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Initial assessment of the chemical state of the water in the upper part of Iskar River

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The ecological status of the water in the Iskar River basin is of utmost importance because it provides more than 70% of Sofia's drinking water. It is considered that the major point source of pollution in the upper Iskar aquatic ecosystems is the discharge from the wastewater treatment plant (WWTP) in the town of Samokov.

This study aims to assess the environmental impact of treated effluent discharge from the WWTP - Samokov in the upper part of the Iskar River. Autumn and spring sampling was carried out (November 2020, March 2021, November 2021 and March 2022) at four sampling points upstream and downstream of the WWTP - Samokov and from a discharge of a local WWTP in the village of Belchin. The contents of macro-, micro- and trace elements, as well as inorganic anions were determined and compared with the requirements of Bulgarian legislation. The concentrations of the macroelements Na, K, Ca, Mg, P, S and Si were relatively stable in the studied sampling points and seasons. The concentrations of the main part of the regulated microelements were below the maximum admissible concentrations (MACs). Seasonal exceedance of the MACs was established for Al, Fe, Hg before and after the discharge, which is an indication of diffuse pollution. The presence of Cl^-, NO_3^- and SO_4^{2-} was found, and the highest concentrations were determined at the discharge, but were below the MACs according to the requirements of Bulgarian legislation.

Keywords: Iskar River, Water pollution, Macroelements, Microelements, Inorganic anions, Seasonal variations

INTRODUCTION

Anthropogenic pollution and protection of the environment are global problems [1-2]. The increase in population leads to industrial, domestic, traffic, and agricultural pollution. Surface waters are carriers of large quantities of various waste materials. Concentrated polluters of surface waters are usually wastewater from households, industrial facilities and large urban agglomerations that are located near rivers or lakes. Pollutants can be heavy metals, hydrocarbons, chlorinated hydrocarbons, organochlorine compounds, nitroaromatic compounds, organophosphates, nonchlorinated pesticides and herbicides, and radionuclides [3]. Heavy metals are extremely hazardous contaminants in various media of the environment due to their extensive persistence, high ecotoxicity, non-degradable feature, and potential bioaccumulation and biomagnification through food chains, posing potential risks to the ecosystem and human beings [4]. The health risk of trace elements in aquatic environment and subsequent uptake in the food chain by aquatic organisms and humans, can result in morphological abnormalities and genetic alteration of cells. In addition, trace elements can affect enzymatic and hormonal activities [5]. In order to assess the risk of water pollution and its adverse impact on the natural environment, accurate determinations of element concentrations, especially of potentially toxic elements are needed. Chemical analysis of surface waters provides an efficient tool for water-quality management. Numerous investigations have been carried out to establish environmental changes in surface waters worldwide using different instrumental methods depending on the number of elements to be determined and the limit of detection (LOD) of the methods [6-10]. Analysis of common inorganic anions in water is also mandatory. Ion chromatography has almost replaced most of the wet chemical methods used in water analysis [11].

In Bulgaria, the quality of surface water intended for household purposes is constantly monitored according to the requirements of Bulgarian legislation [12]. There are sporadic literature data on water quality research, usually for a single element [13], only trace element concentrations and impact assessment of the wastewater treatment plants discharges [14]. The upper Iskar sub-catchment is

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one of the biggest Bulgarian water sources that supplies the capital Sofia with drinking water. The ecological status of the Iskar River can be deteriorated as a result of diffuse pollution from agriculture, penetration of untreated sewage from the small villages, and tourism, etc. It is considered, however, that the main point source, representing a critical factor for water quality in the aquatic ecosystems in the upper Iskar aquatic ecosystems, is the discharge from the wastewater treatment plant (WWTP) of the town of Samokov [15].

Municipal WWTPs have been widely constructed in intensive urban areas with high population densities to reduce the discharge of pollutants into water environments [16, 17]. However, WWTPs discharge remains a major source of nutrients and micropollutants in receiving aquatic ecosystems [18]. As water is uniquely vulnerable to pollution, water pollution control has received considerable attention as one of the most critical environmental challenges [19].

Recently, the effect of the WWTP - Samokov discharge on physicochemical parameters, nutrient concentrations, selected hazardous and specific pollutants, and the abundance and activity of microbial communities were assessed [15].

