

Evaluation of concentrations of bivalent and univalent alkaline cations in water of the Nature Reserve Žitavský luh – wetland

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Abstract

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We evaluated concentrations of bivalent and univalent alkaline cations in the water of the Nature Reserve (NR) Žitavský luh, wetland over the years 2003–2005. According to the results obtained, we can state that the amounts of alkaline cations in water of the wetland followed the ordering: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. The mean share of calcium on the total sum of alkaline cations for the whole monitored period was 52.03%, magnesium 21.02%, sodium 19.83% and potassium 7.13%. Over the whole monitoring period, the ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ was 2.48/1 and the ratio of Na^+/K^+ was 2.78/1. Over the whole monitoring period, there have not been discerned any trends in seasonal dynamics in concentrations of the alkaline cations or their dependence on the sampling site. We calculated characteristic values of concentration of calcium and also magnesium, and compared these with the limit values given by STN 75 7221 “Classification of the water surface quality”. The result was classification of water in all the sampling sites as belonging to the 2nd class of water surface quality (clean water). As no sources of anthropogenic pollution with calcium and magnesium were present in the river basin of the Žitava River, we can conclude that their presence in the wetland water is of natural origin – resulting from the nature of the parent rock in the monitoring area, mostly consisting of calcium loess and from soil genealogy – controlled by presence of basic cations in the surrounding soils.

Key words

wetland, surface water quality, concentration of alkaline cations

Introduction

Wetlands are important elements of a watershed because they serve as a link between the land and water systems. As the link between land and water, wetlands play a vital role in programs for water quality control. They represent a complex of ecosystems, with a wide range of biologic, ecologic, hydrologic and socio-economic functions (HEIMLICH et al., 1998).

Calcium and magnesium are generally main cations in natural waters, where they mostly occur either in form of simple ions Ca^{2+} and Mg^{2+} (DONAHOE and CHONGXUAN, 1998), or in the form of their ion associates (TÖLGYESSY and MELICHOVÁ, 2000). Generally, calcium is represented in higher concentrations than magnesium

in natural waters (DUBOVÁ, 1998). The two elements leached from calcium and magnesium aluminosilicates, dolomites, magnesites and gypsum enter the waters (PITTER, 1999). When carbon dioxide is absent, the solubility of calcite, dolomite and magnesite is very low. In presence of CO_2 , these compounds are dissolved to calcium and magnesium hydrogen-carbonates (BISKUPIČ, 1991). At pH values above 7.0, calcium, magnesium, and sodium become to leach from soils (BANDEL et al., 2002). Possible anthropogenic sources of calcium and magnesium are some industrial waste waters used in such activities as acid neutralization by lime, calcite, dolomite and magnesite (PITTER, 1999). Concentrations of Ca^{2+} in fresh water range from 0.01 to 0.1 millimolar. High concentrations of calcium and/or magnesium

cations in fresh water cause so called hard water (DUESING, 2005). According to STN 75 7221 (Classification of surface water quality), they belong to the indicators of water surface quality.

As for the quantity, sodium and potassium in natural waters usually follow next calcium and potassium. In waters they occur mainly as simple cations Na^+ and K^+ (TÖLGYESSY et al., 1984). In natural waters with high mineralisation, it is possible that sodium content is higher than that of calcium and magnesium. This is possible for some mineral waters (TÖLGYESSY, MELIČHOVÁ, 2000). Sodium and potassium are released to waters by weathering of some alumino-silicates. Sodium is leached especially from field deposits in high quantities. The natural source of sodium is possibly the exchange of Ca^{2+} and Mg^{2+} ions at interface between water and some clay minerals. The anthropogenic source of sodium and potassium is in sewage waters and some industrial waste waters. The sources of potassium are possibly also flushes of applied potassium fertilizers (PITTER, 1999). From the hygienic viewpoint, they are not important in water. Their allowable concentrations in surface waters are not limited.

