

## **Laboratory analyses of key physicochemical parameters in surface water, ground water and run-off in Serbia and Croatia**

The mission and one of the main goals of the SeNs Wetlands Interreg IPA Project is the analysis of the basic quality physicochemical parameters in the Lake surface and ground water determined by standard analytical methods and developed fiber optic sensor methods. The first milestone of the Project is installment of piezometers for sampling of ground water. In the first phase the piezometers will be used for collecting samples to determine key physicochemical parameters by standard analytical methods. In the second phase, the FOS modified by FTS research team will be used for the purpose of conducting the parallel comparative analysis with standard laboratory analytical methods. Installed systems will be a part of integrated continuous monitoring network on cross-border wetland areas Croatia-Serbia.

Physicochemical parameters include pH, air and water temperature, dissolved oxygen, chemical oxygen demand (COD), biological oxygen demand (BOD<sub>5</sub>), total organic carbon (TOC), anions - nitrites (NO<sub>2</sub><sup>-</sup>(aq)) and nitrates (NO<sub>3</sub><sup>-</sup>(aq)), orthophosphates (PO<sub>4</sub><sup>3-</sup>(aq)) and ammonium nitrogen cation (NH<sub>4</sub><sup>+</sup>-N(aq)), total nitrogen and phosphorus, sulfates (SO<sub>4</sub><sup>2-</sup>(aq)), chlorides (Cl<sup>-</sup>(aq)), fluorides (F<sup>-</sup>(aq)), conductivity, total chlorine, organic aromatic compound phenol (C<sub>6</sub>H<sub>5</sub>OH) and cations of metals (nickel (Ni<sup>2+</sup>(aq)), iron (Fe<sup>2/3+</sup>(aq)), zinc (Zn<sup>2+</sup>(aq)), chromium (Cr<sup>6+</sup>(aq)), copper (Cu<sup>2+</sup>(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.

### **Preliminary screening and sampling in Serbia**

Preliminary screening and sampling of Lake Zobnatica surface water, in the vicinity of Bačka Topola, Vojvodina, Serbia, were conducted on 17<sup>th</sup> November of 2017, and 28<sup>th</sup> May of 2018. Surface water of the Lake Zobnatica is the type of freshwater. Zobnatica Lake was formed in 1976 in the valley of a small river, Krivaja, with an area of 226 ha and length of about 5 km. The primary purpose of the lake is the irrigation of agricultural areas, but in recent years the lake has become a real tourist pearl of Bačka Topola municipality, especially in the summer. Constructed beach, sports facilities, fast food restaurants and bars are available for the tourists. There is also the possibility for sport fishing (rich in carp, perch, hamour, catfish and other white fish). In the close vicinity of the Lake is the rich agricultural area, which in some parts comes close to the Lake water, beach for local population and rural settlements.

The classification of surface water quality prescribed by Regulation on emission limit values of polluting substances in surface and groundwaters and deadlines for their achievement (Official Gazette of the RS 50/2012) is shown in Table 1 and Table 2.

**Table 1.** The limit values of physic-chemical parameters for classification of water quality, Regulation on emission limit values of polluting substances in surface and groundwater and deadlines for their achievement (Official Gazette of the RS 50/2012)

Parameter	Unit	Class I	Class II	Class III	Class IV	Class V
pH	-	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	<6.5 or >8.5
Conductivity	µS/cm	<1000 / BLQ	1000	1500	3000	>3000
Dissolved oxygen	mgO <sub>2</sub> /L	- / BLQ	- / BLQ	5	4	<4
PO <sub>4</sub> <sup>3-</sup>	mg/L	- / BLQ	-	0.2	0.5	>0.5
NO <sub>2</sub> <sup>-</sup>	mg/L	0.01 / BLQ	0.03	0.12	0.3	0.3
NO <sub>3</sub> <sup>-</sup>	mg/L	- / BLQ	-	6	15	>15
NH <sub>4</sub> <sup>+</sup> -N	mg/L	- / BLQ	-	0.6	1.5	>1.5
SO <sub>4</sub> <sup>2-</sup> (aq)	mg/L	50 / BLQ	100	200	300	>300
Cl <sup>-</sup> (aq)	mg/L	50 / BLQ	-	150	250	>250
Total chlorine	mg/L	0.005	0.005	-	-	-
TOC	mg/L	- / BLQ	-	15	50	>50
HPK	mgO <sub>2</sub> /L	10 / BLQ	15	30	125	>125
BPK <sub>5</sub>	mgO <sub>2</sub> /L	- / BLQ	-	7	25	>25
Chromium <sup>1</sup> (total)	µg/L	25 / BLQ	50	100	250	>250
Cu <sup>2+</sup> (aq)	µg/L	5/22/40/112*	5/22/40/112*	500	1000	>1000
Zn <sup>2+</sup> (aq)	µg/L	30/200/300/500*	300/700/1000/2000*	2000	5000	>5000
Fe <sup>2/3+</sup> (aq)	µg/L	200	500	1000	2000	>2000
Fenols	µg/L	<1	1	20	50	>50