In the present work, the concentrations of macro-, micro-, trace elements, and inorganic anions were investigated for a 2-year period in water samples taken before the WWTP, at the point of discharge, and at certain distances after the WWTP. On this basis, the impact of the WWTP - Samokov on water quality, as well as seasonal variations were assessed.

EXPERIMENTAL

Sampling points

Four sampling campaigns were carried out in two seasons – November, 2020, March, 2021, November, 2021 and March, 2022. Water samples were taken from 5 locations indicated in Fig. 1. Four of the samples were taken from the Iskar River upstream and downstream of the WWTP - Samokov and for a comparison, water samples from a discharge of a local WWTP from a hotel complex in the village of Belchin into a canal that joins the Palakaria River were also taken.

Sampling and sample preparation

Sampling was carried out in one day. Water samples were taken manually in plastic bottles. Pooled water samples were prepared from several (min. 5) points located in a small area. The physicochemical parameters (temperature, oxygen concentration, conductivity, and pH) were analyzed *in situ* immediately after sampling [15]. In laboratory conditions, they were filtered with 25 mm PES sterile syringe filters (0.45 µm). Afterwards, the samples were divided into 2 aliquots. One of the aliquots was used for the determination of anions without further treatment, and the other one, used for the determination of elemental composition, was acidified to pH 2 with conc. HNO_3 prior to analysis. The samples were stored at 4 °C and analyzed within 24 h.

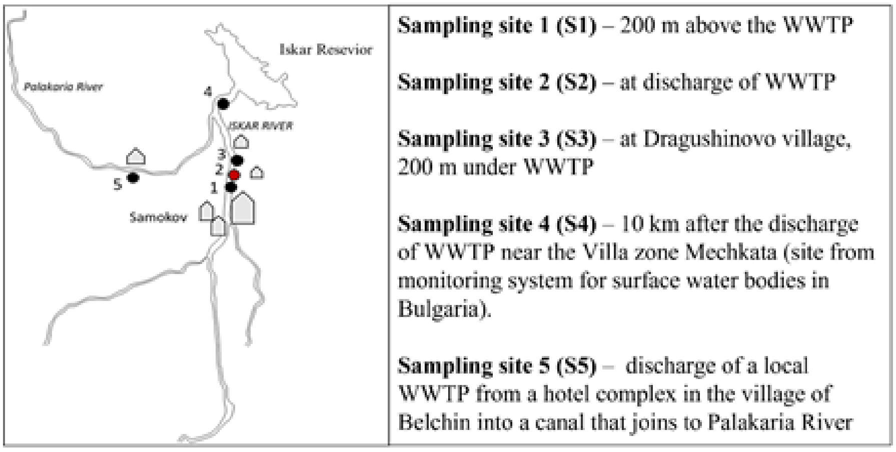

Fig. 1. Sampling locations upstream and downstream of the WWTP-Samokov

Instrumentation

The determination of the elements in the water samples was carried out using ICP-MS (Perkin-Elmer SCIEX Elan DRC-e) with a cross-flow nebulizer. The concentrations of 70 elements were analyzed. The calibration and the determination of macro-, micro-, and trace elements was done simultaneously under experimental conditions and element isotopes described in Lyubomirova *et al.* [20] and Lyubomirova and Djingova [21].

The determination of the inorganic anions was performed by an ion chromatograph model CIC-D160, SHINE (Qingdao Shenghan Chromatograph Technology Co., Qingdao, China), equipped with an anion-exchange column SH-AC-11 (size 4.6×250 mm) purchased from SHINE (Qingdao, China). The separation was performed at the following operating parameters: mobile phase - 15 mM KOH, column temperature - 35 °C and flow rate- 1.0 mL/min (isocratic elution). The volume of the injected sample was 25 μL.

