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SURFACE SPRINGS OF LAKE OHRID - ACCESS OF PHYSICOCHEMICAL COMPOSITION

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Abstract

The goal of the paper is to point out specific characteristics of karst springs of Lake Ohrid as they contribute substantially to the lake's inflow. Supplying with nutrients, dissolved oxygen and constant living conditions surface springs are beneficial for lakes extraordinarity as a special boundary for many endemic species. It was shown that Lake Ohrid undergoes eutrophication, so another goal of our protection is monitoring of sensitive parameters regularly following the tributaries that feed this basin. Of interest was the quantification of basic physico-chemical spring properties in order to better understand how and what kind of groundwater is delivered to Lake Ohrid. As karst systems show heterogeneity and variability of many hydrogeological, ecological and other parameters, seven individual surface springs belonging to a larger spring area were monitored during three years. All of them are used as a source of drinking water. Categorization of the water samples is according to OECD regulations, positive by law regulations of Republic of Macedonia. Investigations are done according to standard limnological methods. It was found that there were no major changes with springs intrusion and runoff.

Key words: Lake Ohrid, surface springs, physico-chemical investigations, drinking water

Introduction

Lake Ohrid is located on the central Balkan with approximately two-third of its surface area belonging to Macedonia and about one-third belonging of Albania. Mediterranean climate and the small drainage basin of 2600 km² (catchment/lake surface ratio of ~7) of Lake Ohrid results in a long hydraulic residence time scale of ~70 years (Albrecht, 2008). The water balance of the lake is characterized by average in- and output rates of approximately 37.9 $m^3 s^{-1}$ (Albrecht, 2008), about two-third of the output occurs via River Crni Drim and one-third through evaporation. Relative to its surface, the catchment area is small. Excluding Lake Prespa, it is even smaller with 1,002 km^2 (Popovska and Bonacci, 2007). Today's water input from tributaries is a minor water source, whereas a significant ratio of inflow is delivered by inflows from karstic aquifers (~53%), direct precipitation on the lake surface (~23%), and river inflow (~23%) (Albrecht, 2008). There are around 40 tributaries which flow into the Lake Ohrid (23 on the Albanian side and 17 on Macedonian side). Most of them carry very poor amounts of water during the dry summer period. The hydrography above all reveals the karstic character of Lake Ohrid. Lakes. Many sub-lacustrine and surface springs, particularly on the South-eastern and Southern side of Lake Ohrid, are charged by neighbouring Lake Prespa as well as by mountain range precipitation seeping through the karstic rocks and mixing with the waters originating in Lake Prespa (Anovski *et al*., 1980; Eftimi and Zoto, 1997; Matzinger *et al*., 2006a; Amataj *et al*., 2007; Popovska and Bonacci, 2007).

The karstic springs are the most interesting phenomenon from a hydrogeological point of view, as they present heterogeneity and variability of many hydrogeological, ecological and other parameters. The aim of this article is to present few important surface spring groups by characterizing some physico-chemical parameters, such as temperature (*T*), electroconductivity, pH, ionic composition, and concentration of dissolved oxygen and some trace elements. These springs are large enough to supply the amount of freshwater needed for human requirements for the city of Ohrid. Inputs *via* springs provide nutrient-rich waters generating areas of enhanced biological activity (Stankovic, 1960; Gilbert *et al*., 1984; Naumoski, 1990; Sywula *et al*., 2003). Different authors determined unique life-forms with impressive percentages of diversity and endemism. The planaria species *Dendrocoelum sanctinaumi*, which is found in the St. Naum surface spring area shows clear genetic difference from littoral forms (Sywula *et al*., 2006) and many other species like freshwater sponge (Hadžišče, 1956; Gilbert and Hadžišče, 1984), forms of *gastropoda* and many others. Because of the crucial effects of springs on Lake Ohrid, they were included in this monitoring program. In this article, we present the temporal variability of spring water properties and show differences of those properties among different sites.