Material and methods

The Nature Reserve was established in 1980, and it originally represented a wetland with an area of about 140 ha. The actual area is 74.69 ha, at an altitude of 132–133 m asl. Geographic coordinates are: 48°12' N and 18°19' E. As for the climate, the territory belongs to the warm and dry region with mild winter and an average annual temperature of 9.5 °C. The annual precipitation total represents 600 mm. In term of geology, the research area belongs to older Quaternary (Pleistocene). This area is created by extensive ground level of Pleistocene sediments, primarily calcium loess, which provide a base rock (bedrock) for large amounts of soil. The territory of the Reserve comprises parts of three cadastral zones belonging to the villages of Maňa, Kmeťovo and Michal' nad Žitavou (district Nové Zámky). The original side channel of the Žitava River, crosses the southern and western part of the territory with a 600 m long segment and belongs to the catchments area of the Žitava River, the bank of the river represents the western boundary. The northern boundary is identical with the boundaries of the districts Nitra and Nové Zámky. The lowest parts in southeast of the considered wetland are typical marshes. The source of water is the surface water of the regulated Žitava River transported through an underground channel, from which the water periodically penetrates onto the wetland surface. By 1994, higher situated, periodically flooded meadows (circa 35 ha) were regularly mowed with machines.

The locality represents a significant habitat, especially because it serves as a foraging and breeding site for several endangered wetland bird species, both nesting and migratory. There have been confirmed 39 at European-level endangered bird species occurring in this area: 7 critical endangered, 16 endangered and 4 migratory (DANKO et al., 1995). The locality represents one of the most significant occurrence localities of the species *Porzana porzana*, *Anas querquedula* and *Circus aeruginosus*. SVOBODOVÁ (1992) confirmed 262 higher plant species, 36 from them were endangered species of the Slovak flora. The critically endangered taxon of a high ecosozological value is *Adonis flammea*, endangered rare taxons are: *Clematis integrifolia*, *Papaver albiflorus*, and *Viola pumila*. From the endangered ones we list here: *Adonis vernalis*, *Carex melanostachya*, *Carex paniculata*, *Catabrosa aquatica*, *Nepeta pannonica*, *Taraxacum palustre*, *Tithymalus salicifolius*, and *Veronica longifolia*. The succession of the main vegetation formation of *Glyceria maxima*, *Typha latifolia* is in progress and has a significant impact on decrease in the nesting bird species. Wood vegetation in the southern part of the Reserve consists of associations and communities of *Salicion albae*, with expanding an invasive North American species – *Negundo aceroides*. At present, the riverine vegetation can only be found on the rest of original, non-regulated flow of Žitava. The dominant woody plants are: *Salix alba*, *Salix fragilis*, *Salix cinera*, *Alnus glutinosa* and *Populus alba*. The shrubs are represented by *Crataegus monogyna*, *Rosa canina* and *Rubus caesius*.

Material sampling and processing

The water from the wetland was sampled regularly, over the whole years 2003–2005, monthly, always about the date of the 15th. The layout of the sampling sites system was proposed in such a way as to obtain the best possible data for evaluation of the changes in concentrations of bivalent and univalent alkaline cations in dependence on space and time. We have established the following five sites:

1. The beginning of the old original bed of the Žitava River. It is the collection spot of the water transported from the Žitava River through the underground channel to the western part of the Reserve in spring and summer months.
2. Pursuing original meander of the old Žitava River with the protective levee on the southern bank.
3. An open water area, with the water outfall regulated with a floodgate to control the flood water level in the southeastern part of the Reserve.
4. and 5. The sampling sites situated on the open water area in the southeastern part of the wetland, with marshy character, adjacent to a road.



