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Assessment on physico-chemical composition of surface karst springs feeding Lake Ohrid

Проценка на физичко-хемискиот состав на површинските карстни извори кои го прихрануваат Охридското Езеро

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The goal of the paper is to characterise the surface karst springs of Lake Ohrid as they contribute substantially to the lake's inflow. As Lake Ohrid is affected by recent eutrophication, another goal of its protection activity is regular monitoring of sensitive parameters 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 inflowing water is delivered to Lake Ohrid. For that purpose, seven individual surface springs (3 major springs of the large spring complex at St. Naum, Spring 1, Church and St. Petka, two spring sites located on higher elevations relative to Lake Prespa, Elšani and Korita; Kališta and Biljana's springs) belonging to a larger spring area were monitored during three years. 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 had individually different physico-chemical signatures. Thus, the fluctuations of temperature and nutrients at Korita and Elšani were caused by mountain range precipitation. The temperature, conductivity, pH and DO variability was minor as indicated by small standard deviations of the measurements. The specific conductance of all subaquatic and surface spring waters was generally less than 400 µS cm^{-1}, indicating that the water contained only small amounts of dissolved minerals. It was also found that the concentration of various heavy metals (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni and Pb) are very low in all of the investigated springs.

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

Целта на овој труд е да се одредат карактеристиките на карстните извори кои се влеваат во Охридското Езеро, а кои значително придонесуваат кон неговиот прилив. Поради тоа што Охридското Езеро подлежи на процесот на еутрофикација, друга цел за неговата заштита е воспоставување на редовен мониторинг на чувствителните параметри на притоките кои го хранат овој слив..Од интерес беше квантификација на основните физичко-хемиски својства на изворите со цел подобро да се процени каков е квалитетот на приливната вода која влегува во Охридското Езеро. За таа цел, седум индивидуални површински извори (3 позначајни извори кај комплексот Св. Наум - Извор 1, Црква и Св. Петка, два извори лоцирани на ниво на Преспанското Езеро, Елшани и Корита; Калишта и Билјанини Извори) кои припаѓаат на поголемо сливно подрачје се следени во текот на три години. Податоците покажуваат ге-

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нерална постојаност на карактеристиките на изворите. Измерените параметри покажуваат многу мали сезонски варијации, што јасно се гледа од евидентираните температури на изворите. Сепак, секој извор се карактеризира со свои индивидуални физичко-хемиски карактеристики. Така, утврдено е дека промените во температурата и нутриентите во водата од изворите Калишта и Елшани се поврзани со дотокот на вода од топење на снегот и атмосферски врнежи. Промените на температурата, електроспроводливоста, pH и DO генерално се многу мали што се гледа и од малите вредности на нивните стандардната девијации од мерењата. Електроспроводливоста на водата во сите извори е под 400 µS cm^{-1}, укажувајќи ма малото присуство на растворени минерални материи. Утврдена е, исто така, многу ниска концентрација на различни тешки метали (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni and Pb) во водите од овие извори.

Клучни зборови: Охридско Езеро, површински извори, физичко-хемиски истражувања, вода за пиење

Introduction

Lake Ohrid is located on the central Balkan with approximately two-thirds of its surface area belonging to Macedonia and about one-third belonging to Albania. The water balance of the lake is characterized by an annual average in- and output rate of 37.9 m^3 s^{-1}. Tributaries contribute only ~23% of today's water loads, whereas karstic aquifers contribute ~53%, and direct precipitation on the lake surface ~23% (Albrecht, 2008). There are around 40 tributaries flowing into Lake Ohrid (23 on the Albanian side, and 17 on the Macedonian side). Most of them carry only small amounts of water during the dry summer period. The hydrography clearly reveals the karstic character of Lake Ohrid. 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 from Lake Prespa (Anovski et al., 1980; Eftimi & Zoto, 1997; Matzinger et al., 2006a; Amataj et al., 2007; Popovska & Bonacci, 2007). About two-thirds of the output occurs via River Crni Drim and one-third through evaporation (Albrecht, 2008). Relative to its surface, the catchment area is small (catchment/lake surface ratio of ~7). The catchment area of Lake Ohrid is 2600 km². Excluding Lake Prespa, it is even smaller with 1002 km^2 (Popovska & Bonacci, 2007). The small catchment and the Mediterranean climate result in a hydraulic residence time of ~70 years (Albrecht, 2008).

