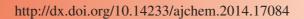




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## Seasonal Change of Physico-Chemical Properties of Thermal Water from Afyonkarahisar Region

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In this study, physico-chemical properties of water samples seasonally collected from well heads of 14 different hot springs in Afyonkarahisar were determined. In water samples, nitrate and nitrite were analyzed by a spectrophotometer, while 26 elements were analyzed by ICP-OES. Temperature of water samples were found to be in the range of 38 to 89 °C, pH values were in the range of 6.31 to 7.91, while conductivity values were in the range of 281 to  $1624 \,\mu\text{S/cm}$ . With respect to water samples, it was discovered that boron and arsenic values in 13 hot springs, calcium values in 5 hot springs, barium values in 2 hot springs, manganese values in 1 hot spring and phosphorus value in 2 hot springs in autumn and summer, potasssium and lithium values in all hot springs were higher than the standard values of WHO and TSE-266. Thermal water from the research site were considered to be used in broader fields and contribute more to economy, while it was concluded that high values should be taken into account during use.

Keywords: Seasonal change, Thermal water, Afyonkarahisar.

#### INTRODUCTION

From early ages to 20th century, mankind have only benefited from therapeutic and relaxing effects of thermal water sources<sup>1,2</sup>. Water is indispensable for a clean and healthy life. Water quality is the most important factor for individuals as well as public health. Considering the fact that most thermal waters are used as mineral springs, it is extremely important to determine the quality of these waters. The best known solvent in nature is water and it is also a good carrier. In its natural state, it contains many dissolved substances, solid particles and living organisms. People take water from a cycle called hydrological cycle to meet their vital and economic needs and give it back to the cycle after using it. Substances mixed with water during these processes change physical, chemical and biological properties of waters, which is referred to as water pollution<sup>3</sup>.

Any substance that can be found in water is harmful to human health above a certain concentration. Even very small concentrations of toxic substances in water may cause harm to human health and result in diseases and even death. Even trace amounts of these substances can be undesirable and the most important group of these substances is comprised of elements<sup>4</sup> such as Sb, Ag, As, Be, Cd, Cr, Pb, Mn, Hg, Ni, Se and Zn<sup>4</sup>.

However, unconscious use of pesticides, industrial wastes and waste waters entering underground environment cause pollution of geothermal resources. As a result, nitrate and nitrite levels of these spring waters vary significantly. Therefore, it is important to determine these parameters for public health<sup>3</sup>.

Afyonkarahisar is a province rich in thermal waters. There are many hot springs within its borders. Some of the major ones are Ikbal, Ömer, Gazligöl, Oruçoglu, Hüdai, Gecek, Heybeli, Soydan, Basak, Yaylakent, Grand Özer, Özdemir, Grand Sönmez and AFJET. For this reason, it'd be appropriate to call the province of Afyonkarahisar as "spa town". Thermal waters in Afyonkarahisar have a capacity of 70.17 MWt with a temperature range of 40 to 98 °C and they are used in heating, hotels, SPA and tourism. These spas are thought to be good for many diseases and visited by thousands of people every year. It is stated that these waters are good for health problems, including rheumatism, disorders of heart and circulatory system, kidneys and urinary tract, liver and gall bladder, digestive system, metabolism disorders, bone and arthritis, skin diseases, nerve and muscle fatigue, neural disorders and gynecological diseases<sup>5-6</sup>.

This study aims to determine physico-chemical properties of thermal waters in Afyonkarahisar region, which has a significant potential for geothermal energy, according to seasons and reveal the current state of these waters in terms of human and environmental health.

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#### **EXPERIMENTAL**

**Sample collection:** Thermal waters were collected from the province of Afyonkarahisar and surrounding towns.

Water samples were stored in 500 mL polyethylene bottles which were previously washed with HCl solution and distilled water and then rinsed with sampled water twice. The bottles were sealed by taking care that no air bubble remained inside and brought to the laboratory. Numbers of each hot spring were carefully written on the sample containers. HCl and HNO<sub>3</sub> were added to refrigerated samples allocated for trace element and heavy metal analyses and their pH was brought down to 2<sup>7</sup>. Prior to analysis, samples were filtered. Water samples used in our study conducted seasonally were collected in July 2004, October 2004, January 2005 and April 2005.

Analysis method: Water samples were collected from the point of emergence of each hot spring. Water temperature was measured at the point of emergence using a thermometer and noted. After temperature of water samples brought to the laboratory came down to room temperature, their pH was measured using pH 890 digital pH meter and noted. Conductivity of water samples was measured at 20 °C using a WTC 330i conductometer. Determination of nitrate and nitrite concentrations, which are important indicators of water pollution, was conducted by spectrophotometric method<sup>8</sup>. The analysis of 26 elements in thermal waters was conducted using an Optima 4300 ICP-OES spectroscopy in Selçuk University, Faculty of Agriculture laboratory.

#### RESULTS AND DISCUSSION

Thermal waters in Turkey are mostly utilized by SPA tourism due to their positive effects on health. The number of SPA facilities in Afyonkarahisar, which has a significant potential for geothermal energy, is much higher than in any other region of Turkey. Seasonal analysis of these thermal waters makes it possible to determine the properties of thermal waters in these facilities, which are believed to have healing effects, on an annual basis. Thus, risk factor is revealed in terms of health.

Mostly K, Na, Ca, Mg and B concentrations of thermal waters have been investigated by researchers. In the present study, values of elements from groups 1A, 2A and 3A group were typically found to be lower in winter compared to other seasons.

