Journal of Chemical Technology and Metallurgy, 59, 2, 2024, 287-300

THERMODYNAMIC MODELING OF RIVER WATER AS A TOOL FOR ENVIRONMENTAL IMPACT EVALUATION

Antonina Kovacheva[1], Rumiana Gergulova[1], Radost Ilieva[1],
Diana Rabadjieva[1], Ivelin Vladov[2], Veselin Nanev[2]

[1]*Institute of General and Inorganic Chemistry*
Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11
1113 Sofia, Bulgaria
[2]*Institute of Experimental Morphology*
Pathology and Anthropology with Museum
Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 25
1113 Sofia, Bulgaria
E-mail: antonina1975@abv.bg

Received 09 July 2023
Accepted 20 August 2023 *DOI: 10.59957/jctm.v59.i2.2024.6*

ABSTRACT

The possibility of applying a thermodynamic approach to calculate the elements' chemical species and thus to more effectively assess the water quality is demonstrated. Iskar river and its three tributaries Lesnovska, Kakach and Blato rivers within Sofia Municipality were chosen as a case study. Experimental field and laboratory studies were done to create an input database for thermodynamic calculations. The obtained analytical data revealed high concentrations of PO_4^{3-}, NH^{4+} *and* NO_2^- *in all studied water samples, which is an indicator for serious domestic pollution. The water was pure in terms of Fe, Co, Ni, Cu, Zn and Cd. Al, Pb and Mn exceeded the maximum allowed concentrations in the water of Iskar river after Sofia city, and along the entire flow of Lesnovska river. The thermodynamically calculated chemical species showed that Na, K, Mg, Ca,* NO_2^-, NO_3^- *and* NH_4^+ *exist mainly as free ions. The presence of dissolved ammonia was calculated for all sample stations, which is a serious problem for aquatic animals, especially for fish.* PO_4^{3-} *showed a great variety of forms depending on pH. Among the trace metals (Al, Pb and Mn), Pb is potentially the riskiest element for plants, as its dominant organometalic species are easily accumulated by them. Free ions of Mn dominate, which is dangerous for aquatic fauna as* Mn^{2+} *ions easily interact with ligands of organic compounds found in the bloodstream and/or within organs. Regarding Al, the dominant hydroxy species are a prerequisite for the precipitation of* $Al(OH)_3$ *and thus, for the self-purification of waters.*

Keywords: thermodynamic modeling, ecological assessment, threshold pollution indices, chemical species, Iskar river.

INTRODUCTION

Thermodynamic models based on quantitative regularities between the concentrations of the components in the solutions and thermodynamic quantities as Gibbs free energy, chemical potential, solubility product, equilibrium formation constants, etc., have been developed to describe the behavior of multicomponent water-salt systems [1 - 3]. They are usually employed to determine the type and concentration range at which stable or metastable crystallization of solid phases occurs, and as a result, to predict system behavior with changes of the conditions. In this way both laboratory and industrial processes can be optimized. Since natural waters can be considered as complex multicomponent electrolyte systems, these models can also be successfully applied to solve environmental problems [4, 5].

The chemical elements contained in natural waters are in different concentrations - macro-, micro- and traces and exist as different species - free ions, inorganic or organic complexes, dissolved gases, etc. Natural or anthropogenic changes in the environment change the chemical species of the elements, and therefore, their bioavailability. This dynamic determines the increased scientific interest to chemical element speciation [6, 7]. In spite of the accumulation of data from these studies, only physico-chemical parameters and total content of some typical pollutants are determined in monitoring studies to control water quality. The developed new analytical methods [8, 9] for determining the chemical species of some elements are not applied to monitoring analysis because they are too expensive. This determines the need to look for and implement another approach that quickly, cheaply and effectively provides information on the chemical species of the elements in natural waters and thus, to carry out a more effective assessment of the ecological state of water. In our previous work, based on a complex approach, including the analysis of the chemical composition of water or aqueous soil extracts and the application of various thermodynamic mathematical models, we established a relationship between the chemical species of trace metals and their bioaccumulation [10, 11].

The aim of the present work is the more effective assessment of the river water quality by combining field and laboratory analytical studies with thermodynamic calculations of the chemical species of elements. The Iskar river and its tributaries Lesnovska, Kakach and Blato rivers in the vicinity of Sofia municipality were chosen as a case study, as the population of Sofia city has almost doubled in the last 20 years, which has led to the expansion of built-up areas and the annexation of nearby villages as neighborhoods of the city. As a result, a mass production of waste enters the aquatic and terrestrial ecosystems and deteriorates their quality.

The physico-chemical characteristics and concentrations of macro-components (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}), nutrients (NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-}), trace metals (Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) and dissolved organic carbon (DOC) were determined at selected points along the Iskar river and Lesnovska river and at one point on each Kakach and Blato rivers, before their confluence with the Iskar river. The threshold pollution indices were applied for standard pollution assessment. Analytical data obtained from experimental field and laboratory studies were used as input data for thermodynamic calculations to calculate the chemical species of major and trace metals under study, as well as of nutrients.

Iskar river is one of the most studied rivers in Bulgaria. 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. In recent years, scientific publications concerned the determination of the trace metals As, Cd, Cu, Hg, Pb, Zn, Mn, Ni, Co, Cr in bottom sediments [12, 13]. It was established that sediments in Iskar river before Sofia city are moderately contaminated in respect of As, Cd, Cu, Hg, Pb, Zn [13]. Yordanova et al. established “good” ecological state of Iskar river water around Samokov town (after Sofia city), according to macrozoobenthos indicators, but registered local deterioration around the outfall of the Wastewater Treatment Plant in Samokov [14].

EXPERIMENTAL

Sampling and preservation

Nine sampling stations along the Iskar river (I1 - I9), six sampling stations along Lesnovska river (L1 - L6), as well as per one point on each the Kakach river (K7) and the Blato river (B8) before their confluence with the Iskar river, were selected (Fig. 1). The samples were collected in May 2020.

Water samples (approximate volume of 1.5 L) were collected from the upper surface layer (0 - 20 cm) of the water basins. 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 dissolved organic carbon (DOC) determination were preserved frozen in glass containers until analysis. Filtrates for ICP-OES (inductively coupled plasma optical emission spectrometry) analysis were acidified with 65 % HNO_3 p.a. (Merck, Darmstadt, Germany) to pH < 2.0 and were stored in polyethylene bottles at 4°C.

