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ANALYSES OF NATURAL WATER QUALITY IN STARA ZAGORA REGION ACCORDING TO THE PARAMETERS SULFATES AND CHLORIDES

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ABSTRACT
The goal of the present work is an initial estimation of natural water quality in Stara Zagora Region, Bulgaria, with respect to the indices - sulfates (SO_4^{2-}) and chlorides (Cl^-). The concentrations of SO_4^{2-} and Cl^- in 13 surface and groundwater samples collected from four municipalities in Stara Zagora Region were determined spectrophotometrically. According to the results, the waters from Chirpan Reservoir (s.p. 2.1) characterized with the highest Cl^- concentration – 59.60 mg/dm^3. The mean determined Cl^- concentrations were 13.15 mg/dm^3 for Stara Zagora (s.p. 1) and 3.95 mg/dm^3 for Gurkovo (s.p. 4) Municipalities. Chloride concentrations in 75 % of the groundwater samples were under the ecological threshold of 50.00 mg/dm^3. The average measured SO_4^{2-} concentrations in the tested surface waters were: 23.45 mg/dm^3 for Stara Zagora (s.p. 1); 19.70 mg/dm^3 for Kazanlak (s.p. 3) and 22.50 mg/dm^3 for Gurkovo (s.p. 4) Municipalities. Thus, they could be classified as I category. SO_4^{2-} concentration in Zetyovo Reservoir waters (s.p. 2.2) (398.00 mg/dm^3) nearly coincided with the III category limit for surface waters (400.00 mg/dm^3). Sulfate concentrations in groundwater samples 1.5 and 4.3 exceeded the ecological threshold (50.00 mg/dm^3).

Keywords: sulfates, chlorides, surface water, groundwater, spectrophotometry

INTRODUCTION

Chlorides and sulfates are major inorganic constituents of surface and groundwater. Regarding groundwaters, sulfate and chloride are present in several minerals, but are most prevalent in evaporites such as sulfate, anhydrite, and halite. Anthropogenic sources of these inorganic compounds include agricultural products (animal manure, fertilizers, and irrigation return flow), oilfield brine, household sewage, landfill leachate, industrial effluent, deicing salt, pumping-induced saltwater intrusion, etc.

According to some scientists the isotopic signature of SO_4^{2-} ions dissolved in freshwaters can give precise information on their origins and biological transformations. Sulphate ions dissolved in lakewater can originate primarily from the inflows to the lake (rivers or/and direct catchment) or,
secondarily, from the internal recycling of S stored in the sediments. Typical primary SO_4^{2-} origins in surface waters are: rainfall SO_4^{2-} ; catchment runoff, i.e. mineralization of C-bound S, organic SO_4^{2-} ; hydrolysis and leaching of soil SO_4^{2-}, runoff from wetlands; pollutants, like fertilizers, or sewage. Occurrence and isotopic signature of secondary SO_4^{2-}origins depend on biogeochemical processes in the lake sediments (1).

Other researchers investigated the hydrogeologic causes of variations in watershed SO_4^{2-} mass balances in the eastern United States. They measured higher average SO_4^{2-} concentrations in summer than in winter, consistent with observations made by other authors and attributed in part to seasonal changes in regional SO_2 emissions and higher rates of photochemical oxidation of SO_2 in summer than in winter (2). Szynkiewicz et al. (3) stated that the isotopic mass balance is an

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important tool for quantitative evaluations of freshwater resources. Among stable isotopes, sulfur and oxygen isotopic compositions of sulfate dissolved in waters are the most suitable for isotope mass balance calculations, because sulfate ions have shown high thermodynamic stability and very low half-time (104–107 years) of isotopic exchange between other sulfur and oxygen-bearing compounds dissolved in waters (3).

