Fluorine Content of Drinking Water in Relation to the Geological-Petrographical Formations From FYROM

SUMMARY

The aim of the study was to determine the association between different concentrations of the fluoride ion in drinking water and some geological variables in FYROM, by using information from Institute for Geological and Mineral studies. From May 2003 to May 2004 we studied the fluoride concentration in the sources of drinking water in 92 localities. Measurements of F-concentration were performed using a special ion-Analyser Model EA 920 produced by ORION and a special F-electrode. For the chemical analysis 10% TISAB-Aluminon (Total Ionic Strength Adjusted Buffer) was used. Starting of the 68 settlements of the republic, 9 were found to have naturally fluoridated drinking water. Highest concentrations were found in 3 thermal baths (Katlanovo, Bansko and Negorci). Optimal fluorine contents were found in the tap water from Gratsko, Kolesino and Stip, and suboptimal in the southern region of the country (Balinci, Marvinci, Brajkovci, Martinovo and Pirava) mainly, with the exception of Kocani, which is situated in the eastern part of the country. As a total, 80.300 people are gaining benefit from the naturally fluoridated water. The water from lake Dojran contained high 5,6 ppm F natural fluoride concentration. The lake is situated in the southern region of the country. Geological-petrographical characteristics of the terrain can help in identifying areas with optimal or high concentrations of the fluorine ion in the drinking water, so the volcanic rocks as well as the geothermal fluids might be considered to be key factors that lead to unusually high concentrations of fluorine within water.

Keywords: Natural Fluoridated Water; Geology

Introduction

Fluorine contents in drinking water samples are affected by factors such as availability and solubility of fluorine-containing minerals, rock’s or soil’s porosity through which the water passes, residence time, temperature, pH and the presence of other elements, e.g. calcium, aluminium and iron, which may complex with fluorine. Water is the major source of consuming fluorine for people. There is no water which does not contain fluorine at all, but there are waters with various fluorine contents, depending on a whole series of factors that have mostly geological origin. Being familiar with the fluorine content of the drinking water for each area is especially important datum for the dentist. In many countries, separate maps of naturally fluoridated drinking water have been made.

There are 150 minerals which contain fluorine, although the most important are as follows: fluorite (CaF₂; 49%F), fluor-apatite (Ca₁₀F₂ (PO₄)₆; 3.4% F), cryolite (Na₃AlF₆; 54%F) and etc. Fluorine distribution is the most intensively expressed within acid magmatic rocks (granites, granodiorites etc). The fluorine contents of within magmatic rocks are as follows: ultrabasic 100 ppm, basic 400 ppm, intermediate 500 ppm, acid rocks 735 ppmF. Fluorine distribution inside sedimentary rocks is as follows: sandstone 270 ppmF, carbonate 330 ppm, clay 740ppm, Shales 740ppm.
The examination revealed as follows: a) 3 thermal baths with fluorine containing waters above the optimal concentrations (1.5 - 5.3 ppm F); b) 3 settlements with optimal F-concentration (0.7 - 1.2 ppm F) with 46.700 inhabitants; c) 6 settlements with suboptimal F-content (0.4 - 0.65 ppm F) beneficial to 33.600 inhabitants; d) 8 settlements with insufficient F-concentration (0.2 - 0.3) with 50.600 inhabitants; e) the remaining 51 communities (including city of Skopje, with population of approximately 1 million) with water containing only traces of F (< 0.3 ppm F).

Information was collected from the local authorities, Geological and Mineral Survey Institute, the Republic Institute for Health Protection, as well as the State statistical Institute of the FYROM.

Material and Method

From May 2003 to May 2004 we studied the fluorine contents in the sources of drinking water for 92 localities (tap water from urban and rural communities, dug wells, thermal baths, natural springs and water from 3 lakes). The collecting method and storing the water samples were predetermined. Plastic (polyethylene) bottles were used, because of the reaction of fluorine with the glass and they were washed out with the water sample. Collected bottles were stored in a cool place until the start of fluorine measurement. Time between collection and measurement was no longer than 2 months.

