3}$). We assume that this above average concentrations in the summer could be due to the lower surface of the water due to higher evaporation. Depending on the places of sampling points, the lowest average concentration (58.10 $mg.dm^{-3}$) for the whole reference period was at the mouth of the Čilizian brook and the top (60.32 $mg.dm^{-3}$) in the first side shoulder. The analysis of variance detected highly statistically significant effect of the year and month of collection on changes in the concentration of calcium. The average concentration of magnesium for the whole reference period was 14.54 $mg.dm^{-3}$. As for the time of collection, the highest average concentrations for the entire observation period were found during the summer, with the maximum average concentration in July (16.94 $mg.dm^{-3}$) and minimum in February (10.81 $mg.dm^{-3}$). The lowest average magnesium concentration for the entire reference period, regarding to the sampling points, was measured in the north-eastern part of the nature reserve (14.28 $mg.dm^{-3}$) and the highest one at the mouth of the Čilizian brook into the National Nature Reserve (14.72 $mg.dm^{-3}$).

Keywords: divalent basic cations; calcium; magnesium; oxbow

Calcium and magnesium are the main cations of natural waters (Razowska-Jaworek, 2014). Calcium concentration in groundwater and surface waters ranges from several dozen up to several hundreds of $mg.dm^{-3}$ and magnesium from the units up to several tens of $mg.dm^{-3}$ (Pitter, 2009). The weight ratio between the calcium and magnesium is in the range of 4 : 1 to 2 : 1, the exception is mineral waters (Poláček et al., 2010). They get into water by decomposition of calcium and magnesium aluminosilicates and in larger concentrations by dissolution of limestone ($CaCO_3$), dolomite ($CaCO_3 . MgCO_3$), magnesite ($MgCO_3$), gypsum ($CaSO_4 . 2 H_2O$) and their minerals (Pitter, 2009). Another source of calcium and magnesium in surface waters may be rainfalls (Babošová and Noskovič, 2014). The concentration of calcium in rainwater is ranging from 0.1 to 10 $mg.dm^{-3}$ and magnesium marks around 0.1 $mg.dm^{-3}$ (Kadlec and Wallace, 2009). Their anthropogenic sources can be some industrial waste waters from the plants, whose acids are neutralized with lime, limestone, dolomite, or magnesite (Pitter, 2009).

Material and methods

The National Nature Reservation 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 on the Danubian Plain 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, belonging to the river-basin of the Danube. The national nature reservation was announced in 1964 on the area of 79.8715 ha, while water area is 79.87 ha, and the protected zone is 55.25 ha. The Čičov oxbow is considered the largest lake in an ox-bow of a river in Slovakia, and appeared after the break of the Danube dyke in 1899. 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 the Danube, from which oxbow waters are fed by subsurface seepage. Depending on the water level, the surrounding area is waterlogged and flooded at high states. From mid-summer, the groundwater drops because the evaporation dominates over precipitation. By the Žitný ostrov, opens into the oxbow channel the Vrbina – Medveďov and Čiližský channel open into the oxbow. It is an area of rain-snow runoff type, with the accumulation of water in December – January, with high water levels in February – April.

The geological structure consists mostly of Neogene clays – Pannonian sediments of the lake, covered by

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quaternary Holocene alluvial sediments of gravel, sand, loess and flood waters. The basic quaternary elements are: fluvial – wetland sediments with organic additives and fluvial – alluvial sediments in the lowlands. In terms of soil conditions, there are predominantly clayey soil types in the western part of the area and clay-loam soils in the eastern part. 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. The 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 hottest month is July, with average monthly temperature 20.5 °C. The territory is not only the warmest zone, but 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 is 59.3 mm) (Table 1).

