**Multi-methodological approach to evaluate trace elements and major components in wetland system with subsaline and freshwater characteristics**

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**Abstract**

~~We showed that the present status of the transboundary wetlands in Central Europe can be evaluated using complementary experimental and statistical methods.~~ In this study, the present status of the transboundary wetlands in Central Europe was evaluated using complementary experimental and statistical methods. Detailed characterization of the complex, subsaline/freshwater system in this study is aimed to be the contribution to the global wetland inventory.

~~For the first time, distribution and behaviour of trace elements and major components in the Neusiedler lake basin (Austria) were obtained.~~ The distribution and behaviour of major and trace elements in water from the Neusiedler lake basin (Austria) were investigated. ~~We propose t~~Two water types were proposed: CaNaHCO3 and CaHCO3. Toxic metals were discussed in comparison with the sediment quality criteria and Ni was above the value that might cause severe toxic effects. TOC/TN ratio in sediments suggested terrestrial origin of organic matter. Significant variation of trace elements in water was noticed among the sampling sites. Although the Wulka River was anthropogenically influenced, only dissolved Zn, As and U were above world average values. This was consequence of precipitation and metal adsorption onto suspended particles. Cd, Zn, Mn and Fe were the highest in acidic spring, where low pH maintains metals in a dissolved form. Uranium amounts near closed coalmine exceeded maximum allowed concentration (20 µg L-1). Majority of elements in water and sediment have normal statistical distribution, with a small number of anomalies, thus indicating moderate anthropogenic influence.

**Keywords**: Transboundary wetlands; Ramsar site no. 271; Sediment and water geochemistry; Mineralogy; Piper trilinear diagram

**1. Introduction**

Saline and subsaline lakes are special wetland ecosystems, the fragile and sensitive characteristics of which deserve special attention. They are especially rare in Europe and other areas of moderate climate in the world. Generally, there is limited knowledge about chemical composition of trace elements in water and sediment and about mineral composition of sediments in subsaline aquatic environments. Biological limnologists often use the classification scheme of freshwaters (less than 1 ‰), subsaline (1-3 ‰), hyposaline (3-20 ‰), as outlined by Last and Ginn (2005) for the saline systems of Western Canada.

One of the first scientific studies of subsaline Lake Neusiedl was a paper of Ascherson (1865), who reported drying up of that lake. He explained that Lake Neusiedl probably has underground connections with the rivers Danube or Raab. Häusler (1992) suggested a new concept of the lake's water balance. His results indicated, opposed to previous assumptions, that the lake's water balance is not influenced significantly by subsurface inflow. Piller and Harzhauser (2005) explained that brackish water conditions could not have prevailed and they rejected the interpretation of the Sarmatian Sea as a brackish basin passing gradually into a terrestrial superlake. Eitzinger et al. (2009) studied impact of climate change on the water balance of Lake Neusiedl, while Ágoston-Szabó and Dinka (2006, 2009) investigated changes in sediment and sediment interstitial water characteristics in Lake Fertő/Neusiedl. Sediment characteristics demonstrated that the changes in the chemical parameters of the sediment interstitial water and in the organic matter content and microbial activity of the sediment are strongly interrelated with the condition of the reed stands. Furthermore, Häusler et al. (2007) explained that the surface geological structure of the Neusiedl area consists of only a few members of the Tertiary and the Quaternary layer.

Between 1970 and 1971, the Austrian Mineral Oil Administration investigated hydrocarbons in the Eisenstadt Tertiary basins and in Seewinkel. A selection of important "holes on Oil" and Counter Flash (CF) flat drills are shown in the geological map of this region. A regionally effective intra Pleistocene faulting in Riss / Mindel Interglacial has led to significant shifts in the drainage network in northern Burgenland. During this time, lacustrine deposits were formed presumably. In the literature they are known as "Interglazialton" and "salt-leading horizon", or as deposits of a paleo-lake Neusiedl. The enrichment of the "salt-leading horizon" with soluble salts, particularly sodium carbonate, results in a very plastic, strong adhesive when wet. This layer is impermeable, so that it accumulates water from precipitation, which results in formation of temporary salt lakes. A result of the "salt-leading horizon" reconstructable interglacial steppe probably occupied the territory of today's Lake Neusiedl, including the entire Seewinkel, the Rust Mountains and the Leitha Mountains, which already (slightly) upscale Parndorfer and a flat ridge to the southeast.

The salt lakes of the Seewinkel are shallow salty coatings that vary seasonally between a maximum of 60 cm water depth and complete dryness. While in 1900 there were still more than 100 such lakes, today there are about 45 of them between the eastern shore of Lake Neusiedl and the Hanságbecken, mostly located within the "National Park Neusiedler See - Seewinkel”. The salt lakes occur in two different areas: on the one hand, just east of Lake Neusiedl and then in the central Seewinkel. Although these coatings represent an extremely sensitive and threatened ecosystem, so far there have been only a few geochemical studies of the relationship between water of those small lakes and groundwater, as well as about the salt origin (Häusler et al., 2014). Lake Neusiedl is hardly fed by groundwater, due to the hydrogeology of the area.

Although a large collection of published data exists from the northern Burgenland aquatic environment, significant lack of chemical data from surface waters, especially trace elements of subsaline lakes ~~directed us toward~~ was one of the main motives to perform this study. Besides the subsaline lakes of northern Burgenland, ~~we~~ it was also aimed to investigate the most interesting aquatic environments in this region due to their exceptional significance for two bordering central European countries (Austria and Hungary), like karstic springs of the Leithagebirge Mountains, the Wulka River feeding Lake Neusiedl, some streams and lakes originating from abandoned coalmines and some thermal springs. Lake Neusiedl was investigated during many decades, but most of research deals with hydrology and hydrogeology of the lake.