BLQ – base-line quality; \* - depending on the water hardness 10, 50, 100 and 500 mgCaCO<sub>3</sub>/L

The Lake Zobnatica is a natural reservoirs type of dynamic and static water bodies, and the sensitivity of this type of eco-system is more fragile and the maximum allowable values of physicochemical parameters in lakes are more restrictive than in rivers. In Table 3 the maximum allowable values of physicochemical parameters for class I and II quality of water for lakes below 200 m of sea level are presented.

**Table 2.** The maximum allowable values of physicochemical parameters for class I and II quality of water for lakes below 200 m of sea level (Official Gazette of the RS 50/2012)

Parameter	Unit	Maximum allowable values for class I of surface water	Maximum allowable values for class II of surface water
pH	-	6.5-8.5	6.5-8.5
Dissolved oxygen	mg/L	8.52	7
TOC	mg/L	2	6
BPK <sub>5</sub>	mg/L	2	5
NH <sub>4</sub> <sup>+</sup> -N	mg/L	0.1	0.3
NO <sub>3</sub> <sup>-</sup>	mg/L	1	3
PO <sub>4</sub> <sup>3-</sup>	mg/L	0.02	0.1
Total phosphorus	mg/L	0.05	0.2
Cl <sup>-</sup>	mg/L	50	100

According to the preliminary results and maximal allowable values Zobnatica Lake can be classified as class IV at best, as poor ecological status and utilization for irrigation and industrial use (process and cooling water). The characteristic of conductivity is only parameter of the water of class I quality, according to Serbian national Law and By-law. Dissolved oxygen in water is the key parameter for maintenance of life in water, e.g. for fish, invertebrates, bacteria and plants. At least 5 ppm (5 mg O<sub>2</sub>/L) is necessary for the survival of fish. Origin of free molecules of O<sub>2</sub> in water derives from the atmosphere and photosynthesis of algae. Dissolved oxygen level that is too low can harm aquatic life and negatively affect water quality. Dissolved oxygen decreases with increasing temperature. Therefore, the content of oxygen in water is higher in winter than in summer. Lower dissolved oxygen values in waters are at higher pressures and reverse proportional with temperature. Aerobic bacteria use dissolved oxygen during decomposition of organic substances in water.

Orthophosphates in water can be present due to the washing out of phosphate rocks, waste water from industry and households and the run off from agricultural land. Increased nutrient (e.g. orthophosphates, nitrite) concentrations in natural waters lead to eutrophication ("flowering water"). Eutrophication is excessive growth of plants and algae, as a response to increased levels of nutrients and is induced by the discharge of nitrate or phosphate containing detergents, fertilizers, or sewage into an aquatic system.

The results of preliminary screening analyses indicated pollution and need for detailed monitoring of surface water as well as ground water and run off water.

### **Sampling campaigns of ground water, surface water and run-off water in Serbia**

Sampling campaigns of ground water, surface water and run-off water in the vicinity of Lake Zobnatica were conducted on 2<sup>nd</sup> July of 2018 and 30<sup>th</sup> of August 2018, after the piezometers (labeled B1 to B9) and collectors were positioned, constructed and installed. During the sampling campaigns there was no precipitation and the air temperatures were 28 °C and 35 °C.

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 (Table 4. and Figures 1-3). 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).

**Table 3.** Geographic coordinates – north latitude and east longitude – of piezometers (B1-9) and collectors (from K-a to K-f)

Location	North latitude	East longitude
B1	45°53'9.15"N	19°36'55.25"E
B2	45°53'8.58"N	19°36'54.78"E
B3	45°53'8.68"N	19°36'55.16"E
K-a	45°53'8.72"N	19°36'54.73"E
K-b	45°53'8.78"N	19°36'55.24"E
B5	45°52'48.69"N	19°37'7.82"E
B4	45°52'45.94"N	19°37'5.01"E
B6	45°51'26.68"N	19°37'0.68"E
B7	45°51'26.94"N	19°36'57.38"E
B8	45°51'21.73"N	19°36'43.64"E
B9	45°51'20.88"N	19°36'41.56"E
K-c	45°51'21.61"N	19°36'43.98"E
K-d	45°51'24.87"N	19°36'56.60"E
K-e	45°51'23.45"N	19°36'56.00"E
K-f	45°51'21.95"N	19°36'53.58"E