Materials and methods

Samples were taken from seven individual springs: three belonging to the larger spring complex at St. Naum (Capture – Spring 1, Church and St. Petka); two spring sites are located on higher elevations relative to Lake Prespa (849 m a.s.l.) named Elšani and Korita; Kališta spring in the North-western part of the Lake and Biljana's springs in the North-eastern part. A map with summary of all monitored surface springs is presented on the Fig. 1. Monitoring was done between June 2005 and September 2008.

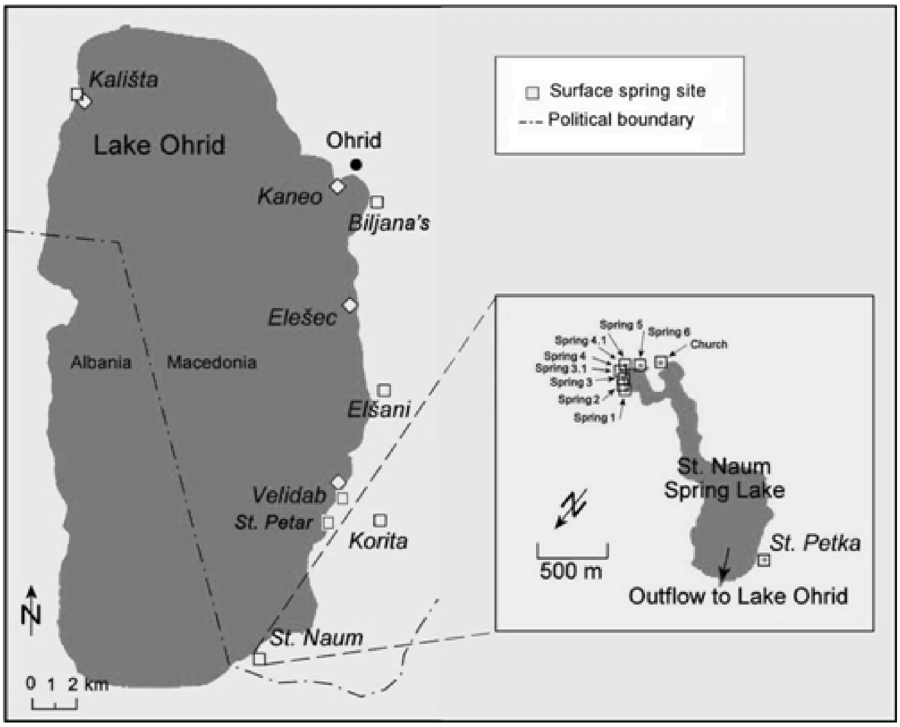

Fig. 1. Locations of surface springs of Lake Ohrid

Water temperature (*T*), specific conductance (κ_T), and pH were measured in-situ on a monthly basis from September 2005 to December 2006, after that quarterly until September 2008 at all sampling sites using hand-held instrument. The instruments' accuracies were 0.2^{o}C, 5% of the measured conductance value, and 0.01 for pH. Values κ_T were transformed to specific conductance at 20 ^{o}C (expressed with κ_{20}) based on ionic composition (Wüest *et al.* 1996).

Water samples were taken at Spring 1, Church and St. Petka, Korita, Elšani, Biljana's spring and Kališta on a monthly basis from September 2005 to December 2006, after that quarterly until August, 2008. Samples were stored in clean plastic bottles for analysis of ions and trace elements, in glass vials for analysis of stable isotopes, and in glass bottles for analysis of dissolved oxygen. The bottles were cooled immediately after sampling. Phosphate was measured using a Procon flow analyzer (DEW, 1996) at Eawag, Kastanienbaum and photometrically (Strickland and Parsons, 1968) at the Hydrobolological Institute, Ohrid. Cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}, NO_3^-) were measured with ion chromatography with an accuracy of <5% of measurement (Weiss, 2004) at Eawag, Kastanienbaum and by atomic absorption spectrometry (Varian, SpectrAA 220). Analysis of dissolved oxygen (DO) and oxygen saturation ($O_{2,sat}$) was carried out following the Winkler method (Clesceri *et al.*, 1989). For trace elements analysis water samples were concentrated with solid phase extraction and after that determined with electrothermal atomic absorption spectrometry (ETAAS). All other lab work was accomplished at Hydrobiological Institute, Ohrid and Faculty of Natural Science and Mathematics, Skopje.

