

Laboratory Analyses of Key Physicochemical Parameters of Targeted Locations of Surface & Ground water and run-off for Protected Water Bodies in Croatia and Serbia in the period December 2018-May 2019

In the period from December 2018 to May 2019, three sampling campaigns were performed in Serbia and Croatia. Sampling campaigns of ground water, surface water and run-off water in the vicinity of Lake Zobnatica and Tompojevacki ritovi were conducted in December 2018, February 2019 and April 2019. Laboratory analyses were performed for selected physicochemical parameters: pH, dissolved oxygen, chemical oxygen demand (COD), biological oxygen demand (BOD₅), total organic carbon (TOC), anions - nitrites (NO₂⁻(aq)) and nitrates (NO₃⁻(aq)), orthophosphates (PO₄³⁻(aq)) and ammonium nitrogen cation (NH₄⁺-N(aq)), total nitrogen and phosphorus, sulfates (SO₄²⁻(aq)), chlorides (Cl⁻(aq)), fluorides (F⁻(aq)), conductivity, total chlorine, phenols and cations of metals (nickel (Ni²⁺(aq)), iron (Fe^{2/3+}(aq)), zinc (Zn²⁺(aq)), chromium (Cr⁶⁺(aq)), copper (Cu²⁺(aq))). All physicochemical parameters were analyzed in Accredited Laboratory for monitoring of landfills, wastewater and air, Department of Environmental Engineering and Occupational Safety, Faculty of technical sciences, University of Novi Sad. The standard EPA and HACH methods were used for all Laboratory measurements - EPA 170.1, EPA 150.1, EPA 120.1, EPA 360.1, EPA 365.3, HACH 8507, HACH 8192, HACH 8155, HACH 8021, HACH 8113, HACH 8023, HACH 8167, HACH 8023, EN ISO 11905-1, Method 8047, Method 8150, Method 8146, Method 8009, Method 8143 and ISO 15705.

Results of surface water analyses in Serbia and Croatia were compared and classified by Regulation on emission limit values of polluting substances in surface and groundwater and deadlines for their achievement (Official Gazette of the RS 50/2012) and Regulation on water classification (77/98 and 137/08), respectively.

Results of ground water analysis in Serbia

Ground water was collected from piezometers B1 to B9. Sampling sites B1, B8 and B9 are located in agricultural area, B2, and B3 are near the Lake. Forest and grass are between B1 and B2, B3 sampling sites. B4 – B7 locations are in green belt area (Figure 1). The sampling procedure was conducted according the Standards SRPS EN ISO 5667-1:2008 (Guidelines for development of sampling programs), SRPS EN ISO 5667-3:2007 (Guidelines for protection and handling of the sample), SRPS EN ISO 5667-6:1997 (Guidelines for abstraction of samples from rivers and streams).



Figure 1. Groundwater sampling sites (B3 and B9) in Serbia

Analysis of key physicochemical parameters in groundwater (B1-B9) was conducted in February and April 2019. High concentrations were obtained for orthophosphates (B9) and total nitrogen (B1, B2, B5, B9) in February 2019 and for conductivity (B2-B8), orthophosphates (B6, B9), ammonium ion (B9) and total nitrogen (B1-B5, B8, B9) in April 2019. Low concentrations of dissolved oxygen (2,63 and 1,54 mg/L) were found in samples from piezometer B9 in both sampling campaigns. In previous sampling period (July – August 2018.), low concentrations of dissolved oxygen and high concentrations of orthophosphates were also noticed. The high values of orthophosphates and total nitrogen indicate pollution from agricultural activities.

Results of surface water analysis in Serbia

Surface water was collected from locations PV1 to PV3. Results of physico-chemical analyses are compared to Regulation on emission limit values of polluting substances in surface and groundwater and deadlines for their achievement (Official Gazette of the RS 50/2012).

According to the results and maximal allowable values Zobnatica Lake can be classified as class III quality water at best (in December 2018. and April 2019.), as moderate ecological status and utilization for bathing and recreation, irrigation and industrial use. The results obtained in February 2019. indicated class V water quality (orthophosphates), with high trophic state and bad eco-status. In the previous period (July 2018.), the water quality also belonged to class V, however the parameter which indicated bad eco-status was pH value.

