ECOLOGICAL ASSESSMENT OF ISKAR RIVER WATER IN THE REGION OF SOFIA CITY, BULGARIA

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Abstract

Ecological assessment of Iskar River water in the region of Sofia city municipality, Bulgaria, was performed through analytical measurements and thermodynamic calculations. The analytical data obtained and the calculated threshold pollution indices of the single nutrients PO_4^{3-}, NO_2^-, NO_3^- and NH_4^+ and their integrated threshold pollution indices showed strong water pollution in respect of NH_4^+ and PO_4^{3-} in all studied stations. The waters were pure as regards the trace metals Al, Fe, Co, Ni, Cu, Zn and Cd. Only Mn and Pb exceeded their maximum allowed concentrations in stations after Sofia city around Novi Iskar town. The chemical species of the trace metals were calculated by thermodynamic modeling and discussed.

Key words: *ecological assessment, Iskar River, thermodynamic modeling, chemical species*

1. INTRODUCTION

The Iskar River is the longest Bulgarian river—368 km with catchment area of 8646 km^2. It crosses seven geographical areas of Bulgaria, namely Rila and Pirin Mountains, Kraishte, Srednogorie, Sofia Plain, Stara Planina (Balkan) Mountains, Predbalkana Mountains and West Danube Plain (Kenderov and Trichkova, 2020). The waters of the river in its upper course, before the city of Sofia, are used mainly for drinking purposes, while those after the city of Sofia - for irrigation. Sofia city is the capital and largest city of Bulgaria with a population of 1.2 million inhabitants. The uncontrolled growth of the city's population, especially in the last 20 years, has led to the expansion of construction boundaries, an increase in garbage, as well as an increase in water in need of treatment (sewage and wastewater). Therefore, it was of interest to us to trace the ecological condition of the Iskar River as it passes through the city of Sofia.

Owing to its importance for the region through which the Iskar River flows, it is subject to monitoring by the Bulgarian National Monitoring System of the Environment, which provides timely information about the state of the environmental elements and the factors having an impact on it. Monitoring studies of natural surface water mainly include analysis of physicochemical parameters, priority substances (toxic, persistent and easily bioaccumulated) and specific pollutants (organic substances, trace metals, metalloids, cyanides, phenols) (Alrumman et al. 2016, Mainali 2020). They do not distinguish between chemical species, although the significance of the latter is very well known (Laderriere et al. 2021, Teramoto et al. 2021). The reason is that experimental methods for speciation are expensive and labor-intensive (Fytianos 2001). Mathematical modeling based on the principles of chemical thermodynamics is an alternate approach for prognosing, studying and interpreting the behavior of the chemical species of trace metals in natural water basins, taking into account a number of interrelated factors and simultaneously occurring processes (Grenthe et al. 1997, Ge et al. 2005). In our former work (Tepavitcharova et al. 2009; Tepavitcharova et al. 2011; Rabadjieva et al. 2018) we have proposed a combined method for complex ecological assessment of surface waters. The method includes analysis of the chemical composition of water and treatment of the obtained data with various mathematical models for thermodynamic modeling of the chemical species of elements.

The goals of the present work were: (i) to determine the physicochemical and chemical characteristics of the river water through field and laboratory research in the river section within the boundaries of

Sofia city municipality; and (ii) to calculate the chemical species of the elements by applying thermodynamic models. This will allow us to perform a complex assessment of the ecological condition of Iskar River. The sampling was conducted in June 2020.

2. MATERIALS AND METHODS

2.1. Sampling, preservation and analyses

Nine sampling stations (Fig. 1) were selected, located as follows: 1 – at the entrance of the Sofia city, under the boulevard Tsarigradsko shosse, 2 – in Dimitar Milenkov quarter; 3 - before Sofia Airport; 4 – in Vrazhdebna quarter; 5 - under boulevard Botevgradsko shosse; 6 – close to Chepintsi career; 7 – close to the Kubratovo village; 8 – in Novi Iskar town, after Lakprom Ltd; and 9 - after the Novi Iskar town.