The appropriate data, e.g. the kind of water sources (surface water, drilled or natural spring), were taken from the local records onsite. The measurements of F-contents were performed at the University of Thessaloniki, department of Preventive Dentistry, Periodontology and Implant Biology, using a special ion-Analyser Model EA 920 equipment produced by ORION, and a special F-electrode. For the chemical analysis 10% TISAB-Aluminon (Total Ionic Strength Adjusted Buffer) was used. The electrode was adjusted against standard F-solutions (0.1 to 1 ppm, and 1.0 to 10 ppm F).

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Results and Discussion

On the basis of the obtained results of each drinking water sample, the cities have been classified into 5 categories (Tab. 1).

Table 1. Summary statistics of determined F values in drinking water samples in the FYROM

<table>
<thead>
<tr>
<th></th>
<th>&gt;1.1 ppmF</th>
<th>0.7-1.0 ppmF</th>
<th>0.4-0.6 ppmF</th>
<th>0.2-0.3 ppmF</th>
<th>&lt;0.2 ppmF</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of samples</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>8</td>
<td>51</td>
</tr>
<tr>
<td>Minimum</td>
<td>1.8</td>
<td>0.75</td>
<td>0.45</td>
<td>0.20</td>
<td>0.021</td>
</tr>
<tr>
<td>Maximum</td>
<td>3.4</td>
<td>0.86</td>
<td>0.59</td>
<td>0.28</td>
<td>0.19</td>
</tr>
<tr>
<td>Mediana</td>
<td>2.6</td>
<td>0.86</td>
<td>0.48</td>
<td>0.24</td>
<td>0.10</td>
</tr>
<tr>
<td>Mean</td>
<td>2.6</td>
<td>0.823</td>
<td>0.495</td>
<td>0.24</td>
<td>0.109</td>
</tr>
<tr>
<td>SD</td>
<td>0.80</td>
<td>0.064</td>
<td>0.048</td>
<td>0.031</td>
<td>0.043</td>
</tr>
<tr>
<td>No of inhabitants</td>
<td>46.700</td>
<td>33.600</td>
<td>50.600</td>
<td>1.050.000</td>
<td></td>
</tr>
</tbody>
</table>

Waters with high F-contents (> 1.1 ppm);
Waters with ideal F-contents (0.7 - 1.0 ppm);
Waters with suboptimal F-contents (0.4 - 0.6 ppm);
Waters with insufficient F-contents (0.2 - 0.3 ppm);
Waters with a lack of F (< 0.2 ppm).

The examination revealed as follows: a) 3 thermal baths with fluorine containing waters above the optimal concentrations (1.5 - 5.3 ppm F); b) 3 settlements with optimal F-concentration (0.7 - 1.2 ppm F) with 46.700 inhabitants; c) 6 settlements with suboptimal F-content (0.4 - 0.65 ppm F) beneficial to 33.600 inhabitants; d) 8 settlements with insufficient F-concentration (0.2 - 0.3) with 50 600 inhabitants; e) the remaining 51 communities (including city of Skopje, with population of approximately 1 million) with water containing only traces of F (< 0.3 ppm F).

The territory of the FYROM is characterised by a very complex geological-petrographical composition. According to the geotectonic structure of the terrain, as well as general evolution of the same, from east to west, in the territory of the FYROM 4 structural facial zones can be distinguished: Serbo-Macedonian Mass, Vardar zone, Pelagonian-horst-anticlinorium, and the Western-Macedonian zone. Different types of rocks are represented from the oldest to the youngest geological formations. The tectonic structure of the terrain, especially the neotectonics, is influencing formation of the thermal, thermonuclear and mineral basins of the aquifer water. These waters are mainly found in direct relation with the tectonically active faults. The largest number of them is found in the area of tectonically very unstable Vardar zone.