Results and discussion

Average spring water temperature in the study area ranged from 8.2 ^{o}C at Spring Korita to 11.9 ^{o}C at Spring St. Petka. Average values for temperature, pH and conductivity are given in the Table 1. The regular annual climate conditions, as well as mountain site explains very low temperature of the Korita spring. Depending of the season its water temperature varies from 7.2 ^{o}C to 10 ^{o}C. At St. Naum spring area, ***in-situ*** measurements of the temperature from the individual springs were in a narrow range of 0.6 ^{o}C. Hence, water temperatures in the entire study area seemed to be constant during the entire year.

Average conductivity lied between 261-385 μS cm^{-1} (Table 1). Springs pH ranges between 7.5-7.9. Temporal constancy of the spring water could be noticed at St. Naum spring area (Table 1). At Kališta and Korita, pH values were 7.4 and 7.8. Alkalinity was determined as a concentration of $CaCO_3$ (in mg l^{-1}) and results were lower than 187 mg l^{-1} at all sampling sites. Only at Kalšita, seasonal changes could be noticed with variations from 160 to 220 mg l^{-1} $CaCO_3$ during the summer periods.

During the present study values of content of free CO_2 fluctuated in high range and pattern of variations were irregular, due to the rate of decomposition. Determined values at all investigated localities demonstrate continued presence in all seasonal periods in all three years. According to the seasonal dynamic there is higher trend in summer than in winter period. DO concentrations were from 6 to 13 mg l^{-1} (Table 1). Variations in DO occur seasonally where lower values were determined in the summer period. Springs at St. Naum area at the East side of the lake showed geographical trend. Starting from the most northern spring at the HBI yard, Biljana's water becomes more under-saturated with DO towards St. Naum spring area. Average values for the amount of biodegradable organic matter all years don't exceed higher value than 2.25 mg l^{-1} O_2 during the whole monitoring.

Table 1. General physico-chemical parameters of the surface spring of the Lake Ohrid

Parameter	Kališta	St. Naum -Spring 1	Church	St. Petka	Korita	Elšani	Biljana's
T (°C), mean	11,47	10,65	11,18	11,88	8,17	10,30	10,93
Range	11-11,9	10,3-11,2	10,3-11,40	10,3-13,60	7,2-10,20	10,01-11	10-15,30
CV	0,02	0,03	0,03	0,09	0,12	0,03	0,15
k_{20}/µS cm^{-1}, mean	316,45	237,82	256,73	261,09	221,96	242,18	234,35
Range	260-365	205-277	208-287	229-286	173,5-255	199,8-293	191,8-263
CV	0,12	0,13	0,13	0,10	0,15	0,14	0,11
pH, mean	7,32	7,52	7,53	7,55	7,78	7,62	7,63
Range	6,84-7,58	6,75-7,87	6,8-7,84	6,85-7,93	6,63-8,28	7,13-7,93	7,22-7,92
CV	0,03	0,05	0,05	0,04	0,06	0,04	0,03
Total alk., mg l^{-1} $CaCO_3$, mean	3,76	3,19	3,19	3,20	2,83	2,99	2,92
Range	3,2-4,44	2,96-3,48	2,8-3,5	2,12-3,44	2,58-3,10	2,78-3,12	2,69-3,2
CV	0,12	0,06	0,07	0,12	0,06	0,04	0,06
DO/mg l^{-1}, mean	8,43	7,75	6,64	6,11	10,20	9,82	10,07
Range	6,68-9,54	6,35-9,21	5,07-8,49	4,55-7,20	8,62-12,96	9,31-10,79	9,79-10,82
CV	0,09	0,10	0,15	0,12	0,12	0,05	0,03
Total P/µg l^{-1}, mean	87,65	34,49	10,78	31,20	10,56	19,00	23,03
Range	0,46- 719	0,41-301	0,45-20,41	0,45-52,4	0,58-22,83	0,24-78,6	2,85-9,05
CV	2,53	2,57	0,49	0,52	0,66	1,17	1,23
Total N/g l^{-1} Mean	446,69	543,40	360,87	388,60	262,38	379,50	379,87
Range	32,8-1203	32,8-1457	38,6-596	0-1192	0-450,06	121,7-706	152,5-671
CV	0,77	0,71	0,45	0,91	0,61	0,42	0,44
Cl^{-1}/µM, mean	107,54	95,17	90,04	108,50	85,92	95,16	72,34
Range	69,5-123	68,2-112	62,3-111	44,5-196	68,5-110	55,6-195,9	44,2-119,0
CV	0,18	0,16	0,21	0,61	0,19	0,55	0,50
Ca^{2+}/µM, mean	1027	919,93	901,89	887,13	900,60	842,25	758,0
Range	868 -1397	511-1454	423-1425	723-1009	679 -1057	499-1132	357 -1021
CV	0,19	0,35	0,38	0,14	0,15	0,22	0,37
Mg^{2+}/µM, mean	128,6	159,96	197,12	163,56	59,81	80,25	64,27
Range	73,6- 205	83,7-225	111-288	35,5-260	19,86-132	40,8-159,2	22,1-139,8
CV	0,33	0,27	0,30	0,48	0,84	0,55	0,71
Na^{+}/µM, mean	71,9	76,01	85,33	82,61	30,88	43,07	49,2
Range	39,5-120,8	42,3-120	35,0-144	24,4-152	14,36-51,9	24,54-55,6	15,8-62,0
CV	0,50	0,38	0,41	0,48	0,52	0,20	0,27
K^{+}/µM, mean	12,63	20,79	22,42	27,03	3,73	10,99	7,40
Range	9,15-16,7	18,3-22,5	18,22-25,15	22,6-32,1	2,8-4,20	9,8-13,46	5,9-8,87
CV	0,21	0,07	0,08	0,10	0,14	0,10	0,12