Therefore, the aim of this study is to assess and describe surface water chemistry (trace and major elements) of the important wetland system in temperate region of Central Europe and also to expand the existing knowledge about sediment chemistry and mineralogy with very precise data. In addition, the pollution status of the subsaline aquatic systems and freshwater springs of the study area is also targeted. The data may be used to identify locations, where risk and vulnerability analyses could be performed in the future. Obtained status of this transboundary wetland (Ramsar site 271) can be added to the global wetland inventory described by Finlayson et al. (1999) and Finlayson (2003).

**2. Study area**

The study area is located around Lake Neusiedl (in the northern part of Burgenland, the easternmost and least populated state (Land) of Austria). Burgenland and Hungary share Lake Neusiedl, known for its reeds and shallowness, as well as its mild climate throughout the year. Lake Neusiedl is Austria's largest lake, and is a great tourist attraction, bringing lots of people into the region north of the lake. Lake Neusiedl is the largest steppe lake in Central Europe. In 2001, the Lake Neusiedl region was proclaimed a UNESCO World Heritage Site and joined the list of 850 cultural and natural monuments worldwide. The region, with sections in both Austria and Hungary, encompasses an area of around 747 km². The unique transboundary National Park Lake Neusiedl - Seewinkel, the Natural Park Lake Neusiedl - Leitha Mountain Ranges (an internationally recognised RAMSAR wetland site no. 271, NATURA-2000 area and Biosphere Reserve), the Rust Hills and the Leithaauen belong to this unique natural landscape which surrounds the Lake. Sampling locations numbered from 1 - 14 are described and presented in Figure 1 and Table 1. The main idea of such sampling strategy was to include the most important natural phenomena of Northern Burgenland in ~~our~~ sampling network of the current study, which can be enlarged in some future project. The most important are saline steppe lakes and marches, among which Neusiedl is the largest and most significant one. Therefore, majority of samples are from those subsaline aquatic environments: four from Neusiedl (Jois-See Jungfrau (2), Rust-Seebad (3), Ilmitz (9) and Mole West (10)) and samples from Zicksee (6), Sechsmahdlacke (7) and Darscholacke, Warmsee (8). Until regulation works in the 19th century, Neusiedl covered a much larger area than today and water was significantly deeper than today, therefore one arm of the lake reached almost to the Jois settlement. Today there is arable land, under which underlie old lake sediments.

The Wulka River is the largest tributary and the main source of water supply for Neusiedl. It is known to be a potential source of pollution to Lake Neusiedl, hence a sampling station (5) was chosen to evaluate its potential anthropogenic influence on the lake.

Leithagebirge, a karstic hill chain located North West from Neusiedl, is rich in karstic features, including karstic springs. ~~We have chosen t~~ Two most significant of them - Ochsenbrunnen (1) and Johannes (4) – were chosen.

Northern Burgenland was also an important mining area, due to large deposits of brown coal in some areas. Therefore, two most significant mining sites were chosen to investigate the influence of past mining activities on the environment. One of them (site 12) is a small spring draining a closed coalmine. The other is Neufelder Lake (site 13) located exactly at an abandoned mining site and today is used for recreational purposes.

In Northern Burgenland there are also several occurrences of thermal and mineral waters. The best known of them is Bad Sauerbrunn, an important SPA touristic centre. One (site 11) of ~~our~~ sampling stations is located there, and the other thermal water sample (site 14) was taken at Leiterbrudersdorf thermal spring, which is currently not being used.

**3. Experimental**

**3.1. Sampling, physico-chemical parameters and statistical evaluation**

The position of the studied area is presented in Figure 1, with sampling locations. The sampling site coordinates were determined by a GPS instrument (Garmin GPS Map 72, Kansas City, USA). Two sampling campaigns were performed during the same season (autumn), during two successive years: October 21st, 2010 and October 27th, 2011. Details about all sampling locations are presented in Table 1, together with measured physico-chemical parameters. Altogether five sampling locations (1 - 5) were chosen during the first and nine sampling locations (6 - 14) during the second sampling campaign. On sampling sites, where it was possible, both sample matrixes (water and sediment) were collected. In some locations there was no available sediment and water (extremely low water level, < 5 cm). There were no conditions for representative sampling.

Surface water samples were collected using a clean sampling technique described by Horowitz (1997). Water samples were collected in 1 L NalgeneTM fluorinated ethylene-poly(propylene) bottles (Thermo Fisher Scientific, Rochester, USA). This material has extremely low capacity for trace metal adsorption (Cuculić and Branica, 1996). Prior to the sampling, bottles were thoroughly washed with 10% nitric acid and rinsed with Milli-Q® water (Millipore, Billerica, MA, USA) in order to remove any residual trace metals. After sampling, bottles were zipped in plastic bags and kept maximum one day at 4 °C before preparation and analysis.

Sediment sampling sites were chosen on representative locations with available fine-grained sediment accumulation. On each sampling site, at least three grab samples of active fine-grained surface sediment (0 - 5 cm deep) were collected from different places in an area of 5 m2. From this material a composite sample was taken weighing up to 1.5 kg. This procedure decreased the possible bias caused by local variability. Sediments were wet sieved using water from sampling sites by standard sieves (Fritsch, Germany) to obtain the silt + clay fraction (< 63 µm). The obtained fraction was air dried at room temperature. That fraction was used to make easier comparison with results of similar studies, because it is usually used in environmental studies. In addition, using of this fraction is strongly recommended in Guidance Document No: 25 – Guidance on chemical monitoring of sediment and biota under the Water Framework Directive (2000/60/EC), Technical Report --- 2010.3991. The results of a routine water analysis, which include physico-chemical parameters (water temperature, pH, electric conductivity and salinity) were measured *in situ* at all sampling sites by using a Hach HQ40D instrument (Loveland, USA). Prior to each sampling event the instrument was checked and calibrated. The pH electrode was calibrated with standard pH 4 and 7 buffer solutions with precision of 0.01 pH unit. Accuracy of electric conductivity measurements was 0.1 µS cm-1, while of temperature was 0.1 °C. Salinity was measured using Practical Salinity Scale (PSS-78) and values are given as dimensionless units. That scale is based on an equation relating salinity to the ratio of the electrical conductivity of seawater at 15 ° C to that of a standard potassium chloride solution (KCl). Symbol S is formulated and adopted by the UNESCO/ICES/ SCOR/ IAPSO (1980).

