

## CONCENTRATION ASSESSMENT OF ORGANIC SUBSTANCES IN A WATER FLOW IN THE SOUTHWESTERN PART OF THE SLOVAK REPUBLIC

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**Abstract:** In the years 2005-2010 concentrations of organic substances in the water flow Čaradice brook were evaluated. For their determination we used an indirect method based on the oxidation of organic matter by potassium dichromate, which is known as chemical oxygen demand by potassium dichromate ( $COD_{cr}$ ), which are oxidized almost all organic substances contained in the water. The watercourse 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 a 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 regularity of dynamics of concentrations of organic substances during the whole monitored period is not reflected. The average concentration of  $COD_{cr}$  in the monitored period ranged from 56.55 (2005) to 66.48 (2006)  $mg\ O_2\ dm^{-3}$ . For the whole period represented value of 64.11  $mg\ O_2\ dm^{-3}$ . Depending on the time of sampling the lowest average concentration for the whole monitored period in winter were recorded, with a minimum value in February (57.08  $mg\ O_2\ dm^{-3}$ ). The highest average concentrations in summer were found, with maximum value in July (72.64  $mg\ O_2\ dm^{-3}$ ). Increase of values of chemical oxygen demand in the summer period is probably related to increasing water temperature, accumulation of organic matter and its intense microbial decomposition. Effect of sampling sites was as significant as the influence of the month. The highest average value for the whole monitored period was in sampling sites situated near Čaradice village (61.33  $mg\ O_2\ mg^{-3}$ ) and Kozárovce village (61.71  $mg\ O_2\ mg^{-3}$ ), which can be considered as major source of organic pollution of water by sewage waste water. The second most significant increase near the water reservoir was found. Can be assumed that the increase in the values of  $COD_{cr}$  in that sampling site is probably related to the release of organic matter from sediment in the water reservoir, into which they got from the basin of the water flow. In the regulation of the Government of the Slovak republic No. 269/2010 Coll. the recommended value for  $COD_{cr}$  is 35  $mg\ O_2\ dm^{-3}$ . Calculated values of 90-th percentile (P90) of this indicator in all sampling locations were higher than the recommended value of government regulations.

**Key words:** organic substances, Slovak Republic, water flow, water quality.

### INTRODUCTION

Organic substances in the water can be natural or anthropogenic origin. A significant part of the surface water is natural organic substances (PIVOKONSKÝ et al., 2006). To establish of organic substances the most expanded are indirect laboratory methods based on the biological or chemical oxidation of organic matter in the water – determination of chemical oxygen demand (PITTER, 2009). On the basis of the oxidizing agent may be chemical oxygen demand determinate by dichromate or permanganate method (WITTLINGEROVÁ ET JONÁŠ, 2004, STREĎANSKÝ, 2010). Origin of organic matter in the surface waters is very diverse. Natural organic pollution of natural waters cause extracts from soil and sediments, life activity

products of plant and animal organisms living in water, growth substances, vitamins and enzymes (AMBROŽOVÁ, 2003). Cause of artificial organic pollution is the human factor and its civilizing activity related to the production of enormous amounts of chemical and organic waste. Organic substances have an impact on the quality and properties of the natural waters. Many organic compounds of anthropogenic origin entering to the hydrosphere are toxic and may exhibit carcinogenic, mutagenic and teratogenic effects. Other negatively affects the oxygen balance of the flow or organoleptic properties of water (BARANČIKOVÁ, et al., 2009).

#### **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 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<sup>-1</sup>year<sup>-1</sup>. In the fall of 2008 2 t ha<sup>-1</sup> of ground limestone were injected. Out of organic fertilizers manure was applied under the roots at a dose of 40 t ha<sup>-1</sup> year<sup>-1</sup> (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' 73" east longitude.
- **2nd sampling site** – in the north point of Čaradice, 48 ° 21 '91" 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 '82" north latitude and 18 ° 30' 50" east longitude.
- **5th sampling site** – behind the water reservoir in the north point of Kozárovce, 48 ° 19 '74" north latitude and 18 ° 30' 50" east longitude.
- **6th sampling site** – in the south point of Kozárovce, 48 ° 18 '77" north latitude and 18 ° 32' 25" east longitude.

In the collected samplings of water the chemical oxygen demand by potassium dichromate ( $\text{COD}_{\text{Cr}}$ ) spectrophotometrically, the method is analogous to the ISO 6060, EPA 410.A. Values of  $\text{COD}_{\text{Cr}}$  have expressed in  $\text{mg O}_2 \text{ dm}^{-3}$ .