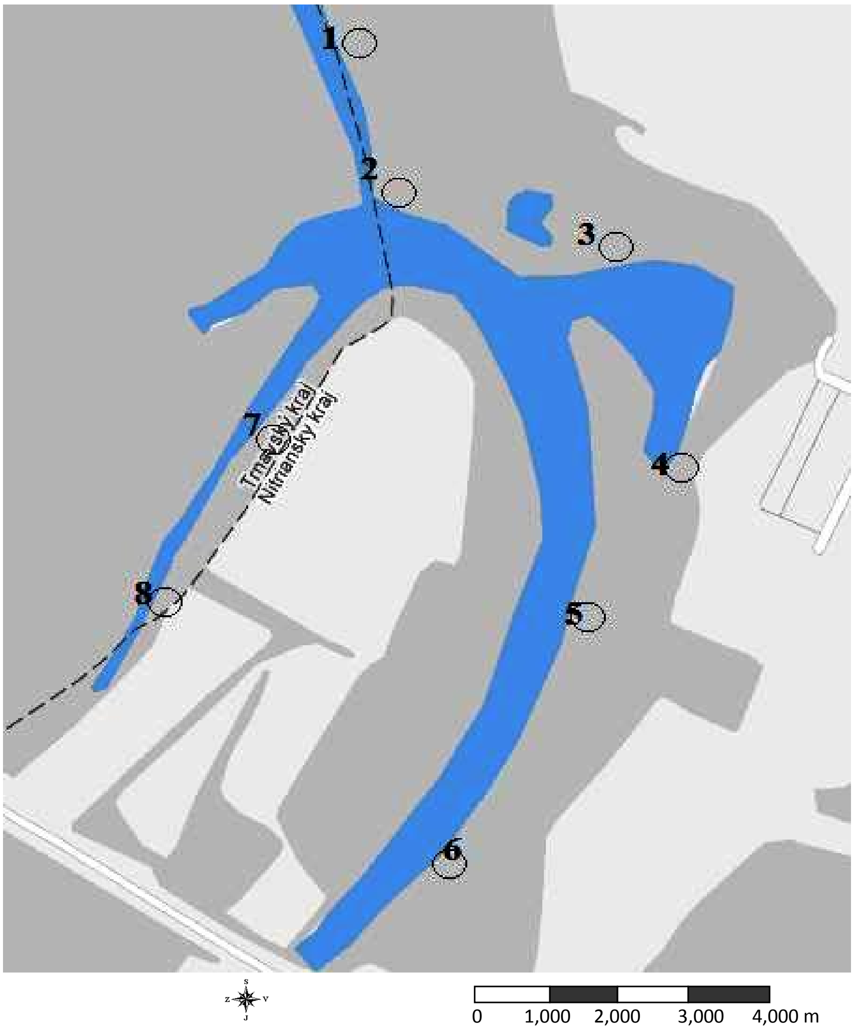

Figure 1 Map of individual sampling places in the National Nature Reserve Čičov oxbow

Table 1 Rainfall in the years 2013–2014

Month	Precipitation 2013	Precipitation 2014	Precipitation 2013–2014
	Σ	Σ	Σ
January	93.40	16.70	110.10
February	91.80	42.20	134.00
March	108.50	7.30	115.80
April	20.80	50.20	71.00
May	64.10	82.20	146.30
Juny	34.60	19.10	53.70
July	5.40	64.50	69.90
August	55.20	110.10	165.30
September	49.60	114.30	163.90
October	14.50	25.00	39.50
November	95.40	34.00	129.40
December	7.50	54.20	61.70
Σ	640.80	619.80	1260.60

Source: SHMÚ

The area is located in one of the windiest regions 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).

Collection and processing of samples

Collections of samples were realized regularly at the monthly intervals, always in about the half of the month during the years 2013 and 2014. Sampling places were determined in order to assess the impact of natural and anthropogenic sources of surface water quality. Specifically, the following eight sampling points were identified (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 channel 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 channel. The average depth of 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 the 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 the average depth 0.39 m.

In the collected water samples there were identified concentrations of divalent cations base Ca^{2+} using flame photometry and Mg^{2+} by the atomic absorption spectrophotometry. To assess the quality of surface water sampling in sampling points according to individual indicators, the 90th percentile (P90) was used. It was calculated from the measured values and the subsequent comparison with their corresponding systems of limit values set out in the Government Regulation No. 269/2010 Coll. The results were processed by mathematical-statistical methods (by the Statgraphics 5.0 plus).