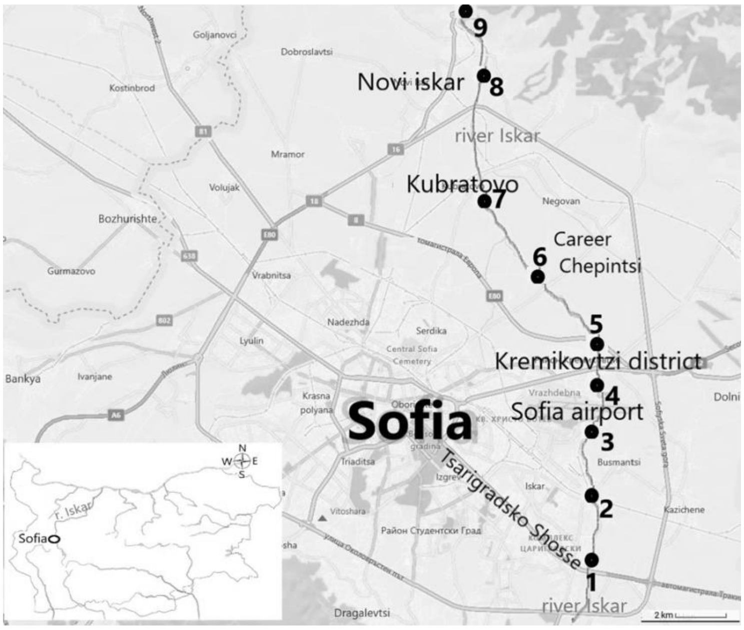

Fig. 1. The Iskar River within the boundaries of Sofia city municipality with sampling stations

Water samples (approximate volume of 1.5 L) were collected from the upper surface layer (0 – 20 cm) of the river. Each sample consisted of 3 sub-samples collected at a distance of 3-5 m from each other. They were filtered through 0.45 µm Millipore (Millipore, Bedford, MA, USA) membrane filters. Filtrates for inductively coupled plasma optical emission spectrometry (ICP OES) analysis were acidified with 65% HNO_3 p.a. (Merck, Darmstadt, Germany) to pH<2.0.

Physicochemical characteristics (temperature, pH, conductivity, dissolved oxygen and salinity) of the water samples were measured *in situ* by a portable Multi 340i-WTW equipment (WTW, Weilheim, Germany) using a series of calibrated temperature–compensated electrodes.

Alkalinity and nutrients (PO_4^{3-}, NO_2^-, NO_3^- and NH_4^+), measured *in situ*, as well as Cl^- and SO_4^{2-} ions were determined spectrophotometrically on a portable NOVA instrument (Merck, NJ, USA). CO_3^{2-} content was calculated from the alkalinity value. Metals (K, Ca, Mg, Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) were determined by ICP OES on a PRODIGY 7 spectrometer (Teledyne Leeman Labs, USA). The Na content was calculated as the difference between ion equivalents of anions and cations.

2.2. Thermodynamic modeling

Chemical species distribution of the dominant dissolved trace metals in the studied water samples was calculated. Data for total concentrations of major and trace metals, DOC and pH were used as input data (Table 1). In case the analytical results for a given element lied below its detection limit, the latter was used in the model. Computer program Visual Minteq, Version 3.1 (Gustafsson 2001) was employed and two thermodynamic models were applied – the classical Ion-Association Model (Grenthe et al. 1997) for calculating inorganic metal species and the Stockholm Humic Model (SHM) (Gustafsson 2001) accounting for the complexation reactions of trace metals with organic matter.