Measurements and chemical analysis

Physico-chemical characteristics (temperature, pH and dissolved oxygen) 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^+) were determined *in situ*, while Cl^- and SO_4^{2-} ions, remotely, all of them spectrophotometrically (portable

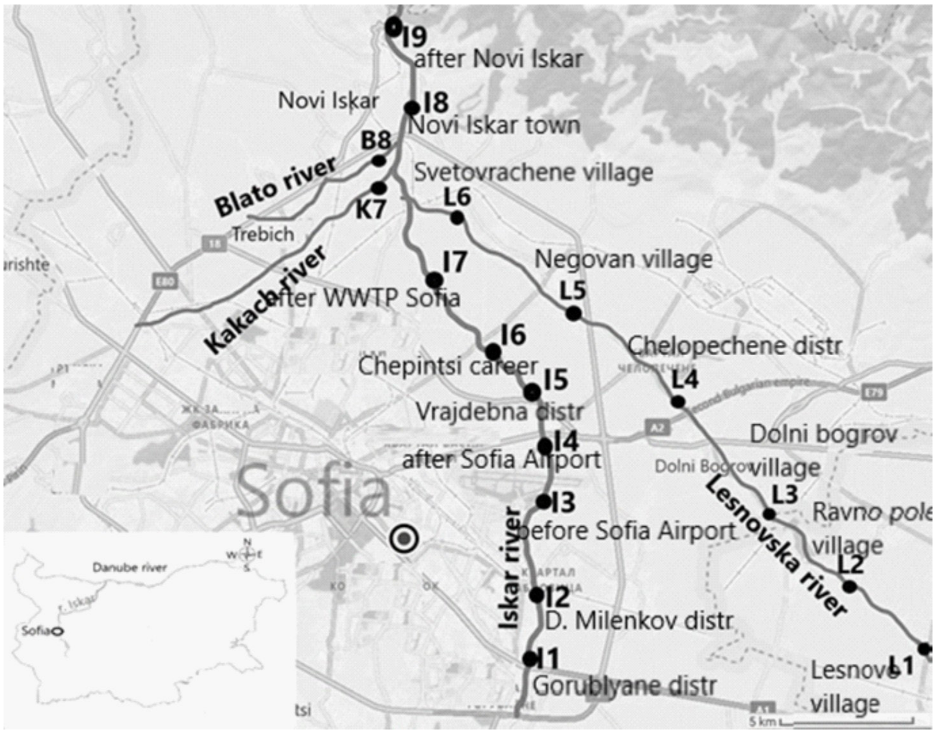


Fig. 1. The studied area with sampling stations.

NOVA, Merck, NJ, USA). The CO_3^{2-} content was calculated from the alkalinity value and the concentration of Na - by the difference of ion equivalents.

Major elements (K, Ca, Mg) and trace metals (Al, Fe, Mn, Co, Ni, Cu, Zn, and Pb) were determined by ICP-OES (PRODIGY 7, Teledyne Leeman Labs, USA). The Na content was calculated as the difference between ion equivalents of the anions and cations determined. Certified Reference Material (Multielement standard solution V for ICP), SIGMA-ALDRICH, Lot: BCCB7069 was used for quality assurance purposes.

Dissolved organic carbon (DOC) content was determined spectrophotometrically (portable NOVA, Merck, NJ, USA) using Merck test kit.

Computational methods

The distribution of dissolved chemical species in water bodies was calculated using the Visual Minteq computer program, Version 3.1 [15]. Two thermodynamic models were applied - the classical ion-association model [16] for calculating the inorganic metal species and the Stockholm Humic Model (SHM) [15] accounting for the complexation reactions of trace metals with organic matter.

The ion-association model is applicable to solutions with ionic strength $I < 0.1$ and accounts for the weak interactions between ions that form ion pairs (complexes). The complex formation was defined by a mass action expression. The stoichiometric formation constant of each complex in a solution was determined by the activity coefficients of the simple and complex ions and the thermodynamic constant at zero ionic strength [17]. Thermodynamic database of Visual Minteq computer program, Version 3.1 was used. It contains updated and expanded data from the NIST Critical Stability Constants database. The activity coefficients of all possible simple and complex species were calculated using the extended Debye-Hückel theory.

The Stockholm Humic Model is a discrete ligand model [15]. It assumes that natural organic substances, presented in the natural solution (humic substances), have a variety of functional groups able to bind metal cations (so-called discrete sites). These sites are characterized by different values of the proton dissociation constant, respectively the complex formation constant. Equilibrium constants for mono- and bidentate coordination and an extra parameter accounting for binding-site heterogeneity were defined to simulate metal binding. All required parameters are included in the program database.

Experimental data for the total concentrations of major and trace metals, nutrients, DOC and pH were used as input data. In case the analytical results of a given element were below its detection limit, the latter was used for the modeling.

The following assumptions were made in order to calculate the species concentrations and their ratios: (i) in the ion-association model a thermodynamic equilibrium was assumed only for complex formation processes; (v) in the Stockholm Humic Model, DOC was only assigned to fulvic acids which are soluble in water; (ii) Mn^{6+} and Mn^{7+} ions were not considered in the calculations, since they are not stable in natural waters [18]; (iii) redox processes were evaluated with the inclusion of all redox pairs that may exist in the systems studied, namely O^0/O^{2-}, N^{3+}/N^{5+}, N^{3-}/N^{5+}, Mn^{2+}/Mn^{3+}; The results showed domination of the O^0/O^{2-} couple. In all cases, insignificant amounts of Mn^{3+} were detected. For this reason, only the Mn^{2+}ions were considered.

RESULTS AND DISCUSSION

Physicochemical parameters

The waters in all studied stations (Table 1 and Table 2) were characterized by neutral to slightly alkaline pH (7.31 - 8.15) which is typical for surface river waters. The exceptions were the water of the Kakach river (K8) and the Blato river (B9), where the values were 6.51 and 9.37, respectively. Dissolved oxygen varied widely, with the highest values in the Lesnovska river (up to 12.3 mg L^{-1}), and significantly lower values (up to 5.06 mg L^{-1}) in the Iskar river, at the places where the water was characterized by low turbulence.

Macro-components

With regard to macro-components, we found that they were within the limits typical of surface waters, but their concentrations were higher in the waters of the three studied tributaries than in the Iskar river.

Thermodynamic calculations of major cation species (Fig. 2) showed dominance of free ions - up to about 95.5 - 99.8 % for Na and K and 80 - 94 % for Ca and Mg. The presence of inorganic and organic complexes was also calculated, the type of which is determined by the nature of the metal, while their amount - by the physico-chemical and chemical characteristics of the water systems.

Na and K (Figs. 2(a), 2(b), 2(c), 2(d)) – electrostatically bound OrgM (M = Na, K) were calculated in the water of the Iskar river, and sulfate complexes in the water of the Lesnovska river. In the water of the Blato river, the presence of Na carbonate and chloride complexes was calculated due to the higher pH.

Ca and Mg (Figs. 2(e), 2(f), 2(g), 2(h)) – a more pronounced tendency to complexation compared to the alkali metals determines the higher concentration (up to 60 % in B8) of the Ca and Mg complex species. It was estimated that electrostatically bound OrgM (M = Ca and Mg) along with monodentately bound organic complexes predominate in the waters of the Iskar river, and sulfate complexes - in the waters of the Lesnovska river, together with carbonate and hydrogencarbonate forms in the waters of the Blato river.