Sulfur in sulfate form also occurs in organic matter such as in polysaccharide sulfates and aromatic sulfates in which the sulfate is bound by ester bond and can be released by hydrolytic reactions carried out by microorganisms. These sulfur-containing organic compounds are added to the water as human and domestic waste in addition to the wide spectrum of industrial effluents and agricultural run off. Unlike flowing waters, stagnant water bodies accumulate sulfur-containing compounds, thus influencing water quality (4).

Literature reported that at high concentrations sulfates could cause catharsis, dehydration and gastrointestinal irritations (5). A group of American scientists stated that SO_4^{2-} concentrations above 500 mg/dm^3 could also cause laxative effect on humans. The high values of this parameter affect the taste of water (6).

The guidelines for drinking water prescribed by the World Health Organization (WHO) for sulfate are 250 mg/dm^3. Generally, sulfate is considered beneficial in irrigation water, especially in the presence of calcium (7).

Chloride concentrations above 150 mg dm^{-3} are toxic to crops and generally unsuitable for irrigation. Water containing more than 350 mg/dm^3 chloride is unsuitable for most industrial uses. According to WHO no health-based guideline value is proposed for chloride in drinking water. Thus, chlorides are not toxicologically alarming, but they can be considered a measure for general pollution (7). Chloride in water may be considerably increased by treatment processes in which chlorine or chloride are used.

The goal of the present study is to assess natural water quality in Stara Zagora Region, Bulgaria, regarding the parameters – sulfates and chlorides. The specific objectives of this investigation are: determination of SO_4^{2-} and Cl^- concentrations in real surface and groundwater samples taken from four municipalities (Stara Zagora, Kazanlak, Chirpan and Gurkovo) in the stated region and analyses of the results from the standpoint of Bulgarian legislation standards for surface (Regulation No. 7/08.08.1986) and groundwater quality (Regulation No. 1/10.10.2007 – currently in force and Regulation No. 1/7.07.2000 – old regulation) (8-10), WHO guidelines for drinking water quality and Environmental Protection Agency (EPA) maximum contaminant levels (MCL) (7, 11).

MATERIALS AND METHODS

Sampling and analyses

Representative sampling points were identified and a total of 13 surface and groundwater samples were collected during the period November – December, 2009, from four municipalities in Stara Zagora Region, Bulgaria **(Table 1)**. The concentrations of chloride and sulfate in all of them were determined. The spectrophotometric analyses were performed on UV/VIS Spectrophotometer DR 5000 (Hach Lange, Germany) using standard Hach Lange cuvette tests for each individual parameter. All measurements were accomplished at room temperature (25^{0}C) at pH 7-9 in triplicate. All the results were referred to the permissible standard values set by the Bulgarian legislation for the quality of surface and groundwaters, WHO guidelines for drinking water quality and EPA limits (7-11).

Study area and environmental data

The administrative district of Stara Zagora Region is located in Central Bulgaria. It occupies an area of 1 151.1 km^2. The district center Stara Zagora ranks sixth in Bulgaria in terms of population. The region covers 11 municipalities. 70 % of its population, a total of 389 574 residents, inhabits the two largest cities: Stara Zagora and Kazanlak.

The present research was provoked as a result of the deteriorated ecological situation in Stara Zagora Region during the last 8 years deriving mainly from atmospheric pollution predominantly with SO_2 and NO_2 emissions. During the past few years frequent ambient air pollution cases in the region have been observed, some of them were very serious and grew up as an ecological and social problem. Until now, however, the sources of these air pollution cases have not been correctly clarified (12, 13).

Table 1. List of the investigated surface and groundwater samples 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
		Novo Selo Village – well	GW	1.5
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

According to previous investigations regarding the ecological evaluation of river ecosystems in the East Aegean Sea Region in Bulgaria and an integrated assessment of the ecological status of the rivers in the Tundzha River sub-basin, it was concluded that the cited region characterized with a high degree of surface water pollution (14, 15). Consequently, the contamination of the natural surface waters in the studied region, due to uncontrolled industrial wastewaters discharge, extensive agricultural fertilizers application and domestic sewage effluents, is of great concern as well. The total number of the basic sources (industrial enterprises, agglomerations with/without wastewater treatment plants) of wastewaters discharge to the sub-basins of Tundzha and Maritsa Rivers defined in the annual report of the Regional Inspectorate of Environment and Waters in Stara Zagora are 55 - 32 licensed, 7 with integrated permits and 5 without permits (16).