Method validation

The estimation of accuracy of the ICP-MS measurements was conducted by the analysis of two water reference materials: SPS-SW2 (Reference Material for Measurement of Elements in Surface Waters, Spectrapure Standards, Norway) and NWTM-23.5 (Environmental matrix reference material, a trace element-fortified sample, Environment and Climate Change, Canada). The accuracy of the determination of the elements not included in the reference materials with possible spectral interference (e.g. ^{107}Ag - $^{91}Zr^{16}O^{+}$, $^{89}Y^{18}O^{+}$, ^{109}Ag - $^{91}Zr^{18}O^{+}$, $^{92}Zr^{16}O^{1}H^{+}$; ^{200}Hg - $^{184}W^{16}O^{+}$, ^{69}Ga - $^{33}S^{36}S^{+}$, ^{71}Ga - $^{38}Ar^{33}S^{+}$) was evaluated by standard addition method. To evaluate the accuracy and precision of the anionic determination, the reference material SPS-NUTR-WW2 (Reference Material for Measurement of Ions in Waste Waters, Oslo, Norway) was used. The experimental results were in very good agreement with the certified/added concentrations. All samples were analyzed in triplicate to assess the precision of the analysis. The precision of the analyses is better than 10 % for the elements and 7% for the anions.

RESULTS AND DISCUSSION

Macroelements composition

Table 1 presents the concentration intervals of the determined elements in the water samples for all sampling campaigns. For the macroelements Na, K, Ca, Mg, P, S and Si maximum admissible concentrations (MACs) are not specified in Bulgarian Regulation No. 12, 2002 on the quality of surface water intended for drinking and household purpose (BG-Reg. 12) [12]. The data in Table 1 show relatively narrow concentration ranges in all the studied regions, especially for Mg, P, S and Si. For Na, K and Ca, no significant differences were also found, but still it can be noted that the minimum concentrations are the highest in the water from the discharge area of the WWTP - Samokov (S2). However, the measured concentrations are far below the indicative values according to Bulgarian Regulation No 9, 2001 (BG-Reg. 9) [22] for drinking water. The evaluation of the data for the presence of seasonal variations showed that the ratios of autumn to spring concentrations ranged from 0.5 to 1.5 regardless the element and the sampling point. These facts are indicative that neither point nor diffuse pollution could be defined. The small fluctuation intervals of the macroelements may be due to other factors such as pH variation [15], water quantity, suspended solids, etc. Distinctly higher concentrations of P were found at the two critical points S2, and S5, which could be due to the use of detergents.

Microelements and trace elements composition

In the present study, the concentrations of 63 micro- and trace elements were determined. The concentrations of Be, Ge, Hf, In, Ir, Tl, Re, Pd, Rh, Pt, Ru, Tm, Sc, Os were below LOD in all the samples. The experimentally determined LODs (3σ) for Ge, In, Ir, Rh were 0.001 μg/L, for Re, Pd, Pt, Ru, Os, REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were 0.002 μg/L, for Hf and Sc were 0.003 μg/L, for Tl was 0.006 μg/L and for Be was 0.008 μg/L.

The elements that are controlled in surface water intended for drinking and domestic water supply are As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn [12]. The last column in Table 1 presents the recommended - MAC (if specified) for waters category A1. Additionally, the average annual concentrations - MAC for inland surface waters according to Regulation H-4, 2012 [23] are presented for Al and U and are marked with an asterisk. The presented data show that the concentration intervals of the main part of the regulated elements (As, B, Be, Ba, Cd, Co, Cr, Mn, Ni, Pb, Se, V, Zn, and U) are below the MACs at all sampling sites. Moreover, relatively narrow and close concentration intervals were observed for As, B, Ba, Co, Cr, Se and U in the studied locations and seasons. The concentrations of the priority pollutants Cd, Ni, and Pb are far below the MACs and relatively similar for the sampling points and seasons. The concentrations of elements, some of which are potentially toxic, with distinct seasonal variations, are presented in Fig. 2.

Table 1. Concentration intervals of macroelements Na, K, Ca, Mg, P, S, Si (mg/L), micro- and trace elements (μg/L) in the water samples.