Nutrients

The studied waters were highly polluted in terms of nutrients. In Iskar river, the content of N - NH_4^+ exceeded the MAC at all studied stations; P - PO_4^{3-} also exceeded the MAC at all stations with the exceptions of I1 and I4, whereas N - NO_2^- exceeded the MAC only at stations I7 - I9 (Table 1). The content of N - NO_3^- did not exceed the MAC for any of the studied stations. In the water of the studied tributaries, the content of nutrients exceeded the MAC at all studied stations, except for L1 about N - NO_2^- and N - NO_3^-, L5 and L6 about N - NH_4^+ and K8 about N - NO_3^- (Table 2).

To assess the pollution, the threshold indices of pollution [19] of an individual element (C_f) were calculated according to the formula $C_f = C/C_{MAC}$, where C is the total concentration of the component and C_{MAC} is the maximum allowed concentration. When the MAC is expressed by a confidence range, then the average value was used. The integrated threshold pollution indices $P_w = \sum C_{fi}/n$ (n - the number of components) were calculated as well.

The results showed that for Iskar river (Fig. 3(a)), N - NH_4^+ displayed the highest degree of contamination ($C_{f\,NH4+}$ = 1.40 - 5.30) followed by P - PO_4^{3-} (C_{fPO43-} = 0.40 - 6.25, with the exception of I8), and N - NO_2^- (C_{fNO2-} = 0.27 - 4.63, with the exception of I8).

In the Lesnovska river (Fig. 2(b)), the highest pollution was shown by P - PO_4^{3-} (C_{fPO43-} = 3.5 - 15), followed by N - NO_2^- (C_{fNO2-} = 1 - 6.67), N - NH_4^+ (C_{fNH4+}

Table 1. Physicochemical characteristics and chemical parameters of the waters of the Iskar river (I1 - I8) in the region of Sofia.

Station/Parameters	MAC	I1	I2	I3	I4	I5	I6	I7	I8	I9
T, °C		16.9	16.8	17.9	18.6	17.8	17.2	20.6	22.5	22.3
pH	6.5 - 8.5[a]	8.04	8.13	8.15	7.89	8.07	7.41	7.31	7.56	7.58
Dissolved O_2, mg L^{-1}	8.00 - 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^+ calc.[b]		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+}		14.3	15.6	9.2	12.1	12.2	15.8	23.4	40.7	23.1
Cl^-		8.2	10.4	7.6	8.9	9.3	8.2	18.3	24.6	43
CO_3^{2-} calc.[c]		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}										
P-PO_4^{3-}	0.025 - 0.075 [a]	0.016	0.044	0.075	0.036	0.06	0.09	0.14	0.25	0.16
N-NO_2^-	0.01 - 0.03 [a]	0.008	0.022	0.022	0.023	0.020	0.025	0.05	0.13	0.14
N-NO_3^-	0.5 - 1.5 [a]	<0.20	0.26	<0.20	<0.20	0.8	0.25	1.2	1.1	0.7
N-NH_4^+	0.04 - 0.4 [a]	0.71	0.87	1.41	0.56	1.16	1.22	2.12	1.79	2.06
DOC		11.8	18.5	23.5	17.3	15.7	13.2	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
Mn	0.05[d]	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.085	0.013
Pb	0.014 [e]	<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]) m_{Na} (mol.L^{-1}) = $\Sigma(m_j.z_j)$ - $\Sigma(m_k.z_k)$, where j – anion; k – ation; ([c]) $C_{CO3-}=(C_{CaCO3}.M_{CO3})/M_{CaCO3}$; ([d]) Bulgarian regulation 4/2012 - annual average; ([e]) European Parliament Directive 2013/39/EC on inland surface waters; < - Below the detection limit of the element.

Table 2. Physicochemical characteristics and chemical parameters of the waters of the Lesnovska river(L1 - L6), Kakach (K7) and Blato (B8) river in the region of Sofia.

Station/Parameters	Lesnovska river							Kakach river	Blato river
	MAC	L1	L2	L3	L4	L5	L6	K7	B8
T, °C		14	15.6	15.3	17.1	12.9	14.1	14	16.4
pH	6.5 - 8.5[a]	7.64	7.72	8.13	8.04	7.86	7.8	6.51	9.37
Dissolved O_2, mg L^{-1}	8.00 - 6.00[a]	11.7	12.8	12.3	10.2	12.9	11.7	6.63	10.5
Alkalinity, mg L^{-1}		206	165	185	190	171	159	176	233
Major ions, mg L^{-1}									
K		5.40	1.22	22.9	11.4	0.69	1.11	16.0	1.78
Na^+ calc.[b]		17.7	31.1	44.3	47.9	43.4	44.0	47.8	35.2
Mg		21.8	24.0	26.2	25.4	25.6	25.6	17.7	19.5
Ca		55.1	48.5	63.2	61.4	66.8	59.3	70.4	74.2
Cl-		12.8	43.7	56.9	54.4	53.5	46.2	52.1	41.3
SO42-		47.7	59.8	121.9	104.9	116	121	119	51.1
CO_3^{2-} calc.[c]		123	99	111	114	102	95.4	105	139
Nutrients, mg L^{-1}									
P-PO_4^{3-}	0.025 - 0.075 [a]	0.14	0.43	0.6	0.44	0.4	0.29	1.28	0.86
N-NO_2^-	0.01 - 0.03 [a]	0.03	0.14	0.2	0.17	0.15	0.09	0.09	0.19
N-NO_3^-	0.5 - 1.5 [a]	0.7	1.6	1.7	2.1	2.6	2.9	0.4	2.6
N-NH_4^+	0.04 - 0.4 [a]	0.65	1.53	1.19	0.96	0.35	0.24	1.84	0.84
DOC		17.7	19.4	13.5	24.6	22.1	20.2	23.9	26.7
Trace metals, mg L^{-1}									
Al	0.025 [a]	0.263	0.271	0.381	0.295	0.287	0.289	0.267	0.321
Mn	0.05 [d]	<0.005	0.175	0.269	0.209	0.071	0.069	0.182	<0.005
Pb	0.014 [e]	0.102	0.109	0.159	0.134	0.112	0.088	0.202	0.031

Notes:([a]) Bulgarian regulation 4/2012 - "quality II good water" for semi-mountain types of rivers;([b]) m_{Na} $(mol.L^{-1}) = \Sigma(m_j.z_j) - \Sigma(m_k.z_k)$, where j – anion; k – cation; ([c]) $C_{CO3-}=(C_{CaCO3}.M_{CO3})/M_{CaCO3}$; ([d]) Bulgarian regulation 4/2012 - annual average; ([e]) European Parliament Directive 2013/39/EC on inland surface waters; - Below the detection limit of the element.