RESULTS AND DISCUSSION

1. Chlorides

1. 1. Surface Waters

The determined chloride concentrations in the surface water samples taken from Stara Zagora, Kazanlak, Chirpan and Gurkovo Municipalities during the autumn period, 2009, are presented on Fig. 1. Obviously, the waters from Chirpan Reservoir (s.p. 2.1) characterized with the highest Cl^- concentration – 59.60 mg/dm^3, which value is approximately 2 times higher than that measured in the surface waters of Zetyovo Reservoir (s.p. 2.2).

The mean determined Cl^- concentrations for Stara Zagora (s.p. 1) and Gurkovo (s.p. 4) Municipalities were 13.15 mg/dm^3 and 3.95 mg/dm^3, respectively. Tundzha River near Rozovo Village (s.p. 3.3) and two of its feeders – Eninska (s.p. 3.1) and Leshnitsa (s.p. 3.2) Rivers, were chosen as representative samples for the water quality characterization of Kazanlak Municipality. From the data displayed on **Fig. 1**, it could be concluded that the feeders contained approximately 6.5 times more chlorides as compared to their concentration in Tundzha River (17.20 mg/dm^3).

The comparative analysis between the spectrophotometrically determined values and the surface water quality standards set in Regulation No. 7 of 8.08.1986 (State Gazette No. 96/12.12.1986), proved that all analyzed surface water samples respond to the I category standard according to the parameter chlorides, as their concentrations are lower than 200.00 mg/dm^3 (8).

1. 2. Groundwaters

The investigations of the present study revealed that Cl^- concentrations in 75 % of the groundwater samples taken from Stara Zagora Region were under the ecological threshold of 30.00 mg/dm^3, set by Regulaton No. 1/7.07.2000 (9). According to the data presented on **Fig. 2**, only the parameter value in the sample taken from Stara Zagora Municipality (s.p. 1.5) surpassed with about 55 % the ecological threshold. Obviously, chlorides could not be classified as potential pollutants of the groundwaters in the selected municipalities, as their concentrations were far below both limits: the pollution threshold (100.00 mg/dm^3) and the quality standard (250.00 mg/dm^3).

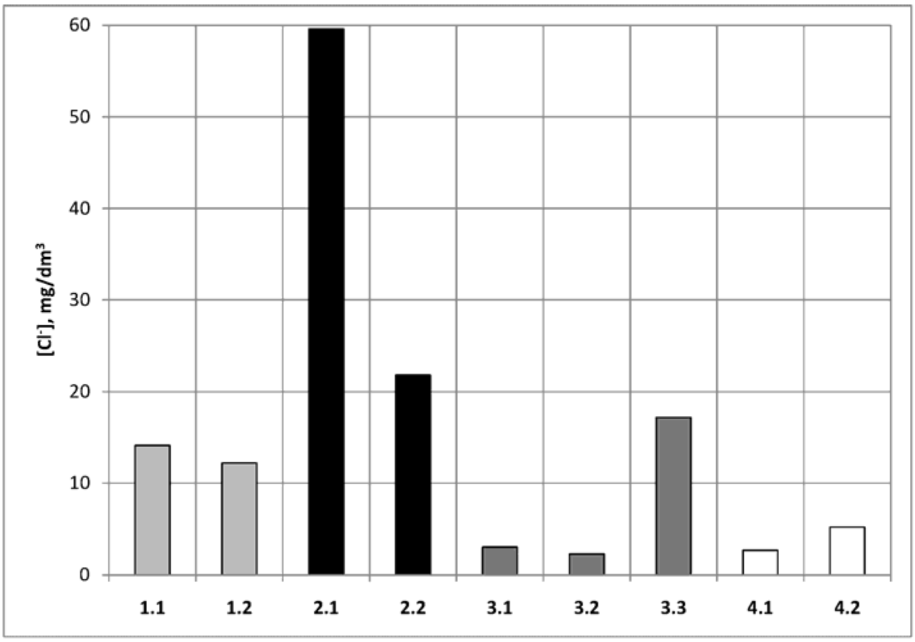

Fig. 1. Average Cl^- concentration values in surface water samples from Stara Zagora Region.