The karstic springs of Lake Ohrid are a most interesting hydrogeological phenomenon, as they introduce heterogeneity and variability of many hydrogeological, ecological and other parameters. Likewise springs can be recognized from inputs of nutrients to the lake water that may occur through subterranean processes (Matter et al. 2010).

The aim of this paper is to present a few important groups of surface springs groups by discussion of physico-chemical parameters, such as temperature (T), specific conductivity, pH, ionic composition, concentrations of dissolved oxygen and trace elements. These springs are large enough to supply the amount of freshwater required by 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 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 species (Sywula et al., 2003). Other endemic species are, for example, the freshwater sponge (Hadžišče, 1956; Gilbert & Hadžišče, 1984), and some gastropods. In this article, we present the specific physico-chemical patterns of major surface karst springs of Lake Ohrid from the Macedonian side. We elucidate temporal variability of the spring water properties and show differences of those properties among different sites.

Materials and methods

Water samples were taken from seven individual springs: three belonging to the larger spring complex at St. Naum (Spring 1, Church and St. Petka); two spring sites are located at higher elevations relative to Lake Prespa (849 m asl) named Elšani and Korita; Kališta spring in the North-western part of the Lake, and Biljana's springs in the North-eastern part (Fig. 1). The monitoring was carried out between June 2005 and September 2008.

Water temperature (T), specific conductivity (κ_T), and pH were measured in-situ at all sampling sites on a monthly basis from September 2005 to December 2006, and after that quarterly until September 2008 using a hand-held instrument (WTW, LF 197 and WTW, PH197). The instruments' accuracies were 0.2^{o}C, 5% of the measured conductivity value, and 0.05 for pH. Values of κ_T were transformed to specific conductivity at 20 ^{o}C (expressed

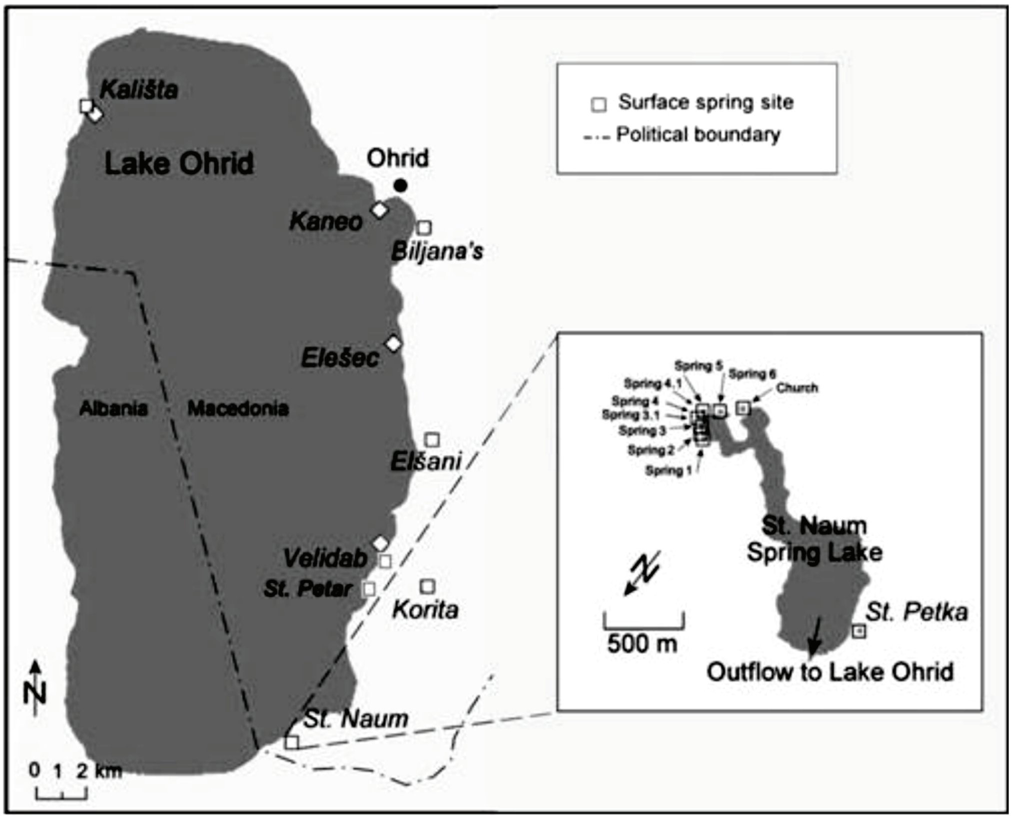

Fig. 1. Locations of surface springs of Lake Ohrid

with κ_{20}) based on ionic composition (Wüest et al., 1996).