Sampling site 1



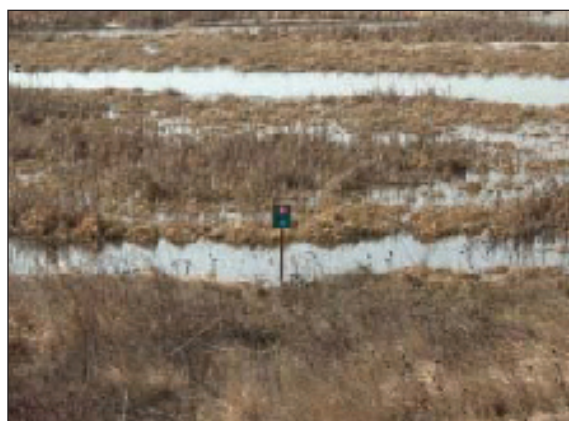
Sampling site 2



Sampling site 3



Sampling site 4



Sampling site 5

In water samples collected the magnesium concentration was determined by the atomic absorption spectrophotometry, and calcium, sodium and potassium concentrations were determined by the flame-metric method. Ca^{2+} and Mg^{2+} are the only alkaline cations indicating the water quality, therefore the water in the sampling sites was ranked in the categories of surface water quality only based on these two indicators. It was performed by comparison of the calculated characteristic Ca^{2+} and Mg^{2+} values and the corresponding system of limit values which are stated by the STN 75 7221 (Classification of the surface water quality). The calculation of Na^+ and K^+ characteristic values was

not realized because, according to the Slovak Technical Standard 75 7221, they are not included as water quality indicators.

Results and discussion

The mean alkaline cations concentrations of Ca^{2+} , Mg^{2+} , Na^+ and K^+ in the NR Žitavský luh in the monitored years and over the whole research period are summarised in Table 1, their shares on the bulk amounts of alkaline cations in monitored years and over the whole research period in percent are in Table 2.

Table 1. The mean alkaline cations concentrations in water of Žitavský luh in monitored years and over the whole research period

Year	Indicator (mg dm^{-3})			
	Ca	Mg	Na	K
2003	62.8	29.7	22.87	8.43
2004	52.28	16.7	21.54	7.7
2005	68.67	27.81	25.61	9.05
Average	61.25	24.74	23.34	8.39

Table 2. Relative representation of alkaline cations in percentage on the whole sum of alkaline cations in wetland in monitored years and over the whole research period

Year (1)	Sum $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ (mg dm^{-3}) (2)	Percentage share of individual cations from the sum $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ (3)			
		% Ca^{2+}	% Mg^{2+}	% Na^+	% K^+
2003	123.8	50.72	23.99	18.47	6.81
2004	98.22	53.22	17	21.93	7.84
2005	131.14	52.36	21.21	19.53	6.9
Average (4)	117.72	52.03	21.02	19.83	7.13

From the data obtained it follows that the quantitatively dominant alkaline cation in the wetland water was calcium because its share in the whole sum of $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ (mg dm^{-3}) ranged from 50.72 (2003) to 53.22% (2004), and the mean share of calcium in the total sum of alkaline cations for the whole monitored period represented 52.03%.

It agrees with opinions of many other authors, according to whom calcium is determinative in water of the Danube branch system (DUBOVÁ and BUBLINEC, 1996) and in the water course Hostianský stream (NOSKOVIČ et al., 2003). Similarly, BENDELL-YOUNG and PICK (1996) confirmed the same relative importance of alkaline cations (Ca/Mg/Na/K) with Ca^{2+} as dominant in mineral-rich fens, moderately-poor fens and mineral-poor fens, too. Mean Ca^{2+} concentrations in the monitored years ranged from 52.28 (2004) to 68.67 mg dm^{-3} (2005). The mean Ca^{2+} concentration over the whole research period represented 61.25 mg dm^{-3} .