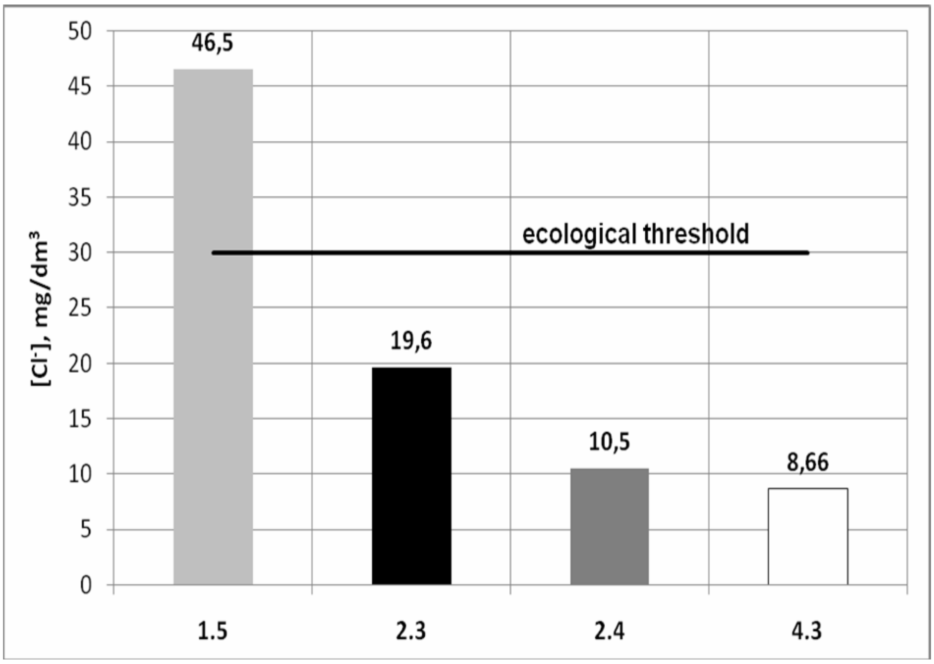

Fig. 2. Average Cl^- concentration values in groundwater samples from Stara Zagora Region

2. Sulfates

The presence of sulfate in surface and groundwater is mostly controlled by dissolution and deposition of mineral and amorphous solid phases, dissolved oxygen, atmospheric deposition, biological interactions, point and nonpoint sources (17).

2.1. Surface Waters

The average spectrophotometrically determined SO_4^{2-} concentrations in 9 surface water samples taken from the four investigated municipalities in Stara Zagora Region (Table 1) are graphically presented on **Fig. 3.** The data clearly diplay that s.p. 2.1 and 2.2 from Chirpan Municipality characterized with the highest values of this parameter. The measured sulfate concentration in Zetyovo Reservoir waters (398.00 mg/dm^3) nearly coincides with the maximum permissible limit for III category surface waters (400.00 mg/dm^3), i.e. the application of these waters even for industrial purposes is not recommended (8). It was established that SO_4^{2-} content in Chirpan Reservoir (s.p. 2.1) was 188.00 mg/dm^3, which is quite close to the I category upper standard value of 200.00 mg/dm^3 (8). Thus, the use of this natural water body is advisable neither for drinking nor for domestic purposes.

