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SPECTROPHOTOMETRIC DETERMINATION OF ZINC AND IRON IN NATURAL WATERS FROM STARA ZAGORA REGION

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ABSTRACT
The goal of the present study was quality evaluation of the natural waters in Stara Zagora Region according to two parameters: total iron and zinc. With regard to the investigations conducted during October-December, 2009: the surface waters of Stara Zagora Region, towards the measured zinc and iron concentrations, could be classified as I category; the groundwaters of Stara Zagora Region, towards the measured iron concentrations, could be classified as waters with increased content of total iron, but below the ecological threshold; the groundwaters of Stara Zagora Region, towards the measured zinc concentrations, could be classified as waters with zinc content below the ecological threshold in Gurkovo Municipality and Gita Village (Chirpan Municipality); above the ecological threshold in Novo Selo Village (Stara Zagora Municipality) and Tekirska River (Chirpan Municipality); above the pollution threshold in Bratya Kunchevi Village (Stara Zagora Municipality).

Key words: Stara Zagora, spectrophotometry, natural waters, zinc, iron

INTRODUCTION

The administrative district of Stara Zagora Region is located in Central Bulgaria (Figure 1) with a population of 389 574 residents. It covers 11 municipalities and 70 % of its population inhabits the two largest cities: Stara Zagora and Kazanlak.

A variety of metals in the form of ions (complexes) with various toxicity, could enter industrial wastewaters as a result of anthropogenic activity. Due to corrosion and geological factors some metal ions in complex form being environmental contaminants could also be present in drinking waters and natural water bodies. By the biological cycle, some of them through the food chain pass into plants, animals and man, thus affecting them negatively. One of the main assumptions of the World Health Organization (WHO) is that "all people, despite their growth stage, social and economic conditions, should have the right and access to adequate supply with harmless drinking water. The basic way for achieving the latter is responsibility (1). With regard to human health prevention and protection of all biological species, the monitoring of some special parameters of drinking waters and natural bodies is essential.

The scientific literature is lacking of information concerning natural water quality in Stara Zagora Region with regard to specific values for zinc, in the form of Zn^{2+}, and total iron (Fe) concentrations. Natural water contamination with zinc and iron turned out as a problem due to various factors: industry, transport, agriculture, lack of sewage systems in heavily populated areas, or from point sources as sewage water leakage, etc. (2, 3).

Iron is an essential nutrient. WHO estimation for iron minimal daily requirements depend on age, sex and man physiological status, and they range from 10 to 50 mg/d (4, 5). The average lethal dose for iron is 200-250 mg/kg body weight. However, literature presents data for death cases resulting from swelling of 40 mg/kg body weight doses (6, 7, 8).

Zinc is a representative of the group of microelements, thus in small quantities it is essential for human, animal and plant growth.

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Zinc influences living processes and displays regulatory functions, as it participates in the content of above 40 enzyme systems. Food zinc deficiency of men has been reported in a number of countries (9-12). The strong toxicity is due to the swelling of too large quantities of zinc resins, accidentally or intentionally (13). At high concentrations in water systems, however, zinc is accepted as a hazardous contaminant.

The data presented undoubtedly prove the necessity of monitoring and assessment of zinc and iron qualities in natural waters that present a significant part of the sources used for drinking and domestic purposes.

The aim of the present study was quality assessment of the natural waters in Stara Zagora Region, regarding two basic parameters – iron and zinc. To fulfill the latter, the following objectives were outlined:

(i) to determine iron and zinc concentrations in real surface and groundwater samples, taken from four municipalities in the region stated;

(ii) to analyze the results obtained from the viewpoint of Bulgarian legislation standards for surface and groundwater quality (14-16), as well as according to WHO guide values for drinking water quality and the permissible by the Environmental Protection Agency (EPA) maximum contamination levels (MCL).

MATERIALS AND METHOD

- *Reagents*

The reagents applied were of analytical grade (p.a. Merck and Fluka).

