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PRELIMINARY INVESTIGATIONS OF FLUORIDE CONTENT IN THE WATER OF THREE MAIN LAKES IN THE REPUBLIC OF MACEDONIA

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A b s t r a c t: The aim of the study was to determine the F^- content in the water of three main lakes in the Republic of Macedonia. The estimation of F-concentration was performed using a special ion-Analyzer Model EA 920 produced by ORION, and a special ion-selective F-electrode. The results were as follows: the water from lakes Dojran, Ohrid and Prespa contained 5.6 ppm F^-, 0.08 ppmF^- and 0.15 ppmF^- respectively. High value on F^- concentration in Dojran Lake could be attributed to it's tectonic genesis and supplying with water courses from mountain of Belasica, which contains granitic rocks, characterized as very rich in fluorides mainly fluorite (CaF_2), such as distribution of zooplankton, phytoplankton, higher aquatic plants. Also the high value on F concentration may be a result of under enormous anthropogenic influences derived from tourism and agricultural practices in the catchment area of the lake.

Key words: fluoride; ion analyzer; lake

INTRODUCTION

Fluoride is an ion of the element fluorine, and is a natural component in most water resources. Fluoride is an essential element notably for health (Frencken J. E., 1992; USNRC, 1993; USPHS, 1991). Fluoride is present in surface, more in ground water and much more in geothermal and mineral water (Allmann R. and Koritnig S., 1974; Deshmukh A. N. and Maple D. B., 1996; Gaciri S. J. and T. C. Davies, 1993; Handa B. K., 1975). Fluoride content varies widely. Fluoride content in water depends on several factors such as: geology of the terrain, type of rocks, depth of source, chemical and physical properties of water-bearing layer, pH values and temperature, content of calcium ion and etc.

Geology plays a key role in defining fluoride concentrations. Specific geological conditions which result in higher concentration of fluoride in water are related to volcanic activity. Acidic rocks which are poor in calcium and rich in fluoride under high temperature activity release fluoride from the rocks or fluids after eruptive processes and hydration in water bodies. Volcanic rocks and geothermal fluids can be regarded as key factor for the high concentration on fluoride in water (Lottermoser B. G. and Cleverley J. S., 2007; Hem, J. D., 1989; Sharma S. K., 2003). Fluoride is dissolved salt whose major sources in ground waters are apatite, mica, hornblende and fluor apatite. They are associated with water with high pH values and low calcium concentration (Karthikeyan G,. A. Shunmugasundarraj, 2008; Alagumuthu G. and Rajan M., 2008).

Ohrid, Prespa and Dojran are biggest natural lakes in the Republic of Macedonia. Location map of these lakes is shown on Fig 1.

Ohrid Lake straddles the mountainous border between the south-western Macedonia and eastern Albania. The lake has a surface area of 358 km^2 a maximum water depth of 289 m, a mean water depth of 155 m, and a volume of 55 km^3.

Fig. 1. Location map of three lakes:Ohrid, Prespa and Dojran

Located in a tectonic graben, the lake is amongst the few worldwide lakes existing since the Tertiary. Geological map of Ohrid Lake and Prespa Lake is shown on Fig. 2.

The Ohrid lake collects water from several small rivers (Cherava, Koselska and Sateska). Crni Drim river represents the most natural flow brings. Over 20% of the lakes water comes from nearby Prespa Lake. A lithological unit around the lakes confirms this assumption. Possibly plunging the water comes from south-west parts of lake where the bottom is composed of Triassic limestone. The lake is surrounded by Palaeozoic metamorphics in the north-east and north and Mesozoic ultramafic, carbonatic and magmatic rocks in the east, north-west, west and south. Pliocene units are present in the south-west. Quaternary sediments are present mostly in Ohrid and Struga fields while in Prespa and Debar fileds are covered with proluvium and alluvium.