Anomalies (extremes and outliers) of elements in sediment and water are determined by program STATISTICA 8.0, using boxplot method. Box-plots are constructed on the basis of the empirical cumulative distribution plots. The box length was the interquartile range, where outlier values were defined as 1.5 and 3 box lengths from the upper or lower edge of the box. Extremes were values more than 3 box lengths from the edge of the box (Tukey, 1977).

**3.2. Mineralogical and elemental analysis of sediments**

Mineral composition of the samples was determined by using X-ray powder diffraction (XRD). A Philips X’Pert PRO powder diffractometer was employed operating at 40 mV and 40 mA. Mineral phases in the samples were identified using Powder Diffraction File (PDF) database (2004). Semi-quantitative mineralogical analysis was performed using the method described in Boldrin et al. (1992).

Concentrations of metal/metalloids (Fe, Al, Zn, Mn, Ni, Cu, Co, Cd, Pb, As, Mo and U) in surface sediments were measured using inductively coupled plasma-mass spectrometry (ICP-MS, Elan 9000, Perkin Elmer, USA), with solution of 20 µg L-1 Ge, Rh, In, Re, and Ce, as internal standard.

Sediment was sieved with a 63 μm sieve, model Retsch AS200, to get rid of impurities and coarser gravel, and then dried in thermostat at a temperature of 40 °C. Aliquots of approximately 0.1 g of the powder sludge sample were degenerated with 2.5 mL of Suprapur® nitric acid and 7.5 mL of Puriss® hydrochloric acid and heated for half an hour at 1000 W in an Anton Paar Multiwave 3000 oven (Graz, Austria). ISO 11466 (Soil quality-Extraction of trace elements soluble in aqua regia) was followed. Digested samples were quantitatively transferred to volumetric flasks and diluted to 50 mL with deionized water. All laboratory glassware were submerged for 24 h in 1% HNO3 solution and rinsed three times with deionized water prior to use. Elements in sediment were detected by Inductively Coupled Plasma Mass Spectrometry at ICP MS Elan 9000 (Perkin Elmer), using a standard reference material (RTC, Trace elements on fresh water sediment).

**3.3. Determination of mineral oils, total P, total N and total organic C in sediments**

Mineral oils in sediments were determined by modified spectrophotometric method SM 5520 (Environmental Protection Agency, 1998) in hexane with previous dichloromethane extraction (Perkin Elmer Lambda 25 instrument). Sediment was sieved with a 63 μm sieve, model Retsch AS200, in order to remove impurities and coarser gravel, and dried for 24 hours at 40 °C. Aliquots of approximately 0.5 g of the powder sludge sample were quantitatively transferred to volumetric flasks with 25 mL of dichloromethane, and shaken by an automatic shaker for 1 hour. Dichloromethane was poured into a flask with a round cap through a glass funnel with filter paper. This procedure was repeated two more times. The extract of 75 mL of dichloromethane was evaporated to dryness on a water bath (at 45 °C). After the flask has cooled, 10 mL of n-hexane and a bit of aluminium oxide were added. The sample was mixed well and left for 5 - 10 min. Aluminium oxide binds oils of animal origin, but not mineral oils. Total hydrocarbons (mineral oils) are sum of long-chained and branched aliphatic, alicyclic, aromatic or alkil-substituted aromatic hydrocarbons between C10H22 (n-decane) and C40H82 (n-tetracontane). Absorbance was measured at 256 nm according to the blind test method. Measurement was performed in a 10 mm quartz cuvette.

Total phosphorus (TP) and total nitrogen (TN) in sediment were determined using spectrophotometric method with a PerkinElmer Lambda 25 UV/VIS spectrophotometer. Before determination, samples were digested with concentrated reagents (H2SO4, K2SO4 and SeO2) and treated with hydrogen peroxide, releasing organic N as ammonium and organic P as phosphate. Total organic carbon (TOC) was determined in dried and acidified sediment using TOC analyser TOC-VCPH with solid sample module SSM-5000A (Shimadzu, Kyoto, Japan). Sediment is combusted at 1350 oC in an oxygen atmosphere. Carbon is oxidized to form CO2. The mass is converted to percentage of carbon based on the dry weight.

**3.4. Dissolved major elements and organic carbon in waters**

Dissolved major elements (anions and cations) were determined by ion chromatography on a Dionex ICS 3000 (Thermo Fisher Scientific). Before the analysis, the samples were filtered through a 0.45 μm filter (Acrodisc® Syringe Filters, Sigma-Aldrich, St. Louis, USA) in order to remove sample residues that might cause various problems, blockages and damage to the valves and column and in order to prevent the breakdown of cations by bacterial contamination. Sample contamination is also prevented by discarding the first portion of the filtrate. It is necessary to adjust the pH value of the sample in accordance with the pH values allowed by the column. If the concentrations of the analyte are too high (especially if they exceed column capacity), it is necessary to dilute the sample with deionized water (eluent can also be used for this purpose).

Samples for DOC collection, their preservation and storage were according to the procedure of Tupas et al. (1994).

Dissolved organic carbon (DOC) was determined using the TOC-VCPH device. Samples were collected in pre-cleaned 250 mL dark glass bottle, transported and stored in a refrigerator between 2 °C to 8 °C. Samples were not preserved by freezing in refrigerator because they were analyzed within 8 days. The method is based on incineration of a sample at high temperatures (680 °C) until gas CO2 is generated. Before incineration, the sample must be filtered through a 0.45 μm filter paper and acidified with 2 M HCl (pH<2) which removes inorganic carbon that is removed from the sample by blowing using synthetic air.