- *Sampling*

16 sampling points from four municipalities (Chirpan, Kazanlak, Gurkovo and Stara Zagora) were selected for the qualification of the surface and groundwaters, from shallow wells (3-25 m), in Stara Zagora Region **(Fig. 1).** The sampling and analyses were conducted during the autumn period (October-December), 2009. The examined water samples were collected, conserved and analyzed according to standard methods (17). The parameters pH, conductivity and temperature were determined at the time of sampling. Four parallel samples were taken for chemical analysis: (i) non-filtrated, acidified sample conserved with HNO_3 for cations determination, (ii) filtrated sample for anions and alkalinity determination, (iii) filtrated acidifies sample conserved with HNO_3 for dissolved cations determination, as well as (iv) filtrated sample acidified with H_2SO_4, for COD and BOD determination. The water samples were filtered through 0.45 μm membrane filters. Acidification and filtration were accomplished at the very sampling point. The natural water samples were collected in clean polyethylene bottles.

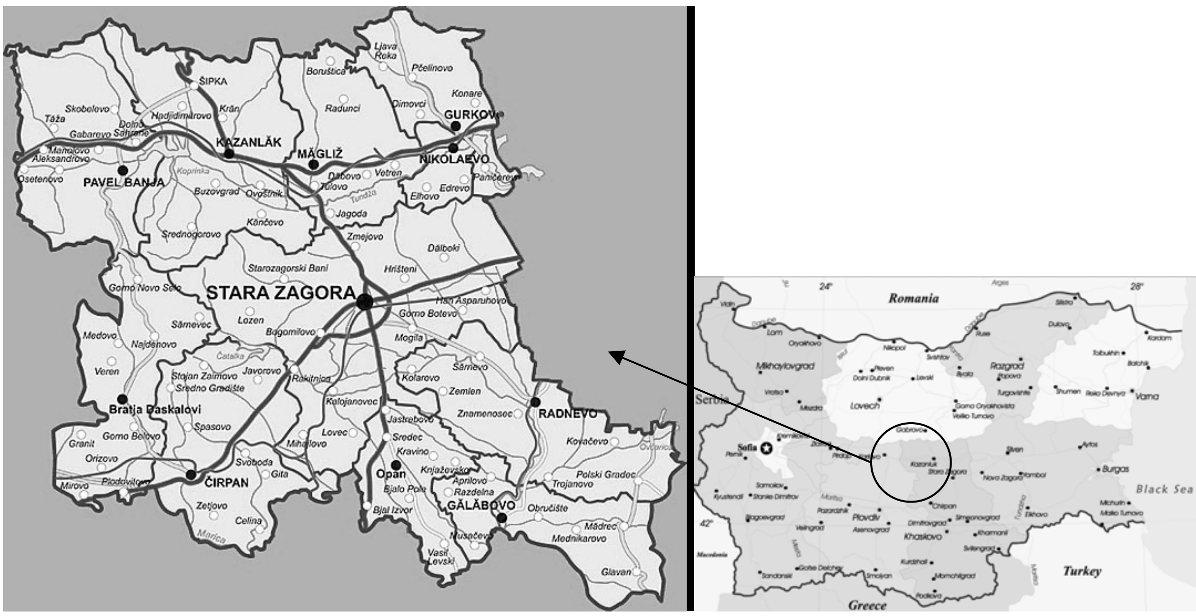

Fig. 1. A map of Stara Zagora Region.

- *Spectrophotometric analyses*

Iron and zinc concentrations were determined on UV/VIS DR 5000 spectrophotometer (Hach Lange, Germany) using standard Hach Lange cuvette tests for each individual parameter.

- *pH measurement*

pH and conductivity measurements of the water samples tested were accomplished by pH-meter Consort C932, Belgium.

All measurements were accomplished at room temperature (25^0C) at pH 7-9 in triplicate.

