

TIME AND PLACE CHANGES OF CHLORIDES CONCENTRATIONS IN THE SOUTHWESTERN PART OF THE SLOVAK REPUBLIC

J. NOSKOVIČ, Mária BABOŠOVÁ, Jana PORHAJAŠOVÁ, Alena RAKOVSKÁ, Terézia ČERYOVÁ

*Department of Environmental Science and Zoology, Faculty of Agrobiolgy and Food Resources
Slovak University of Agriculture in Nitra, Tr. A. Hlinku 2, 949 76 Nitra
Slovak Republic
Jaroslav.Noskovic@uniag.sk*

Abstract: In the years 2005-2010 concentrations of chlorides in the water flow Čaradice brook were evaluated. For their determination we used measuring method according to Mohr. Čaradice brook springs in the mountains of Pohronský Inovec in the southern foot of Drienka hill and it is the right tributary of the Hron River, into which mouth near the village Kozárovce. Its length is 11.1 km. Samples of the water in longitudinal profile of the watercourse were carried out from six sampling sites, on a regular basis, in the second decade of the month. The places of taking samples were localized to include all real sources causing the pollution of watercourse. Seasonal dynamics regularity of concentrations of chlorides during the whole monitored period is not reflected. The average concentration of chlorides in the monitored period ranged from 12.52 (year 2010) to 28.01 (year 2007) mg dm^{-3} and for the whole period represented value of 20.54 mg dm^{-3} . Depending on the time of sampling the lowest average concentrations for the whole monitored period in spring season were recorded, with a minimum average value in the month of March (13.93 mg dm^{-3}). From that month occurs generally gradual increase in chloride concentration until the month of October, when we found the highest average concentration in the water flow throughout the period (23.35 mg dm^{-3}). Effect of sampling sites on the chloride concentration in the water flow was as significant as the influence of the month. In the longitudinal profile of the watercourse, we recorded the tendency of its gradual increase in concentration from the first (12.06 mg dm^{-3}) to the last sampling site near village Kozárovce (27.46 mg dm^{-3}). Low concentrations in first and second sampling site are likely related to the fact that the sampling sites were located near the natural ecosystems (forest ecosystem and agroecosystem of permanent grassland). Their most significant increase in the water flow near villages' Čaradice and Kozárovce was recorded. It can be assumed that the increase in Cl⁻ values in mentioned sampling sites is probably due to the fact that villages do not have drainage networks or wastewater treatment. In the regulation of the Government of the Slovak republic No. 269/2010 Coll. the recommended value for chlorides is 200 mg dm^{-3} . Calculated values of 90-th percentile (P90) of this indicator in all sampling sites were lower than the recommended value of government regulations.

Key words: chlorides, Slovak Republik, water flow, water quality.

INTRODUCTION

The most widespread form of chlorine compounds is chlorides which are present in the water predominantly as simple anion Cl⁻ (PITTER, 2009). Along with hydrogen carbonate and sulphates are major anions in waters (RAO, 2008). Into the water are getting by weathering and leaching of rocks. In waters are chemically and biochemically stable (BARANČÍKOVÁ et al. 2009). On the solid phases are absorbed only to small extent, therefore are easy drift out from soil. With increasing degree of mineralization of water their content increases (PITTER, 1999). In natural waters are in very low concentrations (RAO, 2008). Their natural resources may be rainfall or geologic bedrock containing chloride (MASHBURN, 2004). Chloride concentration can be affected by anthropogenic activities. Higher content often indicates fecal contamination of water (STREĎANSKÝ, 2010, NOLLET et al., 2013). In surface waters is usually their concentration in amount of 10 to 100 mg dm^{-3} (DIMKIC et al., 2008). Into the watercourses are

receiving from different sources including natural mineral resources, agriculture, irrigation systems, water runoff from cities due to use of road salt, sewage and industrial waste water (TWORT, 2001). Chlorides are hygienically clean in waters but at higher concentrations affect the taste of water (BISKUPIČ, 1991).