Result and discussion

In the waters of the National Nature Reserve of Čičov oxbow calcium was mostly represented by a bivalent basic cation. Its average concentration in the monitored years ranged from 47.56 (2014) to 71.72 mg.dm^{-3} (2013) and for the entire reference period it reached the value 59.63 mg.dm^{-3} (Fig. 2). Higher average concentrations of calcium are stated in the river Bebrava (77.33 mg.dm^{-3}) and in the river Nitra (81.1 mg.dm^{-3}) by Gregor (2012) and in the water of National Nature Reserve of Žitava wetland (61.25 mg.dm^{-3}) by Noskovič et al., (2010) and lower ones in the water course of Kadaň (47.69 mg.dm^{-3}) by Noskovič et al., (2007).

The percentage ratio of calcium on the total amount of bivalent basis cations ranged from 76.2 (2014) to 83.43% (2013), and reached the value of 79.82% for the entire monitored period. The weight ratio of the Ca^{2+} : Mg^{2+} in the course of the years 2013–2014 was 4.09 : 1 (Table 2). It agrees with the statement of Poláček et al., (2010), who claim that the ratio between calcium and magnesium in natural waters can be up to 4 : 1.

The effect of sampling time on the concentration of calcium in the water of the National Nature Reserve is shown in Figure 3. From this Figure it may be seen that seasonal regularity in the dynamics of its concentrations in the course of monitoring was not proved. The highest average concentration of Ca^{2+} for the entire reference period were found in the spring and summer, with the maximum concentration in July (70.73 mg.dm^{-3}) and the lowest in winter, with the minimum average concentration in November (48.42 mg.dm^{-3}). Higher average concentrations of calcium in summer (118.80 mg.dm^{-3}) and lower in the winter season (75.71 mg.dm^{-3}) in the lake of Bharawas was also found by Sahni, Yadav (2012). We assume that the rise in the concentration of calcium in the summer period was due to the lower surface of water in consequence of higher evaporation and by increasing its concentration in the water of the National Nature Reserve.

Depending on the location of sampling, average concentration

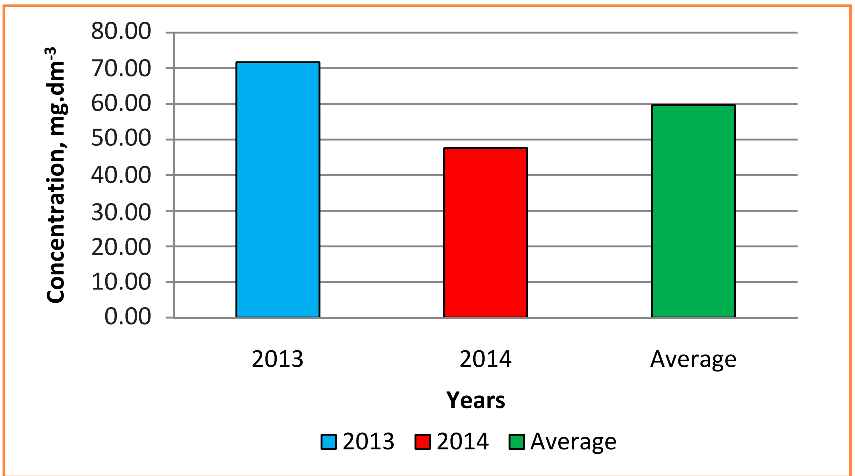

Figure 2 The average concentrations of Ca^{2+} in mg.dm^{-3} in the years 2013–2014

Table 2 Percentage of calcium and magnesium to the total amount of divalent base cations and their mass ratio

