TEMPORAL VARIABILITY IN PHYSICO-CHEMICAL PROPERTIES OF ST. NAUM KARST SPRINGS FEEDING LAKE OHRID

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TEMPORAL VARIABILITY IN PHYSICO-CHEMICAL PROPERTIES OF ST. NAUM KARST SPRINGS FEEDING LAKE OHRID

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ABSTRACT

Jordanoska, B., Kunz, M. J., Stafilov & T., Wüest, A. (2010). Temporal variability of physico-chemical properties of St. Naum karst springs feeding Lake Ohrid, Ekol. Zašt. Život. Sred., Vol. 13, No. 1-2, 3-11, Skopje.

Lake Ohrid is strongly affected by karstic springs. Sub-aquatic as well as surface springs provide ~27% to the overall water input of ~38 m^3 s^{-1}. This particularity of cool, clean and oxygen-rich inflowing water was an important prerequisite for the establishment of the extraordinary biodiversity of Lake Ohrid. The aim of this article is to present physico-chemical properties of the spring water located in the southern part of the lake. Eight individual springs, belonging to the larger spring complex of St. Naum, were monitored for three years. The first part of the data record revealed long-term stability of spring water characteristics. The water temperature remained constant with variability of only ~0.1 °C to ~0.2 °C. Similarly, small changes in electrical conductivity, pH, dissolved oxygen and stable isotopes emphasize the low variability of the water properties. In turn, a comparison of the datasets reveals substantial differences between the eight springs in spite of their close proximity to each other. Temporal stability and spatial heterogeneity of the water properties suggest the existence of a complex and voluminous groundwater system feeding the springs, in which the spring waters are expected to be stored in large reservoirs for a long period of time. These observations imply that changes in the Lake Ohrid spring water quality may take effect with a substantial delay relative to alterations in its catchment.

Key words: Karst springs, Lake Ohrid, Republic of Macedonia, temporal stability, ancient lake, spring water temperature

ИЗВОД

Јорданоска, Б., Kunz, M. J., Стафилов, Т. и Wüest, A. (2010). Временска стабилност на физичко-хемиските карактеристики на карстните извори во Св. Наум, Охридско Езеро, Екол. Зашт. Живот. Сред., Том 13, Бр. 1-2, 3-11, Скопје.

Значително влијание на приливот во Охридското Езеро имаат карстните извори кои се богати со нутриенти. Површинските како и подводните извори обезбедуваат ~27% од вкупниот прилив на Езерото од ~38 m^3 s^{-1}. Оваа ладна, чиста и богата со кислород вода претставува важен предуслов за формирање на исклучителниот биоверзитет на Охридското Езеро. Целта на ова истражување е да се презентираат некои физичко-хемиски карактеристики на изворската вода од јужниот дел на Езерото. За таа цел, во текот на три години, се истражувани осум одделни извори кои припаѓаат на една поголема изворска област. Добиените резултати укажуваат на константност на специфичните особености на изворите, во текот на целиот период на истражување. Занемарливата варијабилност на температурата, која се движеше во граници од 0.1°C до 0.2°C, како и малите промени на електроспроводливоста, pH, растворениот кислород и стабилните изотопи, ја потенцираат постојаноста на изворската вода. Но сепак, споредувајќи ги изворите индивидуално, се откриваат значителни разлики помеѓу осумте извори и покрај краткото растојание на кое се распределени. Временската стабилност на параметрите и просторната хетерогеност на изворската вода, укажуваат на постоењето на сложен подземен систем кој ги храни изворите и се очекува истиот да биде складиран во големи акумулации и во подолг временски период. Ова би значело дека промените во квалитетот на изворите ќе се одразат, иако со одредено доцнење, на квалитетот на водата на Охридското Езеро.

Клучни зборови: Карстни извори, Охридско Езеро, Република Македонија, временска стабилност, прастаро езеро, темепература на изворската вода.

INTRODUCTION

Lake Ohrid, located in the border region of Macedonia, Albania and Greece, south-eastern Europe, is protected under the UNESCO World Heritage program (UNESCO, 2006). Lake Ohrid‘s rich biodiversity and endemism was of main scientific attention in the past (Stankovic, 1960; Martens, 1997; Sell et al., 2004). Unfortunately, this valuable ecosystem is endangered by anthropogenic impacts resulting from ecologically adverse alterations, which have already been observed and documented (Watzin et al., 2002). In the worst case, irreversible future changes of the ecosystem must be anticipated if the trophic level of Lake Ohrid is significantly increasing (Matzinger et al., 2007). The ongoing eutrophication, in combination with global warming, could lead to a complete depletion of oxygen in the deep water (Matzinger et al., 2007).