To the evaluation of the quality of surface water in the sampling sites under the indicator  $\text{COD}_{\text{Cr}}$  we used the values of the 90-th percentile (P90) 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.

## RESULTS AND DISCUSSION

Average values of  $\text{COD}_{\text{Cr}}$  in the water of Čaradice brook in the years 2005-2010 ranged from 56.55 (2005) to 66.48 (2006) and during the whole monitored period represented 64.11  $\text{mg O}_2 \text{ dm}^{-3}$  (fig. 1). Ďurčíková (2011) on the Danube, Bratislava profile – right bank, found a lower average value (40.0  $\text{mg O}_2 \text{ mg}^{-3}$ ).

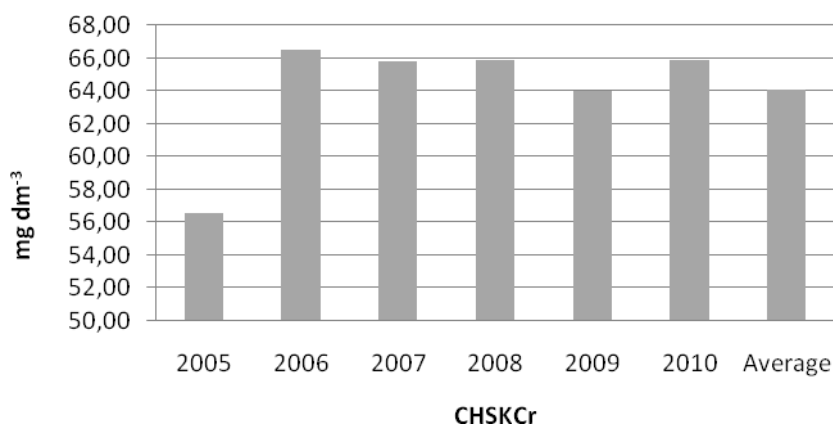


Fig. 1 Average values of  $\text{COD}_{\text{Cr}}$  in the water of Čaradice brook during the years 2005-2010

Depending on the time of collection the lower average values of  $\text{COD}_{\text{Cr}}$  during the whole monitored period in winter and spring period were recorded (fig. 2), with a minimum average value in February (57.08  $\text{mg O}_2 \text{ dm}^{-3}$ ). In that month in the year 2005 its absolute the lowest value (35.50  $\text{mg O}_2 \text{ dm}^{-3}$ ) was measured. Pollution of water of Čaradice stream by

organic substances to be seen the most significantly in the summer months, when they were recorded the highest values of chemical oxygen demand by potassium dichromate. The highest average concentrations in summer were found, with maximum value in July ( $72.64 \text{ mg O}_2 \text{ dm}^{-3}$ ), when in 2008 the highest average value of  $\text{COD}_{\text{Cr}}$  ( $101.0 \text{ mg O}_2 \text{ dm}^{-3}$ ) was measured. Increase of values of chemical oxygen demand in the summer period is probably related to increasing of water temperature, accumulation of organic matter and its intense microbial decomposition. Analogous conclusion of seasonal dynamic of concentration of organic substances also mentioned Pivokonský et al., (2001), Ženišová et al., (2005) and Šulvová et al., (2009). Seasonal regularity of dynamics of concentrations of organic substances during the whole monitored period is not reflected.