Table 1. Physicochemical characteristics and chemical parameters of the waters of the Iskar River in the region of Sofia

Station/Parameters	**MAC**	**1.**	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**
T, ºC		16.9	16.8	17.9	18.6	17.8	17.2	20.6	22.5	22.3
pH	6.5-8.7[a]	8.04	8.13	8.15	7.89	8.07	7.41	7.31	7.56	7.58
Conductivity, μS/cm	750[a]	140	144	158	135	151	145	216	357	278
Dissolved O_2, mg L^{-1}	7.00-6.00[a]	8.22	7.37	7.13	6.8	7.34	6.53	5.76	5.18	5.06
Alkalinity, mg L^{-1}		58	53	27	38	35	39	48	84	56
Major ions, mg.L^{-1}										
Na^+		8.64	7.20	0.54	0.71	1.18	1.32	0.68	7.61	18.0
K^+		3.9	3.8	4.0	4.0	3.4	4.4	4.6	5.4	5.8
Mg^{2+}		3.35	3.80	3.37	3.72	3.80	3.54	4.09	7.86	6.05
Ca^{2+}		14	15	9.2	12.1	12	15	23	40	23
Cl^-	300	8.2	10	7.6	8.9	9.3	8.2	18.3	24.6	43
CO_3^{2-}	300	34.8	31.8	16.2	22.8	21.0	23.4	28.8	50.4	33.6
SO_4^{2-}		2.7	5.9	4.9	1.5	4.0	9.0	7.1	33.4	11.2
Nutrients, mg.L^{-1}										
PO_4^{3-}	0.025-0.06 [a]	0.016	0.044	0.075	0.036	0.06	0.09	0.14	0.25	0.16
N-NO_2^-	0.03-0.06 [a]	0.008	0.022	0.022	0.023	0.020	0.025	0.05	**0.13**	**0.14**
N-NO_3^-	0.8 - 2 [a]	<0.20	0.26	<0.20	<0.20	0.8	0.25	1.2	1.1	0.7
N-NH_4^+	0.1-0.3 [a]	**0.71**	**0.87**	**1.41**	**0.56**	**1.16**	**1.22**	**2.12**	**1.79**	**2.06**
DOC	12[a]			23.5				12.5	13.0	39.4
Trace metals, mg.L^{-1}										
Al	0.025 [a]	<0.005	0.008	<0.005	<0.005	<0.005	0.046	0.018	<0.005	<0.005
Fe	0.1[c]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mn	0.05 [c]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	**0.085**	0.013
Co	0.1 [c]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ni	0.034 [b]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	0.006 [cc]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Zn	0.04 [cc]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	0.0015 [b]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	0.014 [b]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	**0.013**	**0.053**	**0.029**

Notes:([a]) Bulgarian regulation 4/2012 - "quality II good water" for semi-mountain types of rivers; ([b]) European Parliament Directive 2013/39/EC on inland surface waters; ([c]) Bulgarian regulation 4/2012 -

annual average; (cc) Bulgarian regulation 4/2012 - annual average, at $CaCO_3$ content in the water between 50 – 100 mg L^{-1}**.**The following assumptions were made in order to calculate species concentrations and their ratios: (i) the activity coefficients of all possible simple and complex inorganic species were calculated using the extended Debye-Hűckel theory; (ii) Mn^{6+} and Mn^{7+} ions were not considered in the calculations, since they are not stable in natural water (ATSDR 2012); (iii) redox processes were evaluated by considering all the redox pairs that may exist in the systems studied, namely O^0/O^{2-}, N^{3+}/N^{5+}, N^{3-}/N^{5+}, Co^{3+}/Co^{2+}, Cu^+/Cu^{2+}, Fe^{2+}/Fe^{3+}. The results revealed that irrespectively of the relatively high oxygen content (> 5 mg.L^{-1}), the high content of N-NH_4^+ reduces the *pE* of the medium from 12.1, characteristic for O^{2-}/ O_2, to values between 5 and 6, characteristic for NO_3^-/NH_4^+ (Table 2). As a result, the simultaneous presence of Cu^+ and Cu^{2+} in some of the studied waters was calculated and their forms were included in the calculations for the distribution of the forms of the elements. With regard to Fe, Mn and Co, the concentrations of Fe^{2+}, Mn^{3+} and $Co^{3+}$are between 5 and 10 orders of magnitude lower than those of Fe^{3+}, Mn^{2+} and Co^{2+}, therefore only the latter forms were considered; (iv) in the Ion-Association Model a thermodynamic equilibrium was assumed only for the complex formation processes; (v) in the Stockholm Humic Model, DOC was assigned only to fulvic acids which are soluble in water.