The analyses of the results obtained outlined the following average values of SO_4^{2-} concentrations in the surface waters of Stara Zagora Region: 23.45 mg/dm^3 for Stara Zagora Municipality (s.p. 1); 19.70 mg/dm^3 for Kazanlak Municipality (s.p. 3) and 22.50 mg/dm^3 for Gurkovo Municipality (s.p. 4). Consequently, they respond to the I category limit for surface waters.

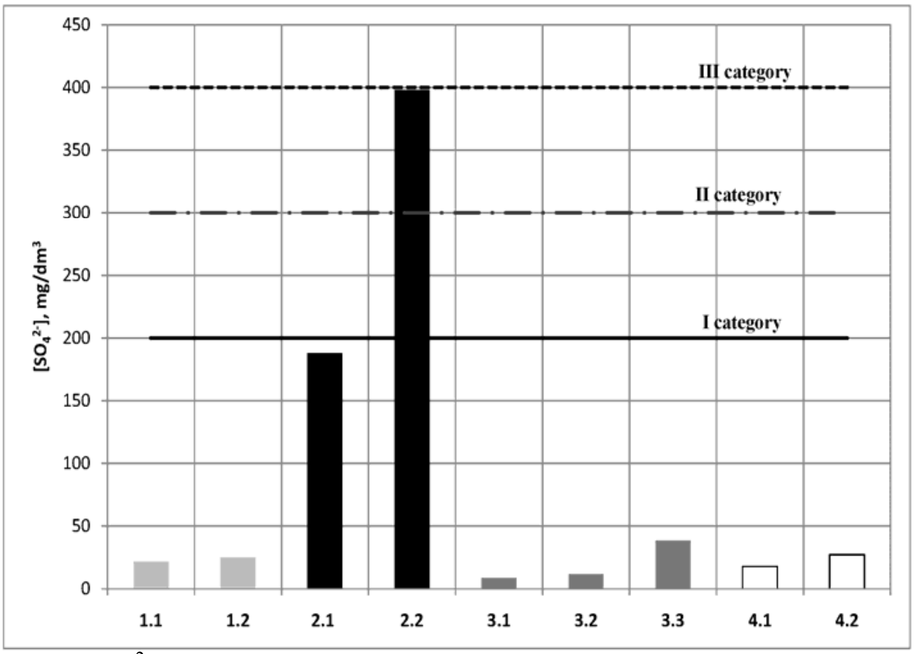

Fig. 3. Average SO_4^{2-} concentration values in surface water samples from Stara Zagora Region

2.2. Groundwaters

Sulfates present in the groundwaters, are mostly a combination of potassium, sodium and magnesium sulfate. Due to the low solubility of calcium sulfate (2.00 g/dm^3 at 20^{0}C), the more soluble Na_2SO_4, $MgSO_4$ and $FeSO_4$ contained in the soil layers dominate quantitatively in the groundwaters (18).

The average values of the measured SO_4^{2-} concentrations in some groundwater sources of Stara Zagora Region are displayed on **Fig. 4**. It was established that the groundwaters in Chirpan Municipality characterized with the lowest content of these inorganic salts: 4.38 mg/dm^3 and 12.00 mg/dm^3, respectively in s.p. 2.3 and 2.4. Taking into account the ecological threshold of 50.00 mg/dm^3 SO_4^{2-} set by the Bulgarian legislation (9), however, it could be concluded that the measured sulfate content in sampling point 4.3 is approximately 24 % higher. The 2.7 fold exceedance of the latter limit detected in s.p. 1.5 – groundwater from Novo Selo Village, turned out even more significant.

The comparative estimation between the spectrophotometrically determined SO_4^{2-} concentrations in the four groundwater sampling points and the Bulgarian legislation standards of 150.00 mg/dm^3 pollution threshold and 250.00 mg/dm^3 quality standard, proved that the investigated groundwaters in Stara Zagora Region meet the groundwater quality requirements according to the parameter sulfates. Besides, WHO and EPA have not regulted quide values for permissible sulfate concentrations in drinking water from the viewpoint of human health. The thorough investigations of both international organizations, however, ascertained increase of complaints associated with deterioration of the taste of drinking water containing SO_4^{2-} concentrations above 500.00 mg/dm^3 (7).