RESULTS AND DISCUSSION

The 16 analyzed sampling points (name, type and code) of surface and groundwaters from four municipalities in Stara Zagora Region are presented in **Table 1.**

All the results obtained were compared with the permissible standards – BDS (Regulation № 1/2007 and Regulation № 7/1986), WHO and EPA.

Table 1. *List of the sampling points of natural surface and groundwaters in Stara Zagora Region*

№	*Municipality*	Sampling Point (s.p.)	Type of water	Code
1.	*Stara Zagora*	Sazliika River before Chatalka Reservoir	FSW	1.1
		Sazliika River after Chatalka Reservoir	FSW	1.2
		Bedechka River before Zagorka Lake	FSW	1.3
		Tundzha River (bridge Yagoda Village)	FSW	1.4
		Novo Selo Village – well	GW	1.5
		Bratya Kunchevi Village - well	GW	1.6
2.	*Chirpan*	Chirpan Reservoir	RSW	2.1
		Zetyovo Reservoir	RSW	2.2
		Tekirska River – well (before Chirpan City)	GW	2.3
		Gita Village - shaft well in a drinking water pumping station	GW	2.4
3.	*Kazanlak*	Eninska River (after Enina Village)	FSW	3.1
		Leshnitsa River (after Dunavtsi Village)	FSW	3.2
		Tundzha River (after Rozovo Village)	FSW	3.3
4.	*Gurkovo*	Lazova River	FSW	4.1
		Radova River	FSW	4.2
		Gurkovo City - well	GW	4.3

FSW – flowing surface water; RSW – reservoir surface water; GW – groundwater

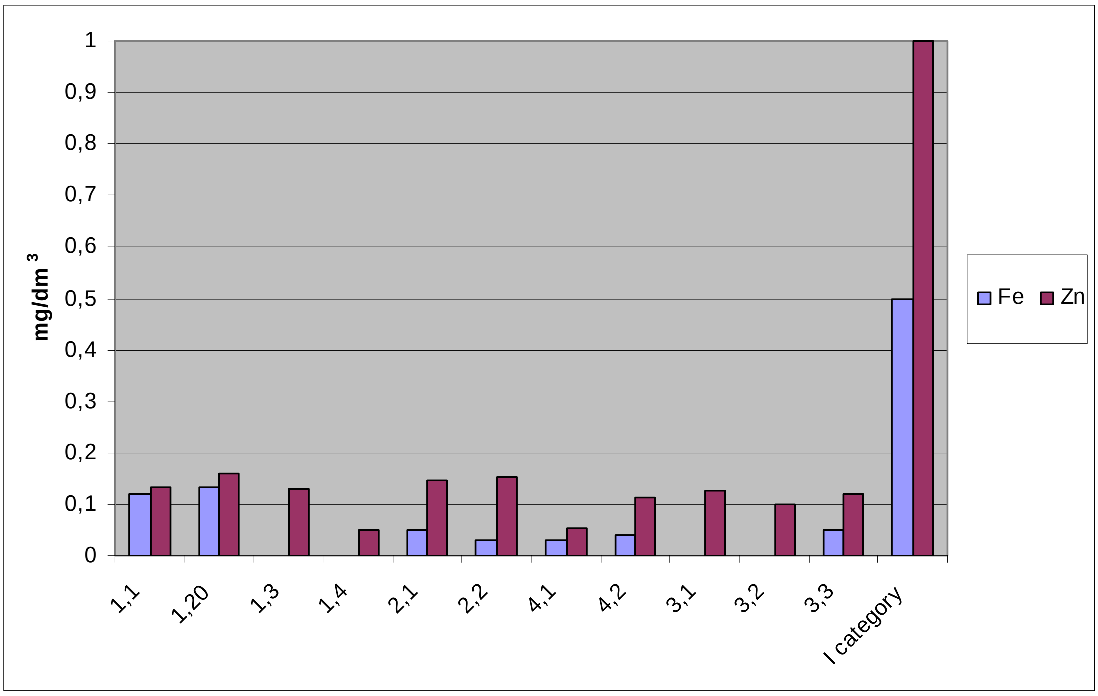

Fig. 2. Fe and Zn concentrations in surface water samples.