	S1	S2	S3	S4	S5	Reg. 12
Na	4.3-7.2	14.5-19.0	4.6-15.6	5.7-21.3	5.0-61	
K	1.4-2.4	6.3-8.0	1.8-11.2	1.9-3.8	2.3-5.1	
Ca	7.1-14.6	15.9-24.2	8.1-23.9	8.9-20.3	11.2-15.5	
Mg	1.9-2.1	2.0-3.4	1.4-6.6	2.4-2.7	2.9-3.7	
P	0.01-0.13	0.41-0.68	0.01-0.15	0.01-0.10	0.04-0.80	
S	1.1-3.9	2.4-6.9	2.2-3.7	1.1-4.4	3.7-5.3	
Si	3.9-5.3	5.1-7.4	4.5-4.7	4.1-17	9.3-13.5	
Al	9.0-80	4.1-14.0	10.1-88	12.2-117	38-3710	(15-25)*
As	0.16-1.15	0.41-0.85	0.15-0.90	0.23-0.51	1.22-1.97	10-50
B	3.6-13.0	17.2-26	2.4-76	5.4-7.5	9.2-69	1000
Ba	1.0-9.5	1.1-12.2	1.1-8.4	0.4-9.0	1.9-23.9	100
Cd	0.01-0.05	0.07-0.35	0.03-0.07	<0.001-0.07	0.01-0.02	1-5
Co	0.08-0.17	0.13-0.22	0.07-0.17	0.11-0.34	0.30-0.57	20
Cr	0.20-3.3	0.53-4.3	1.1-3.8	0.50-1.6	3.4-4.9	50
Cu	1.31-21.6	1.48-44.0	1.32-21.3	1.53-24.2	2.13-9.22	20-50
Fe	27-120	5.6-166	27-184	29-363	304-3880	100-300
Hg	0.12-1.11	0.13-0.93	0.65-1.42	0.24-0.63	<0.001-2.76	0.5-1
Mn	0.51-2.2	0.18-1.45	0.37-1.13	0.90-4.1	18.5-108	50
Ni	0.48-1.04	0.74-3.49	0.30-2.31	0.46-2.14	1.81-4.73	20
Pb	0.05-0.15	0.01-0.70	0.02-0.16	0.01-0.38	0.08-1.18	50
Se	<0.012-1.45	<0.012-1.88	<0.012-2.6	<0.012-1.01	<0.012-0.72	10
V	0.33-1.21	0.72-1.46	0.14-1.58	0.50-1.30	1.20-8.23	10
Zn	0.63-62	8.1-45	2.7-58	2.3-76	10.8-12.9	500-3000
U	0.25-0.52	0.14-0.25	0.28-1.41	0.36-0.82	0.29-0.33	(5-40)*
Ag	<0.003-0.13	<0.003-0.13	<0.003-0.09	<0.003-0.04	0.004-1.98	
Au	0.02-0.14	0.02-0.15	0.02-0.17	0.03-0.43	<0.001-0.13	
Bi	0.01-0.14	0.01-0.21	<0.001-0.06	0.006-0.15	0.01-0.08	
Cs	0.01-0.05	0.01-0.02	0.01-0.02	0.004-0.04	0.24-0.36	
Ga	0.01-0.05	0.02-0.04	0.03-0.08	0.01-0.47	0.59-1.31	
Li	0.42-1.03	0.84-1.47	0.70-1.21	0.52-1.54	2.33-17.6	
Mo	0.30-2.56	0.67-2.62	0.38-1.79	0.43-4.20	0.53-22.2	
Nb	0.02-0.04	0.01-0.04	0.003-0.05	0.01-0.06	0.06-0.37	
REEs	<0.002-0.15	<0.002-0.73	<0.002-0.08	<0.002-0.40	<0.002-1.43	
Rb	0.14-1.61	2.86-7.17	1.01-45.3	0.92-1.90	4.50-8.50	
Sb	0.03-0.20	0.13-0.29	0.06-0.33	0.04-0.30	0.15-0.27	
Sn	0.01-0.73	0.03-0.53	0.10-0.25	0.58-1.26	0.26-0.29	
Sr	47.3-67.2	68.0-130	50.8-142	54.8-72.0	88.5-103	
Ta	0.01-0.04	<0.002-0.02	0.004-0.04	<0.002-0.15	0.03-0.10	
Te	0.15-0.22	0.09-0.27	0.05-0.34	0.002-0.58	<0.001-0.12	
Th	0.01-0.08	0.003-0.07	0.02-0.05	0.01-0.12	0.05-0.58	
Ti	0.04-105	0.06-115	0.03-93	0.04-32	13.0-189	
W	0.11-2.91	0.43-2.05	0.19-1.33	0.20-5.32	0.40-63	
Y	0.06-0.19	0.03-0.10	0.04-0.07	0.04-0.10	0.04-0.86	
Zr	0.10-0.20	0.04-0.11	0.01-0.24	0.02-0.66	0.12-2.62	