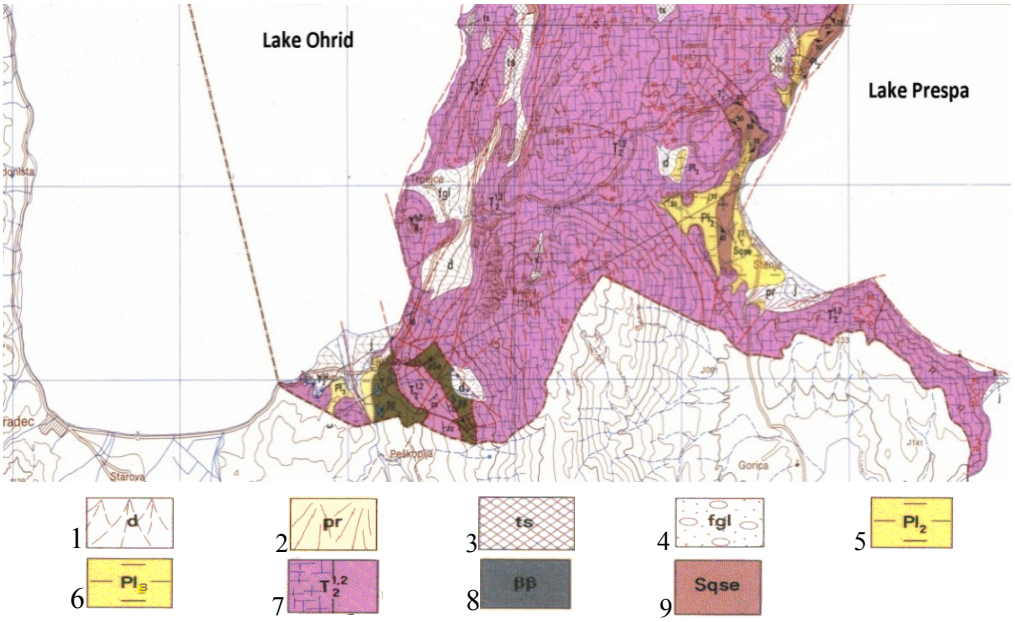

Fig. 2. Geological map of Prespa Lake
1. Deluvium; 2. Proluvium; 3. Terra rossa; 4. Glaciofluvial sediments; 5. Gravel, sand, clay, marl; 6. Gravel, sand, clay; 7. Limestone and dolomite; 8. Diabase; 9. Quartz sericite schists

The surface area of neighbouring Prespa Lake is only 254 km^2. Of the total surface area, 190 km^2 belongs to Macedonia, 84.8 km^2 to Greece and 38.8 km^2 to Albania. Maximum and mean water depths are 58 m and 14 m, respectively, and its volume is 3.6 km^3.

According to Micevski, E. (2000), the Ohrid–Prespa region is characterized by fairly complex-geological-tectonic structures with rocks from the oldest Paleozoic formation to the youngest Neogene and Quaternary sedimentary rocks. This region is composed of rocks varying in their age, mineralogical composition and origin. The calcareous rocks are dominant and to a small extent are distributed between magmatic rocks and granodiorites. Syenites are present at the higher elevation areas, but Triassic carbonate rock masses are also present in many areas. Different types of Quaternary sediments, such as alluvial, fluvioglacial, proluvial and deluvial sediments, are dominant in the valley, especially at the riverbeds.

Dojran Lake is located in the south-west part of Macedonia, on the border with Greece, in the Dojran ridge of the regional tectonic rupture (rift zone), between the Serbo-Macedonian Mass and the Vardar zone. The total area of it is 43.1 km^2. The lake is divided in two pieces, one belongs to Republic of Macedonia 27.3 km^2, and the other to

Greece 15.8 km^2. The lake has a rounded shape, a maximum depth of 10 m and north-to-south length of 8.9 km and is 7.1 km at its widest, making it the third largest lake partially in the Republic of Macedonia, after Ohrid Lake and Prespa Lake. Dojran Lake is the smallest tectonic lake that was formed in the Neogene's Quarter period and is of the tectonic-volcanic genesis. Geological map of Dojran Lake is shown on Fig 3.