The average values of Fe and Zn content in the investigated surface water samples are presented on Fig. 2. The surface water samples characterizing Stara Zagora Municipality were taken from Sazliika, Bedechka and Tundzha Rivers. The highest Fe concentration was measured in Sazliika River (1.1, **Table 1**) – 0.12 mg/dm^3 **(Fig. 2)**. The average determined Fe concentration in the surface waters of Chirpan Municipality was 0.04 mg/dm^3. In Kazanlak Municipality Fe content - 0.05 mg/dm^3, was detected only in the sample taken from Tundzha River (3.3, **Table 1**). Our investigations did not determine presence of Fe in the other three points from Kazanlak Municipality. It was supposed that the measured Fe concentration in Tundzha River after Rozovo Village is a result of anthropogenic pollution due to the fact that this region is close to the industrial area of Kazanlak City. The comparative analyses of the results obtained proved that according to the parameter Fe, all of the investigated surface waters from the four municipalities **(Table 1)**, could be classified as I category, i.e. waters that can be used for drinking purposes and other activities requiring water of that quality.

The concentrations measured correspond to the standards set by WHO and EPA for the permissible Fe limits in drinking water. The concentrations of iron in the examined surface waters from all sampling points of Stara Zagora Region are below 0.5 mg/dm^3, which is the maximum permissible Fe concentration for I category surface waters according to Regulation № 7/1986.

The standards for drinking water quality set by EPA are classified in two categories – primary and secondary. The primary standards are based on health assumptions and are designed for man protection from the three contaminant types: pathogens, radioactive elements and toxic substances. The secondary limits include taste, odour, colour, corrosivity and foaming. The standard for Secondary Maximum Contamination Level (SMCL) for iron in drinking waters is 0.3 mg/dm^3. Waters containing lower iron concentrations are not supposed to have unpleasant taste, odour, appearance and side reactions caused by a secondary contaminant. The obtained in the present study results for Fe and Zn content in the surface water samples from Stara Zagora were analyzed according to Regulation № 4, 20.10.2000 for the quality of waters supporting fish and shellfish organism's life (15). It was concluded that the fresh surface waters are capable of supporting fish life according to both parameters: iron and zinc.