Year	Total of Ca^{2+} + Mg^{2+}, mg.dm^{-3}	The share of individual cations in the total of Ca^{2+} + Mg^{2+}		Ca^{2+} : Mg^{2+}
		% Ca^{2+}	% Mg^{2+}	
2013	85.94	83.43	16.56	5.03:1
2014	62.41	76.2	23.79	3.20:1
Average	**74.18**	**79.82**	**20.18**	**4.09:1**

of calcium for the entire monitored period ranged from 58.10 (sample no. 2 – the mouth of the Čilizian brook to the reservation) up to 60.32 mg.dm^{-3} (sample no. 6 – in the first side of distributary). In individual years of monitoring, the differences in its average concentrations were slightly significant. Their average concentration in 2013 ranged from 69.88 (sampling place no. 2) up to 72.55 mg.dm^{-3} (place of sampling no. 5), and in 2014 these were from 46.32 (place of sampling no. 2) up to 48.17 mg.dm^{-3} (sampling place no. 6). From the given above it follows that in 2013 we noticed a higher interval of fluctuation in its concentrations. The results obtained during the reference period, however, show that the effect of sampling places on average concentrations of Ca^{2+} was not expressed more significantly (Fig. 4). We assume that natural sources of both calcium (and magnesium) in the water of the National Nature Reserve of Čičov distributary are the interaction products between water and the primary and secondary minerals (geological and pedological environment). In the monitored region it concerns carbonate minerals (calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$, magnesite Mg and their transitional isomorphic components), as well as the component of clay minerals being recorded in the soil systems. In the area of interest there are primarily 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. Anthropogenic sources of pollution by calcium (and magnesium) in the vicinity of the National Nature Reserve were not found.

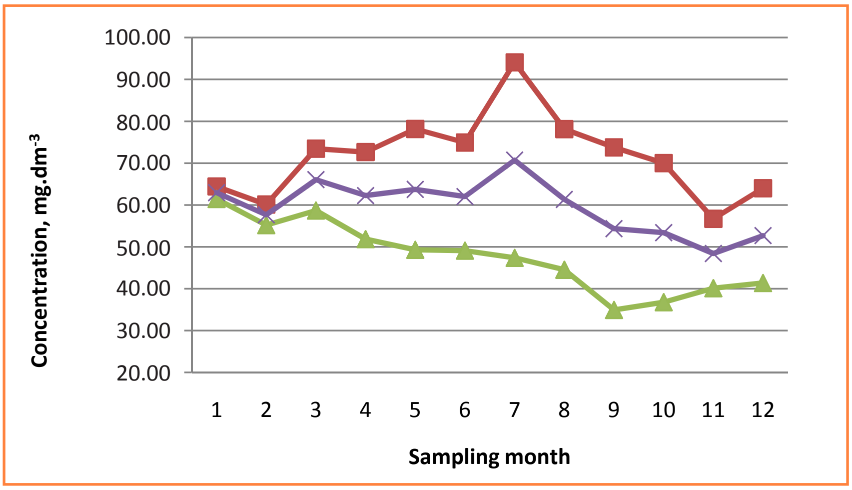

Figure 3 The average concentrations of Ca^{2+} in mg.dm^{-3} depending on the sampling time

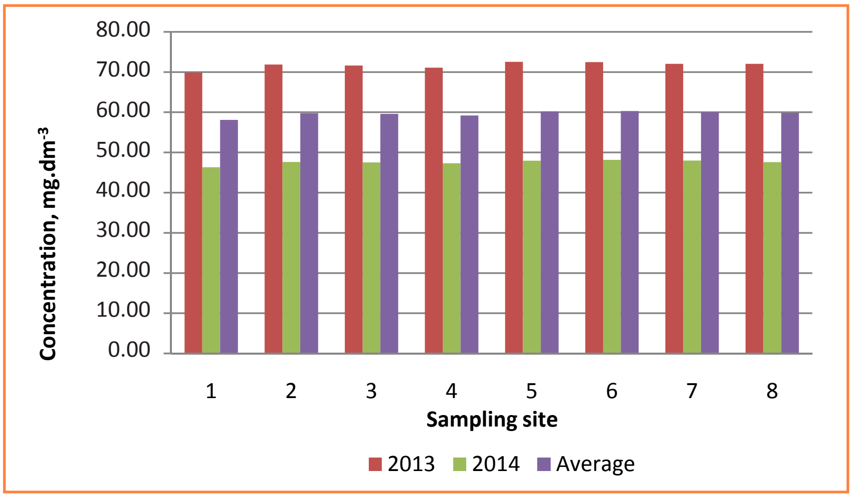

Figure 4 The average concentrations of Ca^{2+} in mg.dm^{-3} depending on the sampling site

A highly statistically significant influence of the year and month of collection has been detected by the variance analysis. The influence of the sampling place was statistically insignificant. As for the interactions, only the interaction between the year and the month of collection was confirmed as a highly statistically significant one (Table 3).