**3.5. Determination of metal/metalloids in waters**

Concentrations of dissolved and total metal/metalloids (Fe, Al, Zn, Mn, Ni, Cu, Co, Cd, Pb, As, Mo, Ba and U) were measured in surface water samples using both inductively coupled plasma-mass spectrometry (ICP-MS, Elan 9000) and voltammetry. Fe, Al, Mn, Ni, Co, As, Mo, Ba and U were determined by ICP-MS method that was described in detail in Matić et al. (2012, 2013). In order to assess accurately low concentrations of Cd, Cu, Pb and Zn in water samples, they were measured using voltammetric methods, due to their very low detection limits and consistent reproducibility. Two kinds of measurements were performed:

a) Concentrations of total metals measured in unfiltered water samples, include particulate, colloidal, large complexes and dissolved metals;

b) Concentrations of dissolved metals, after sample filtration, under nitrogen pressure through 0.45 µm cellulose nitrate membrane filters (Sartorius, Göttingen, Germany).

Prior to voltammetric analysis, unfiltered and filtered water samples for determination of trace metals were acidified with Suprapur® nitric acid (Merck, Darmstadt, Germany) to a pH < 2 and UV irradiated for 24 hours (150 W mercury lamp, Hanau, Germany). Trace metal concentration measurements were performed by the ECO Chemie μAUTOLAB multimode potentiostat (Utrecht, The Netherlands) connected with a three-electrode system Metrohm 663 VA STAND (Herissau, Switzerland). A hanging mercury drop was used as a working electrode (VA stand 663, Metrohm, Herissau, Switzerland), with a drop surface of 0.25 mm2. A platinum wire was used as a counter electrode and Ag|AgCl with saturated NaCl as a reference electrode. The electrochemical method used for Cu, Cd, Pb and Zn was differential pulse anodic stripping voltammetry (DPASV) with standard addition method for determination of trace concentrations in water samples. Limits of quantification, LOQ, obtained in acidic Milli-Q® water (Millipore, Billerica, USA) were 1, 2, 5 and 10 ng L-1 for Cd, Pb, Cu and Zn in water samples, respectively (based on a standard addition method and 10σ rule for 10 min accumulation time). Concentrations of total and dissolved Ni and Co in water samples were measured by adsorptive cathodic stripping voltammetry (ACSV) with standard addition method. LOQ for Co and Ni obtained in acidic Milli-Q® water were 1 and 10 ng L-1, respectively.

Quality control of the applied voltammetric method was verified by determining trace metal concentrations in the River Water Reference Material for Trace Metals (SLRS-5) of the National Research Council Canada. All measured metal concentrations were within 10 % of certified values.

**4. Results and discussion**

**4.1. Physico-chemical parameters**

Spatial variations of physico-chemical parameters presented in Table 1 can be discussed. As expected, trends of salinity and EC variations are related, with the lowest values at two karstic wells, Ochsenbrunnen (S = 0.30 and EC = 491 µS/cm) and Johannes (S = 0.32 and EC = 553 µS/cm). These EC values are comparable with those that Stojanovic et al. (2009) found at Donaukanal 1 site (400 µS/cm) which is in the same area. Also, ~~our~~ EC values in two karstic springs from the current research were somewhat higher than values ~~we~~ found by ~~(~~Frančišković-Bilinski et al.~~,~~ (2013) in the karstic rivers Kupa and Rječina in central Croatia (204 - 340 µS/cm) and in karstic springs of Biokovo mountain on the Croatian Adriatic coast (230 - 368 µS/cm) (Matić et al., 2012, 2013). Generally, EC values were significantly higher than 1000 µS/cm in the rest of the samples. The highest EC value was measured at site 8 (Darscholacke, Warmsee), 2650 µS/cm, which is approximately 5 times higher compared to karstic springs due to higher content of dissolved inorganic salts. Consequently, at the same site, the highest salinity of 1.36 was recorded. At the nearby site Darscho, Stojanovic et al. (2009) also found the highest EC = 6200 µS/cm.

Distribution of pH was relatively wide, from 5.98 - 10.05. ~~We found t~~The highest pH (10.05) was found at Sechsmahdlacke, while the lowest, acidic pH 5.98 was recorded at Bad Sauerbrunn site (acidic spa). Values of pH at Zicksee (9.05), Darscholacke (9.13) and Illmitz (9.09) were almost in perfect agreement with pH values reported by Stojanovic et al. (2009). Alkaline pH values reflect characteristics of Pannonian small subsaline lakes described in this study and earlier by Krachler (1992) and Stojanovic et al. (2009). Neutral pH values (6.94, 6.96 and 7.34) at thermal spring Leiterbrudersdorf and karstic springs Johannes and Ochsenbrunnen were measured, respectively. That was similar to pH values recorded (around 7.2) at karstic springs of Biokovo mountain (Matić et al., 2012, 2013). The pH values of karstic springs of the Rječina and Kupa Rivers were higher (8.30 and 8.14, respectively).

The lowest temperature (7.6 °C) was measured in the water of Ochsenbrunnen karstic spring, which was similar to 7.3 °C measured at Rječina and Kupa River karstic springs (Frančišković-Bilinski et al. 2013). However, at Johannes karstic spring higher water temperature was found, 12.2 °C. The most probable cause was the sub-thermal characteristics of the Johannes spring area. Interestingly, at the sites with the lowest pH values, the highest temperatures were recorded at thermal spring Leiterbrudersdorf (16.8 °C) and at Bad Sauerbrunn (14.0 °C).

**4.2. Semi-quantitative mineralogical analysis**

Results of semi-quantitative mineralogical analysis of lake, spring and stream sediments from the investigated area of Northern Burgenland are presented in Table 2, together with an overview of detected minerals, including PDF database number and complete chemical formula. All eleven studied sediment samples are complex mixtures of minerals, among which eight minerals have been detected: calcite, quartz, muscovite/illite, chlorite, ankerite, dolomite, smectite and plagioclase. Possibly, there could be several more minerals in traces, but they could not be detected due to limitations of XRD method. In addition, semi-quantitative percentages from Table 2 are calculated approximation, due to complexity of the studied sediments and limitations of used method.