Samples were stored in clean plastic bottles for analysis of major ions and trace elements. Dissolved oxygen was determined with the Winkler method. The bottles were cooled immediately after sampling. Water samples for the measurements of major ions and nitrates were filtrated using nitro cellulose filters (pore diameter of 0.45 μm). For phosphate analysis, glass fiber filters were used (pore diameter of 0.7 μm). Phosphates were measured photometrically according to standard methods (DEW, 1996) at Eawag, Kastanienbaum, and photometrically (Strickland & 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% (Weiss, 2004) at Eawag, Kastanienbaum. Analysis of dissolved oxygen (DO) was carried out following the Winkler method (Clesceri et al., 1989). Alkalinity was titrated to the endpoint at pH 4.3 with 0.1M HCl (Clesceri et al., 1989). The method of solid phase extraction was used for the pre-concentration and determination of ten trace elements (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni and Pb) and then determined by electrothermal atomic absorption spectrometry - ETAAS (Varian SpectrAA 640Z) and by flame AAS (Varian, SpectrAA 220). This laboratory work was accomplished at the Hydrobiological Institute, Ohrid, and Faculty of Natural Science and Mathematics, Skopje.

Results

The average spring water temperature ranged from 8.2 °C at Spring Korita to 11.9 °C at Spring St. Petka (Table 1). The low water temperature of the Korita spring results from the geographic location in the Galicica Mountains and seasonal variations from 7.2 °C to 10 °C. At St. Naum spring area, *in-situ* measurements of the temperature from the individual springs indicated a narrow range of 0.6 °C and relatively constant conditions throughout the year.

The average conductivity of the springs ranges between 222-310 μS cm^{-1} and the pH ranges between 7.32-7.78 (Table 1). At Kališta and Korita, pH values were 7.4 and 7.8, respectively. Alkalinity was expressed as the concentration of $CaCO_3$ (in mg l^{-1}), and results were from 283 to 376 mg l^{-1} $CaCO_3$.

During the present study, the content of free CO_2 fluctuated in a wide range depending on the rate of decomposition. According to the seasonal dynamic the content of free CO_2 is higher in summer than in winter, but persists throughout the entire monitoring period. DO concentrations ranged from 6.11 to

10.07 mg l^{-1} (Table **1**). Variations in DO occur seasonally, with lower values during the summer period. Springs at the East side of the lake showed geographical trend: starting from the most northern spring at the HBI yard, Biljana spring, the water becomes more under-saturated with DO towards the south, where the St. Naum spring area is. The highest value for calcium is detected at Kališta (Table **1**). Average values for SO_4^{2-} were 0.4 mg l^{-1} at Elšani, 0.32 mg l^{-1} at St. Petka, while the lowest value of 0.12 was observed at Kališta, St. Naum and Korita. The concentrations of NO_3^- range from 0.04 to 0.8 mg N l^{-1} (Fig 2). Nitrite concentrations in these freshwaters were below the detection limit of 0.001