Although the concentration intervals do not pose any environmental threat, a trend of increasing Cd and Ni in the spring seasons and once for Pb in the risk point S_2 is worth noting. Higher levels of the toxic elements Ni and Pb, but within the admissible limits, as well as V (close to the limit) and Mn (twice the limit) were found in S5. Mn is an essential element for humans. Based on the upper range value of Mn intake of 11 mg/day, a health-based value of 0.4 mg/L is derived in WHO [24] which is much higher than the measured concentrations in S5. The increased concentration may be due to the widespread use of Mn-manufacture of iron and steel alloys, an oxidant for cleaning, bleaching and disinfection, and as an ingredient in various products. Manganese greensands are used in some locations for potable water treatment. At concentrations higher than 0.05 mg/L in the water undesirable color and turbidity may ensue. At a concentration of 0.2 mg/L, Mn can often form a coating on pipes, which may slough off as a black precipitate [24]. Cu and Zn are also essential trace elements with high admissible concentrations in BG-Reg. 9 [22] (2 mg/L, resp. 4 mg/L). In BG-Reg. 12 [12], the admissible values are lower, especially for Cu. For both elements, a uniform trend of the measured concentrations was observed, which shows an increase in the autumn of 2020 in all sampling sites, followed by a permanent decrease until the spring of 2022. The Cu concentrations in this season exceeded the recommended value in all sampling sites but were below the admissible value. The highest concentration of Cu was measured in S2 and of Zn in S4. Their seasonal increase and the fact that Zn concentration was the lowest in S2 indicate that the variations are not due to a defined point source of pollution. Increased Cu and Zn in surface waters may be attributed to long-term manure-borne copper and zinc inputs to grassland and arable soils which could result in their catchment in water [25]. The concentration of Fe exceeded the MAC in S4 and the recommended value in all sampling sites. A curious result was also the dynamics in the concentration of Al, which exceeded the admissible levels according to Regulation H-4 in S1, S3 and S4, but was below the recommended limit in S2, probably due to a precipitation. An exceedance of the limits is observed in both seasons. According to WHO, naturally occurring Al and Fe. as well as their salts used as coagulants in drinking-water treatment, are their primary sources in drinking water [24]. Typical coagulant doses are 2–5 mg/L as Al or 4–10 mg/L as Fe. The presence of Al at concentrations over 0.1–0.2 mg/L often leads to consumer complaints due to the deposition of aluminium hydroxide floc. At high concentrations of Al and Fe, undesirable turbidity and color to the water may also appear [24]. The data in Fig. 2 show, however, that all values for Al and Fe in the water samples from the Iskar River, with the exception of a single value of 363 µg/L for Fe in S4, are below the indicative value of 200 µg/L in drinking water according to BG-Reg. 9 [22]. Better process optimization is needed in the local WWTP from a hotel complex in the village of Belchin, where the concentrations of Al and Fe were 3710 µg/L, resp. 3880 µg/L in the spring of 2021.