Table 2. Oxidation-reduction characteristics of the modeled water systems

Station/Parameter	3	7	8	9	3	7	8	9
	mg.L^{-1}				%			
I	0.001	0.002	0.004	0.003	0.001	0.002	0.004	0.003
pE	12.1	5.656	6.217	5.123	12.1	5.656	6.217	5.123
Fe^{2+}	2.2E-18	3.6E-09	2.8E-10	1.8E-10	4.5E-14	7.3E-05	5.7E-06	3.6E-06
Fe^{3+}	5.0E-03	5.0E-03	5.0E-03	5.0E-03	100	100	100	100
Mn^{2+}	0.005	0.005	0.085	0.013	100	100	100	100
Mn^{3+}	5.5E-12	1.2E-22	7.7E-21	5.5E-12	1.1E-07	2.4E-18	9.1E-18	4.2E-08
Co^{2+}	0.005	0.005	0.005	0.005	100	100	100	100
Co^{3+}	2.9E-17	6.2E-24	6.2E-24	1.1E-24	5.8E-13	1.2E-19	1.3E-19	2.2E-20
Cu^{1+}	1.2E-18	6.5E-06	9.4E-11	1.3E-04	2.4E-14	0.13	1.9E-06	2.55
Cu^{2+}	5.0E-03	5.0E-03	5.00E-03	4.8E-03	100	99.87	100	97.45

3. RESULTS AND DISCUSSION

3.1. Physicochemical and chemical assessment

The results for the physicochemical characteristics and chemical parameters of the waters of the Iskar River in the studied section are shown in Table 1. The waters in all studied stations are characterized by neutral to slightly alkaline pH (7.31 - 8.15), which is typical for surface river waters. The electrical conductivity varies from 135 to 357 µS cm^{-1} which is below the maximum allowable concentration (MAC) (750 µS cm^{-1}), according to ORDINANCE No. H-4 of 14.09.2012 of the Bulgarian legislation for characterization of surface waters of semi-mountain type. Dissolved oxygen varies widely - from 8.22 at station 1, where the river enters the urban area, down to 5.06 at station 9, where the waters are already characterized by low turbulence, this being also a signal of possible pollution.

With regard to macro-components, we found that they are within the limits typical of surface waters. There is a general tendency to increase their concentrations along the river from station 1 to station 9, passing through a maximum at station 8.

The studied waters are highly polluted in terms of nutrients. The content of $N\text{-}NH_4^+$ is particularly high, exceeding the MAC at all studied stations; $P\text{-}PO_4^{3-}$ exceeds the MAC at stations 3 and 5 - 9, whereas $N\text{-}NO_2^-$ exceeds the MAC at stations 8 and 9 (Table 1). To assess the pollution, the threshold indices of pollution of an individual element (C_f) according to the formula $C_f = C/C_{MAC}$, where C is the concentration of the element and C_{MAC} is the maximum allowed concentration (when the MAC is expressed by a confidence range, then the upper value is used), as well as the integrated indices of threshold pollution $P_w = \sum C_{fi}/n$), where n is the number of nutrients, were calculated.