Karstic springs, adjacent to the entire coast line, play an important role for Lake Ohrid (Fig. 1). The overall contribution to Lake Ohrid‘s total inflow account for more than ~50% (Matzinger et al., 2006b). The springs are fed by aquifers that are recharged from precipitation and, along the eastern shoreline, also entirely from upstream Lake Prespa (Anovski et al., 1980; Amataj et al., 2005; Matzinger et al., 2006a). Due to its organic productivity, Lake Prespa is an important source of nutrient and oxygen-rich water for oligotrophic Lake Ohrid, although significant portions of phosphorus are retained during the underground passage (Matzinger

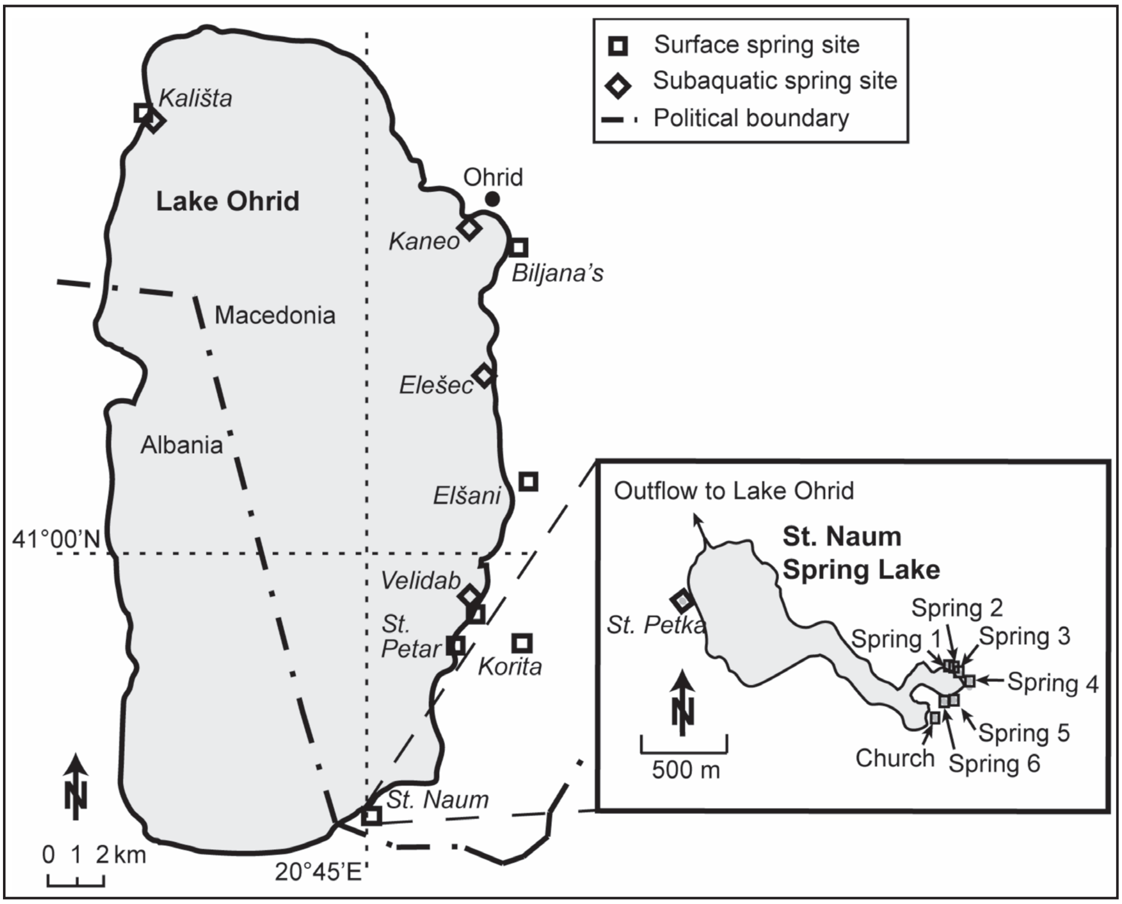

Fig. 1. Lake Ohrid including the positions of the springs indicated: The springs located at St. Naum Spring Lake, examined in this study, are marked by open symbols (see inset).