MATERIAL AND METHODS

Čaradice brook springs in the mountains of Pohronský Inovec in the southern foot of the hill Drienka (751.1 m) at an altitude of about 600 above sea level. The brook flows through the territories of Zlaté Moravce and Levice districts. It is a right tributary of the river Hron, its length is 11.1 km. Near the village of Kozárovce a uniform reservoir called "Dam" was built, which is located between the villages Čaradice and Kozárovce. It is used for irrigation and sports fishing. From the right, from the area of Sejovský hill (295.2 m above the sea level) flows the largest tributary of Čaradice brook - the Svätý brook, from the left side it has only short tributaries. The flow direction is predominantly north-south, on the lower reaches northeast. Čaradice creek flows into the river Hron near the village Kozárovce, in the area called Slovak gates, at an altitude of about 174 above sea level in relation to hydrographic conditions. Čaradice stream flows in the uplands - lowland area which is characterized by the type of rainsnow runoff with the highest flow rate in March and lowest in the month of September. According to the geological characteristics of the soil it has been shaped over the several stages of volcanic activity with rotation periods of destruction and denudation of volcanic complexes. Andesine, rhyolite and basalt neovolcanites are interspersed there (Konečný, 1998). The territory belongs to the warm area and slightly dry subarea. The average temperature in 2005 was 9.1 °C, in 2006-9.7 °C - 8.9 °C in 2007, in 2008 - 9.4 °C, in 2009 9.8 °C, 2010 - 10.03 °C. The average rainfall in 2005 represented 711.4 mm, in 2006 - 842.7 mm, in 2007-569.8 mm, in 2008 - 679.7 mm, 2009 - 684.4 mm and 687.7 mm in 2010 (source: Kozárovce precipitation measuring stations). In the upper segment of the river basin watercourse forest ecosystems and permanent grassland are situated. The greater part of the stream flows through the agroecosystem of agricultural crops on the arable land. In terms of agro-productions the territory ranks to the corn - sugar beet region. Plant production is focused mainly on cereals growing (wheat, winter rye, and spring barley, maize for grain and for silage), perennial forage crops (Lucerne) and oilseeds (rapeseed, sunflower). Livestock production is oriented on the cattle breeding. Farmed land near the watercourse belongs to the cadastre of the agricultural cooperative of Volkovce. During the monitored period industrial fertilizers were applied such as urea (N = 46 %), the DAM 390 (N = 30 %), NPK 15 : 15 : 15 at a dose of 200 kg.ha⁻¹ (N = 12 %, P₂O₅ = 19 %, K₂O = 19 %), LAV - 350 kg.ha⁻¹ (N = 27 %), DASA - 250 kg.ha⁻¹ (N = 26 %, S = 13 %). Nitrogenous fertilizers were applied in the average batch 138 kg.ha⁻¹.year⁻¹, phosphate 39 kg ha⁻¹.year⁻¹ and potassium at a dose of 6.01 kg ha⁻¹ year⁻¹. In the fall of 2008 2 t.ha⁻¹ of ground limestone were injected. Out of organic fertilizers manure was applied under the roots at a dose of 40 t.ha⁻¹.year⁻¹ (source: Volkovce Agricultural Cooperative). Samples of the water from Čaradice brook were carried out on a regular basis, in the second decade of the month in the years 2005 - 2010. The places of taking samples were localized in a longitudinal profile of the watercourse to include all sources causing the changes of dissolved oxygen concentration. Samples of water were collected from six sampling sites. Water samples were taken from the middle of the main stream.

- **1st sampling site** - the forest ecosystem Pohronský Inovec, 48° 22' 56" north latitude and 18° 29' 7.3" east longitude.
- **2nd sampling site** - in the north point of Čaradice, 48° 21' 9.1" north latitude and 18° 30' 53" east longitude.

- **3rd sampling site** – in the south point of Čaradice, 48° 21' 35" north latitude and 18° 30' 55" east longitude.
- **4th sampling site** - before the water tank, 48° 19' 8.2" north latitude and 18° 30' 50" east longitude.
- **5th sampling site** – behind the water reservoir in the north point of Kozárovce, 48° 19' 7.4" north latitude and 18° 30' 50" east longitude.
- **6th sampling site** – in the south point of Kozárovce, 48° 18' 7.7" north latitude and 18° 32' 25" east longitude.

In the collected samplings of water we used for their determination measuring method according to Mohr. Values of Cl⁻ have expressed in mg dm⁻³.

To the evaluation of the quality of surface water in the sampling sites under the indicator Cl⁻ we used the values of the 90-th percentile (P90), it was calculated from the measured values and then compared with limit values referred in the Regulation of the Government of the Slovak Republic No. 269/2010 Coll.