The results (Fig. 2) show that the highest degree of contamination is displayed by $N\text{-}NH_4^+$ (C_f=1.87 – 6.87) followed by $P\text{-}PO_4^{3-}$ (C_f=0.27 – 4.17), and $N\text{-}NO_2^-$ (C_f=0.13 – 2.17). The content of $N\text{-}NO_3^-$ does not exceed the MAC for any of the studied stations. According to the calculated integrated indices of threshold pollution P_w, the most polluted in terms of nutrients are the waters at station 8 with P_w = 3.21. These results point to a strong municipal pollution and only partial water purification in the Sofia wastewater treatment plant near the village of Kubratovo, located before station 7 (Fig. 1).

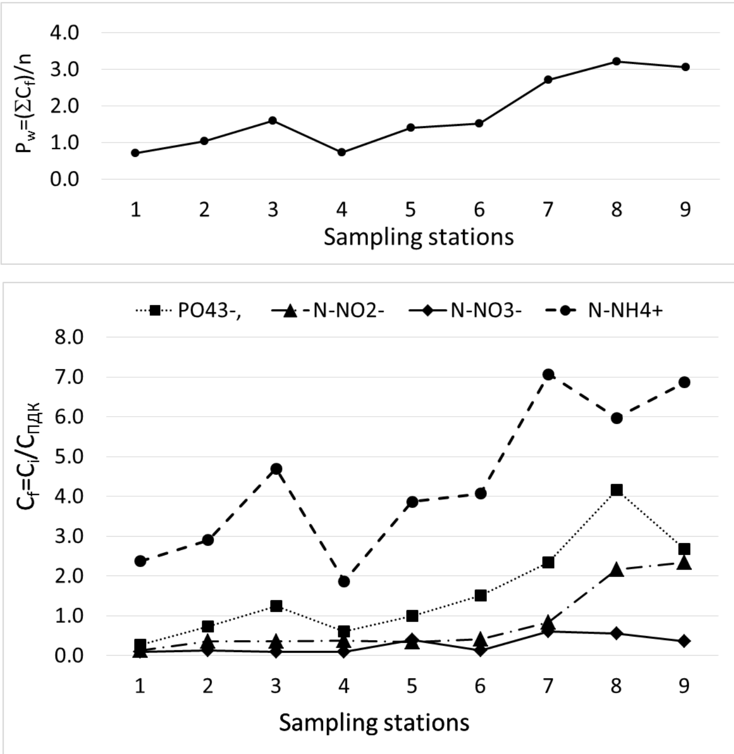

Fig. 2. Threshold indices of pollution of a single element (C_f) and integrated threshold indices of pollution (P_w) of the studied water samples

The studies show that the waters are pure in terms of the trace elements Al, Fe, Co, Ni, Cu, Zn and Cd. Values of Mn and Pb exceeding the MAC were measured at stations 8 and 9.

3.2. Thermodynamic modelling

Trace metals include elements of key interest in terms of biogeochemical cyclic processes, owing to their specific properties, reactivity and significance as pollutants. Therefore, object of thermodynamic calculations was the species distribution of the trace metals under study. A thermodynamic ion-association Visual Minteq computer program version 3.1, was applied for simulating the soluble inorganic and organic species of trace elements in the waters studied. The calculations were done for the waters of stations 3, 7, 8 and 9 with maximum nutrient and trace metals (stations 8 and 9) pollution. The concentration of dissolved organic matter (DOM) in natural water is represented by dissolved organic carbon (DOC) which was measured in the waters of stations 3, 7, 8 and 9 (Table 1) by the method of spectrophotometric analysis of catalytically decomposed organic matter. Multiple functional groups in DOM represent potential bonding sites for metals and therefore a wide variety of metal-organic species is expected. Organic ligands in natural water form complexes with metal ions which are thereby mobilized and transported towards different reservoirs within the aquatic system. Complexation by organic ligands generally decreases metal uptake, simultaneously enhancing their residence time in the surface water. Metal associations with organic matter can be characterized as surface complexation reactions, whereby cations associate with negatively charged functional groups of the organic molecule (Yamashita et al. 2020, Cherkasova et al. 2021).