Over the whole monitoring period, there were found no regular seasonal trends in calcium concentrations depending on the sampling time. The highest mean concentration over the monitored period occurred in March 2003. In this month, the maximum mean calcium concentration for the whole research period was obtained (75.61 mg dm^{-3}). It corresponds to the beginning of water supply to the Reserve from the Žitava River; therefore, Žitava can be considered as the main source of Ca^{2+} entering the wetland (Fig. 1). Mean calcium concentration over the whole research period varied in dependence on the sampling time, from 53.40 (January) to 75.61 mg dm^{-3} (March).

An interesting finding is that the trend in changes of mean calcium concentrations is very similar to the trend in mean magnesium concentrations over the monitoring period (Fig. 2).

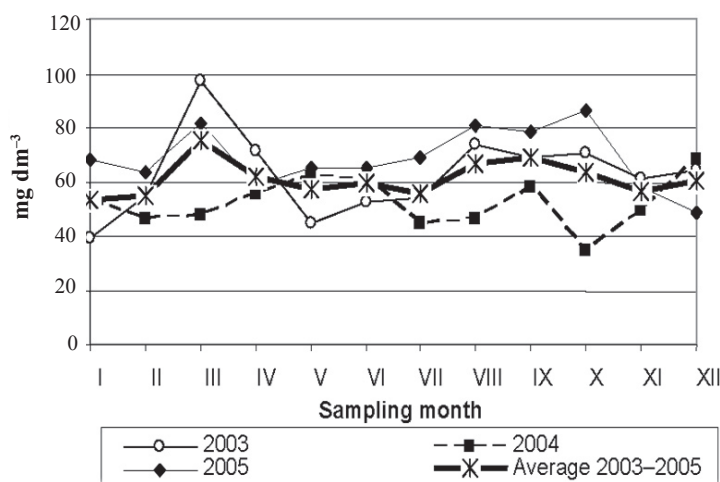


Fig. 1. Dynamics of the mean Ca^{2+} concentrations in wetland in monitored years 2003–2005

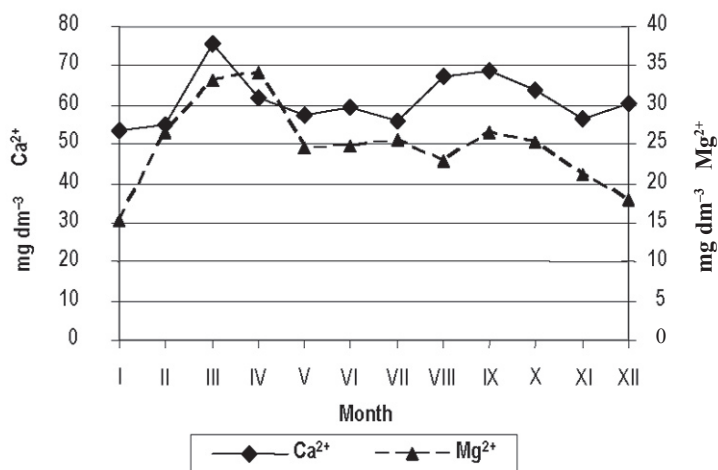


Fig. 2. Dynamics of the mean Ca^{2+} and Mg^{2+} concentrations depending on the sampling time

The sampling site had not significant effect on the changes in calcium concentrations. The lowest mean Ca^{2+} concentrations in dependence on the sampling site were recorded in sampling site No. 3 (58.73 mg dm^{-3}) by 17 (2004) to 23.99% (2003), with the mean of 21.02% over the whole monitored period (Table 2). The weight ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in the individual years was **2.11/1** (2003), **3.13/1** (2004) and **2.47/1** (2005), over the whole monitored period it was **2.48/1**. It corresponds to data reported by GÁBRIŠ et al. (1998), TÖLGYESSY and MELICHOVÁ (2000), according to whom the weight ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in natural waters varies from 4/1 to 2/1. The mean magnesium concentration over the whole research period represented 24.74 mg dm^{-3} and its mean values ranged from 16.7 (2004) to 29.7 mg dm^{-3} (2003) (Table 1).