Results of run-off water analysis in Serbia

Run-off water from the agricultural fields was collected at locations K-a to K-f. Sampling sites are presented in Figure 2.



Figure 2. Run off water sampling sites (K-a, K-d, K-c) in Serbia

High concentrations of orthophosphates up to 1,592 mg/L were measured in all sampling campaigns and indicate run off from agricultural land especially at sampling site K-b. The total nitrogen was measured in high concentrations from 12,59 to 73,26 mg/L (K-a, K-b, K-c) in sampling campaigns in February and April 2019. Nitrite were measured in high concentration of 0,436 mg/L at sampling site K-c in February 2019. Influence of green belt was noticed in reduction of total nitrogen and nitrite concentrations for locations K-c and K-f. Location K-c presents the most contaminated location and influence of agricultural activities could be noticed, since K-c is located close to the agricultural field. Location K-f is near location K-c, but it is surrounded by the green belt.

Results of ground water analysis in Croatia

Sampling campaigns of ground water in Tompojevacki ritovi were conducted in three campaigns (December 2018., February and April 2019.) from the piezometers labeled P1 to P6. Groundwater sampling sites (P1, P2, P3) in Croatia are presented in Figure 3. The sampling procedure was conducted according the Standards SRPS EN ISO 5667-1:2008 (Guidelines for development of sampling programs), SRPS EN ISO 5667-3:2007 (Guidelines for protection and handling of the sample), SRPS EN ISO 5667-6:1997 (Guidelines for abstraction of samples from rivers and streams).



Figure 3. Groundwater sampling sites (P1, P2, P3) in Croatia

In December 2018, ammonium ion and chromium (VI) concentrations were high in water from piezometers P5 and P2, respectively. High concentrations for both pollutants were noticed in the previous sampling campaign in September 2018. At sampling sites P2 and P3, pH values were 10,14 and 9,08, indicating alkaline groundwater. Dissolved oxygen was measured in concentration lower than 4 mg/L (3,66 mg/L) in water from piezometer P3. In February and April 2019, low concentrations of dissolved oxygen were also noticed in groundwater from piezometers P6 and P8. High values of conductivity (P4), orthophosphate (P1-P8), ammonium ion (P6) and COD (P6, P7) were measured in groundwater in February 2019. In April 2019, orthophosphates were detected in high concentrations in five of eight piezometers (P1, P3, P4, P6, P8). Also, high values were measured for conductivity (P3-P5, P8), TOC (P3) and total nitrogen (P6).

Results of surface water analysis in Croatia

Surface water was collected from locations P0V1 and P0V2 (Figure 4). Results of physico-chemical analyses were compared to Regulation on water classification.



Figure 4. Surface water sampling sites (POV1 and POV2) in Croatia

According to the results and maximal allowable values Tompojevacki ritovi belongs to the class IV or class V water quality (orthophosphates and dissolved oxygen), with high trophic state and bad eco-status. High values of nutrients and decrease in dissolved oxygen indicate a significant impact of the degradation of organic matter on water quality. Increased orthophosphates in natural waters lead to eutrophication, excessive growth of plants and algae, which could be also noticed in Figure 4.

Results of run-off water analysis in Croatia

Run-off water from the agricultural fields was collected at locations KH1 to KH4. Locations KH1 and KH4 are surrounded by green belts. Sampling sites are presented in Figure 5.



Figure 5. Run off water sampling sites (KH1, KH2, KH3) in Croatia

High ranges of orthophosphates concentrations from 1,112 to 1,823 mg/L and from 7,705 to 10,01 mg/L were measured in run off water from collectors in both sampling campaigns, in February and April 2019. Dissolved oxygen values were lower than 1 mg/L in both sampling campaigns at sampling location KH4. Total nitrogen was detected in very high concentration (275,68 mg/L) at the same sampling site. Also, TOC and COD concentrations were high in run off water from collector KH4 and amounted to 79,90 and 180 mg/L, respectively.

The main problem of pollution was caused by orthophosphates and total nitrogen which originated from run off from agricultural land. Most of the nitrogen in water is the product of organic matter degradation. Additional nitrogen is introduced into the water by run off from the agricultural land, where artificial fertilizers are used.

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