Table 1. General physico-chemical parameters of the surface springs 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	10.3-13.6	7.2-10.20	10.01-11	10-15.3
CV	0.02	0.03	0.03	0.09	0.12	0.03	0.15
k_{20}/µS cm^{-1} Mean	316.4	237.8	256.7	261.1	222.0	242.2	234.3
Range	260-365	205-277	208-287	229-286	173.5-255	200-293	192-263
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
Tot alk., mg l^{-1} $CaCO_3$ Mean	376	319	319	320	283	299	292
Range	320-444	296-348	280-350	212-344	258-310	278-312	269-320
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	8.62-13.0	9.31-10.8	9.79-10.8
CV	0.09	0.10	0.15	0.12	0.12	0.05	0.03
TP/µg l^{-1} Mean	87.6	34.5	10.8	31.2	10.6	19.0	23.0
Range	0.46- 719	0.41-301	0.45-20.4	0.45-52.4	0.58-22.8	0.24-78.6	2.85-99.0
CV	2.53	2.57	0.49	0.52	0.66	1.17	1.23
TN/mg l^{-1} Mean	446.7	543.4	360.9	388.60	262.38	379.50	379.87
Range	33-1203	33-1457	38.6-596	0-1192	0-450	122-706	152-671
CV	0.77	0.71	0.45	0.91	0.61	0.42	0.44
Cl^{-1}/µM Mean	107.5	95.2	90.0	108.5	85.9	95.2	72.3
Range	69.5-123	68.2-112	62.3-111	44.5-196	68.5-110	55.6-196	44.2-119
CV	0.18	0.16	0.21	0.61	0.19	0.55	0.50
Ca^{2+}/µM Mean	1027	919.9	901.9	887.1	900.6	842.2	758
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	160.0	197.1	163.6	59.8	80.2	64.3
Range	73.6- 205	83.7-225	111-288	35.5-260	19.9-132	40.8-159	22.1-140
CV	0.33	0.27	0.30	0.48	0.84	0.55	0.71
Na^+/µM Mean	71.9	76.0	85.3	82.6	30.99	43.1	49.2
Range	39.5-121	42.3-120	35.0-144	24.4-152	14.4-51.9	24.5-55.6	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	18.2-25.1	22.6-32.1	2.8-4.20	9.8-13.5	5.9-8.87
CV	0.21	0.07	0.08	0.10	0.14	0.10	0.12

CV- Coefficient of variation

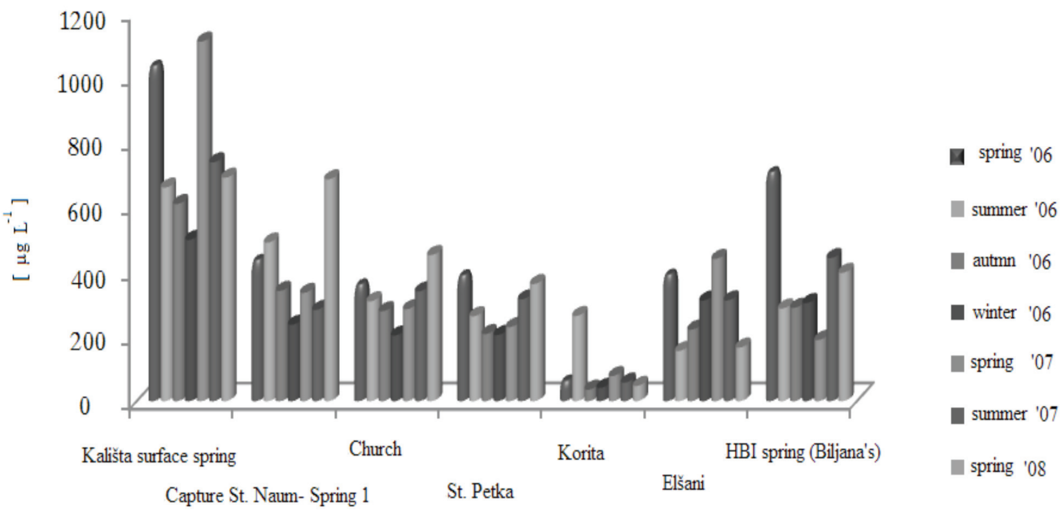

Fig. 2. Seasonal dynamics of NO3--N concentration

mg N l^{-1}. Generally, the concentrations of total organic nitrogen content determined in the entire study area spanned a large range. Surface springs contained less than 0.03 mg l^{-1} total phosphorus except Kališta surface spring, which showed seasonal fluctuations and had average phosphorus values of 0.08 mg l^{-1}. Peak concentrations were usually observed in the summer period during the tourist season with highest values at spring Kališta in August 2006 (0.7 mg l^{-1}) and St. Naum spring area (0.3 mg l^{-1}). Chloride concentrations were generally below 0.3 mg l^{-1}.

The concentrations of different metals in waters vary over a wide range and are generally in very small concentrations, below permissible limits. As and Co were below detection limits in all samples.