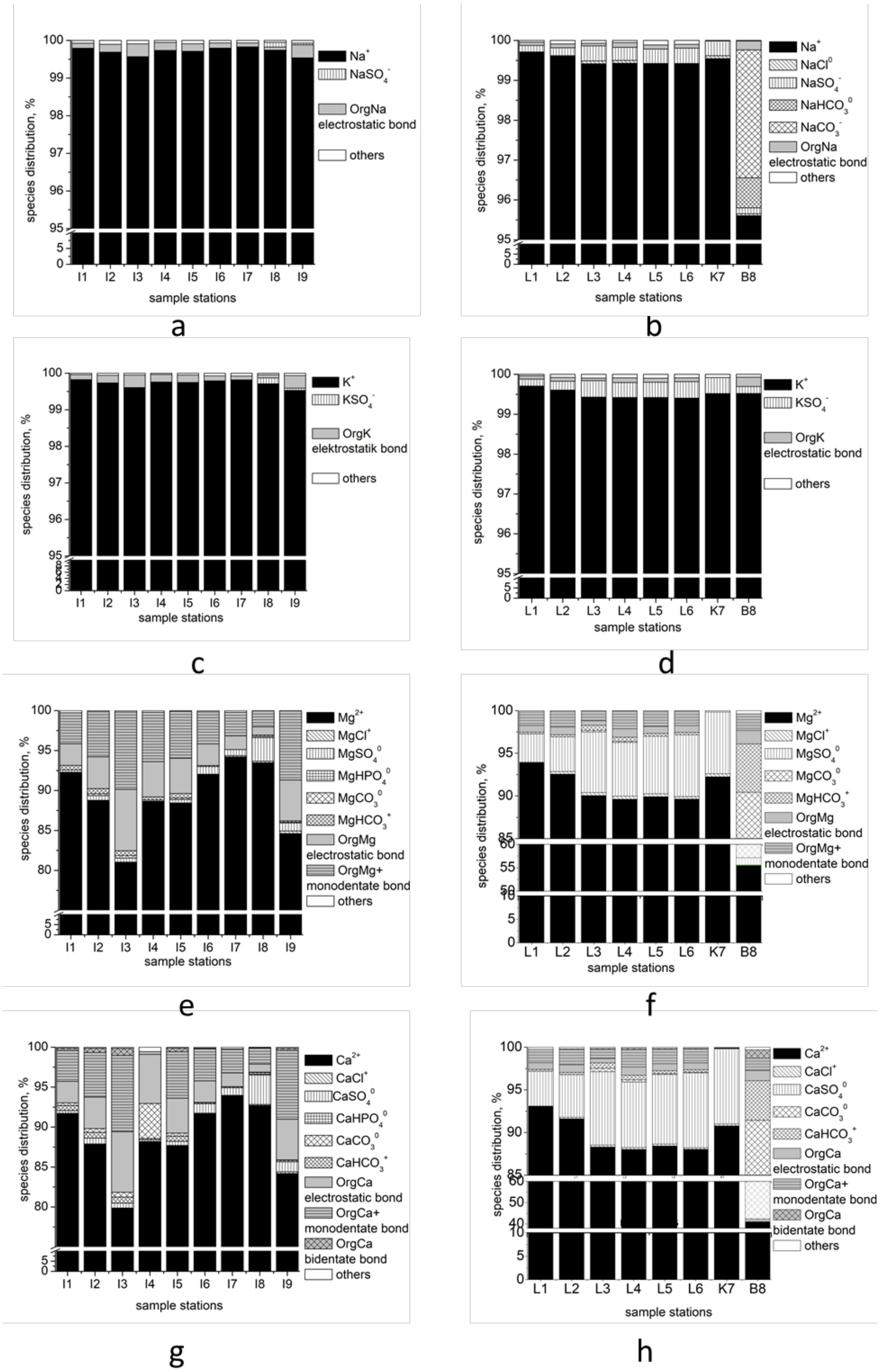


Fig. 2. Distribution of the chemical species of Na, K, Mg and Ca in the water of sampling stations in Iskar river (a, c, e, g) and its tributaries (b, d, f, h).

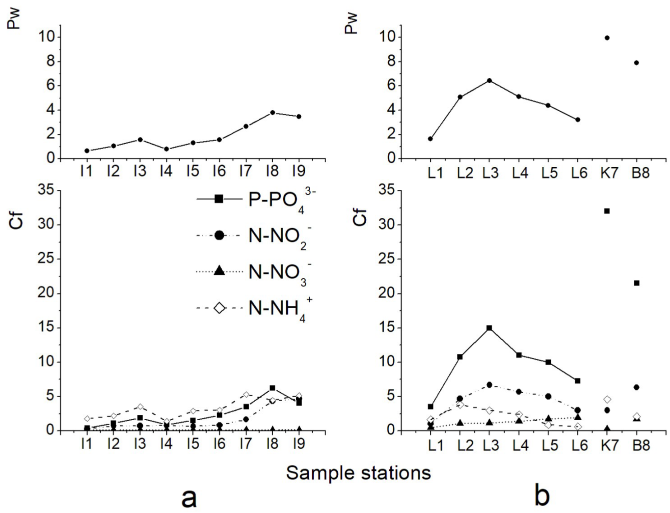


Fig. 3. Threshold pollution indices (C_f) and integrated threshold pollution indices (P_w) with regard to nutrients of the studied water samples from the Iskar River (I1 - I9) (a), and its tributaries (b) (Lesnovska River L1 - L6, Kakach river K7 and Blato river B8).

= 0.60 - 3.83) and N - NO_3^- (C_{fNO3-} = 0.47 - 1.93). There was a tendency to increase pollution concerning P - PO_4^{3-}, N - NH_4^+ and N - NO_2^- from station L1 to station L3, where it reached a peak and then decreased to point L6, but remained higher than that in the Iskar river. The concentration of N - NO_3^- rised smoothly along the entire course of the river. The highest threshold pollution indices $C_{fPO_4^{3-}}$ and C_{fNH4+} were calculated for stations K7 and B8.

According to the calculated integrated threshold pollution indices, P_w, the most polluted in terms of nutrients were the water of Kakach river (P_w = 9.96), followed by the water of Blato river (P_w = 7.91), Lesnovska river (max P_w = 5.11) and Iskar river with P_w = 0.64(I1) - 2.65(I7) before the inflow of studied tributaries (Figs. 3(a) and 3(b)). After the inflow of tributaries (sample stations I8 and I9) P_w increased almost twice.

The results pointed to a strong domestic pollution in Kakach and Blato rivers and both agricultural and domestic pollution in Lesnovska river. Although the water of the Iskar river was less polluted, the high value of P_w at station I7 revealed only partial water purification in the wastewater treatment plant in Sofia located before station I7 (Figs. 1 and 3(a)).

Nitrogen and phosphorus are essential for the growth of aquatic plants and microorganisms. A change in the concentration of nutrients can change the nutrient ratio (N : P) required for primary productivity and can lead to changes in the composition and function of the biological species [20, 21]. The N : P ratio of 16 : 1 is required for optimum growth of phytoplankton and diatoms.