The Government Regulation no. 269/2010 Coll. provides the recommended value for calcium 100 mg.dm^{-3}. Based on the calculated

Table 3 Analysis of variance for Ca^{2+} concentration

Effect	The sum of squares	Degrees of freedom	Mean square	*F*	*p*
Year	27962.3	1	27669.2	3110.53	0.000000
Month	7234.2	11	649.9	73.06	0.000000
Simple site	85.7	7	12.4	1.39	0.220029
Year* month	7502.6	11	682.1	76.68	0.000000
Year* simple site	6.0	7	0.9	0.10	0.998379
Month* simple site	647.3	77	8.4	0.95	0.597367
Error	676.0	76	8.9	–	–

F – value, *p* – value

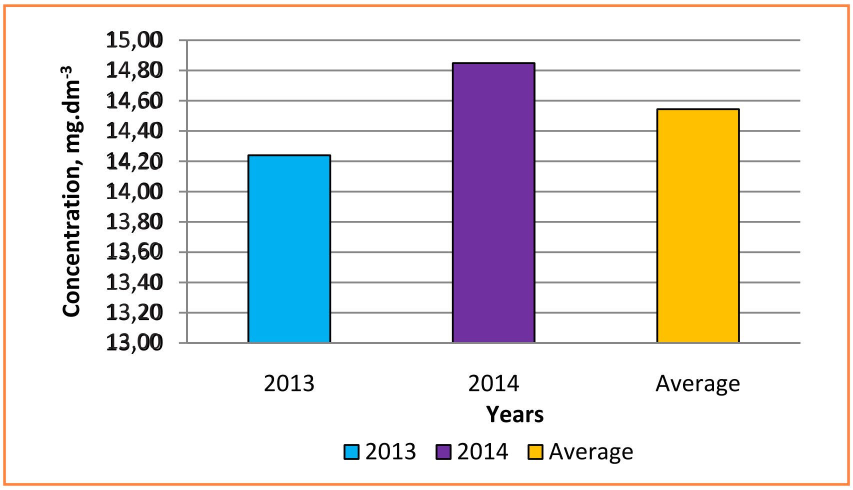

Figure 5 The average concentrations of Mg^{2+} in $mg.dm^{-3}$ in the years 2013–2014

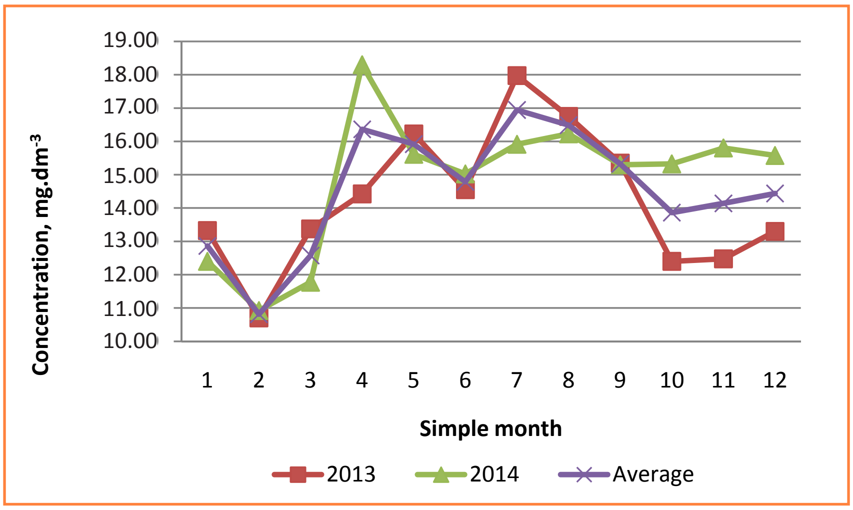

Figure 6 The average concentrations of Mg^{2+} in $mg.dm^{-3}$ depending on the sampling time