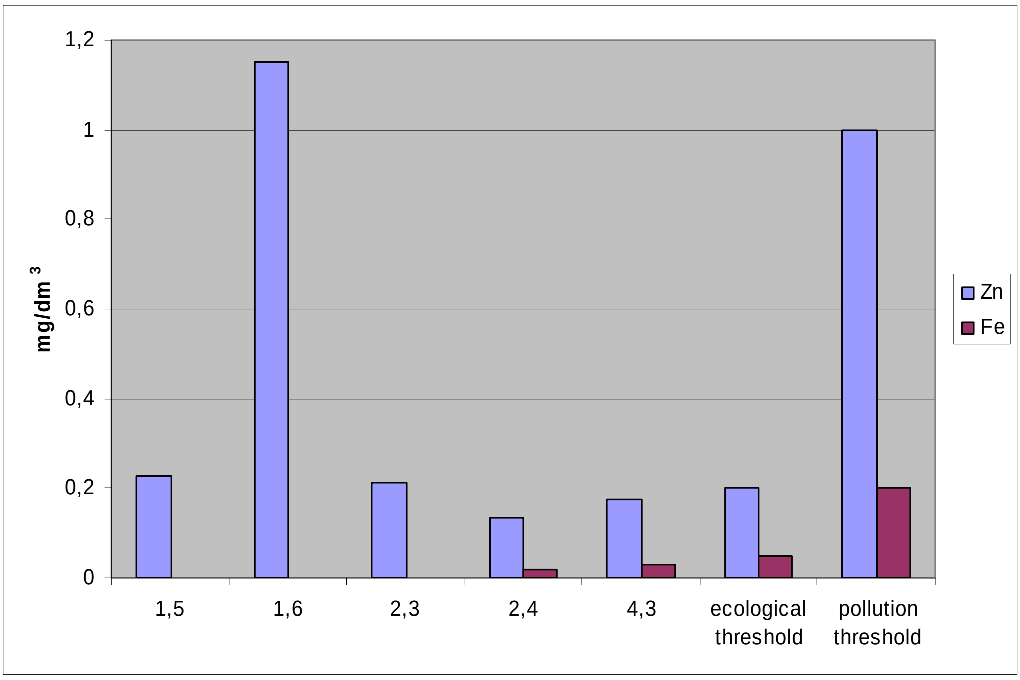

Fig. 3. Fe and Zn concentrations in groundwater samples.

Groundwater samples from the same four municipalities were taken for the quality determination of zinc and iron content **(Table 1)**. The analyses of the results and all resulting conclusions for groundwater quality were made on the basis of the standards set by the Bulgarian legislation (16-18).

The concentrations of Zn and Fe in the tested groundwater samples, as well as the corresponding ecological and pollution thresholds are presented on **Fig. 3.** The results obtained ascertained the highest Zn content in the groundwaters from Stara Zagora Municipality as compared to the analyzed groundwater samples from the other three municipalities (Chirpan, Kazanlak and Gurkovo). Zn concentrations in groundwater samples from Stara Zagora Municipality above the pollution threshold (1 mg/dm^3, Regulation №1/2007) were measured in samples taken from wells in Bratya Kunchevi Village (1.6, **Table 1**) - 1.15 mg/dm^3. All the other analyzed groundwater samples (1.5, 2.3, 2.4, Tab.1) characterized with Zn concentration below the pollution threshold (1 mg/dm^3, Fig. 3). The measured zinc concentrations in the waters from sampling points 1.5 (Zn 0.229 mg/dm^3) and 2.3 (Zn 0.212 mg/dm^3) exceeded the ecological threshold (0.2 mg/dm^3, **Fig. 3**). According to the measured Zn concentrations the groundwaters of Stara Zagora Region could be classified as: waters with zinc content under the ecological threshold from a well in Gurkovo City, Gurkovo Municipality and from Gita Village, Chirpan Municipality - shaft well in a drinking water pumping station; above the ecological threshold – Novo Selo Village, Stara Zagora Municipality and Tekirska River, Chirpan Municipality; above the pollution threshold - Bratya Kunchevi Village, Stara Zagora Municipality.

The results from the present study revealed that Fe concentrations in the investigated groundwaters of Stara Zagora Region did not exceed the pollution threshold **(Fig. 3)**.

It should be emphasized that the data obtained during the present investigations is the initial stage of a significant research (Ref. № 2008/115236) directed to a detailed qualitative and quantitative assessment of the surface and groundwater quality in Stara Zagora Region.

Water pollution of surface and groundwater streams can be resumed in a hydrodynamic mass transport accompanied by a mass transfer due to physical, chemical and biochemical processes. Entry of pollutants into shallow aquifers occurs by percolation from ground surface (disposal of wastes, agricultural fertilizers), from surface waters, through injection wells, sanitary septic tanks, sewer leakage and by saline water intrusion (18,19).

CONCLUSIONS

- The surface waters in Stara Zagora Region could be classified as I category according to the measured zinc and iron concentration values;
- The groundwaters of Stara Zagora Region could be classified as waters with increased content of total iron, but below the ecological threshold according to the measured iron concentration values;
- According to the measured zinc concentration values the groundwaters of Stara Zagora Region could be classified as waters with zinc content below the ecological threshold in Gurkovo Municipality and Gita Village, Chirpan Municipality; above the ecological threshold in Novo Selo Village, Stara Zagora Municipality and Tekirska River, Chirpan Municipality; above the pollution threshold in Bratya Kunchevi Village, Stara Zagora Municipality.

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