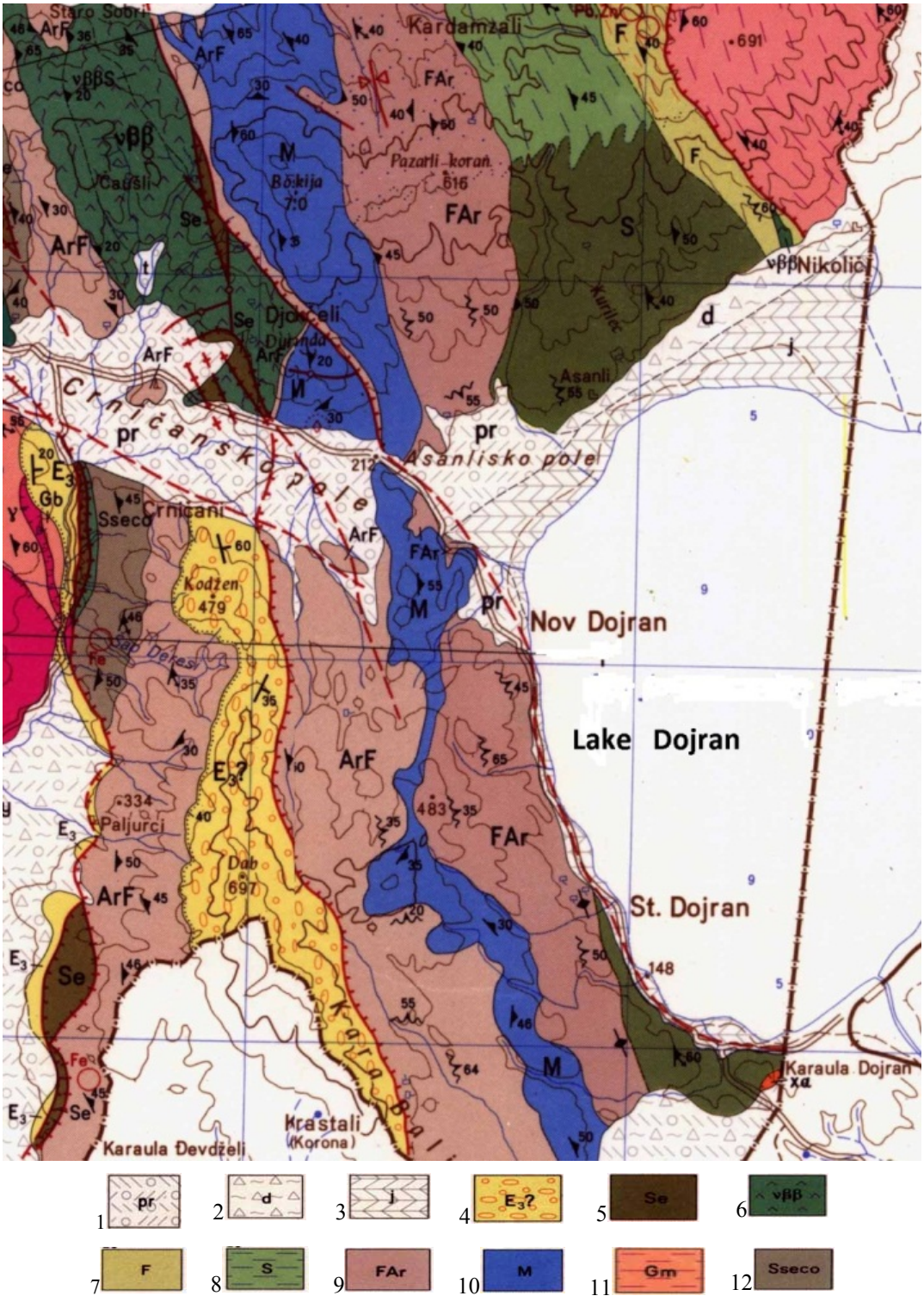

Fig. 3. Geological map of Dojran Lake
1. Proluvium; deluvium; 3.Lacustrine sediments; 4. Conglomerates; 5. Serpentinite; 6. Metamorphic gabbro diabasse; 7. Filites with calcalerous shale and marble; 8. Green shists; 9. Filites, argiloshists and sandstone with limestone schists and marbles; 10. Marbles; 11. Muscovite gneiss; 12. Sericite-chlorite schists and sandstone

Materials and methods. The water samples were collected in 2005 during the summer. The estimation of F-concentration was performed using a special ion-analyzer Model EA 920, produced by ORION, and a special ion-selective F electrode. For the chemical analysis 10% TISAB (Total Ionic Strength Adjusted Buffer) Aluminon was used.

Results and discussion. Obtained results for the concentration of F^- in waters from three natural biggest lakes in the Republic of Macedonia and concentration of F from water for public supplies of the settlements which are located on the shores of the biggest natural lakes in the Republic of Macedonia are shown in Table 1.

Table 1

Concentration of F in water from three natural lakes and concentration of F from water for public supplies of the settlements which are located on the shores of the lakes in the Republic of Macedonia

Name of the lake and town	F^-content (ppmF)	Total surface area
Ohrid of Lake	0.08	358 km^2
Town of Ohrid	0.06	Number of inhabitants – 41 989
Town of Struga	0.04	Number of inhabitants – 16559
Lake of Prespa	0.15	254 km^2
Town of Resen	0.07	Number of inhabitants – 8748
Lake of Dojran	5.60	43.1 km^2
Town of Star Dojran	0.11	Number of inhabitants – 361

Comparisons of the fluoride concentrations of water sample of lakes and towns which are located on the shores show that the fluoride concentration is higher in lakes (Figs. 5, 6 and 7). Dojran Lake has highest content of F. The F concentration in the other two lakes is within the permissible limits. Concentration of F in the towns is in the normal range. Smallest concentration of F has the town Struga (0.04 ppm). A study in the USA showed that the optimum fluoride concentration is 1.0–1.2 mg/l [Lalumandier, J. A. & Jones, J. L. 1999]. Estonian and EU requirements set a limit at 1.5 mg/l [Joogivesi. Üldnõuded. 1995]. WHO 0.5–1.5 [WHO 1993].