Сл. 1. Охридското Езеро и истражуваните локалитети: Истражуваните локалитети околу изворите кај Св. Наум се прикажани во зголемениот дел et al., 2006a). In this context, springs may compromise Lake Ohrid's ecosystem by becoming a source of pollution, especially if future nutrient concentrations in Lake Prespa increase substantially (Matzinger et al., 2006a).

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). These zones are likely to be found where intruding spring water stratifies, i.e. between 15 and 40 m depth depending on the season (Matzinger et al., 2006b). Hypothetically, this setting may have been crucial in supporting the evolution of endemic species, and of habitats populated by those organisms.

It was suggested that monitoring of Lake Ohrid is of high relevance in respect to establishing a reference of anthropogenic impacts, which are anticipated to increase further (Matzinger et al., 2007). Because of the crucial effects of springs on Lake Ohrid, they were included in such a monitoring program. Therefore, it is of great interest to quantify their basic physico-chemical water properties, in order to better understand how and what kind of groundwater is delivered to Lake Ohrid by those karst springs. This study has focused on the water quality of the springs in the St. Naum area by characterizing some physico-chemical parameters, such as temperature (*T*), conductivity, pH, ionic composition, dissolved oxygen and stable isotopes. In this article, we present the temporal variability of spring water properties and show differences of those properties among different sites.

MATERIALS AND METHODS

The studied springs are located at the St. Naum spring area close to the border between Macedonia and Albania (Fig. 1). Due to the various springs, a tiny lake developed (Fig. 1), which collects their waters before draining into Lake Ohrid. At its outflow, a relatively constant mean discharge of ~7.5 $m^3 s^{-1}$ was reported, which accounts for ~20% of the total inflow to Lake Ohrid (Watzin et al., 2002). Eight springs located around St. Naum Spring Lake were examined between June 2005 and August 2008 (hereafter called „Spring 1" to „Spring 6", „Spring Church", and „Spring St. Petka"; inset of Fig. 1).

Water temperature (*T*), specific electrical conductance (κ_T), and pH were measured *in-situ* using handheld instruments. Subsequently, seasonal measurements were done. The instruments' accuracies were 0.2°C, 5% of the measured conductance value, and 0.01 for pH. κ_T values were transformed to specific conductance at 20°C (expressed with κ_{20}) based on ionic composition (Wüest et al., 1996).

An important aspect is the potential seasonal variability in the spring activity. In order to observe such changes, moorings with *T* loggers were placed into the flow of a few selected springs, Spring 1, Spring 4, Spring 6 and Spring Church. Data was recorded from November 2005 to March 2009 with an accuracy of ~0.1°C.

Water samples were taken at Springs 1, Church and St. Petka on a monthly basis from September 2005 to December 2006, and quarterly until August 2008. Samples were stored in clean plastic bottles for analysis of ions, in glass vials for analysis of stable isotopes, and in glass bottles for analysis of dissolved oxygen (DO). The bottles were cooled immediately after sampling. Phosphates were measured using a Procon flow analyzer (method in DEW, 1996) at Eawag, Kastanienbaum and photometrically (Strickland and Parsons 1968) at the Hydrobiological 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 (methods in Weiss, 2004) at Eawag and by atomic absorption spectrometry (Varian, SpectrAA 220). Analysis of DO and oxygen saturation ($O_{2,sat}$) was carried out following the Winkler method (Clesceri et al., 1998).

Analysis of stable isotopes of oxygen and hydrogen was carried out with isotope ratio mass spectrometry (method adapted from Werner et al., 2001) at Eawag. The instrument's accuracies were 0.3‰ and 0.8‰ for ^{18}O and deuterium (D), respectively. The resulting $^{18}O/^{16}O$ and D/H ratios were compared to internationally accepted Vienna Standard Mean Ocean Water (VSMOW). Differences were expressed in the delta-notation as a per mille deviation (i.e. $\delta^{18}O$, and δD).