The modeling data showed that the trace metals Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb formed a great variety of complexes. The chemical species of trace metals (in amounts higher than 0.1%) are presented in Figs. 3 and 4.

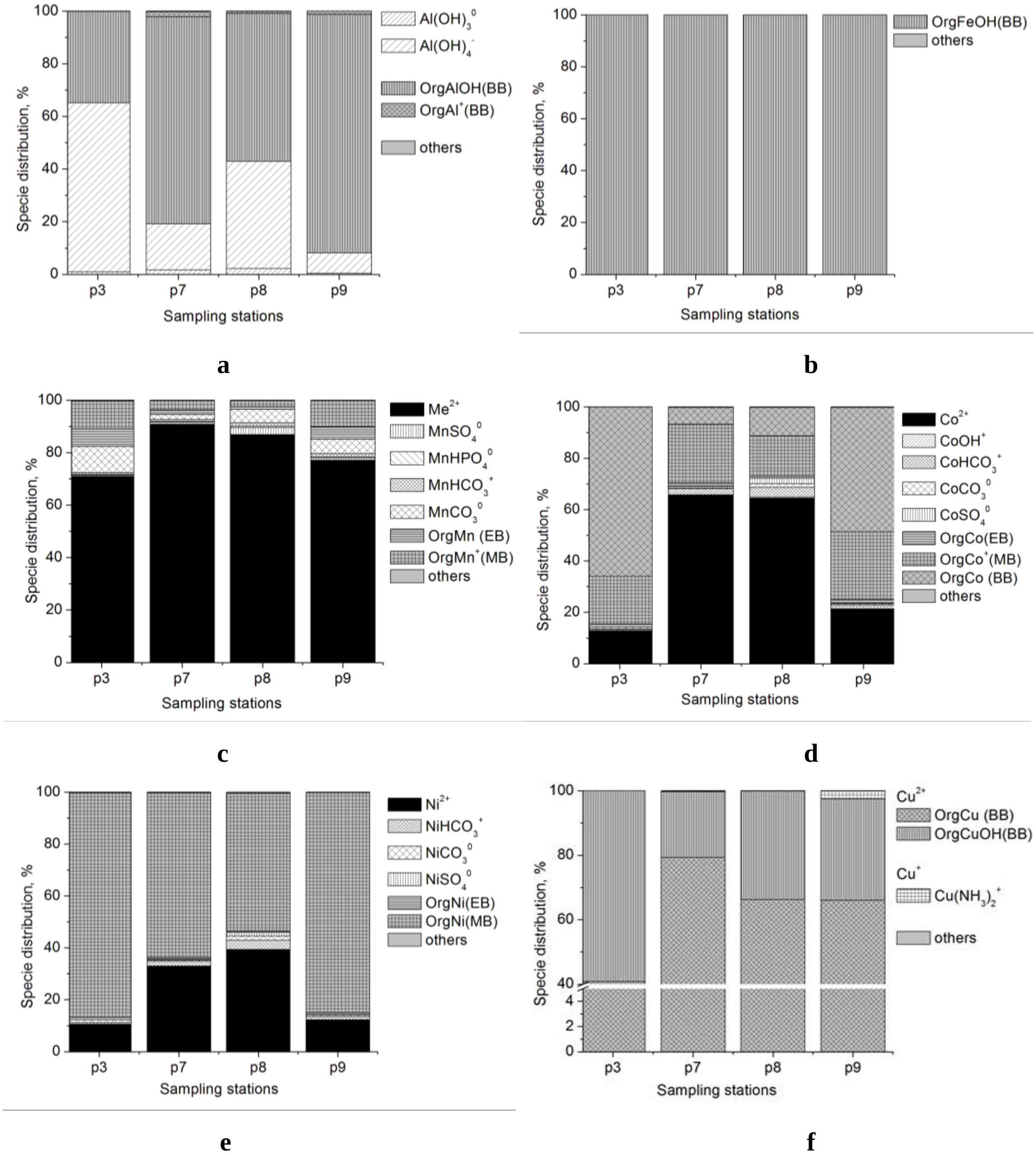

Fig. 3. Specie distribution of Al (a); Fe (b); Mn (c); Co (d), Ni (e) and Cu (f) in the water of Iskar River at stations 3, 7, 8 and 9. EB denotes electrostatic bond; MB denotes monodentate bond and BB denotes bidentate bond.