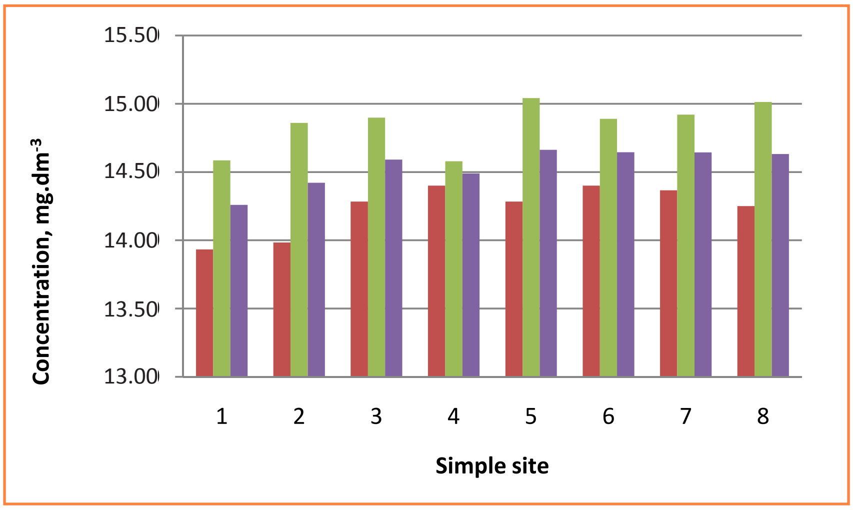

Figure 7 The average concentrations of Mg^{2+} in $mg.dm^{-3}$ depending on the sampling site

values of 90th percentile (P90) of this indicator, we found out that the calculated characteristic values were lower (Table 4).

The average concentrations of magnesium in the monitored years ranged from 14.24 (2013) to 14.85 $mg.dm^{-3}$ (2014) and for the entire monitored period reached 14.54 $mg.dm^{-3}$ (Fig. 5). Higher average concentrations of magnesium (22.2 $mg.dm^{-3}$) were found by Nedzarek et al., (2015) in the river Ina in Poland and by Sharma et al., (2013) in Lake Kundh (31.35 $mg.dm^{-3}$). Its lower average concentration (7.4 $mg.dm^{-3}$) in Lake Manatee in Florida was stated by Toor et al. (2012).

The proportion of magnesium on the total amount of bivalent basic cations ($Ca^{2+} + Mg^{2+}$) ranged from 16.56 (2013) up to 23.79% (2014) and for the entire monitored reference period it reached 20.18% (Table 1). Magnesium, as a quantitatively less represented bivalent basic cation in the water of the Nature Reserve of Žitavian wetland was also found by Noskovič et al., (2010).

Depending on the time of sampling, the average concentrations of magnesium for the whole monitored period ranged from 10.81 (February) to 16.94 $mg.dm^{-3}$ (July) (Fig. 6). Similarly as in calcium, higher average concentrations of Mg^{2+} were found in the summer period, with the maximum average concentration in July (16.94 $mg.dm^{-3}$) and lower in the winter period, with the minimum average concentration in February (10.81 $mg.dm^{-3}$). The rise of its concentration in the summer period in the Lake Dal was detected by Mukhtar et al. (2014). Waghmare and Kulkarni (2013) state that in the course of the year, magnesium concentrations in the river Lendi ranged from 9.6 (December) to 26.4 (July) $mg.dm^{-3}$. During the monitored years was not shown the seasonal regularity in the dynamics of its concentrations.