Discussion

Data presented in the study indicate that the temperature of water from the surface springs from the Macedonian side of Lake Ohrid is relatively stable throughout the year. Chemical variations are more significant. The variations of temperature and nutrients at Korita and Elšani can probably be explained by their location in the mountains. The specific conductivity of all subaquatic and surface spring waters is generally less than 400 µS cm^{-1}, indicating that small amounts of ions are dissolved in the water. The relative constant composition of the water is confirmed by stable isotopes studies ($\delta^{18}O$ and δD) on water samples from St. Naum springs (Spring 1, Church and St. Petka (Jordanoska et al., 2010).

The water from all investigated surface springs was usually remarkably clear. The quality of spring water represents the general water quality of the ground-water system. However, springs showed individual physico-chemical signatures. Variations of ion concentrations were relatively high but not systematic. At St. Naum spring area outflows, neither signals from precipitation events nor seasonal changes in Lake Prespa‘s outflow are detected in the spring water. As previously stated by Matzinger (2006a), these karst aquifers that are connecting lakes Prespa and Ohrid not only mineralize the entering phosphorus to SRP (Soluble reactive phosphorus), but also retain 65 % of the phosphorus load from Lake Prespa. Anthropogenic influence is still visible at some locations, e.g. the increasing P load measured at all sampling sites during the tourist season (summer period). Thus, it is important to provide regular monitoring of essential indicators for the lake ecology in all larger groups of karst aquifers and in order to qualify the groundwater input.

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References

Albrecht, C. & Wilke, T. (2008). Ancient Lake Ohrid: biodiversity and evolution. *Hydrobiologia*, **615**: 103–140.

Amataj, S., Anovski, T., Benischke, R., Eftimi, R., Gourcy, L.L., Kola, L., Leontiadis, I., Micevski, E., Stamos, A., Zoto, J. (2007). Tracer methods used to verify the hypothesis of Cvijić about the underground connection between Prespa and Ohrid Lake. *Environmental Geology*, **51**: 749–753.

Anovski, T., Naumovski, J. , Kacurkov, D., Kirkov P. (1980). A study of the origin of water of St. Naum Springs. Lake Ohrid. *Fizika*, **12**: 76–86.

Anovski, T., Andonovski, B., Minceva, B. (1991). Study of the hydrologic relationship between Ohrid and Prespa lakes. In: Proceedings of an IAEA International Symposium, IAEA-SM-319, 62 p., Vienna.

Clesceri, L., Greenberg, A., Eaton, A. (Eds.) (1998). *Standard Methods for the Examination of Water and Wastewater.* 20th ed., 4–129 pp. APHA, AWWA, WEF Washington DC.

DEW (1996). *German Standard Methods for Water Analysis, Volume II*. VCH, Weinheim.

Eftimi, R. & Zoto, J. (1997). Isotope study of the connection of Ohrid and Prespa lakes. In: International Symposium “Towards Integrated Conservation and Sustainable Development of Transboundary Macro and Micro Prespa Lakes”, Korcha, Albania.

Gilbert, J. J. & Hadzisce, S. (1984). Taxonomic notes on the shallow-water endemic sponges of Lake Ohrid, Yugoslavia, with a description of two new species and a redescription of *Spongilla stankovici*. *Archiv für Hydrobiologie,* **99**: 331-339.

Hadžišče, S. (1956). III. Beitrag zur Kenntnis der Gastropodenfauna des Ohridsees. - Beschreibungen der bis jetzt unbekannten Schnecken und Beispiele der Speciation bei den Gastropoden des Ohridsees. *Zbornik na rabotite, Hidrobioloski Zavod - Ohrid*, 4.

Jordanoska, B., Kunz, M., Stafilov, T., Wüest, A. J. (2010). Temporal variability in physico-chemical properties of St. Naum karst springs feeding Lake Ohrid. Ecology and Protection of the Environment, 13: 3-11.

Karadjova, I. (1999). Determination of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb in natural waters, alkali and alkaline earth salts by electrothermal atomic absorption spectrometry after preconcentration by column solid phase extraction. *Mikrochimica Acta*, **130**: 185-190.

Lokoska, L. & Noveska, V. (2008). Microbiological investigations of some surface springs around lake ohrid and subaquatic springs at Kalista during December 2005 December 2006, Balwois, Ohrid.

Manga, M. (2001). Using springs to study groundwater flow and active geologic processes. *Annual Review of Earth and Planetary Science*, **29**: 201–229.