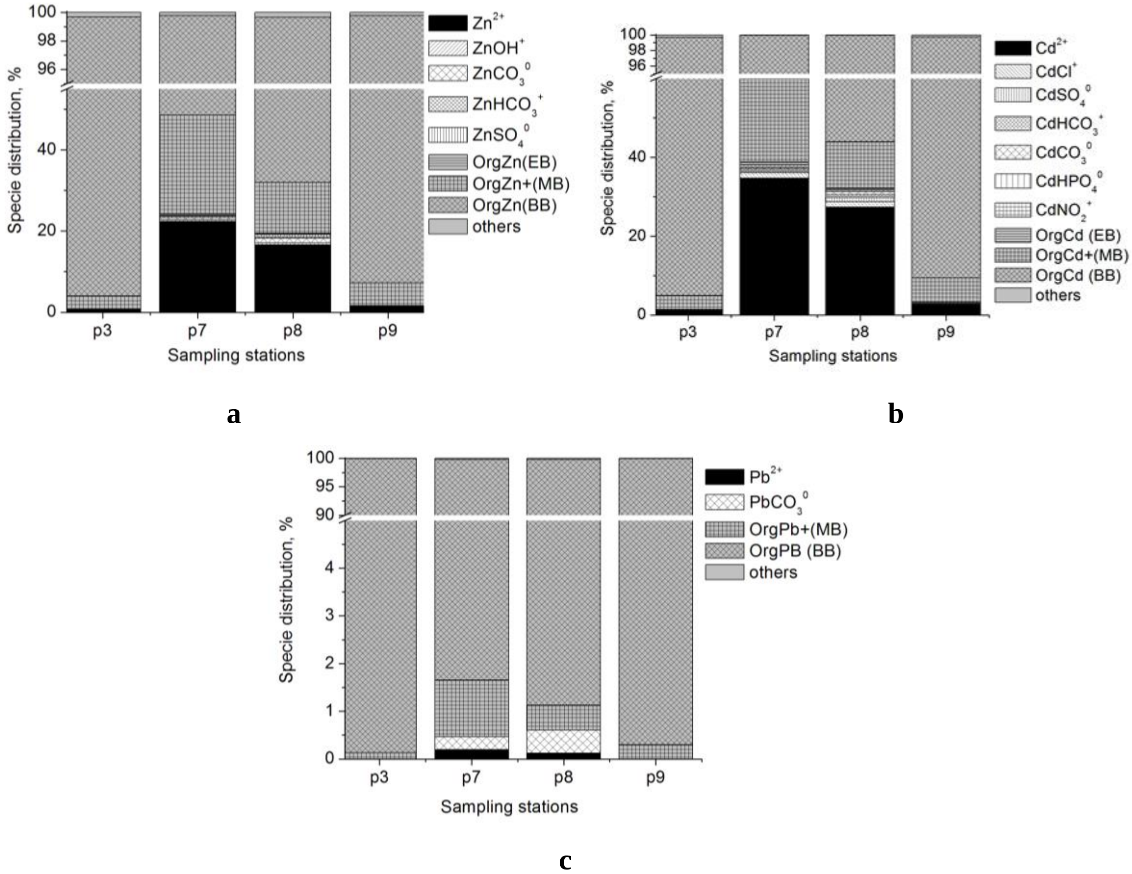

Fig. 4. Specie distribution of Zn (a), Cd (b), and Pb (c) in the water of Iskar River at stations 3, 7, 8 and 9. EB denotes electrostatic bond; MB denotes monodentate bond and BB denotes bidentate bond.