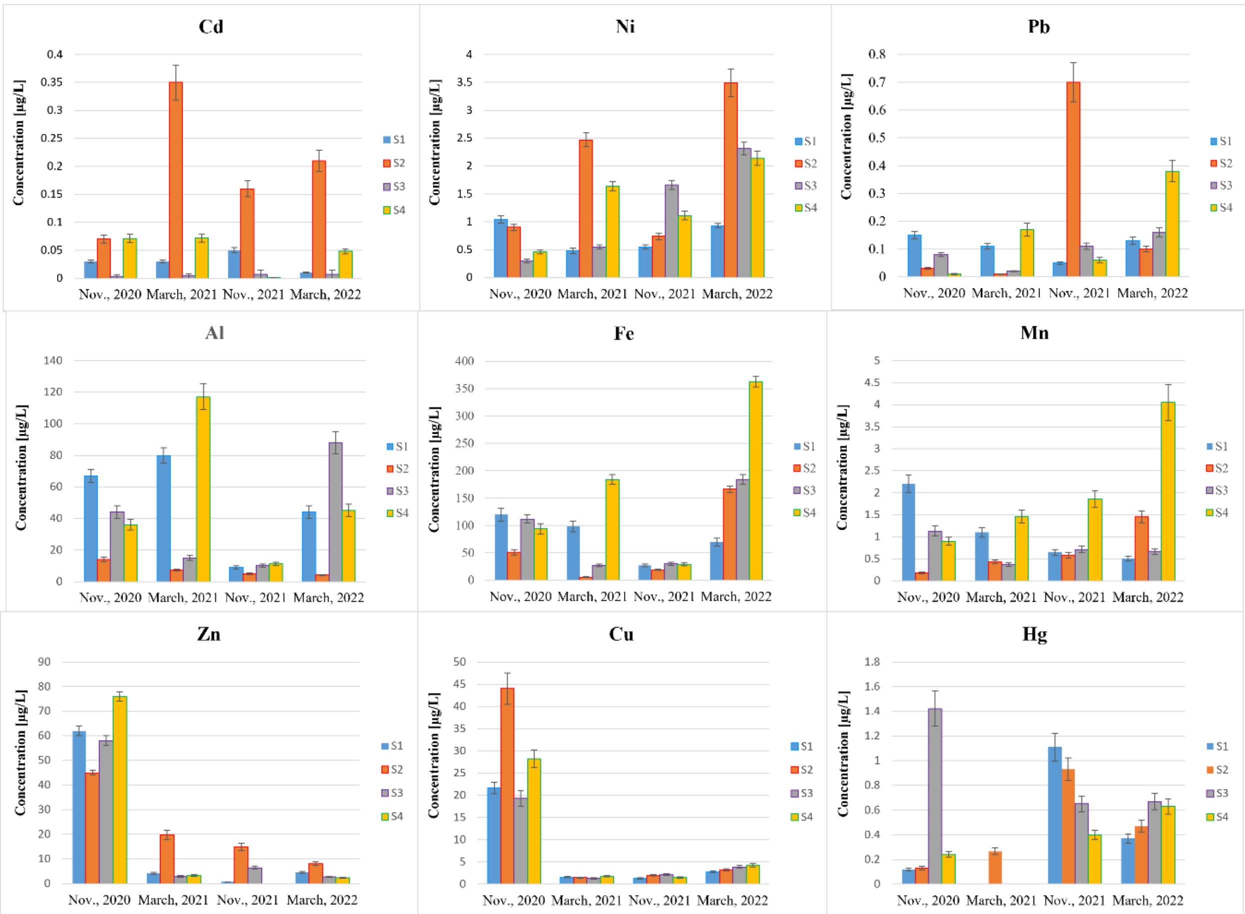

Fig. 2. Concentrations of selected elements with distinct seasonal variations

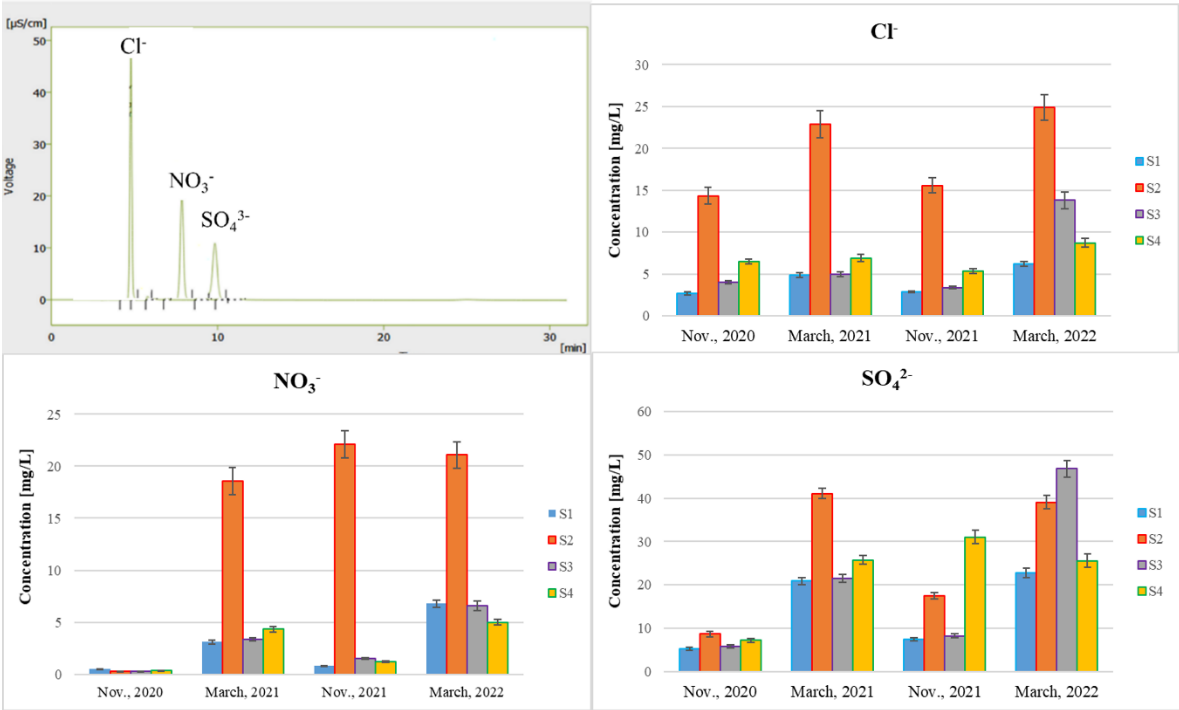

Fig. 3. Ion chromatogram of Iskar River water from sampling site S1 and seasonal variations of Cl^-, NO_3^- and SO_4^{2-} in the water samples from the Iskar River

A marked increase from spring to autumn was found for Hg which is also a priority pollutant. The seasonal increase and exceeding the MAC only in certain places (S1, S3, S5), and slightly below the limit in S2 (Nov., 2021) is an indication of diffuse pollution, probably due to the use of Hg in biocides.

The remaining micro- and trace elements do not have a defined MAC in BG-Reg. 12 [12]. Relatively narrow and close intervals were observed between the individual points of the Iskar River and occasional seasonal variations. For some of the trace elements, e.g., Ag, Cs, Ga, Li, Mo, Nb, Rb, REEs, Th, W, Y and Zr higher maximum values were established in the discharge of the local WWTP from a hotel complex in Belchin (S5). The reasons for this result could be the natural higher microelement concentration in the water springs of the Palakaria River, as well as the effect of soil cover structure, and the biogeochemical status of drainage on the surface water [26].

Anionic composition

The anionic composition of the surface waters was determined using ion chromatography. A chromatogram of a water sample from the Iskar River and the concentration of the registered anions in the sampling points during the studied seasons are presented in Fig. 3. The obtained chromatograms show that in the water samples from the Iskar River only Cl^-, NO_3^- and SO_4^{2-} were found to be present. According to BG-Reg. 12 [12] the recommended/admissible values for water in Category A1 are: Cl^- - 200 mg/L, NO_3^- - 25/50 mg/L and SO_4^{2-} - 150/250 mg/L. The concentrations of all three anions, despite certain variations, are below the admissible levels.