Manga, M. (1996). Hydrology of spring-dominated streams in the Oregon Cascades, *Water Resources Research*, **32**: 2435-2439.

Matter, M., Anselmetti, F. S., Jordanoska, B., Wagner, B., Wessels, M.,Wüest, A.(2010). Carbonate sedimentation and effects of eutrophication observed at the Kališta subaquatic springs in Lake Ohrid (Macedonia), *Biogeosciences*, **7**: 3755–3767.

Matzinger, A., Jordanoski, M., Veljanoska-Sarafiloska, E., Sturm, M., Wüest, A. (2006a). Is Lake Prespa jeopardizing the ecosystem of ancient Lake Ohrid? *Hydrobiologia* **553**: 89–109.

Matzinger, A., Spirkovski, Z., Patceva, S., Wüest, A. (2006b). Sensitivity of ancient lake Ohrid to local anthropogenic impacts and global warming. *Journal of Great Lakes Research,* **32**: 158-179.

Matzinger, A., Schmid, M., Veljanoska-Sarafiloska, E., Patceva, S., Guseska, D., Wagner, B., Müller, B., Sturm, M., Wüest, A. (2007). Eutrophication of ancient Lake Ohrid: Global warming amplifies detrimental effects of increased nutrient inputs. *Limnology and Oceanography*, **52**: 338–353.

Moore, W. S. (2006). *Submarine groundwater discharge with special reference swoam.* Willard - Department of Geological Sciences, University of South Carolina, Columbia, SC 29208.

Naumoski, T. (1990). *Phosphorus supply in Lake Ohid, Macedonia, Yugoslavia*. Verhandlung International Verein Limnology **24**: 253-257.

Popovska, C. & Bonacci, O. (2007). Basic data on the hydrology of Lakes Ohrid and Prespa. *Hydrological Processes*, **21**: 658-664.

Stafilov, T., Pavlovska, G., Čundeva, K. (2002). Lead(II) and cobalt(III) heptyldithiocarbamates as new coflotation reagents for preconcentration of cadmium before its ETAAS determination. *Journal of Institute of Sciience and Technology - Balikesir University*, **4**: 85-89.

Stankovic, S. (1960). The Balkan Lake Ohrid and its Living World, Volume IX of *Monographiae Biologicae*. Uitgeverij Dr. W. Junk, Den Haag, Netherlands.

Strickland, J. & Parsons, T. (1968). *A Practical Handbook of Seawater Analysis*. Second ed., 71–76 pp. Fisheries Research Board of Canada, Ottawa, Canada.

Sywula, T., Krstanovski, Z., Tasevska, O., Sell, J., Kretowicz, T. (2003). Genetic differences among several species of tricladida from the relict Lake Ohrid as revealed by enzyme electrophoresis. *Folia biologica*, **51**: 105–109.

Sywula, T., Krstanovski, Z., Biała, A., Wysocka, A., Kilikowska, A., Sell, J. (2006). Phylogenetic position of *Dendrocoelum lacteum* (Tricladida) from the Balkan Lake Ohrid evidenced by allozyme data. *Biochemical Systematics and Ecology*, **34**: 212-218.

Wagner, B., Wilke, T., Krastel-Gudegast, S., Grazhdani, A., Reicherter, K., Trajanovski, S., Zanchetta, G. (2009). Scientific Collaboration on Past Speciation Conditions in Lake Ohrid, SCOPSCO Workshop Report.

Watzin, M., Puka, V., Naumoski, T. (Eds.) (2002). Lake Ohrid and its watershed, State of the Environment Report. Tirana, Albania and Ohrid, Macedonia: Lake Ohrid Conservation Project, Tirana/Ohrid.

Weiss, J. (2004). *Handbook of Ion Chromatography*. Wiley-VCH, Weinheim.

WHO (1996). *Guidelines for Drinking-Water Quality-Health Criteria and Other Supporting Information*, 971.

Wüest, A., Piepke, G., Halfman, J. D. (1996). Combined effects of dissolved solids and temperatue on the density stratification of Lake Malawi. In: Johnson, T.C., Odada, E.O. (eds.). *The Limnology, clymatology and paleoclimatology of the East African Lakes*. 183-202 pp., Gordon and Breach, Toronto.

Wüest, A. (2005). Scientific co-operation between Eastern Europe and Switzerland. Project proposal - SCOPES 2005-2008.