RESULTS

Results from *in-situ* measurements are listed in Table 1. Mean *T* in the study area ranged from 10.4 °C at Spring 1 to 12.6 °C at Spring St. Petka. Average conductivity lay between 261 to 284 µS cm^{-1} for Spring 1 and Spring St. Petka, respectively. At all measured springs, pH was virtually the same (7.63 to 7.65). Averaged values of *in-situ* measurements had generally small standard deviations (Table 1).

Fig. 2 describes the *T* development over three years. At Spring 1, *T* was 10.4 °C during the three years of measurements and between 10.7 and 10.8 °C at Spring 4. *T* of both springs did fluctuate only marginally in time. Compared to Spring 1 and 4, Spring Church was warmer, where *T* was measured between 11.3 and 11.5 °C. Similarly, at Spring 6, *T* varied between 11.1 and 11.2°C.

Results from the analyses of DO and of stable isotopes are presented in Table 2. The highest concentration of DO was measured for Spring 1 (7.8

Tab. 1. Averages resulting from sporadic *in-situ* measurements. The "± values" represent experimental standard deviation of the mean (n=11).

Таб. 1. Просечни вредности од поединечните in-situ мерења на испитуваните извори. „±" вредностите ја претставуваат експерименталната стандардна девијација (n=11).

Spring name*	**Temperature [°C]**	**Elecytroconductivity, κ_{20} [µS cm^{-1}]**	**pH**
Spring 1	10.5 ± 0.2	261 ± 1	7.6 ± 0.05
Spring 2	10.6 ± 0.05	268 ± 1	7.6 ± 0.05
Spring 3	10.7 ± 0.05	272 ± 1	7.6 ± 0.05
Spring 4	10.7 ± 0.05	273 ± 1	7.6 ± 0.05
Spring 5	10.8 ± 0.05	275 ± 2	7.6 ± 0.05
Spring 6	11.2 ± 0.05	298 ± 1	7.6 ± 0.05
Spring Church	11.2 ± 0.3	317 ± 41	7.5 ± 0.3
Spring St. Petka	11.9 ± 0.3	317 ± 32	7.6 ± 0.3

*Number of samples = 11

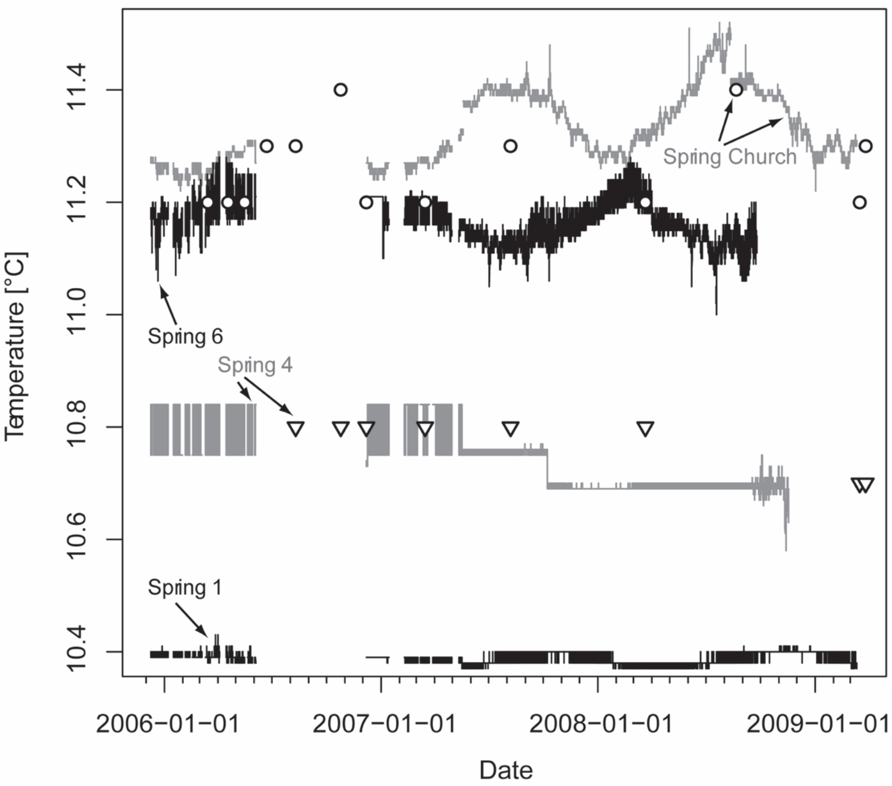

Fig. 2. Spring water temperatures at St. Naum Spring Lake (Spring 1, Spring 4, Spring 6 and Spring Church). Temperature series, recorded by thermistors, are shown by lines, whereas open circles and triangles display individual *in-situ* measurements at Spring Church and Spring 4, respectively. As obvious from the line-plots, thermistors products with different resolutions (Vemco: low resolution; Richard Bancker: high resolution) have been used.