Fig. 4(a) presents a diagram of nitrogen vs. phosphorus in the river waters under study. Waters in the sample stations are divided in three groups:

Group A - with low concentration of phosphopus (0.016 - 0.16 mg L^{-1}) and nitrogen which varies widely (0.7 - 3.37 mg L^{-1}). This group includes all points from the Iskar river (except I8) and only L1 from the Lesnovska river (Fig. 4(a)). The N : P molar ratio exceeded the optimum between 1.3 and 6.2 times (Fig. 4(b)).

Group B - with close values for the total nitrogen content (3.02 - 3.27 mg L^{-1}) and phosphorus (0.25 - 0.6 mg L^{-1}). All points from the Lesnovska river (except L1) and one point from the Iskar River (I8) fall here (Fig. 4(a)). The N : P molar ratio is relatively close to the optimum (varying between 11.4 and 26.7), being equal to it at stations L2, L4 and L5 (Fig. 4(b)).

Group C - with the highest phosphorus content of all the waters studied (Fig. 3(a)). The waters of both small tributaries - the Kakach river and the Blato river belong to this group. The N : P molar ratio is much lower than optimal (Fig. 4(b)).

Waters in group A and group C significantly deviate from the optimal ratio N / P = 16 and represent a potential danger for plant and animal microorganisms in them. Already in 2009 bad ecological conditions

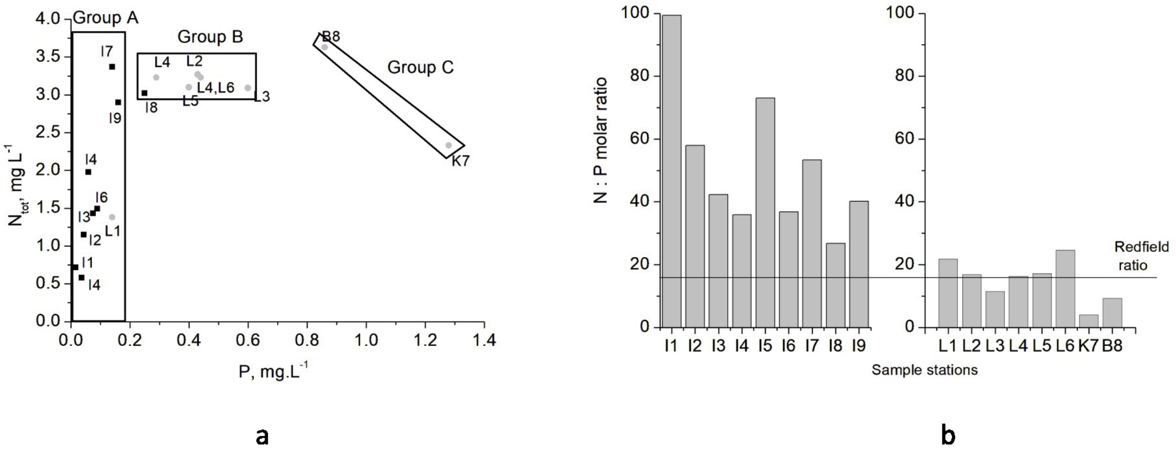


Fig. 4. Diagrams of: (a) nitrates vs. phosphates and (b) N : P molar ratio in the studied waters.

were observed in the waters of the Iskar river around the town of Novi Iskar [22]. The authors reported about disruption of the macrozoobenthic communities and high organic loading.

Thermodynamic modeling revealed that NO_3^- and NO_2^- are present only as free ions. A greater variety of forms is shown by PO_4^{3-} and NH_4^+ ions (Fig. (5)).

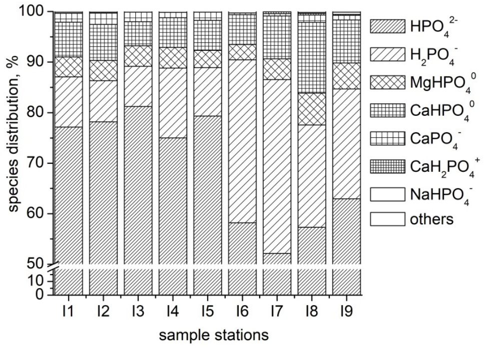
PO_4^{3-} (Figs. 5(a) and 5(b)) – Calculated dominant $H_nPO_4^{n-3}$ (n = 1, 2) species are related to the measured pH values. For Iskar river domination of HPO_4^{2-} (55 - 80 %) and $H_2PO_4^-$ (10 - 30 %) was calculated together with $Ca_nH_mPO_4^{(2n+m-3)}$, (n=1, m=0, 1, 2), $MgHPO_4^0$ and $NaHPO_4^-$. Analogous species were calculated for Lesnovska river. Exceptions are the waters of the Blato and Kakach rivers. The lowest pH (6.61 at station K7) determines the dominance of $H_2PO_4^-$ (70 %) over HPO_4^{2-} (10 %), as well as the presence of $AlHPO_4^+$ species, while the highest pH (9.37, station B8) determines minimal amounts of $H_2PO_4^-$ and an increase in the amount of $CaPO_4^-$ species.

NH_4^+ (Figs. 5(c) and 5(d)) - the calculated dominant species are analogous to those of the alkali metals. Free NH_4^+ ions dominate, namely 92.5 - 99 % for the Iskar river, 96 - 98.5 % for the Lesnovska river, 99 % for the Kakach river and 60 % for the Blato river. Small amounts (up to 5 % for Iskar river and 5 - 8 % for its tributaries) of sulfate and electrostatically bound organic complexes were calculated. In all stations, the presence of dissolved ammonia was also calculated, the amount of which varies, depending on the pH, between 1 and 40 % of the total content of NH_4^+ ions. High amount of ammonia is a serious problem for aquatic animals, especially for fish [23]. Although the concentration of dissolved NH_3 does not reach the critical value of 2 mg L^{-1} in the studied waters of all stations, thermodynamic calculations are an indicator of deteriorated living conditions for aquatic fauna [23].

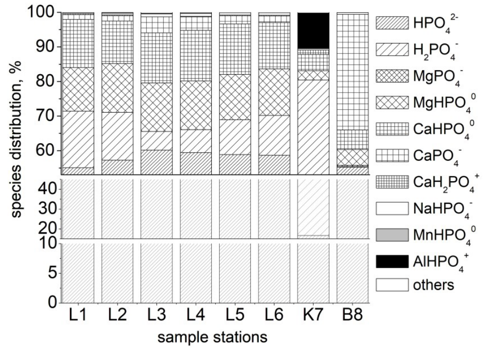
Trace metals

The research shows that the studied waters are pure in terms of trace elements Fe, Co, Ni, Cu Zn and Cd. Their values were below the detection limits of the ICP-OES apparatus used and, accordingly, below the maximum permissible concentrations according to the Bulgarian regulation 4/2012 and European Parliament Directive 2013/39/EC on inland surface waters. Therefore, these elements were not included in Tables 1 and 2. In the Iskar river, the values of Mn and Pb exceeded the MAC at stations I8 and I9 (Table 1). Unlike the Iskar river, Al, Mn and Pb were detected in the waters of all sample stations on the Lesnovska river except in L1 in relation to Mn (Table 2). High contents of Al, Mn and Pb were also reported in points K7 and B8 of the Kakach and Blato rivers, probably as a result of unregulated pollution in the areas of the city of Sofia through which the rivers pass.