RESULTS AND DISCUSSION

The average concentration of chlorides in the monitored period ranged from 12.52 (year 2010) to 28.01 (year 2007) mg dm⁻³ and for the whole period represented value of 20.54 mg dm⁻³. The slightly lower average concentration of chloride (18.84 mg dm⁻³) in the water flow Čerešnový brook between years 2002-2004 found NOSKOVIČ et al. (2008) and HRUŠKA et al. (2006) in small forest catchment in Modrý dol in Krkonoše during the years 1994-2002 (18.10 mg dm⁻³). Seasonal dynamics regularity of concentrations of chlorides during the whole monitored period is not reflected.

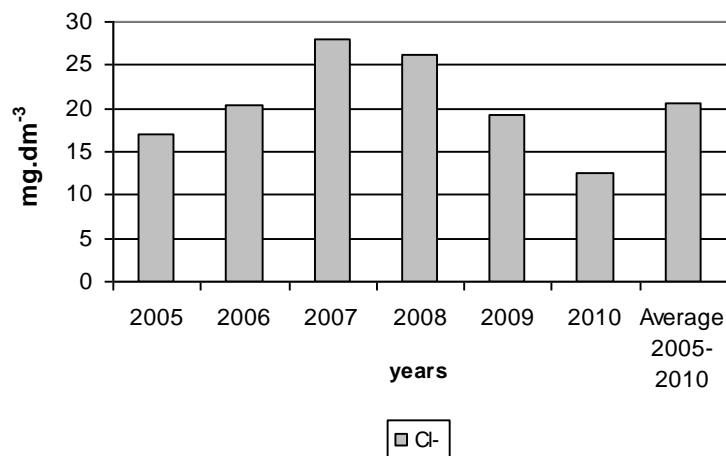


Fig. 1 Average concentration of Cl⁻ (mg dm⁻³) in the water of Čaradice brook in years 2005 – 2010

Depending on the time of sampling the lowest average concentrations for the whole monitored period in spring season were recorded (fig.2) with a minimum average value in the month of March (13.93 mg dm⁻³). The decrease in concentration could be due to higher flow of water in the water course (fig. 3), it is probably connected with the snow melt in its catchment. From that month occurs generally gradual increase in chloride concentration until the month of October, when we found their highest average concentration in the water flow throughout the

period (23.35 mg dm^{-3}). By ĎURIČKOVÁ (2011) increasing of chlorides concentrations in the water course is associated with decrease in flow of water.