Al (Fig. 3a) – Inorganic $Al(OH)_4^-$ (8 – 64%) and organic OrgAlOH (bidentate bond) (35 – 90%) species were calculated to dominate in all studied waters. Only in station 3, $Al(OH)_4^-$ species prevail due to a higher pH (8.15). Another hydroxy form ($Al(OH)_3^0$) and $OrgAl^+$ (bidentate bond) were calculated to exist in small amounts (0.3 – 2 %) in the waters.

Fe (Fig. 3b) – Only one organic species, OrgFeOH (bidentate bond), was calculated to exist in all waters.

Mn (Fig. 3c) – Inorganic species, free Mn^{2+} ions (70 – 90%) and $MnCO_3^0$ (2-10%) ion pairs dominated in all studied waters. Organic species $OrgMn^+$ (monodentate bond) and OrgMn (electrostatic bond) (14-15% total) were calculated for stations 3 and 9 due to higher DOC concentration.

Co (Fig. 3d) and ***Ni*** (Fig. 3e) – Combination of inorganic (mainly Me^{2+} ions) and organic chemical species in different ratios were calculated for both Co and Ni in all water samples. For Co the dominating species in stations 7 and 8 were the free Co^{2+} (64-65%) ions followed by $OrgCo^+$ (monodentate bond) (15-22%) and OrgCo (bidentate bond) (6.5 - 11%), while in stations 3 and 9 organic species (19 – 27% total) prevail. Organic species (53 – 86%) are typical for Ni in all stations.

Cu (Fig. 3f) – Only organic species, OrgCu (bidentate bond) and OrgCuOH (bidentate bond) were calculated as typical for all studied waters. Small amount of $Cu^+(NH_3)_2^+$ species was calculated in stations 7 (0.2% and 9 (2.3%) due to the higher content of NH_4^+ in the water (Table 1).

Zn (Fig. 4a), ***Cd*** (Fig. 4b) and ***Pb*** (Fig. 4c) – Organic species were calculated as dominant (more than 50%) for the three metals in all studied waters. In the case of Zn and Cd up to 35% of free Me^{2+} ions were calculated in stations 7 and 8 due to lower DOC concentration.

Based on our previous publications related to the dynamics of transition metals in the system *water* - *soil* - *soil solution* - *uncultivated vegetation* - *small mammals* (Kovacheva et al. 2020; Rabadjieva et al. 2021), it can be concluded that Fe, Cu and Pb in all tested stations, as well as Co Ni, Zn and Cd in stations 3 and 9, would accumulate in the adjacent plants, as they are in the form of easily digestible organometallic complexes. On the other hand, Mn in all studied stations and Co Ni, Zn and Cd in stations 7 and 8 are dangerous for the animal world, as they are mainly in the form of free ions, which easily interact with ligands of organic compounds found in the bloodstream and/or within organs.

4. CONCLUSIONS

Monitoring studies were carried out in June 2020 on different water stations situated along the Iskar River within the boundaries of Sofia city municipality. The samples from nine water pools were subjected to physicochemical and chemical analyses. The analytical data showed strong water pollution in respect of NH_4^+ and PO_4^{3-} in all studied stations. The waters were pure in respect of the trace metals Al, Fe, Co, Ni, Cu, Zn and Cd. Only Mn and Pb exceeded their maximum allowed concentrations in the stations after Sofia city, around Novi Iskar town.

By application of two different thermodynamic models we have calculated chemical species distribution. The results show that Fe, Cu and Pb in all studied stations, as well as Co Ni, Zn and Cd in stations 3 and 9 are dangerous for the adjacent plants, as they are in the form of easily digestible organometallic complexes. Mn in all studied stations and Co Ni, Zn and Cd in stations 7 and 8 are dangerous for the animal world, as they are mainly in the form of free ions.

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