Сл. 2. Температура на изворската вода во подрачјето на изворите кај Св. Наум (Извор 1, Извор 4, Извор 6 и Црква). Податоците добиени со помош на термистори се прикажани со линии, круговите и триаголниците ги претставуваат индивидуалните *in-situ* мерења во изворот Црква и Избор 4, соодветно. Според графикот, очигледна е различната резолуција на употребените термистори (Vemco: ниска резолуција; Richard Bancker: висока резолуција)

Tab. 2. Averages resulting from analysis of dissolved oxygen (DO) and of stable isotopes. The "±" values represent experimental standard deviations of the mean (n=11).

Таб. 2. Просечни вредности за растворен кислород и стабилните изотопи во водата од истражуваните извори. „±" вредностите ја претставуваат експерименталната стандардна девијација (n=11).

Site name	**DO [mg L^{-1}]**	**$O_{2,sat}$ [%]**	**$\delta^{18}O$ [‰]**	**δD [‰]**
Spring 1	7.7 ± 0.7	78.1 ± 7.4	-6.9 ± 0.1	-40.8 ± 4.4
Spring Church	6.6 ± 0.9	65.7 ± 9.9	-5.5 ± 0.3	-43.2 ± 3.8
Spring St. Petka	6.1 ± 0.7	63.2 ± 7.9	-6.1 ± 0.1	-47.0 ± 0.9

*Number of samples = 11

Tab. 3. Concentrations of ions (all values in µmol L^{-1}). The "± values" represent experimental standard deviation of the means (n = 11).

Таб. 3. Концентрација на јоните (вредностите се дадени во µmol L^{-1}). „±" вредностите ја претставуваат експерименталната стандардна девијација (n = 11).

Spring	**Cl^-**	**SO_4^{2-}**	**NO_3^-**	**PO_4^{3-}**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
Spring 1	96 ± 14	27.3 ± 2.0	13.9 ± 5.6	0.3 ± 0.2	76 ± 30	20.8 ± 1.4	933 ± 43	160 ± 44
Spring Church	90 ± 19	40.3 ± 3.5	10.4 ± 4.2	0.4 ± 0.1	91 ± 32	22.4 ± 1.8	858 ± 100	197 ± 58
Spring St. Petka	109 ± 67	31.7 ± 0.6	10.0 ± 3.5	0.9 ± 0.3	95 ± 39	27.0 ± 2.8	974 ± 21	164 ± 78

mg L^{-1}). Lower concentrations were determined for Springs Church and St. Petka (6.6 and 6.1 mg L^{-1}, respectively). Similarly, $O_{2,sat}$ was highest at Spring 1 compared to the other three springs. Springs Church and St. Petka were clearly undersaturated in O_2. Distribution of stable isotopes was similar for all sites. $\delta^{18}O$ ranged from -5.5 to -6.9‰, while δD varied between -40.8 and -47.0‰.

Average concentrations of anions and cations are listed in Table 3. Concentrations of ions showed the same sequence for all measured springs. For cations, the highest values were recorded for Ca^{2+}, followed by Mg^{2+}, Na^+ and K^+. Anions were dominated by Cl^-, followed by NO_3^-, SO_4^{2-} and PO_4^{3-}. Generally, the estimated concentrations of the entire study area spanned a large range resulting in large relative differences (e.g., mean concentration of PO_4^{3-} at Spring St. Petka was at least three-fold the value measured for Spring 1).

DISCUSSION

Data collected in this study indicate a remarkable stability of spring water characteristics. Measured parameters showed only little temporal variation, as demonstrated most distinctly by records of *T*. However, each spring was found to be individually characterized by its physico-chemical signature.