Figure 1. Sampling locations of piezometers (B1-B3) and collectors (K-a, K-b)





Figure 2. Sampling locations of piezometers (B4-B5)

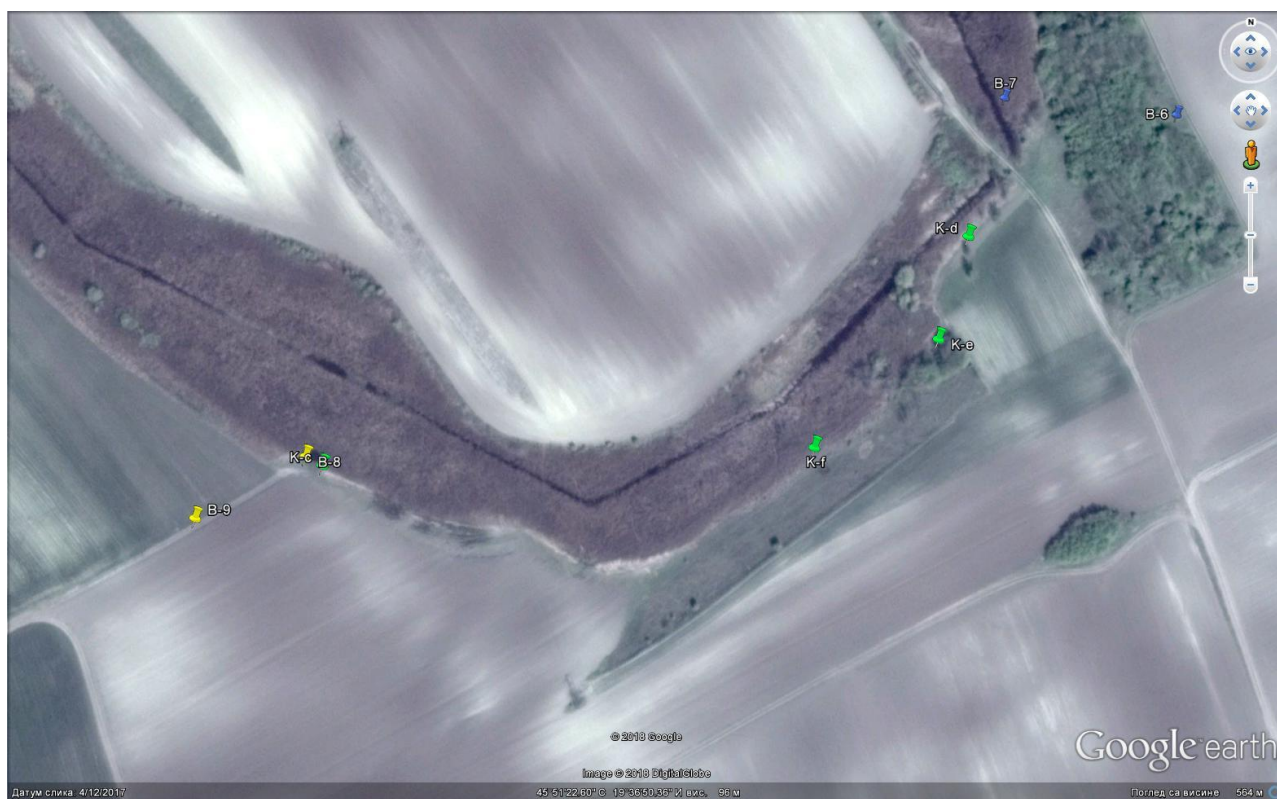


Figure 3. Sampling locations of piezometers (B6-B9) and collectors (K-c to K-f)



Figure 4. Pictures of the sampling performed on 30<sup>th</sup> August of 2018.

### **The first sampling campaign of ground water, surface water and run-off water in Serbia**

Key physicochemical parameters in groundwater (B1-B9) were collected and analyzed in the first sampling campaign (2<sup>nd</sup> July of 2018).

The chemical parameter of pH value indicates whether the solution is acidic, neutral or alkaline. In natural unpolluted waters the pH value depends on free CO<sub>2</sub>, carbonate and bicarbonate. Natural waters have a pH value of 6.5 to 8.5. pH values in samples B3 and B6-B9 of ground water were higher than 8.5, which point out pollution of ground water. Concentration of nitrite in samples B1 and B2 indicate anthropogenic pollution.