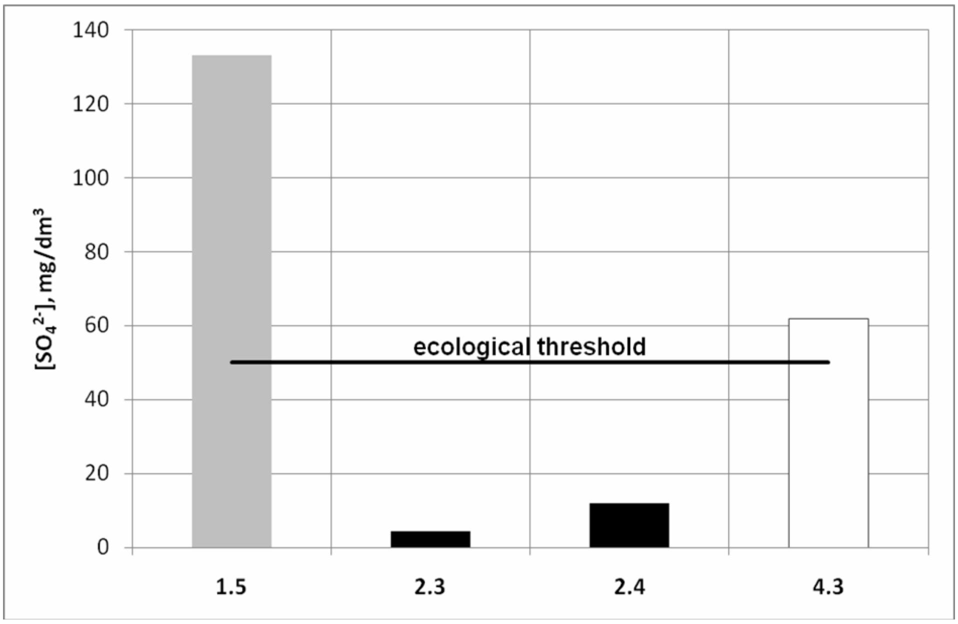

Fig. 4. Average SO_4^{2-} concentration values in groundwater samples from Stara Zagora Region

3. Tundzha River Quality

The results obtained during the present investigations allowed tracking SO_4^{2-} and Cl^- concentration variations in the surface waters from the Southeastern downstream of Tundzha River (s.p. 3.3) between Koprinka Reservoir (Kazanlak Municipality – s.p. 3) and Gurkovo City (Gurkovo Municipality, s.p. 4), including the four feeders: s.p. 3.1, 3.2, 4.1 and 4.2. The concentration profiles presented on **Fig. 5** display analogous trends. The highest values of the determined parameters were measured in the surface water samples from the very river (s.p. 3.3) (38.6 mg/dm^3 SO_4^{2-} ; 17.2 mg/dm^3 Cl^-) and relatively lower – in the feeders surface waters. The approximately 2 times lower SO_4^{2-} and Cl^- concentrations in s.p. 4.1, as compared to those in s.p. 4.2, probably are due to the fact that Lazova River is a left feeder of Radova River, while the latter which crosses meridianally the territory of Gurkovo Municipality, is a left feeder of Tundzha River, i.e. it is characterized with greater catchment area.

The latter conclusions seemed logical as the feeders selected for the present investigations flow through weakly populated areas without significant industrial activities.

The investigations of a group of scientists revealed that regarding SO_4^{2-} content, the influence of polluted atmospheric precipitation is the most dramatic on small water streams with low water mineralization whose catchment areas are in the influence zone of large sources of industrial air emissions. For large rivers with industrially developed basins the main amounts of the ingredients under consideration enter into the river network together with wastewater discharged by industrial and agricultural enterprises, as well as by the communal and household sector. The involvement of substances from the atmosphere in the form of dry and wet deposition in the formation of chemical composition of waters is considerably lower (19).