Temporal stability

Typically, the individual springs' *T* was found in a narrow range of less than 0.2°C (Table 1). This is reflected by time series recorded at springs 1, 4, 6 and Church by installing thermistors into the springs' flow (Fig. 2). Taking into account the thermistors' accuracy, no significant changes have been detected over time.

At first sight, Spring Church exhibited higher variability relative to the other two sites (Fig. 2). It has to be considered that daily and seasonal changes in air temperature may have influenced measured *T* depending on how well the thermistor was covered by spring water. For Spring Church, it was not possible to install the thermistors exactly at the mouth of the spring. Hence, spring water may have been cooled or warmed by the air resulting in the observable daily *T* peaks. However, baseline *T* differed by less than 0.2 °C. This range is expected to agree with the actual *T* that is not influenced by changes in air temperature.

Similar to thermistor data, monthly *T* measurements suggest small temporal fluctuations of *T*. Standard deviations of the mean values are generally small, and in accordance to the *T* range documented by thermistor records. Note that this dataset covers all eight sites. Hence, *T* in the entire study area seems to be constant during the entire year.

Similarly, other measurement properties do not seem to vary in time. In the case of κ_{20}, pH, DO, and $\delta^{18}O$, variability was again minor as indicated by small standard deviations of the mean values (Tables 1 and 2). Variations of ion concentrations and of δD were relatively high but not systematic (Table 2). Larger deviations of the mean values may be due to poor reproducibility related to the applied analysis.

Given 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 apparent at spring outflows in the St. Naum area.

Temporal stability can even be anticipated over long periods by inspecting stable isotopes. Herein presented measurements (Table 2) did not vary significantly from values measured in 1977 (Anovski et al., 1980), and from more recent results (GNIP, 2004; Matzinger et al., 2006a). These findings underline the accuracy of the measurements achieved during this study, and reflect the long-term stability of the examined karst system.

Low temporal variability of spring water characteristics demonstrate the diffuse character of the aquifer feeding the examined springs in contrast to conduit springs (Bonacci, 1987). For the latter type of springs, physico-chemistry and hydrology of groundwater are greatly affected by meteorological conditions (Aquilina et al., 2005). For diffuse springs, standard deviation of *T* is expected to be ~1 °C resulting from deep circulation of groundwater (Bonacci, 1987). However, the herein presented results show an up to 30-fold lower variation.

The most likely explanation for temporal stability to this remarkable extent is the existence of large reservoirs within the karst system in which groundwater is stored for a long period of time. Owing to the high amount of spring water draining into Lake Ohrid, the groundwater reservoirs feeding the springs must be extremely large. 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 reside. Evidently, the residence time has to be longer than one year in order to balance the seasonality of *T*.

Springs combine water from different groundwater sources exhibiting very different residence times. Indeed, a certain portion of groundwater reaches the spring outflow much faster than the anticipated average travel time. This was shown in a dye tracer experiment, during which water originating from Lake Prespa emerged at spring Тиљемiљте, Albania after only six hours (Amataj et al., 2005). However, *T* signals of water traveling in these „fast channels“ were not detected in this study. An estimation of mean residence time could be derived in future using radiogenic tracers (Manga, 2001).

Spatial variability

Several parameters varied considerably when comparing individual springs. Measurements of *T* and of DO revealed a geographical gradient in the St. Naum spring area. Lowest *T* was measured in the south eastern corner of St. Naum Spring Lake. *T* then gradually increased following clockwise around the lake towards St. Petka (Fig. 1, Table 1).

Meanwhile, DO and $O_{2,sat}$ decreased from Spring 1 towards Spring Church and Spring St. Petka, where the minimum $O_{2,sat}$ as well as minimum DO was recorded (Table 2). Oxygen may be consumed during oxidative processes including mineralization of organic matter. Such biological mineralization is illustrated by examining phosphorus contribution from Lake Prespa to Lake Ohrid: most phosphorus measured in spring water is found in its mineralized, thus bio-available form whereas Lake Prespa delivers partly phosphorus incorporated in organic particles (Matzinger et al., 2006a).

Mean concentrations of ions varied greatly from one spring to another. Thus, ion concentrations clearly demonstrate the characteristics of the individual St. Naum springs. In most cases, concentrations were lowest at Spring 1 relative to Spring Church and Spring St. Petka (Table 3). Accordingly, κ_{20} increased from Spring 1 towards St. Petka, showing a similar trend to the warming of the water (Table 1).