According to the results of several studies reported to be conducted in hot springs in the provinces of Aksaray, Konya, Eskisehir, Izmir, Ankara, Kütahya and Denizli, temperature values of thermal waters were in the range of 28 to 150 °C, pH values were in the range of 6.1 to 9.42 and K, Na, Ca, Mg concentrations were in the range of 2.2 to 388 mg/L, 11.2 to 1300 mg/L, 2.8 to 1551 mg/L and 0.1 to 720 mg/L, respectively<sup>9-24</sup>.

Temperature values of 14 hot springs located in Afyonkarahisar and included the study were in the range of 38 to 89 °C, while their pH values were in the range of 6.31 to 7.91. These values correspond to standard values of TSE-266 (6.5-9.2) and WHO (6.5-8.5), demonstrating that acidity and alkalinity are not harmful to public health<sup>25,26</sup>. Temperature values of thermal waters investigated in Afyonkarahisar region were

found to be higher than most temperature values reported by other studies mentioned above. These results show that hot springs in that region are extremely convenient for SPA tourism and they can be used efficiently for heating. The use of thermal waters in the research area in house heating, greenhouse heating, fishery business, thermal tourism and balneological practices is expected to cause a positive impact on local economy and the environment.

Mean K, Na, Ca, Mg and B concentrations of samples from 14 hot springs included in the study were in the range of 43.6 to 244.9, 6.7 to 14.3 mg/L, 82.3 to 279.1 mg/L, 13.6 to 33 mg/L and 0.932 ile 14.573 mg/L, respectively. Boron values in 13 hot springs, Ca values in 5 hot springs, Ba values in 2 hot springs, P values in 2 hot springs in autumn and summer, K and Li values in all hot springs (1-2, 200, 0.3, 0.4-5, 12, 0.1 mg/L, respectively) were found to be above standard values of WHO and TSE-266.

Potassium is involved in many vital functions in human body such as metabolism, growth, repair and cell conductivity. Excess phosphorus disturbs Ca balance and results in problems related to calcium imbalance and a decrease in bone density and strength. As a result, bones lose their strength and become brittle. Excess phosphorus also raises blood pressure<sup>26-28</sup>. Boron is one of the most common pollutants in hot waters and it is dangerous for irrigation water. High concentrations of boron in drinking water have harmful effects on plants and humans. Calcium and magnesium ions which are available in water in high concentrations can be easily absorbed by gastrointestinal system. According to the assessments conducted by diet commissions, it was reported that minimum 800 mg Ca and 350 mg Mg must be taken per day<sup>29</sup>. Calcium is effective in every part of the body, including bones, muscles, nervous system, cell structure, etc. The death rate from cardiovascular disease of people living in places where Ca and Mg content of water is low is 10-30 % greater than that of people living in places where Ca and Mg content of water is high. Intake of high doses of Ba and its accumulation in the body cause weakening of muscles, brain and liver damage and heart rhythm disorders<sup>26-30</sup>.

It is an important factor that heavy metals, which are difficult to remove from the body, disturb the balance of organisms and cause poisoning and even death, are not present in waters. Although they are hazardous for health (due to their toxic effects), heavy metal levels in hot spring waters covered by the research were generally found to be below standard valued of TSE-266 and WHO. As values in 13 hot springs, Fe and Mn values in 1 hot spring were found to be above limit values specified by WHO and TSE-266 (As:0.01 mg/L, Fe:0.2, Mn:0.1 mg/L), suggesting adverse effects on health<sup>25,26</sup>.

Co, Cr, Fe, Mn, *etc.* are among the essential elements required for growth and development. However, their high concentrations are detrimental to human health. A study conducted on 10 year old children in Bangladesh reported that high concentrations of Mn affect mental functions<sup>31-33</sup>. 10 to 50 mg/day of iron is used per day depending on age, physiological state and gender. Despite this, high iron intake has a risk of cancer, albeit low. Long term consumption of drinking waters with high concentrations of iron leads to liver diseases<sup>34</sup>. Arsenic concentration in some geothermal sites situated in

Aegean region was found to be above standard values<sup>24</sup>. Relatively high concentrations of arsenic with respect to standards in drinking and municipal waters have toxic effects on all organisms in the ecosystem<sup>25,26</sup>. If high concentration of arsenic is present in irrigation water, it passes into the plant and is stored as inorganic arsenic, causing the plant to dry out. Long term consumption of drinking water with high arsenic content leads to damage to skin and internal organs in humans. Waters with high As content should be particularly investigated in detail due to its carcinogenic effects in humans. Total daily intake of arsenic in general population was determined as 0.200 mg/kg35. Release of industrial waste containing arsenic into the environment without treatment has caused major problems in terms of human health. In many countries, including Bangladesh and India, arsenic pollution in underground and drinking waters and accordingly acute cancer cases were reported<sup>36</sup>. It was found that 53 members of 17 families (67 %) living near a factory manufacturing copper acetoarsenite in South Calcutta had chronic arsenic poisoning due to consumption of arsenic contaminated water and arsenic concentration in surface well waters was determined as between 5 and 558 mg/ $L^{37}$ .

Nitrate and nitrite concentrations are of great importance in terms of public health so especially drinking waters should be analyzed for nitrate and nitrite and it must be determined whether their values correspond to standard values. Considering that many hot spring waters in our region are used as mineral springs, it emerges once more that these values should be determined. According to TSE-266 and WHO standards, maximum nitrate concentration must be 50 mg/L, while maximum nitrite concentration must be 0.1 mg/L<sup>25,26</sup>. Nitrate and nitrite values in hot springs included in the study were in the range of 4.20 to 9.45 mg/L and 0.069 to 0.084 mg/L, respectively, which are below standard values of TSE-266 and WHO. Hence, the thermal waters included in this investigation do not have any detrimental effects on health.

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