From the viewpoint of quantitative abundance, the second most abundant alkaline cation was magnesium, sharing on the total sum of $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}$ (mg dm^{-3}) by 17 (2004) to 23.99% (2003), with the mean of 21.02% over the whole monitored period (Table 2). The weight ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in the individual years was **2.11/1** (2003), **3.13/1** (2004) and **2.47/1** (2005), over the whole monitored period it was **2.48/1**. It corresponds to data reported by GÁBRIŠ et al. (1998), TÖLGYESSY and MELICHOVÁ (2000), according to whom the weight ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in natural waters varies from 4/1 to 2/1. The mean magnesium concentration over the whole research period represented 24.74 mg dm^{-3} and its mean values ranged from 16.7 (2004) to 29.7 mg dm^{-3} (2003) (Table 1).

On the basis of the calculated characteristic values of calcium (Table 3) according to the STN 75 7221, the water of all sampling sites was ranked into the 2nd class of the water surface quality (clean water).

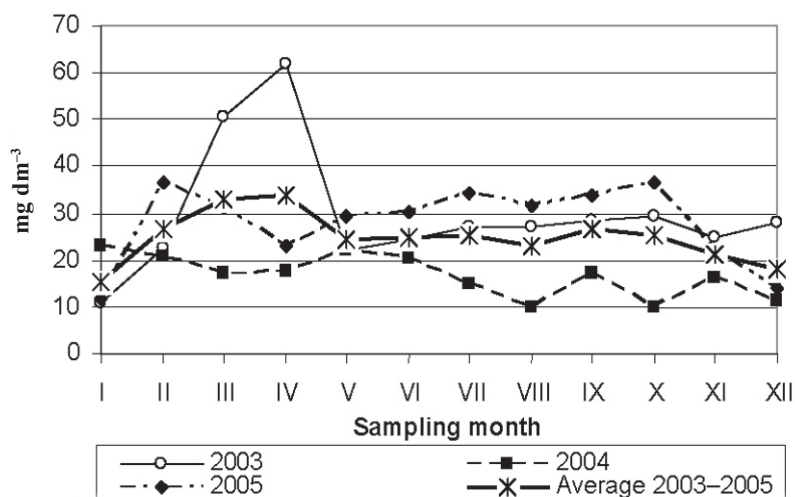


Fig. 3. Dynamics of the mean Mg^{2+} concentrations in wetland in monitored years 2003–2005

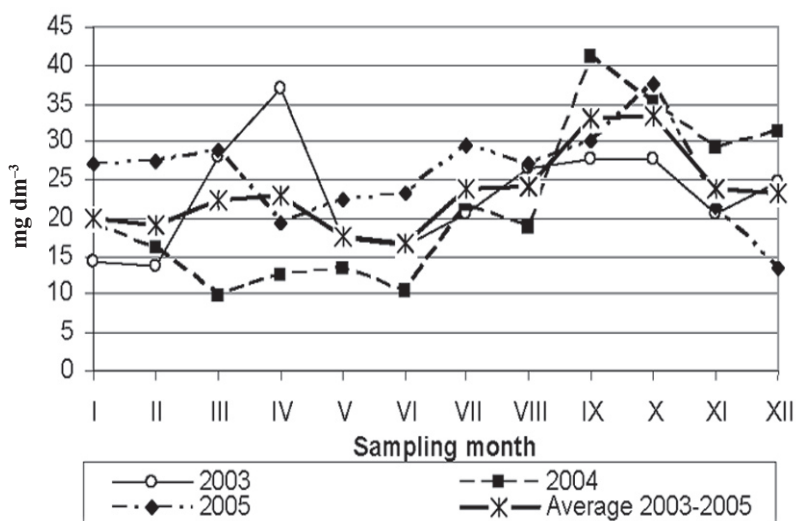


Fig. 4. Dynamics of the mean Na^{+} concentrations in wetland in monitored years 2003–2005

The Mg^{2+} concentration in the years of experiment was changing in dependence on sampling time, but seasonal regularity in its dynamics was not manifested. The highest mean concentration of this cation over the whole research period was identified in April (34.05 mg dm^{-3}), the lowest one in January (15.19 mg dm^{-3}) (Fig. 3).