According to the recent examinations given in this paper, the water from the Dojran lake contains 5.6 ppm F.
Dojran Lake is of tectonic-volcanic genesis. The lake is a natural rarity and unique in the region and its surrounding. It has been located on the main tectonic regional structure that represents a border line between the Rodop mass and the Vardar zone. The special geological conditions that lead to high concentrations of fluorine within water are connected to the volcanic activity, acid rocks very poor with calcium and fluorine abundant, which along with high temperatures leads to release of fluorine from the rocks or fluids after eruptive processes, and hydration within water bodies.

According to the geologic formations through which the water drains, using the geological map of our country (Fig. 3), we grouped the samples (Tab. 2) of water into waters that drain through volcanic rocks, granites, schists, basites and carbonates (marble, limestone). So, the drinking waters originated from carbonate faces (limestone, marbles, etc) show lowest fluorine contents (0.096 ppm in average). The drinking waters originating from mafic rocks show a little bit higher value (0.129 ppm in average), the schists much higher (0.249 ppm in average), and the volcanic rocks show highest fluorine contents (2.2 ppm in average).

According to the achieved results, the fluorine contents in the drinking water from the FYROM can be quite well compared with the geological-petrographic composition. In the contributed figure 1 a correlation between the average fluorine values in the water samples and the geological formations through which water drain can be seen. The results are depicted on a chart of FYR of Macedonia (Fig. 2).

Table 2. Summary statistics of measured F values in drinking water samples that originate from different groups of rocks (geological formations)

<table>
<thead>
<tr>
<th></th>
<th>Volcanic rocks</th>
<th>Granites</th>
<th>Schists</th>
<th>Mafic rocks</th>
<th>Carbonates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nor of samples</td>
<td>3</td>
<td>12</td>
<td>13</td>
<td>4</td>
<td>39</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.26</td>
<td>0.071</td>
<td>0.11</td>
<td>0.09</td>
<td>0.021</td>
</tr>
<tr>
<td>Maximum</td>
<td>5.6</td>
<td>1.8</td>
<td>0.86</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>Mean</td>
<td>2.2</td>
<td>0.533</td>
<td>0.249</td>
<td>0.129</td>
<td>0.096</td>
</tr>
<tr>
<td>Median</td>
<td>0.75</td>
<td>0.48</td>
<td>0.20</td>
<td>0.113</td>
<td>0.098</td>
</tr>
<tr>
<td>SD</td>
<td>2.95</td>
<td>0.449</td>
<td>0.210</td>
<td>0.043</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Fig. 1. Correlation between the average contents of F in the water samples and the geological formations from which the water originate.

Figure 2. Map of naturally fluoridated drinking waters in the FYROM

Figure 3. Geological map of the FYROM N-Neogen, ne-volcanic rocks, K-Creta, sßß-gabbros and diabases, T-Triassic, G-granites, Pz-Paleosocial, RCm-Reef Cambrian, M-marbles and G-gneisses
Conclusions

Starting of the 68 settlements of the republic, 9 were found to have naturally fluoridated drinking water. The highest concentrations were found in three thermal baths (Katlanovo, Bansko and Negorci); optimal fluorine contents were found in the tap water from Gratsko, Kolesino and Stip and suboptimal mainly in the southern region of the country (Balinci, Marvinci, Brajkovci, Murtino and Pirava), with the exception of Kocani, which is situated in the eastern part of the country.

As a total, 80,300 inhabitants are gaining benefit from the naturally fluoridated water. Geological-petrographical characteristics of the terrain can help identify areas with optimal or high concentrations of the fluorine ion in the drinking water, so the volcanic rocks, as well as the geothermal fluids, might be considered to be key factors that lead to unusually high concentration of fluorine within water.

Most of the children population in the FYROM during the period of their teeth formation drink water with very low concentration of fluorine, which is insufficient for prevention of dental caries.

Reference


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