Depending on the place of sampling, average concentrations of Mg^{2+} for the whole reference period ranged from 14.28 (sample no. 4 – in the northeastern part of the nature reserve), up to 14.72 $mg.dm^{-3}$ (sample no. 1 – the mouth of the Čilizian brook into the reservation) (Fig. 7). Similarly as in calcium, the results obtained show that the effect of the

Table 4 Analysis of variance for Mg^{2+} concentration

Effect	The sum of squares	Degrees of freedom	Mean square	*F*	*p*
Year	17.35	1	17.35	44.3	0.000000
Month	586.11	11	53.28	136.0	0.000000
Simple site	3.51	7	0.50	1.3	0.271233
Year * month	176.00	11	16.00	40.8	0.000000
Year * simple site	1.85	7	0.26	0.7	0.691880
Month * simple site	28.89	77	0.38	1.0	0.574682
Error	29.77	76	0.39		

F – value, *P* – value

Table 5 The calculated characteristic values of the 90th percentile (P90) for Ca^{2+} and Mg^{2+}

Calculated characteristic value	Sampling sites							
	1.	2.	3.	4.	5.	6.	7.	8.
Ca^{2+}	40.84	41.63	41.18	41.02	41.59	44.33	42.12	38.63
Mg^{2+}	12.16	12.35	12.18	11.98	11.99	11.80	11.99	12.38

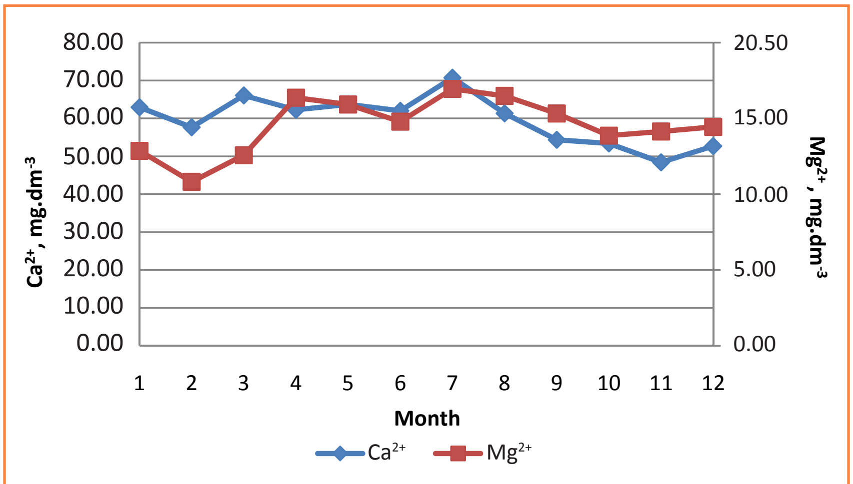

Figure 8 Changes of concentrations of Ca^{2+} and Mg^{2+}

The results show that the effect of sampling sites on the concentration of calcium and magnesium was not significant. We assume that their origin in the water Čičov tributary was of geogene and pedogenic origin. In the cases of both calcium and magnesium, the analysis of variance detected statistically highly significant impacts of the year and month of collection on their concentrations. The proportion of the total amount of bivalent base cations (Ca^{2+} : Mg^{2+}) for the whole reference period amounted to 79.82% and 20.18%. The weight ratio of the Ca^{2+} : Mg^{2+} in the monitored years was 4.09 : 1.

places of sampling did not affect the average concentration of Mg^{2+} more significantly. We assume that the origin of magnesium in the water of the Čičov tributary similarly as in calcium was of the geogene and pedogenic origin. During the reporting period, we saw a very similar trend in changes in average concentrations of calcium and magnesium (Fig. 8), which is confirmed by the high positive correlation detecting the dependence between these two cations bases.

From the analysis of variance for the measured concentrations of magnesium, it is clear that had the year and month of collection marked statistically highly significant impacts, while the impact of sampling points was statistically insignificant. As for the interactions, only the interaction between year and month of collection was statistically highly significant (Table 4).

The Government Regulation no. 269/2010 Coll. provides the recommended value for magnesium at 200 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 (Table 5).

Conclusions

During the years 2013–2014, the concentrations of bivalent basic cations Ca^{2+} and Mg^{2+} were evaluated in the water of Čičov tributary, which belongs to the National Nature Reserve of the basin of the river Danube.

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