In the majority of the studied samples quartz prevails. In general, carbonates are not abundant in larger quantities and in majority of samples calcite was less abundant compared to dolomite with rather small amounts of ankerite in some samples. The only sample with high amount of calcite is sample 1 from Ochsenbrunnen karstic spring, which was completely expected, because Leitha Mountains are mostly a carbonate area. On that location dolomite is not detected. Sample 2 from harbour at Jungfrau Lake near Jois also has a slightly increased percentage of calcite in comparison with the rest of the samples, and dolomite is present. This location is located near the slopes of Leitha Mountains, so carbonate content most probably originates from there. Locations with the highest amount of dolomite are 9 - Neusiedler See at Ilmitz, 12 - stream flowing from closed coalmine and 14 - thermal spring Leiterbrudersdorf. Muscovite/illite is the most abundant or the second abundant mineral in the majority of all the studied samples. Chlorite is present in much lower quantities and is present in all samples in which muscovite/illite is present, except in sample 3 - Rust Seebad. Halite is only suspected, (but not proved) mostly in traces in samples 3, 6 and 7, while in sample 9 halite represents about 2 %. However, it was omitted from Table 2, due to uncertainty because the strongest value d (2.81) is not present in all XRD patterns.

Plagioclase has been detected only on four locations: in three small shallow saline lakes (sites 6, 7 and 8) and in thermal spring Leiterbrudersdorf (site 14), where it is the least abundant. Plagioclase feldspars are the members of the series between NaAlSi3O8 and CaAl2Si2O8. Presence of plagioclase at those sampling sites is expected, as shallow saline lakes are locations with the highest pH values in the area (up to 10.05). One exception is sample 14, which has low pH. The unambiguous characterization of feldspar requires knowledge not only of the chemical composition but also of the structural state of the species, which is out of scope of the present paper.

**4.3. Elemental composition of sediments**

Results of 23 major and trace elements in sediment samples (fraction <63 µm) obtained by ICP-MS analysis are presented in Table 3, while results of boxplot statistical evaluation of anomalies are shown in Table 4.

Grain size effect was not studied in this work, although some studies in other regions exist (Guagliardi et al., 2013; Von Eynatten and Tolosana-Delgado, 2011). Recently Kogelbauer and Loiskandl (2015) have shown that all samples in Neusiedler See are rich in fine grained sediments, what is in support of ~~our~~ the choice ~~of~~ to use~~d~~ fine sediment fraction in the current study.

Most trace metals have normal statistical distribution and there is only a small number of anomalies determined by boxplot statistical method (mostly slight outliers and only a few extremes), which indicates that sediments have not been under significant anthropogenic pressure. Only at six locations, some statistical anomalies in sediments have been observed (see Table 4).

For 13 potentially toxic metals (Cd, Pb, Cr, Mn, Zn, Cu, Ni, Sb, Mo, Fe, Ag, Co and Ba), which are included in existing sediment quality criteria (SMSP and FALCONBRIDGE NC SAS, 2005), their total concentrations and potential toxicity will be discussed according to available British Columbia legislative, Canada (BCL), Ontario legislative, Canada (OL) and US federal criteria (USFC). Their concentrations will also be compared with available data for aqua regia dissolved sediments, from FOREGS Geochemical atlas of Europe (available at <http://weppi.gtk.fi/publ/foregsatlas/>). Cadmium shows one extreme at the Ochsenbrunnen karstic spring. The Cd concentration of 1.42 mg/kg at that location is slightly above the concentration which might cause lowest toxic effects (0.6 mg/kg - BCL, OL), but it is far below the value which might cause significant toxic effects (10 mg/kg - BCL, OL). For Cd there are no available FOREGS data for stream sediments dissolved in aqua regia. Lead shows one outlier, at the Mole West location in Lake Neusiedl. The Pb concentration of 49.6 mg/kg at that location is above the value that might cause lowest toxic effects (31 mg/kg - BCL), but it is far below the value which might cause significant toxic effects (250 mg/kg - BCL). Average concentrations of Pb according to FOREGS Geochemical atlas in sediments of the studied region are 11-14 mg/kg. Concentrations higher than those values are present in sediments of Darscholacke, Lake Neusiedl at Illmitz and Mole West and thermal spring Lieterbrudersdorf. Chromium does not show any anomaly. However, its concentrations in sediments were above the value that might cause lowest toxic effects (26 mg/kg - BCL) at the four locations: at Ochsenbrunnen karstic spring (54.0 mg/kg), at Jois (Lake Neusiedl) 35.8 mg/kg, in the Wulka River (31.4 mg/kg) and in the stream flowing from the abandoned coalmine (40.9 mg/kg). All those values are still far below the value that might cause significant toxic effects (110 mg/kg - BCL). Average concentrations of Cr according to FOREGS Geochemical atlas in sediments of the studied region are 16-27 mg/kg. Concentrations higher than those values are present in sediments of Ochsenbrunnen karstic spring, Lake Neusiedl at Jois, Wulka River and abandoned coalmine. Manganese shows one outlier, in sediments of the stream flowing from the abandoned coalmine. On that location Mn concentration (746 mg/kg) is above the value that might cause lowest toxic effects (460 mg/kg - BCL), but it is still far below the value which might cause significant toxic effects (1100 mg/kg - BCL). On location 8 at Darscholacke there is no statistical anomaly, but Mn concentration (483 mg/kg) is slightly above the value which might cause lowest toxic effects. Average concentrations of Mn according to FOREGS Geochemical atlas in sediments of the studied region are 452-795 mg/kg. All studied sediments, even the one from abandoned coalmine with the highest value, have Mn concentrations within expected values reported by FOREGS or below them. Zinc does not show any statistical anomaly, also all its concentrations are far below the threshold value under which sediments are considered to be unpolluted (90 mg/kg - USFC). Average concentrations of Zn according to FOREGS Geochemical atlas in sediments of the studied region are 45-60 mg/kg. In comparison with that, all studied sediments have very low Zn concentrations, all of them below those values reported by FOREGS. Copper does not show any statistical anomaly, but at two locations, Ochsenbrunnen karstic spring (16.2 mg/kg) and the Wulka River (22.8 mg/kg), its concentrations are slightly above the value which might cause lowest toxic effects (16 mg/kg - BCL). Even those values are still under the USFC for unpolluted sediments (25 mg/kg). Average concentrations of Cu according to FOREGS Geochemical atlas in sediments of the studied region are 14-19 mg/kg. In all studied sediments Cu concentrations are within or lower than those values, except in sediment of the Wulka River, whose concentration is slightly above values reported by FOREGS. Nickel shows one outlier, at Mole West location at Lake Neusiedl. On this location, its concentration (134 mg/kg) is significantly above the value that might cause severe toxic effects (75 mg/kg - BCL). On two more locations, which are statistically not anomalies, the concentrations are above the value that might cause lowest toxic effects (35 mg/kg - BCL, OL): at Ochsenbrunnen karstic spring (38.4 mg/kg) and at Zicksee (46.9 mg/kg). Average concentrations of Ni according to FOREGS Geochemical atlas in sediments of the studied region are 16-23 mg/kg. Concentrations higher than those values are present in sediments of Ochsenbrunnen karstic spring, Zicksee and in Lake Neusiedl at Mole West. Although antimony shows one outlier as statistical anomaly, its concentrations are very low, e.g. existing USFC for disposal of sediments in water is for Sb 500 mg/kg. For Sb there are no available FOREGS data for stream sediments dissolved in aqua regia. Barium does not show any statistical anomaly. Its concentrations are rather low, e.g. existing criteria for disposal of dredged sediments in water is 500 mg/kg (USFC). Molybdenum shows two extremes: at Ochsenbrunnen karstic spring (16.8 mg/kg) and at Zicksee (24.5 mg/kg). Both extremes are also above the value for disposal of dredged sediments (4 mg/kg - OL). For Mo there are no available FOREGS data for stream sediments dissolved in aqua regia. Silver, iron, cobalt and barium do not show any extremes and outliers, their concentrations are under toxic effect threshold and below or within the values reported by FOREGS Geochemical atlas.