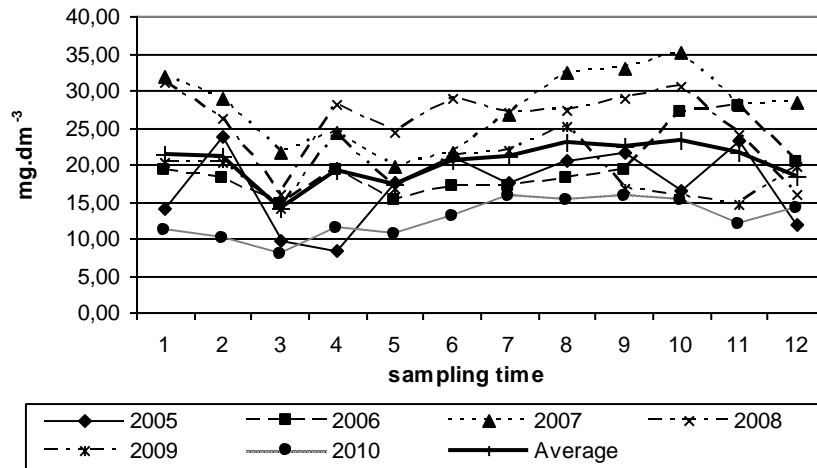


Fig. 2 Average concentration of Cl^- (mg dm^{-3}) depending on time of sampling

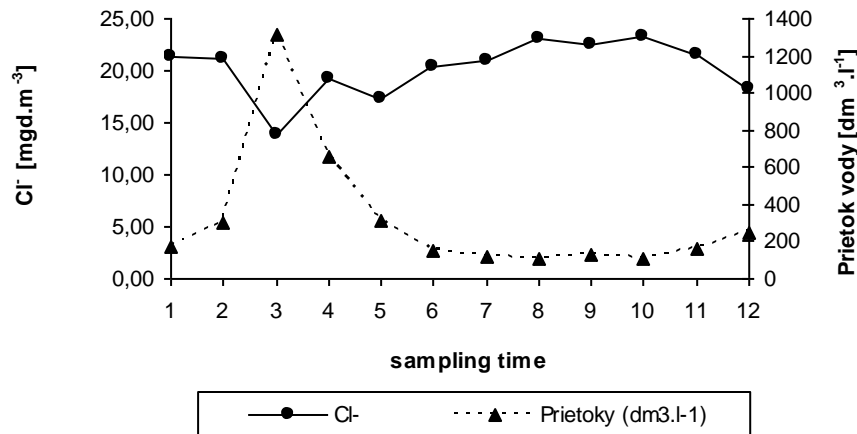


Fig.3 the relationship between the concentration of Cl^- (mg dm^{-3}) and flow of water ($\text{dm}^3 \text{l}^{-1}$)

The chloride concentration was affected by sampling sites (fig. 4). In the longitudinal profile of the watercourse, we recorded the tendency of its gradual increase in concentration from the first (12.06 mg dm^{-3}) to the last sampling site near the village Kozárovce (27.46 mg dm^{-3}). Low concentrations in first and second sampling site are likely related to the fact that the sampling sites were located near the natural ecosystems (forest ecosystem and agroecosystem of permanent grassland) which were not affected by anthropogenic pollution sources. Steele, AITKENHEAD-PETERSON (2011) indicate that the major sources of Cl^- in surface water are domestic waste water, especially human faeces (urine) and runoff from winter road salting. This is confirmed by us identified the most significant increase in their concentrations near the

villages' Čaradice and Kozárovce that do not have drainage networks and sewage treatment. In the sampling site no. 2 (near the village Čaradice) compare with the sampling site no. 3 (below the village Čaradice) their concentration increased by 6.38 mg dm^{-3} (ie 28.31 %). Slight increase in the concentration of Cl^- we recorded in the sampling site no. 4 located near agroecosystems of agricultural crops on arable land, near the water reservoir Priehrada. NOLLET et al. (2013) states that flushing soil by water erosion into the watercourses their concentration increases. By PITTER (2009) chlorides easy leach from soil and in the water environment are chemically and biochemically stable.

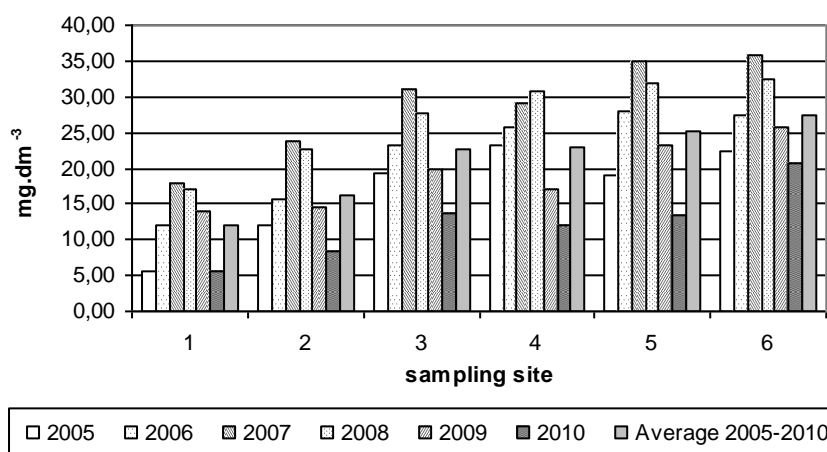


Fig. 4 Average concentration of Cl^- (mg dm^{-3}) depending on sampling site

In the regulation of the Government of the Slovak republic No. 269/2010 Coll. the recommended value for chlorides is 200 mg dm^{-3} . Calculated values of 90-th percentile (P90) of this indicator in all sampling sites were lower than the recommended value of government regulations.