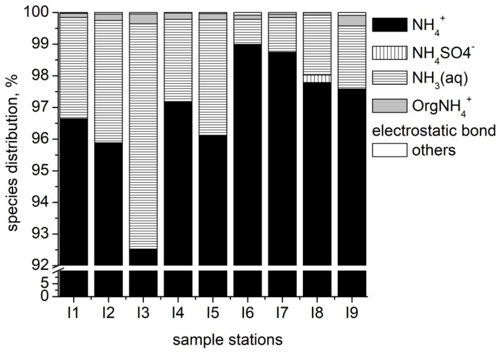
Calculated threshold indices of pollution of an individual element (C_f) and integrated threshold indices of pollution (P_w) show that Lesnovska river was the most polluted river followed by the rivers Kakach, Blato and Iskar (Fig. 6). The contamination is highest in terms of Al, followed by Pb and Mn. A probable reason for this is



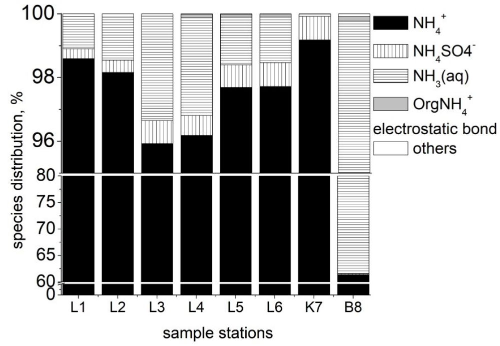
a



b



c



d

Fig. 5. Distribution of the chemical species of PO_4^{3-} and NH_4^+ in the waters of sampling stations in Iskar river (a, c) and of its tributaries (b, d).

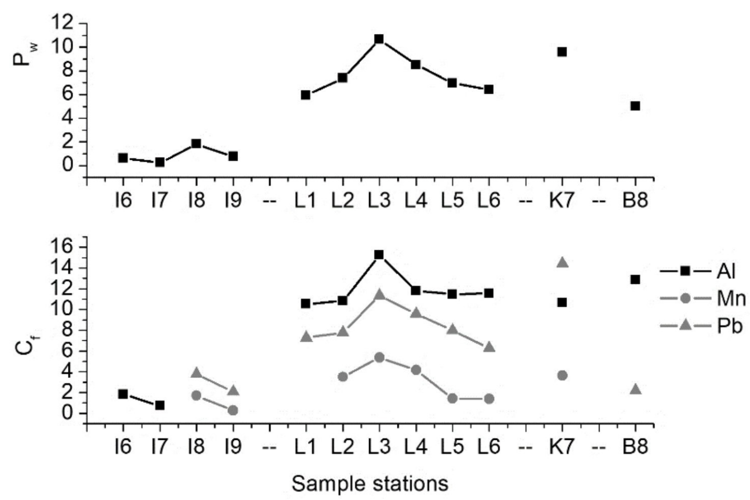


Fig. 6. Threshold pollution indices (C_f) and integrated threshold pollution indices (P_w) with regard to Al, Mn and Pb of the studied water samples from the Iskar river (I6 - I9) (a) and its tributaries (b) (Lesnovska River L1 - L6, Kakach river K7 and Blato river B8).

the airport located next to the village of Lesnovo, which since 2001 has been managed by a private company Intersky, engaged in services and trade in the field of aviation (https://intersky.bg/).

Thermodynamic calculations for samples from Iskar river are presented only for selected points, I6, I7, I8, I9, in which values for Al, Mn and Pb were detected.

Calculated data of species distribution (Fig. 7) showed that the trace metals formed a great variety of complexes. The chemical species of trace metals in amounts higher than 0.1 % are only presented in the figures.

Al (Fig. 7(a)) – Inorganic $Al(OH)_4^-$ (7.6 - 99.7 %) and organic OrgAlOH (bidentate bond) (16.3 - 95 %)