In general, ecological status of analysed sediment samples in the studied area is very good and most of the studied sediment samples are unpolluted or only slightly polluted. Several elements on few locations have concentrations only slightly above threshold for lowest possible toxic effects, which is not worrisome. Only Ni might cause severe toxic effects. However, high Ni concentration in sediment is present at only one location (Lake Neusiedl - Mole West). Increased Ni concentration at this location is assumed to be of anthropogenic origin, especially as Pb concentration has outlier at the same location. In addition, this location is surrounded by a marina and is close to Neusiedl am See, the largest settlement in the whole region of lake Neusiedl. Elevated Mo and Sb concentrations in sediments of Zicksee Lake (site 6) could be due to a major association with the silicate phase, according to Kim et al. (2003). Elevated concentration of Na in sediments of saline Sechsmahdlacke Lake (site 7) could be due to the highest pH (10.05) of all studied waters of the Burgenland region and the highest content of plagioclase.

In addition to major and trace elements, organic matter and mineral oils buried in sediments were determined and presented in Table 5. Sediment nutrients TN and TP can have inorganic as well as organic sources. Mineral oils, composed of a vast mixture of hydrocarbons, were expected to be found on contaminated sites (Becker et al., 2006). The ratio TOC/TN is generally considered a good proxy to discriminate origin of organic matter (Sampei and Matsumoto, 2001). The ratio changes from 13.93 (in sample 7) to 93.28 (in sample 14). In all samples except in sample 7, there is evidence that the organic matter is of terrestrial origin, according to Bordowsky (1965), Meyers (1997) and Gulia et al. (2004).

**4.4. Chemical analysis of water**

From analysis of dissolved anions and cations in water samples (Table 6), a Piper diagram, one of the most useful ways of comparing water quality (Todd and Mays, 2005), was constructed and shown in Figure 2. Comparing Figure 4 given by Manoj et al. (2013) with ~~our~~ results of the current study, ~~we defined~~ two bicarbonate types of waters were defined: mixed calcium and sodium type (CaNaHCO3 in samples 8, 9 and 10) and calcium type (CaHCO3 in samples 6, 11, 12, 13 and 14). These specific water types are in direct relation with their interactions with the geological formations of the basin, dissolution of feldspars and chloride and bicarbonate minerals, as well as with anthropogenic activities (Jayaprakash et al., 2012). Similar hydrochemical facies (CaHCO3, CaNaHCO3) were found by Hagras (2013) in Punjab, Pakistan, while shallow groundwaters and hot springs from north-eastern Guangdong Province, China are mainly (NaK)CaHCO3Cl type, as reported by Jianfei et al. (2014). There was no good correlation between EC and pH, and also between EC and several ions measured, because here studied waters are very few and very different. However, the highest correlations of EC were obtained for Na+ (0.6354) and for SO42- (0.4781). Water analysis accuracy tester Lenntech was used to determine cation-anion balance of water analyses, from analyses presented in Table 6. The sum of cations and sum of anions in meq/L shows low percent difference (0.442-3.84) for samples 8, 9, 10 and 11. The sum of anions, calculated using the same table, shows that it is larger than the sum of cations used in calculation, for samples 6, 12, 13 and 14. Percent difference is greater than accepted difference of 5%, obviously some cations or complexes are missing in the calculation.