Surface water was collected from locations PV1 to PV3. According to pH value higher than 8.5, Lake water belongs to class V quality water, with high trophic state and bad eco-status (Regulation on emission limit values of polluting substances in surface and ground waters and deadlines for their achievement (Official Gazette of the RS 50/2012)).

Run-off water from agricultural fields was collected at locations K-a to K-f. On the date of sampling, 2<sup>nd</sup> of July, in collectors K-a, K-e and K-f there was no water for sampling. Results of examined key physicochemical parameters indicate pollution of run-off water. pH value higher than 8.5 and values for dissolved oxygen lower than 4 mg/L indicate anthropogenic



pollution. Values for orthophosphates in concentrations from 1.7 to 4.5 mg/L point out pollution from agricultural activities. Dissolved oxygen values lower than 4 mg/L also caused a concern and indicated presence of anthropogenic pollution.

### **The second sampling campaign of ground water, surface water and run-off water in Serbia**

Key physicochemical parameters were analyzed in groundwater (B1-B9) for the second sampling campaign (30<sup>th</sup> of August 2018).

The high values of orthophosphates in range of 0.621 to 2.459 mg/L were measured in ground water samples and indicate pollution from agricultural activities. Concentration of nitrites was high in groundwater sample from piezometer B2.

Most of the nitrogen (e.g. ammonia, nitrate, nitrite) 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. In the presence of oxygen in water, nitrogen from ammonia bacteriologically degrades to nitrates and nitrites in nitrification process.

Run-off water from the agricultural fields was collected at location K-a. On the date of sampling, 30<sup>th</sup> of August, in collectors K-b to K-f there was no water for sampling.

The concentration of orthophosphates was very high (4.021 mg/L), which point out the pollution of run -off water from agricultural land. Additional analysis of samples from run off collector didn't indicate influence of "green belt area", due to technical reasons (water was collected only from collector K-a, collectors K-b to K-f were empty).

Results of both sampling campaigns showed the pollution of water with nutrients (orthophosphates and nitrites), alkaline water with pH value higher than 8.5 and lower values of dissolved oxygen than 5 mg/L in the most of the samples. Both sampling campaigns were performed in summer, hence the influence of seasonal variations could not be noticed.

### **Preliminary screening and sampling in Croatia**

Preliminary screening and sampling of surface water in protected area of Tompojevacki ritovi, Croatia, were conducted on 24<sup>th</sup> January of 2018, and 24<sup>th</sup> April of 2018.

Tompojevacki ritovi are wetlands in the length of 48 km. This depression is filled with water, lower than surrounding terrain for 10 to 15 m. The water flow is from the underground sources at the margins of the low parts of the depression. Tompojevacki ritovi were earlier richer in water, and therefore with flora and fauna. Tompojevacki ritovi were surrounded by green belts which protected reservation from the effects of natural phenomena, especially from eolic erosion.

According to the results of key physic-chemical parameters and maximal allowable values Tompojevacki ritovi belongs to the class V water quality (orthophosphates and dissolved oxygen), with high trophic state and bad eco-status. The results of preliminary screening analyses in

Tompojevacki ritovi indicated pollution and need for detailed monitoring of surface water as well as ground water and run off water.

### Sampling campaign of ground water and surface water in Croatia

The first sampling campaign of ground water and surface water in Tompojevacki ritovi was realized on 7<sup>th</sup> September of 2018, after the piezometers (labeled P1 to P6, Figure 5) were placed, constructed and installed. During the sampling campaign there was no precipitation and the air temperature was 28 °C.

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 5. Sampling locations of piezometers (P1-P6)

In ground water samples (P1-P6 for the first sampling campaign) the key physicochemical parameters were analyzed according to standard procedures. Chemical parameter of pH value in samples P2-P6 of ground water was higher than 8.5, which could indicate pollution of ground water (alkaline groundwater). Concentration of orthophosphates in samples P1 to P5 could indicate anthropogenic pollution from agricultural activities.

Surface water was collected from locations POV1 to POV3. According to the results and maximal allowable values (dissolved oxygen and orthophosphates) Tompojevacki ritovi belongs to the class V water quality, 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.



Report made by dr Ivana Mihajlović, prof. dr Mirjana Vojinović-Miloradov, dr Dragan Adamović, dr Maja Petrović, dr Maja Sremački and Boris Obrovski.

Date: 30.11.2018.