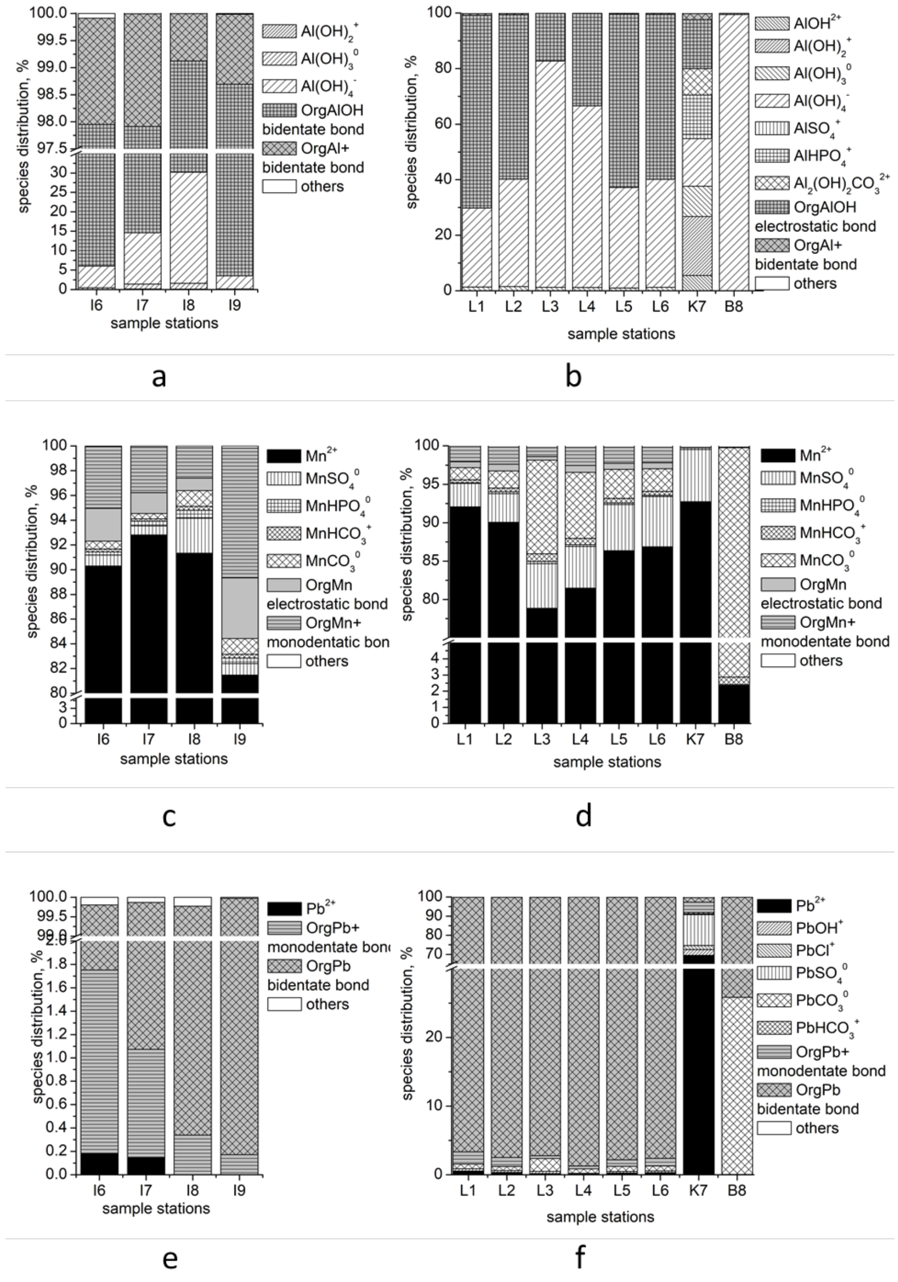


Fig. 7. Distribution of the chemical species of Al, Mn and Pb in the waters of the sampling stations in Iskar river (a, c, e) and its tributaries (b, d, f).

species were calculated to dominate in all studied waters. The ratio between them depends on the pH and the concentration of dissolved organic carbon. At station B8 with the highest pH the amount of $Al(OH)_4^-$ was the highest, while the highest amount of OrgAlOH (bidentate bond) was calculated at station I9 with the highest DOC. The greatest variety of species was calculated in the water with the lowest pH (station B7), where hydroxy ($Al(OH)_n^{n-3}$ n = 1 - 3), carbonate sulfate, phosphate and $OrgAl^+$ (bidentate bond) were also calculated to exist in the waters.

Mn (Fig. 7(b)) – Inorganic species, free Mn^{2+} ions (15.9 - 91.4 %), $MnCO_3^0$ (1.89 - 82 %), $MnHCO_3^+$ (up to 1.6 %) and $MnSO_4^0$ (up to 6.6 %) dominated in all studied waters. Organic species $OrgMn^+$ (monodentate bond) and OrgMn (electrostatic bond) (total 5 - 17 %) were calculated for the stations in Iskar river due to higher DOC concentration.

Pb (Fig. 7(c)) **-** bidentate organic species OrgPb (bidentate bonds) were calculated as dominant (95.4 - 99.7 %) in the waters. An exception is the water from station K7 with the lowest pH, where Pb^{2+} (47.8 %), carbonate (total 35 %) and sulfate (10.9 %) species were calculated as dominant. Additional monodentate $OrgPb^+$, $Pb(OH)_n^{n-2}$ n = 1, 2 and $PbCl^+$ species in amounts below 1.5 % were calculated in the different waters.

The obtained results for trace metal complexation are in accordance with the species of the elements that may exist in surface waters predicted in our previous study [24], as well as with the "hard and soft acids and bases" (HSAB) principles [25, 26]. The Pearson concept that soft Lewis acids preferably coordinate with soft Lewis bases and hard Lewis acids-with hard Lewis bases [26], as well as the Klopman scale [27] for hardness determine the type of metal complexes formed in water systems. Al^{3+} ions are considered as the hardest Lewis acid among the studied metals and they prefer to coordinate with OH^-ions (the hardest Lewis bases in the system) forming hydroxy complexes, which were calculated in our modeling (Figs. 7(a) and 7(b)). In contrary, Pb^{2+} is considered as the softest Lewis acid preferring to coordinate mainly with the soft organic ligands, as calculated in Figs. 7(e) and 7(f). Mn^{2+} takes the medium position, but its hardness [27] is closer to that of Al^{3+}, so hydrated Mn^{2+} ions can be considered since the hardness of H_2O molecules [27] is less than the hardness of OH^- ions.

Based on our previous publications related to the dynamics of trace metals in the system *water - soil - soil solution - uncultivated vegetation - small mammals* [10, 11], it can be concluded that Pb in all sample stations (with exception of K7) would accumulate in the adjacent plants, as it is in the form of easily digestible organometallic complexes. On the other hand, Mn is more dangerous for the animal world, as it exists mainly as free ions, which easily interact with ligands of organic compounds found in the bloodstream and/or within organs. With regard to Al, hydroxy species stimulate precipitation of $Al(OH)_3$ and decrease Al concentration.

CONCLUSIONS

Combined approach for ecological assessment including monitoring studies and thermodynamic calculations of element chemical species was applied to the water bodies of Iskar river and its three tributaries Lesnovska, Kakach and Blato rivers within Sofia Municipality. Physico-chemical characteristics and concentrations of macro-components (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}), nutrients (NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-}), trace metals (Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) and dissolved organic carbon (DOC) were measured to create an input database for thermodynamic calculations. The threshold pollution indices of the individual elements (C_f) and the integrated threshold pollution indices (P_w) were calculated. The data revealed that the studied water bodies were highly polluted in terms of nutrients PO_4^{3-}, NH_4^+ and NO_2^-, which is an indication of serious domestic pollution. The waters were pure in terms of Fe, Co, Ni, Cu, Zn and Cd. Al, Pb and Mn exceeded the maximum allowed concentrations in the water of Iskar river after Sofia city, and along the entire flow of Lesnovska river.

Two thermodynamic methods were applied to calculate chemical species – classical ion-association method for inorganic chemical species and Stockholm Humic Method for organic ones. The thermodynamically calculated chemical species showed that Na, K, Mg, Ca, NO_2^-, NO_3^- and NH_4^+ mainly exist as free ions. The presence of dissolved ammonia was calculated in all sample stations, which is a serious problem for aquatic animals, especially for the fish. PO_4^{3-} shows a great variety of forms depending on pH. Among the trace metals (Al, Pb and Mn), Pb is potentially the riskiest element for plants as its dominant organometalic species are easily accumulated by them. Free ions of Mn dominate, which is dangerous for aquatic fauna as Mn^{2+} ions easily interact with ligands of organic compounds found in the bloodstream and/or within organs. Regarding Al, its dominant hydroxy species are a prerequisite for the precipitation of $Al(OH)_3$ and the self-purification of waters. Our results are in good agreement with the principle for "hard and soft acids and bases".

Acknowledgements

This work has been carried out in the framework of the National Science Program „Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters", approved by the Resolution of the Council of Ministers No 577/17.08.2018 and supported by the Ministry of Education and Science (MES) of Bulgaria (Agreement No Д01-271/09.12.2022).