As for the sampling site, the lowest mean magnesium concentration was 15.31 mg dm^{-3} at sampling site No. 2, the highest was 32.63 mg dm^{-3} at sampling site No. 2, too (Fig. 6). Because there did not occur anthropogenic sources of pollution with calcium and magnesium in the Reserve, we can hypothesise about their natural origin in the wetland, partly from the geologic bedrock, consisting of layers of Pleistocene sediments – mainly calcium loess; partly from the soil itself – the surrounding soils are rich in basic cations.

The characteristic values of magnesium (Table 3) calculated according to the STN 75 7221 classified the water in all sampling sites into the 2nd class of water surface quality (clean water).

Univalent alkaline sodium and potassium cations occurred in water in lower concentrations than bivalent calcium and magnesium cations. The mean share of Na^+ on the whole cation sum $Ca^{2+} + Mg^{2+} + Na^+ + K^+$ (mg dm^{-3}) over the whole monitored period was 19.83%. The share of K^+ represented 7.13% (Table 2). The weight ratio of Na^+/K^+ varied from 2.71/1 (2003) to 2.83/1 (2005) and its mean over the whole monitored period equalled to 2.78/1. Higher concentrations of sodium compared to potassium in water were also confirmed by VALTÝNI and LALKOVIČ, 1995; DUBOVÁ and BUBLINEC, 1996; DUBOVÁ, 1998. According to PITTER (1999), biological and physical-chemical sorption of potassium in soil is much

more intensive than sodium sorption; therefore (hence) potassium concentration in waters is lower, except that it can be transformed into non-exchangeable forms in soil (HUDCOVÁ and SÍROVÝ, 1978). BENDELL-YOUNG and PICK (1996) determined by the comparison of the relative importance of Ca/Mg/Na/K for the various bedrock types as well as for the exchangeable cation presence in soils that the relative occurrence of base cations in waters of wetlands is very similar to the exchangeable cation concentration in the surrounding soils.

The mean Na^+ concentration in the monitored years moved from 21.54 in 2004 to 25.61 mg dm^{-3} in 2005, and mean K^+ concentration from 7.7 in the year 2004 to 9.05 mg dm^{-3} in the year 2005. Over the monitored period, the mean sodium concentration was 23.34 and potassium concentration was 8.39 mg dm^{-3} (Table 1). Maximum mean Na^+ concentration over the monitored period was found in October (33.5 mg dm^{-3}) (Fig. 4), and maximum K^+ in November (11.4 mg dm^{-3}) (Fig. 5). The lowest mean values of Na^+ were recorded in June (16.66 mg dm^{-3}), K^+ in April (5.75 mg dm^{-3}).

In term of the sampling site, the concentration of both univalent cations was moving approximately at the same level, so dependency of their concentrations on the sampling sites was not manifested (Fig. 6). This finding also supports their natural origin.

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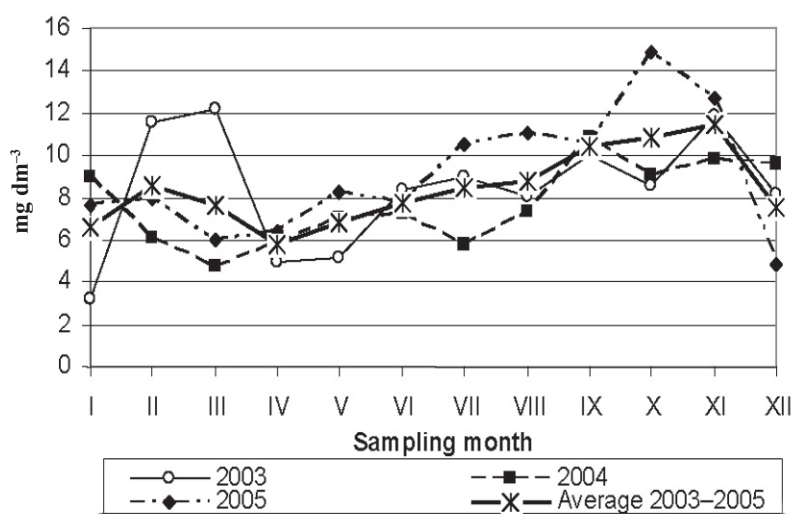