In contrast to the elements, the highest concentration of the anions was found mainly in S2 with a pronounced increase in the spring season. The noticeably higher concentrations in S2 are indicative of a point pollution from the WWTP - Samokov. The observed increase in the spring season could be explained by the use of nitrate and sulfate fertilizers in the summer and autumn and salt during the winter and their subsequent soil infiltration in the surface water.

CONCLUSIONS

The analysis of the water samples from the Iskar River and its tributary Palakaria River showed that the highest concentrations of the macroelements (Na, K, Ca, Mg, S, and Si) were present in the waters from the discharge areas of WWTP - Samokov (S2), followed by the local discharge of a local WWTP in the village of Belchin (S5). No significant seasonal variations were established for the macroelements. For some of the microelements, e.g., Al, Fe, Cu and Hg, a seasonal exceedance of the respective MAC in the BG-Reg. 12 was found, but in most cases, it was not at the discharge of WWTP - Samokov, considered as a point of high potential risk. The analysis of inorganic anions showed the presence of Cl^-, NO_3^- and SO_4^{2-} in the water samples from the

Iskar River with a distinct spring increase, but being below the MACs.

The chemical composition of the waters of the Iskar River is extremely important for maintaining the ecological condition of the river ecosystem and the quality of its water. From this position, the research and analysis carried out can also be viewed. Further, these data are an excellent basis for upgrading them with biological indicators and a comprehensive assessment of the ecological condition of the Iskar River in the upper part, which is of extreme importance for feeding the Iskar Dam - water supply to the city of Sofia.

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