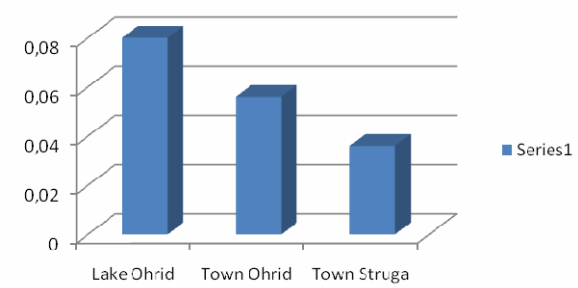

Fig. 5. F^- content in Ohrid Lake and in the town of Ohrid and Struga

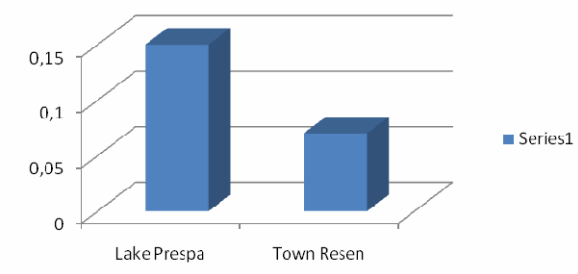

Fig. 6. F^- content in Prespa Lake and in the town of Resen

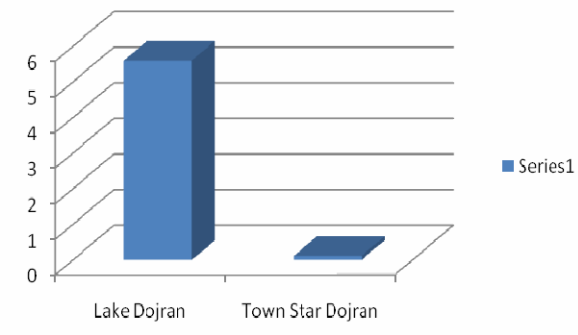

Fig. 7. F^- content in Dojran Lake and in the town of Star Dojran

CONCLUSION

From the presented facts above it can be concluded that the water from lakes Dojran, Ohrid and Prespa contained 5.6 ppm F^-, 0.08 ppmF^- and 0.15 ppmF^-, respectively.

The F content in the water of the lakes depends from the geological terrains in which lakes lie on. The water from Dojran Lake contained 5,6 ppmF^-, value which is beyond the permissible limits set by World Health Organization. Waters with high fluoride content are found mostly in calcium-deficient ground waters in many basement aquifers, such as granite and gneiss, in geothermal wa-

ters and in some sedimentary basins. High value on F concentration in Dojran Lake could be attributed to its tectonic genesis and supplying with watercourses from Belasica mountain, which contains granitic rocks, characterized as very rich in fluorides mainly fluorite CaF_2 and fluor apatite $Ca_5(PO_4)_3F$.

Also the high value on F concentration may be a result of distribution of zooplankton, phytoplankton, higher aquatic plants such as enormous anthropogenic influences derived from tourism and agricultural practices in the catchment area of the lake.

This high value on F concentration can affect on plants and animals in the water. The effects of fluorides on plants depends upon a number of factors such as the concentration, time of exposure, type and age of plant, temperature, type of light and intensity, composition of the air, and its rate of circulation. Also, the effects of fluorides on animals depend upon a number of factors such as the physical and chemical properties of the compounds, dosage or amount given.

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Р е з и м е

ПРЕЛИМИНАРНИ ИСПИТУВАЊА ЗА ОДРЕДУВАЊЕ КОНЦЕНТРАЦИЈАТА НА ФЛУОР ВО ТРИТЕ ПОГОЛЕМИ ЕЗЕРА ВО РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: флуориди; анализа на јони; езеро

Од изнесените податоци може да се заклучи дека водите од Дојранско, Охридско и Преспанско езеро содржат 5,6 ppmF^-, 0,08 ppmF^-и 0,15 ppmF^-, соодветно. Содржината на флуор во вода зависи од геологијата на теренот на кој лежат езерата. Водата од Дојранското езеро содржи 5,6 ppmF^-, вредност која е над од дозволените граници поставени од страна на Светската здравствена организација. Водите со високи концентрации на флуор се наоѓаат главно во подземните води со дефицит на калциум,во геотермалните води и во некои седиментни басени. Високата вредност на F во Дојранското езеро може да е резултат на тектонски постанок на езерото и снабдување со воите од планината Беласица, која содржи гранитски карпи кои се карактеризираат со богатство на флуориди, главно флуорит CaF_2 и флуорапатит $Ca_5(PO_4)_3$.Високата концентрација на F исто така може да биде резултат на дистрибуција на зоопланктонот, фитопланктонот, повисоките водни растенија, но и на антропогените влијанија кои произлегуваат од туризмот и земјоделските активности во сливното подрачје на езерото.

Високата вредност на F може да влијае на растенијата и животните во водата. Влијанието на флуорот врз растенијата зависи од голем број фактори: концентрацијата, времето на изложеност, видот и возраста на растенијата, температурата, видот и интензитетот на светлината, составот на воздухот, како и степенот на циркулација. Неговото влијание врз животните исто така зависи од бројни фактори како што се физичките и хемиските својства на соединенијата, нивната концентрација, и количината која животнитеја примаат.