CV- Coefficient of variation

Average cationic composition is given in the Table 1. The highest value for calcium is detected at Kališta. Average values for (SO_4^{2-}) exceeded from 0.4 mg l^{-1} at Elšani, 0.32 mg l^{-1} at St. Petka surface and lowest value of 0.12 at Kališta, St. Naum and Korita. Concentrations of NO_3-N exceed 0.04-0.8 mg l^{-1} for NO_3-N (Fig 2). Nitrite concentrations in these freshwaters were usually very low, 0.001 mg l^{-1} for NO_2-N. Generally, the determined concentrations of organic nitrogen content in the entire study area spanned a large range resulting in large relative differences (e.g. average concentration of organic nitrogen at springs Elšani and Korita was at least three fold the value measured for spring St. Petka and almost five fold measured at St. Naum Spring 1). Surface springs contained less than 0.03 mg l^{-1} phosphorus except Kališta surface spring which showed seasonal fluctuations and had average phosphorus values of 0.08 mg l^{-1} (Fig 3). Consequently, increase was usually in the summer period when is the tourist season with highest values at spring Kališta measured in august, 2006 of 0.7 mg l^{-1} and St. Naum spring area of 0.3 mg l^{-1}.

The method of solid face extraction (Karadjova, 1999; Stafilov, 2002) was used for concentrating and determination of eight trace elements: Pb, Cd, Cr, Cu, Fe, Hg, Ni, Co, Mn, As. The concentration of different metals in waters varies over a wide range: from 11 µg l^{-1} for iron till 0.02 µg l^{-1} for Cd, generally very small concentrations, below permissible limits. As and Co were under detection limits for all gathered samples.