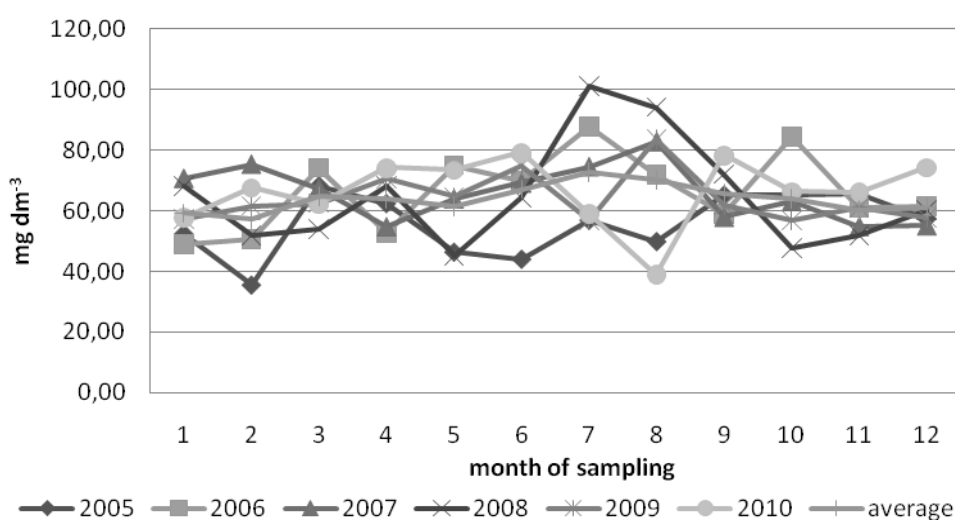


Fig. 2 Average values of  $\text{COD}_{\text{Cr}}$  depending on the time of sampling

Effect of sampling sites was as significant as the influence of the month (fig.3) The highest average value for the whole monitored period was in sampling sites situated near Čaradice village ( $61.33 \text{ mg O}_2 \text{ mg}^{-3}$ ) and Kozárovce village ( $61.71 \text{ mg O}_2 \text{ mg}^{-3}$ ), which can be considered as major source of organic pollution of water by sewage waste water. This agree with the statement of STŘELCOVEJ et al., (2007) and ŠULVOVEJ et al., (2009), according them the main source of organic pollution of surface water are sewage water originating from urban agglomerations. The second most significant increase near the water reservoir (sampling site 5) was found. Can be assumed that the increase in the values of  $\text{COD}_{\text{Cr}}$  in that sampling site is probably related to the release of organic matter from sediment in the water reservoir, into which they got from the basin of the water flow. Elevation of  $\text{COD}_{\text{Cr}}$  near the water reservoirs of Čerešňový brook also found SOZANSKÝ (2004).

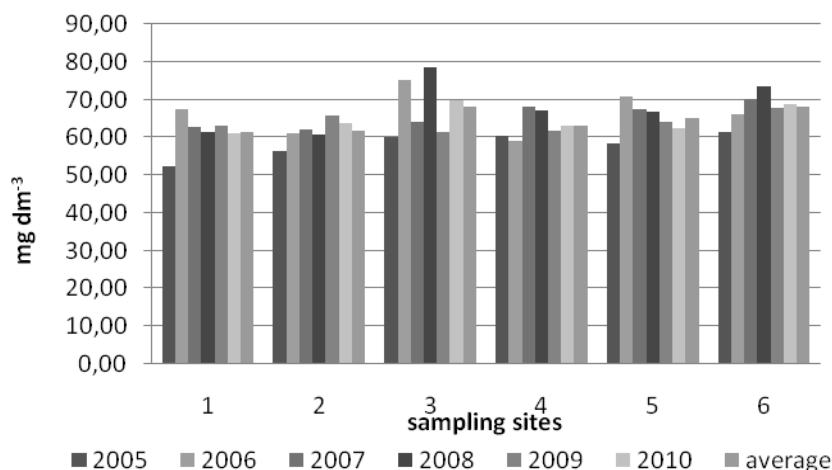


Fig. 3 Average values of COD<sub>Cr</sub> depending on the sampling sites

In the regulation of the Government of the Slovak republic No. 269/2010 Coll. the recommended value for COD<sub>cr</sub> is 35 mg O<sub>2</sub> dm<sup>-3</sup>. Calculated values of 90-th percentile (P90) of this indicator in all sampling locations were higher 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 the years 2005-2010 concentrations of organic substances were evaluated, by indirect method, which is known as chemical oxygen demand by potassium dichromate (COD<sub>Cr</sub>). Its average concentration for the whole period represented value of 64.11 mg O<sub>2</sub> dm<sup>-3</sup>. Depending on the time of sampling the lowest average concentration for the whole monitored period in winter were recorded, with a minimum value in February (57.08 mg O<sub>2</sub> dm<sup>-3</sup>). The highest average concentrations in summer were found, with maximum value in July (72.64 mg O<sub>2</sub> dm<sup>-3</sup>). Depending on the sampling sites the highest average value for the whole monitored period was in sampling sites situated near Čaradice village (61.33 mg O<sub>2</sub> mg<sup>-3</sup>) and Kozárovce village (61.71 mg O<sub>2</sub> mg<sup>-3</sup>), which can be considered as major source of organic pollution of water by sewage waste water. The second most significant increase near the water reservoir was found. Calculated values of 90-th percentile (P90) of this indicator in all sampling locations were higher than the recommended value of government regulations.

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