DOC values in waters are comparable with results obtained by Stojanovic et al. (2009). The highest DOC values (average 12.6 mg L-1) were found at sites 8, 9 and 10, where the highest salinity and pH were observed. This is consistent with results published by Jirsa et al. (2013), where DOC was positively correlated with salinity and electrical conductivity, due to processes of evaporation, and consequently concentration of DOC even in highly saline solutions. Furthermore, the lowest DOC amounts were determined in waters at site 11 (acid spring, 0.49 mg L-1) and site 14 (thermal spring, 0.51 mg L-1), due to lower pH (see Table 1). With respect to trace elements in saline lakes around the Burgenland area (State Archives of Eisenstadt 1963) concentrations of total and dissolved metals and metalloid concentrations (Cd, Pb, Ni, Co, Cu, Al, As, U) were not measured. The first such measurement was performed ~~by us~~ within the current study and presented in Figure 3. As suggested by Cuculić et al. (2009), the precise method can be used for preliminarily distinguishing natural from anthropogenic influence, even at very low concentration ranges.

Ochsenbrunnen (site 1) and Johannes (site 4) karstic springs exhibited low concentrations of all presented elements. Moreover, concentrations of ecotoxic metals and metalloids (Cd, Pb, Ni and As), both dissolved and total, were the lowest determined and were in the range characteristic for clean and unpolluted karstic rivers (Cukrov et al., 2008; Frančišković-Bilinski et al., 2013; Matić et al., 2013). However, moderately elevated concentrations of Cd, Mo, K and Tl in sediments of the Ochsenbrunnen karstic spring (Table 3) probably originate from erosion of the nearby soil rich in clays, which was transported to a small lake to which the spring water flows and sediment sample was taken from there. Contrary to the sediment, water at this spring is extremely clean and concentrations of elements in water are low at this location. On the other hand, the majority of total metal concentrations were the highest at the Wulka River site. Exceptions were As, U, Mn and Fe. It was not a surprise, since the Wulka River accepts the anthropogenic inputs from the surrounding area, which is confirmed by boxplot analysis showing extremes of total Pb, Co, Fe and outliers of total Zn, Cu, Mn and dissolved Co (Table 7). Moreover, Figure 4 presents percentage of dissolved metal fractions in waters. Generally, majority of metals at all sampling sites were present dominantly in dissolved fraction. However, Pb and in lesser extent Mn and Fe showed the lowest dissolved/total ratios in some samples. It is known from the literature that these elements and especially Pb have strong adsorption affinity for natural particles, mainly for Mn oxides (Bilinski et al. 1991). Consequently, the lowest dissolved/total ratios of Pb, Co, Mn and Fe were found in the water sample from the Wulka River indicating that these metals exist significantly in the form which does not pass the filter 0.45 µm at site 5.

Whereas sites 4 (Johannes karstic spring), 11 (acidic spring) and 12 (closed coalmine) supply their waters and belong to the Wulka River catchment, concentrations were presented ~~concentrations~~ (Table 8) for 10 dissolved trace elements from these sites and compared ~~them to~~ with the literature data (Gaillardet et al., 2003; Matić et al., 2013). In the Wulka water all presented trace elements in dissolved form were enriched compared to Johannes spring (site 4), from factor 2 for Cd up to factors 20 and 34 for Co and Zn, respectively. This was expected since this pristine karstic spring was not under anthropogenic influence, unlike the Wulka River. However, notably different physico-chemical conditions in acidic spring water (pH = 5.98) altered dissolved trace metal distribution. While in the Wulka River water (site 5) dissolved Pb, Cu, Ni, Co, As and U were enriched compared to other three sites (4, 11, 12), in acidic spring (site 11) dissolved Cd, Zn, Mn and Fe were the most abundant. That was due to the naturally low pH (5.98), which maintains existing metals in a dissolved form. At the acidic spring and the closed coalmine, concentrations of dissolved Cd and in larger extent Mn and Fe from their discharge drastically dropped upon mixing with the Wulka water. The most probable processes for the loss of dissolved elements were precipitation of elevated Fe and Mn and formation of low soluble ferrihydrite and Mn oxide particles in contact with more alkaline Wulka water. Subsequently, adsorption of dissolved metals, such as Cd and Zn, onto these particles occurs (Bilinski et al., 1991; Casiot et al., 2009). Comparing the Wulka levels of dissolved elements with the world averages (Table 8), one can see significantly higher loads of Zn, As and U (5.7, 4.2 and 33.6-fold, respectively). It is suggested that Zn in the Wulka is most probably of anthropogenic origin, while As and U are naturally enhanced. The Wulka levels of Cu, Ni and Co are quite similar and comparable (Table 8) to the world averages and significantly higher in comparison with values in water of Croatian coastal karstic spring (Matić et al., 2013). These metals in the Wulka have lower amounts compared to the Seine water at Paris where probably larger anthropogenic input exists (Gaillardet et al., 2003).

Higher abundances of U and Mn in sediment were reflected in their elevated concentrations in the water sample at the abandoned coalmine site (12). Water concentrations of both dissolved (22.0 µg L-1) and total (26.7 µg L-1) uranium were the highest of all sampling sites, 10-fold higher compared to Ochsenbrunnen karstic spring (2.0 and 2.6 µg L-1 of dissolved and total U, respectively) and 6-fold above uranium concentration at Johannes spring (3.7 and 4.4 µg L-1 of dissolved and total U, respectively). Both dissolved and total uranium concentrations in the water of the closed coalmine were 2 orders of magnitude (more than 100-fold) higher compared to Bad Sauerbrunn water sample (0.18 and 0.20 µg L-1 of dissolved and total U, respectively). Total uranium concentrations in the majority of sampling sites (except sites 6 and 12) were below 20 µg L-1 which is maximum acceptable concentration of uranium in Canadian drinking water (Health Canada, 2009). Elevated uranium concentrations in water at site 12 were comparable with values determined in two saline lakes of Southern Siberia where Parnachev and Degermendzhy (2002) found maximum values 16.4 and 24 µg L-1 of total uranium, which were the result of anthropogenic pressure. Uranium water concentrations at the majority of ~~our~~ the sites studied in the current study were in the concentration range of other unpolluted Siberian lakes. Moreover, in polluted springs of central Bosnia and Herzegovina, Lenoble et al. (2013) found up to 40 µg L-1 of dissolved uranium, while in a local river up to 0.7 µg L-1 were detected. Additionally, at the closed coalmine (site 12), statistical extremes of both dissolved and total Mn were calculated, which is expected, while uranium did not show any anomaly, both in water and sediment (Table 7 and Table 4).