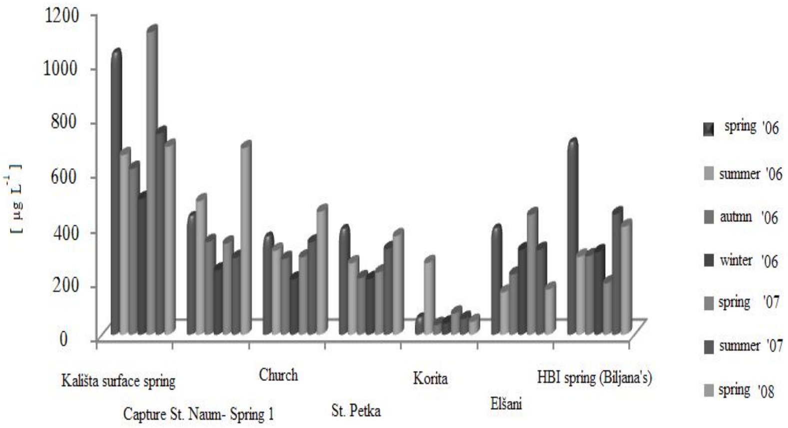

Fig. 2. The NO_3-N and concentration in surface springs, seasonal dynamic in µg l^{-1}

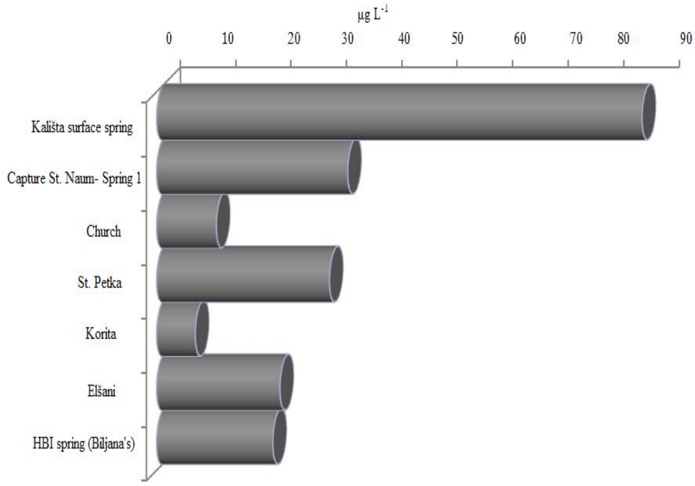

Fig. 3. Seasonal changes in TP for subaquatic springs in µg l^{-1}

Conclusions

Data gathered in this study indicate general stability of spring water characteristics. Measured parameters showed only little seasonal variation, as demonstrated most distinctly by records of water temperature. However, springs were found to be individually characterized by physico-chemical signatures. Similarly, other measurement parameters do not seem to vary in time. In the case of conductivity, pH, DO, variability was minor as indicated by small standard deviations of the averaged values. Variations of ion concentrations were relatively high but not systematic. At St. Naum spring area beside the fact that sources of spring water vary in their physical and chemical properties over time, the temporal stability of these properties measured in spring water is surprising. Neither signals from precipitation events nor seasonal changes in Lake Prespa's outflow are detected at spring outflows at this area. The most likely explanation for temporal stability to this remarkable extent is the existence of large reservoirs within the karsts system in which groundwater is stored for long periods. Owing to the high amount of spring water draining into Lake Ohrid, the groundwater reservoirs feeding the springs must be huge. Large underground lakes may exist inside the mountains between Lake Ohrid and Lake Prespa. Alternatively, large porous channels may be present through which groundwater flows slowly towards Lake Ohrid. The greater the scale of such reservoirs the longer groundwater will be stored. Naturally, residence time has to be longer than one year that temperature can be balanced. Biljana's and St. Naum general characteristics of the spring regime are the direct correlation between precipitation and spring discharge.

Water from all surface springs was usually remarkably clear. The quality of spring water represents the general water quality of the ground-water system. Most spring water was of excellent quality. The specific conductance of all subaquatic and surface springs water generally is less than 400 $\mu S\ cm^{-1}$, indicating that small amounts of minerals are dissolved in the water. Chloride and sulphate concentrations generally are less than 0.3 and 5 $mg\ l^{-1}$, respectively. Spring-water temperatures range from 8 to 12 °C. Higher water temperatures in spring Church indicate that the water originates from deeper parts of the karstic aquifer system, or due seismic activities. Fluctuations of temperature and nutrients at Korita and Elšani are regarding the mountain area, thus, variations were explainable.
Even though general conclusions, anthropogenic influence is still presented with higher amounts of phosphorus measured at Kališta spring area.

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