Contrarily, pH values lack trends comparing the measured sites. Data by EMEP (2005) show that pH in precipitation measured in south western Macedonia is ~5.5 ± 0.5 (mean of annual measurements from 1977 to 1991). This value is much lower compared to source water from Lake Prespa (8.6 ± 0.05; unpublished data by A. Matzinger, mean of a vertical CTD profile).

In conclusion, it is to be expected that the structure of the groundwater flow is complex. The small scale variations in spring water properties suggest that the St. Naum spring area is fed by more than one single groundwater source. Depending on the flow path of water from a certain spring, its characteristics such as *T* and the chemical composition are determined. Overall, the individual characteristic of each spring produces a physico–chemical fingerprint owing to different origins of water of the associated spring, and different geochemical processes altering the spring water properties. This finding is remarkable considering the proximity of the spring outlets (Fig. 1). It also disagrees with the concept that all groundwater discharging in the St. Naum area is stored in a single large underground reservoir.

CONCLUSIONS

The long residence time of the groundwater has important implications concerning the transport of substances to Lake Ohrid. If groundwater is retained for several years in the underground, currently estimated loads to Lake Ohrid may basically show past pollution. As a result, changes in upstream Lake Prespa are detected with substantial delay at the spring inflows. Moreover, due to Lake Ohrid‘s long hydraulic residence time (~70 yr), effects will show up with an even larger delay in Lake Ohrid.

The spatial variability of physico-chemical properties leads to the assumption that spring water is delivered heterogeneously to Lake Ohrid. Each spring discharges water with a characteristic quality, which is differing substantially from other springs. It is thus important to examine all spring waters from Lake Ohrid's entire catchment to be able to qualify the groundwater input.

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ВРЕМЕНСКА СТАБИЛНОСТ НА НЕКОИ ФИЗИЧКО-ХЕМИСКИ КАРАКТЕРИСТИКИ НА КАРСТНИТЕ ИЗВОРИ ВО СВ. НАУМ, ОХРИДСКО ЕЗЕРО

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Резиме

Охридското Езеро претставува еден од највредните и најстарите екосистеми и претставува прибежиште на над 200 ендемични видови. Докажано е дека Езерото е во опасност од антропогеното влијание, подлегнувајќи на процесот на еутрофикација која заедно со глобалното затоплување може да доведе до целосна деплеција на кислородот во длабокиот хиполимнион. Значително влијание на приливот во Охридското Езеро имаат карстните извори кои се богати со нутриенти. Целта на ова истражување е да се презентираат некои физичко-хемиски карактеристики на изворската вода од јужниот дел на Езерото. За таа цел, во текот на три години, се истражувани осум одделни извори кои припаѓаат на една поголема изворска област, кои се лоцирани во близина на Св. Наум. На испитуваните извори беа мерени *in-situ* следните параметри: температура на водата (T), кондуктивитет (κ_T) и pH, употребувајќи теренски инструменти. Потенцијалните сезонски промени се разгледувани преку постојаното мерење на температурата во период на три години во неколку извори со помош на термистори, со точност од ~0.1°C. Во водните примероци се испитувани следните параметри: растворен кислород (DO), фосфор, катјони (Na^+, K^+, Ca^{2+}, Mg^{2+}) и некои анјони (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-) како и стабилните изотопи ($\delta^{18}O$, и δD).

Добиените резултати укажуваат на константност на специфичните особености на изворите, во текот на целиот период на истражување. Занемарливата варијабилност на температурата, која се движеше во граници од 0.1 °C до 0.2 °C, како и малите промени на електроспроводливоста, pH, растворениот кислород и стабилните изотопи, ја потенцираат постојаноста на изворската вода. Но сепак, споредувајќи ги изворите индивидуално, се откриваат значителни разлики помеѓу осумте извори и покрај краткото растојание на кое се распределени. Временската стабилност на параметрите и просторната хетерогеност на изворската вода, укажуваат на постоењето на сложен подземен систем кој ги храни изворите и се очекува истиот да биде складиран во големи акумулации и во подолг временски период. Ова би значело дека промените во квалитетот на изворите ќе се одразат, иако со одредено доцнење, на квалитетот на водата на Охридското Езеро.