Dissolved arsenic concentrations in water samples ranged from 0.17 µg L-1 at site 11 (Bad Sauerbrunn) up to 10.0 µg L-1 at site 2 (Jois at Jungfrau Lake). Maximum concentration (10 µg L-1) at Jois site is the threshold for the WHO guideline and the European drinking water standard. All other concentrations are equal to or well below 6 µg L-1. However, these values are quite low compared to the As concentrations found in groundwaters in eastern Croatia (up to 491 µg L-1) where geology and hydrochemistry govern speciation and elevated content of As (Ujević et al., 2010). Furthermore, in Bosnia and Herzegovina acid mine drainage was responsible (Lenoble et al., 2013) for extremely high arsenic content in local rivers (up to 6.6 mg L-1). The highest amount of dissolved arsenic (10 µg L-1, site 2) in this study is comparable to the lowest levels found in two Kenyan saline lakes where authors measured from 9 - 132 µg L-1 (Jirsa et al. 2013). At the majority of ~~our~~ the studied sites, arsenic in waters was predominantly present in dissolved fraction (>80 %) (Figure 4). In the waters at sites 1 - 4, dissolved/total ratio is well above 90 %. Lower percentage of dissolved form (44 - 66 %) was detected at sites 6, 8, 9, 10. This is due to the highest measured pH values (8.90 - 9.13), which favour precipitation and adsorption processes of arsenic on particulate matter (Lenoble et al. 2013). Furthermore, most of the measured elements at these four sites (6, 8, 9, and 10) showed the lowest percentage of dissolved form. However, at site 11 (acidic spring) with the lowest pH 5.98, the highest concentrations in water, both dissolved and total trace metals (Cd 0.015, 0.016; Zn 7.1, 7.6; Mn 312, 327 and Fe 4018, 7828 µg L-1) were detected, respectively. The concentrations are high in comparison to literature data presented in Table 8. Moreover, the elevated concentrations of total Cd and Zn were similar to their concentrations in the Wulka River (site 5), but unlike the Wulka River, elevated metals in acidic spring (site 11) probably were of natural origin showing statistical anomaly by boxplot evaluation (Table 7).

**5. Conclusions**

Surface sediments and waters of subsaline and freshwater environments of one of the largest wetlands in Central Europe were investigated in detail. The knowledge about chemistry, mineralogy and pollution status extends the earlier hydrogeological studies.

Eight minerals have been detected in sediments: calcite, quartz, muscovite/illite, chlorite, ankerite, dolomite, smectite and plagioclase feldspars, among which quartz prevails in the majority of samples. Terrestrial origin of organic matter in sediments, based on quoted literature, was suggested from the TOC/TN ratio >20, with the only exception at site 7. Concentrations of 13 potentially toxic metals (Cd, Pb, Cr, Mn, Zn, Cu, Ni, Sb, Mo, Fe, Ag, Co and Ba) were compared to the existing sediment quality criteria and FOREGS data. Thus, Cd, Pb, Cr, Mn and Cu were slightly above the values that might cause the lowest toxic effects, while Ni at one location with notable anthropogenic influence (134 mg/kg at site 10) was above the value that might cause severe toxic effects (75 mg/kg - BCL).

Concentrations of major cations and anions were used to construct a Piper trilinear diagram. Two water types were obtained, CaNaHCO3 and CaHCO3, which are in direct relation with the geological formations of the basin, dissolution of feldspars, chloride, bicarbonate minerals and with anthropogenic activities. Comparison of dissolved and total fractions of trace elements confirms that the water quality of the Lake Neusiedl catchment is good, in general. Trace element levels in waters exhibited significant variation among investigated locations, due to the natural and/or anthropogenic influence. Trace elements showed no significant anomalies in most of the water samples, except for the anthropogenically influenced Wulka River. However, only dissolved Zn, As and U in the Wulka River water were above the world average values for unpolluted rivers, due to the precipitation and metal adsorption onto suspended particles. Moreover, acidic spring contained the highest concentrations of dissolved Cd, Zn, Mn and Fe, due to the lowest pH. Enhanced arsenic levels (up to 10 µg L-1) in some water samples were of natural origin and its speciation is governed by hydrochemistry and geology, characteristic for the region. Anthropogenically elevated uranium amounts (up to 27 µg L-1) in the water near the closed coalmine, with high proportion of its dissolved form (above 80 % of total U), exceeded maximum allowed concentration of 20 µg L-1. However, concentrations of all trace elements in waters of two karstic springs were found to be low and in the range characteristic for unpolluted waters. Boxplot statistical analysis showed that most of the trace elements in water and sediment have normal statistical distribution and there is a small number of anomalies, which indicates that the study area has not been under substantial anthropogenic pressure.

Based on the present study, the locations of the Wulka and the closed coalmine region may be potential targets for future monitoring and risk and vulnerability analyses.

This extensive geochemical research of the fragile mixed aquatic systems that are partly located in protected areas would be of benefit for their further protection and we hope that similar research can be applicable to the similar wetland environments elsewhere.

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**Figure captions**

**Figure 1** Map of study area with sampling sites

**Figure 2** Piper diagram according to the major cations and anions in waters

**Figure 3** Concentrations of dissolved (Diss.) and total (Tot.) elements in water samples with 95% confidence intervals

**Figure 4** Percentages of dissolved vs. total element concentrations from Figure 3