REFERENCES

1. A. Lassin, L. André, A revised description of the binary $CaCl_2$-H_2O chemical system up to solution-mineral equilibria and temperatures of 250°C using Pitzer equations. Extension to the multicomponent HCl-LiCl-NaCl-KCl-$MgCl_2$-$CaCl_2$-H_2O system, J. Chem. Thermodyn., 176, 2023, 106927.
2. S. Kournopoulos, M.S. Santos, S. Ravipati, A.J. Haslam, G. Jackson, I.G. Economou, A. Galindo, The Contribution of the Ion-Ion and Ion-Solvent Interactions in a Molecular Thermodynamic Treatment of Electrolyte Solutions, J. Phys. Chem. B, 126, 47, 2022, 9821-9839.
3. D. Li, D. Zeng, D. Gao, Phase diagrams and thermochemical modeling of salt lake brine systems. V. Li^+-Na^+-K^+-Mg^{2+}-Ca^{2+}-SO_4^{2-}-H_2O system, Chem. Thermodyn. Thermal Analysis, 3-4, 2021, 100008.
4. F.Z. Karmil, N. Bounouar, S. Mountadar, A. Rich, M. E. Belghiti, A. Zeroual, M. Mountadar, Phosphate removal from contaminated seawater and RO water using magnetically modified reactive CaO derived from reject brine: Experimental studies maintained by theoretical simulations, Surf. Interfaces, 35, 2022, 102438.
5. K. Michael, A.W. Wilson, P.P. Govender, Modelling of manganese-contaminated groundwater through batch experiments: Implications for bone char remediation, Environ. Adv., 10, 2022, 100323.
6. C. Abate, A. Scala, O. Giuffrè, A. Piperno, A. Pistone, C. Foti, From speciation study to removal of Pb^{2+} from natural waters by a carnosine-based polyacrylamide/azlactone copolymer, J. Environ. Manage, 335, 2023, 117572.
7. D.B. Facco, E. Trentin, G.L. Drescher, R.K. Hammerschmitt, C.A. Ceretta, L.S. Da Silva, G. Brunetto, P.A.A. Ferreira, Chemical speciation of copper and manganese in solution of a copper-contaminated soil and young grapevine growth with amendment application, Pedosphere, 33, 3, 2023, 496-507.
8. V.A. Procópio, R.M. Pereira, C.N. Lange, B.M. Freire, B.L. Batista, Chromium Speciation by HPLC-DAD/ICP-MS: Simultaneous Hyphenation of Analytical Techniques for Studies of Biomolecules, Int. J. Environ. Res. Public Health, 20, 6, 2023, 4912.
9. M. Borelli, A. Bergomi, V. Comite, V. Guglielmi, C.A. Lombardi, S. Gilardoni, B. Di Mauro, M. Lasagni, P. Fermo, Development of a New Analytical Method for the Characterization and Quantification of the Organic and Inorganic Carbonaceous Fractions in Snow Samples Using TOC and TOT Analysis, Atmosphere, 14, 2, 2023, 371.
10. A. Kovacheva, I. Vladov, M. Gabrashanska, D. Rabadjieva, S. Tepavitcharova, V. Nanev, M. Dassenakis, S. Karavoltsos, Dynamics of trace metals in the system water - soil - plant – wild rats – tapeworms (Hymenolepis diminuta) in Maglizh area, Bulgaria, J. Trace Elem. Med. Biol., 58, 2020, 126440
11. D. Rabadjieva, S. Tepavitcharova, A. Kovacheva, R. Gergulova, R. Ilieva, I. Vladov, V. Nanev, M. Gabrashanska, S. Karavoltsos, Trace metals accumulation in the eco-system water – soil – vegetation (Agropyron cristatum) – common voles (Microtus arvalis) – parasites (Hymenolepis diminuta) in Radnevo region, Bulgaria, J. Trace Elem. Med. Biol., 66, 2021, 126750.
12. Z. Cholakova, Peculiarities of heavy metal content in the bottom sediments of some tributaries of the Iskar river in the Stara planina mountain (Iskretska and Batuliyska rivers), Annual of Sofia University "St. Kliment Ohridski", Livre 2, Geographie, 113, 2021, 140-160.
13. Y. Todorova, S. Lincheva, I. Yotinov, Y. Topalova, Contamination and ecological Rrisk assessment of

long-term polluted sediments with heavy metals in small hydropower cascade, Water Resour. Manag., 30,12, 2016, 4171-4184.
14. V. Yordanova, Y. Todorova, M. Belouhova, L. Kenderov, V. Lyubomirova, Y. Topalova, In: S. Chankova, V. Peneva, R. Metcheva, M. Beltcheva, K. Vassilev, G. Radeva, K. Danova (Eds), Current trends of ecology. BioRisk 17, 2022 59-71.
15. J.P. Gustafsson, Modeling the acid–base properties and metal complexation of humic substances with the Stockholm humic model, J. Colloid. Interface Sci. 244, 2001, 102-112.
16. I. Grenthe, I. Puigdomenech, W. Hummel, In: I. Grenthe, I. Puigdomenech (Eds) Modelling in aquatic chemistry, OECD Publications, 1997.
17. D. Turner, M. Whitfield, An equilibrium speciation model for copper in sea and estuarine waters at 25°C including complexation with glycine, EDTA and NTA. Geochim. Cosmochim. Acta, 51, 1987, 3231-3239.
18. ATSDR (Agency for Toxic Substances and Diseases Registry), Toxicological Profile for Manganese, US Department of Health and Human Services, Public Health Service, Atlanta USA, 2012, https://www.atsdr.cdc.gov/toxprofiles/tp151.pdf.
19. C.A. Yan, W. Zhang, Z. Zhang, Y. Liu, C. Deng, N. Nie, Assessment of water quality and identification of polluted risky regions based on field observations&GIS in the Honghe River Watershed, China, PLoS One 10, 3, 2015, e0119130.
20. G. Weigelhofer, T. Hein, E. Bondar-Kunze, In: S. Schmutz, J. Sendzimir (Eds), Riverine Ecosystem Management. Aquatic Ecology Series, 8, 2018, Springer, Cham, Switzerland.
21. N.K. Ravi, A. Srivastava, K. Ram, P.K. Jha, Nutrient chemistry and eutrophication risk assessment of the Ghaghara river, India, Water Supply 21, 7, 2021, 3486.
22. L. Kenderov, I. Yaneva, Ecological Characteristics of the Iskar River Catchment, Biotechnol. Biotechnol. Equip., 23, 2009, 276-280.
23. A.F. Dasan, L.L. Edward, Ammonia toxicity and adaptive response in marine fishes - A review, Indian J Mar Sci. 48, 3, 2019, 273-279
24. D. Rabadjieva, A. Kovacheva, S. Tepavitcharova, R. Gergulova, R. Ilieva, I. Vladov, S. Karavoltsos, Modelling of chemical species of Al, Mn, Zn, and Pb in river body waters of industrial areas of West Rhodope Mountain Bulgaria, Environ. Monit. Assess. 193, 2021, 430.
25. R.G. Parr, R.G. Pearson, Absolute hardness: Companion parameter to absolute electronegativity. J. Am. Chem. Soc, 105, 1983, 7512-7516.
26. R.G. Pearson, Hard and soft acids and bases. J. Am. Chem. Soc, 85, 1963, 3533-3539.
27. G. Klopman, Chemical reactivity and the concept of charge- and frontier-controlled reactions. J. Am. Chem. Soc, 90, 1968, 223-234.