CONCLUSION

In the water of Čaradice brook which springs in the mountains of Pohronský Inovec in the southwestern part of the Slovak Republic, during years 2005 – 2010 we evaluated the chloride concentration. Their average concentration for the whole period represented value of 20.54 mg dm^{-3} . Depending on the time of sampling the lowest average concentrations in spring season were recorded, with a minimum average value in the month of March (13.93 mg dm^{-3}), it was probably due to higher flow of water in the water course. The highest average concentration in the month of October (23.35 mg dm^{-3}) was found. During the whole monitored period seasonal dynamics regularity of its concentrations is not reflected. In the longitudinal profile of the watercourse, we recorded the tendency of its gradual increase in concentration from the first (12.06 mg.dm^{-3}) to the last sampling site near the village Kozárovce (27.46 mg.dm^{-3}). The lowest we found in sampling sites located near the natural ecosystems (forest ecosystem and agroecosystem of permanent grassland), which was not affected by anthropogenic source of pollution. The most significant increase of concentration of Cl^- near villages' Čaradice and Kozárovce was recorded, that villages do not have drainage networks or wastewater treatment. Base on the calculated values of 90-th percentile (P90) of

this indicator we found that in all sampling sites were lower values than the recommended value of government regulations.

Acknowledgement: *This research was supported by the grant project VEGA 1/0513/12 „Research of agro-ecosystems for mitigate climatic change, production of bio-products and improve of nutritional and health parameters of the people“.*

BIBLIOGRAPHY

1. BARANČIKOVÁ, G., FAZEKAŠOVÁ, D., MANKO, P., TORMA, S., 2009. *Chémia životného prostredia*. Prešov, 2009, 251 s., ISBN 978-80-555-0082-9.
2. BISKUPIČ, F. 1991. *Chémia vody*. Bratislava: Slovenská technická univerzita, 1991, 160 s. ISBN 80-227-0447-4.
3. DIMKIC, M. A. et al., 2008. *Groundwater Management in Large River Basins*, Intl Water Assn, 704 p. ISBN 978-1843391906.
4. ĎURIČKOVÁ, A., 2011. Hodnotenie kvality vody v Dunaji. In: IX. Konferencia mladých vodohospodárov, ZZVH Banská Bystrica, 2010.
5. HRUŠKA, J., MAJER, V., FOTTOVÁ, D., 2006. Vliv kyslé Depozice na chemizmus povrchových vod v Krkonoších. In: *Opera Cocotoca*, 43, 2006, s. 95 – 110.
6. KONEČNÝ, V., 1998. *Vysvetlivky ku geologickej mape Štiavnických vrchov a Pohronského Inovca (štiavnické stratovulkány)*. Geologická služba Slovenskej republiky. Vydavateľstvo Dioníza Štúra, Bratislava, 1998, 473 s.
7. MASHBURN, S. L., 2004. Chlorine in ground water and surface water in the vicinity of selected surface water sampling sites of the Beneficial Use Monitoring Program of Oklahoma, University of Michigan Library, 52 p.
8. Nariadenie vlády SR č. 269/2010 Z. z., ktorým sa ustanovujú požiadavky na dosiahnutie dobrého stavu vôd.
9. NOLLET, L. M.L., DE GELDER, L. S. P. 2013. *Handbook of Water Analysis*, 3. Edition, CRC Press, 995 p. ISBN 978-1-4398-8964-0.
10. NOSKOVIČ, J. et al., 2008. Monitorovanie a hodnotenie koncentrácií chloridov a síranov vo vodnom toku Čerešňový potok. In *Acta Hydrologica Slovaca*, vol. 9, no. 2, pp. 179-185, ISSN 1335-6291.
11. PITTEK, P., 1999. *Hydrochemie*. VŠCHT Praha, 1999, 568 s., ISBN 80-7080-340-1.
12. PITTEK, P., 2009. *Hydrochemie*. 4th ed. VŠCHT Praha, 2009, 568 s., ISBN 978-80-7080-701-9.
13. RAO, A. A., 2008. *Chemistry of Water*. 1st. edition, New Age International Pvt Ltd Publishers, 424 p. ISBN 978-8122423617.
14. STEELE, M. K., AITKENHEAD-PETERSON, J. S., 2011. Longterm sodium chloridesurfacewater expots the Dallas/fort Worth region, *Science of The Total Environment*, Vol. 409, Issue 16, 2011, p. 3021 – 3032.
15. STREĎANSKÝ, J., 2010. *Hodnotenie kvality životného prostredia*. 1. vydanie. Slovenská poľnohospodárska univerzita Nitra, 2010, 125 s. ISBN 978-80-552-0423-9.
16. TWORT, A. C., RATNAYAKA, D. D., BRANDT, M. J., 2001. *Water supply*, 5th edition, Butterworth - Heinemann, Elsevier, Oxford, UK, 669p. ISBN 978-0-340-72018-9.