CONCLUSIONS

- All analyzed surface water samples respond to I category standard for surface waters according to the parameter chlorides, as their concentrations are lower than the maximum permitted limit of 200.00 mg/dm^3;
- Chlorides could not be classified as potential pollutants of the groundwaters in the four selected municipalities, as their concentrations were far below the quality standard (250.00 mg/dm^3);
- The highest measured SO_4^{2-} concentration - 398.00 mg/dm^3 in Zetyovo Reservoir waters (s.p. 2.2) nearly coincides with the maximum permissible limit for III category surface waters (400.00 mg/dm^3), i.e. the application of these waters even for industrial purposes is not recommended;
- Sulfates content in the surface waters from Stara Zagora (s.p. 1.1, 1.2), Kazanlak (s.p. 3.1, 3.2, 3.3) and Gurkovo (s.p. 4.1, 4.2)

Municipalities are certainly below the I category limit for surface waters regarding this parameter;

- The investigated groundwaters in Stara Zagora Region meet the groundwater quality requirements according to the parameter SO_4^{2-} set by the Bulgarian legislation;
- Cl^- and SO_4^{2-} concentration profiles for the downstream of Tundzha River and four of its feeders in Stara Zagora Region displayed analogous trends: with the highest measured values in the surface water samples from the very river (s.p. 3.3) – 17.20 mg/dm^3 Cl^- ; 38.6 mg/dm^3 SO_4^{2-}, and relatively lower – in the feeders surface waters (s.p. 3.1, 3.2, 4.1, 4.2).

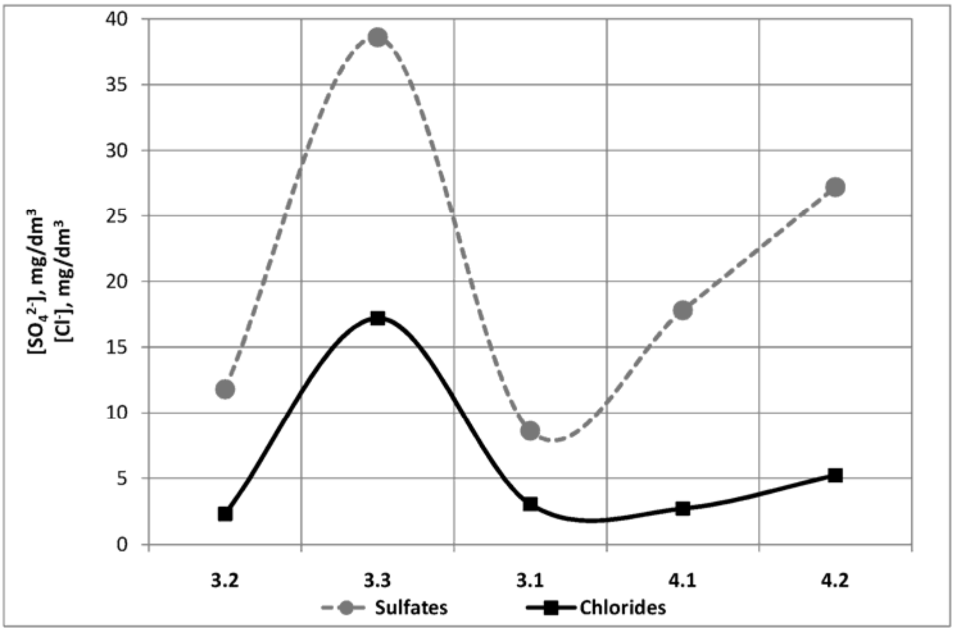

Fig. 5. Concentration curves of Cl^- and SO_4^{2-} for surface water samples from the downstream of Tundzha River and four of its feeders in Stara Zagora Region.

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