Fig. 5. Dynamics of the mean K^+ concentrations in wetland in monitored years 2003–2005

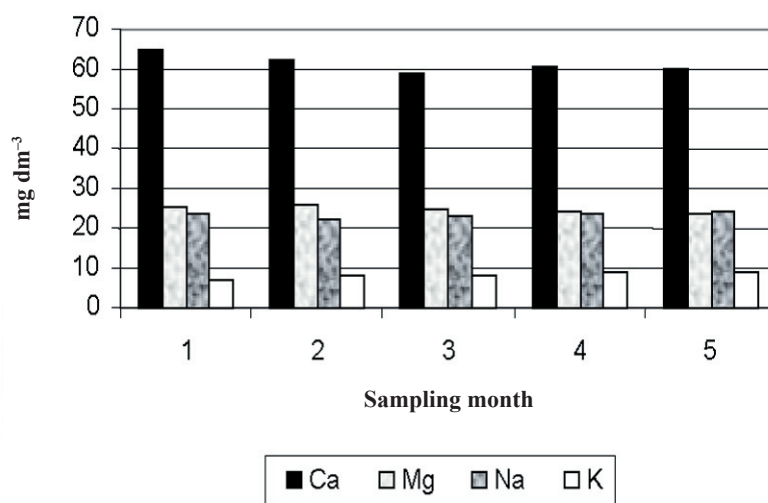


Fig. 6. Mean cations concentrations over the years 2003–2005 depending on sampling site

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Hodnotenie koncentrácií dvojmocných a jednomocných bázických katiónov vo vode prírodnej rezervácie Žitavský luh – mokrad'

Súhrn

Vo vode prírodnej rezervácie (PR), ktorá je mokrad'ou sa v rokoch 2003–2005 hodnotili koncentrácie dvojmocných a jednomocných bázických katiónov. Na základe získaných výsledkov môžeme konštatovať, že obsah bázických katiónov vo vode mokrade bol v poradí $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. Priemerný podiel vápnika na celkovej sume bázických katiónov za celé sledované obdobie bol 52,03 %, horčíka 21,02 %, sodíka 19,83 % a draslíka 7,13 %. Za celé sledované obdobie bol pomer $\text{Ca}^{2+} : \text{Mg}^{2+} = 2,48 : 1$ a pomer $\text{Na}^+ : \text{K}^+ = 2,78 : 1$. Sezónna zákonitosť v dynamike koncentrácií bázických katiónov sa v priebehu sledovaného obdobia neprejavila tak ako ani ich závislosť z hľadiska miesta odberu. Vypočítané charakteristické hodnoty vápnika a tiež horčíka zaraďujú vodu vo všetkých odberových miestach podľa STN 75 7221 Klasifikácia kvality povrchových vôd do II. triedy kvality (čistá voda). Nakoľko v povodí rieky Žitavy sa nenachádzajú antropogénne zdroje znečisťovania vápnikom a horčíkom, môžeme konštatovať, že ich pôvod vo vode luhu bol prírodného charakteru, a to jednak z geologického podložia, ktoré je tvorené vrstvami pleistocénnych sedimentov – hlavne vápenatých spraší ako aj pedogénneho charakteru – tvorený skladbou základných katiónov okolitých pôd.