



Research article

Heavy metal contamination assessment and potential human health risk of water quality of lakes situated in the protected area of Tisa, Romania

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ABSTRACT

Protected areas are significant due to the high value of natural resources they shelter. This study's primary objective is to assess the quality status of the water resources (13 lakes and Tisa River) localized in the protected area of Tisa River on the territory of Romania. A number of 13 lakes and surface water (Tisa River) situated in the protected area through the Natura 2000 ecological network are studied. The chemistry and potential pollution status were analyzed by measuring and analyzing a set of twenty elements and sixteen physico-chemical parameters. The potential impact of anthropogenic activities was settled through the applied analysis and obtained results. A potential human health risk was noticed. Results indicated that waters are rich in Ni and Fe probably due to interaction with groundwater rich in Fe and Ni. Waters are characterized by potential contamination, which if directly or through the food chain consumed could negatively influence the human health. Piper and Gibbs plots indicated that the studied waters are divided into three categories based on water-rock interactions: mixed $\text{Ca}^{2+}\text{-Na}^+\text{-HCO}_3^-$, CaCO_3^- , and $\text{Na}^+\text{-HCO}_3^-$. Likewise, the applied pollution indices (Heavy metal Pollution Index, HPI and Heavy metal Evaluation Index, HEI) indicated three pollution categories correlated to the As, Ni and Fe amounts. The findings of this research imply that the chemistry of the studied lakes and surface waters is influenced by the geogenic origin and emergence of anthropogenic activities. The significance of this research is related to understanding of mechanisms that influence the water quality, improving and conserving the natural water resources, and correspondingly understanding if any potential human health risks could be identified.

1. Introduction

In its essentiality and simplicity, water supports biodiversity, aquatic biota and all terrestrial living creatures (biota and human life); water is the condition of life [1–3]. Worldwide, lakes cover a surface of around 100 km² (0.01 % of the global water resources, together with other bodies), including 1400 bodies (plus reservoirs), supporting over 100,000 species [4,5]. There are different lake categories, including saline, fresh and brackish (based on the salinity level and chemistry), eutrophic, oligotrophic, hyper-eutrophic, and mesotrophic (based on the nutrient concentrations) [6]. The physicochemical conditions and chemistry of lakes influence and depend on the plankton and other associated biota [7]. The natural variations including atmospheric settlement and hydrodynamic

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conditions, along with rapid urbanization and the quickening pace of industrialization, socioeconomic development, and agriculture (economic needs) destabilize habitats, ecosystems, and biodiversity impact the drinking water sources [4,5,8,9]. Hydrological factors (flow velocity, river water discharge and level) influence the nutrient level in lakes, which could trigger the algae development, leading to eutrophication and decrease of the dissolved oxygen [5,10,11]. Climate change has the potential to worsen eutrophication in the area by increasing temperatures and reducing precipitation. By increasing the emission of greenhouse gases from the sea, such as nitrous oxide and methane, eutrophication would accelerate global warming, disrupt food chains, cause biodiversity losses, and deteriorate ecosystem services. Other repercussions of eutrophication include the dominance of blue-green algae, deep water anoxia, macrophyte issues, algal scums, toxic byproducts, inverse effects on the fishery industry and economic losses, decline in ecosystem services, and decreased appreciation of the environment's aesthetic qualities [12]. Eutrophication has direct effects on the quality of lake water, biodiversity, socioeconomic benefits, recreational and tourism opportunities. It alters the amount of dissolved oxygen in the water, increases fish mortality and phytoplankton organism development, and creates toxins and cyanobacteria blooms. In the meantime, knowledge of the dynamics of eutrophication under regular phytoplankton community monitoring is necessary for the restoration of lakes and the life-supporting functions they provide. Global warming has the potential to exacerbate the eutrophication trend and jeopardize the health of the aquatic ecosystems, as nearly all existing legislative agreements to safeguard the lake environment and its abundant resources have not yet been put into effect [13]. The loading of agricultural wastewater and urban sewage water, which causes eutrophication of the river, is the primary cause of the nutrient loading (especially of phosphorous and nitrogen) in surface water bodies (such as rivers and lakes) [14]. Rejuvenation should limit cattle activity near surface water; otherwise, pollution can harm all living things, including humans, and lessen environmental and socioeconomic disasters like climate change [14]. The decreasing or lack of oxygen leads to the death of fish, which allows the mosquito population to overgrow and spread malaria. Furthermore, the emissions caused by industry impact climate change, implying a change in the precipitation regime, modifying the connectivity of lakes with biological implications [6]. The degradation of sediments and wastes affects, on long term, the swan population [15].

The quality of lakes is directly connected, influenced and altered by the physical, biological and chemical indicators and the interaction between them. Lakes are considered unique systems, considering the interactions and chemistry, processes and mechanisms [16,17]. Water salinity, temperature, turbidity, nutrient availability, bacterial losses caused by sedimentation and death, solar radiation influence the natural processes of lakes, as well as the bacterial charge [18].

Heavy metals in high amounts of toxic wastes are considered a significant contamination category due to their bioaccumulation, persistence and high toxicity level [19,20]. The low solubility in water characterizes the heavy metals and the majority of metals, so they are adsorbed and deposited by sediments and suspended particulate matter implying a small content of metals remains and migrates in water [21,22]. Therefore, the solid deposits of heavy metals make the self-purification process very hard to implement and make the sediments the secondary source of metals in the water ecosystems [22,23]. Due to the desorption and resuspend of heavy metals in the overlying water, variations in the hydrological circumstances (waves, wind), physico-chemical indicators (dissolved oxygen, pH, redox potential), and benthic bioturbation will result in secondary contamination [23]. When ingested in large quantities, metals are not metabolized by organisms and instead bioaccumulate in the soft tissues, causing cell structures damage, impeding the production of proteins and nucleic acids, and interfering with the processes of photosynthesis and energy transfer [2,6]. The main sources of trace and heavy metals are the anthropogenic activities (industry, agriculture, mining, aquaculture, household and urban activities). The occurrence of natural processes (degradation of rocks rich in minerals caused by erosion and weathering, suspended solids and sediments) is also responsible for the incidence of heavy metals in the water sources, air, soil and vegetation [19,20,23–25]. Conversely, some metals (first- and second rows of transition metals) are essential in plant growth [26].

In this term, monitoring, quantifying and assessing the quality status of waters concerning the metal content is significant in identifying, preventing and mitigating the contamination process. Different tools are used in achieving this goal, such as the heavy metal pollution indices. The most used indices are the heavy metal pollution index and the heavy metal evaluation index, developed by Horton [27]. The importance of using specific indices is determining the contamination status with heavy metals by converting the obtained numerical score into qualitative data.

The main objective and implicitly the novelty of this research was to evaluate the quality of lakes and rivers situated in the protective area of Tisa River, in Romania. In order to achieve this objective, a set of physico-chemical parameters was determined and analyzed. Based on this data, the typology of water was determined with the help of variate diagrams (Piper, Gibbs and Total Ionic Salinity). Likewise, the heavy metal pollution status was studied with the help of heavy metal pollution indices. The quality of lakes, and also their limitations as a nonrenewable resource are essential to be monitor and assess due to their critical demands for the humans and biota needs. The possible limitation of this study is the fact that only one sampling station was chosen.

The outcomes gained will successfully execute management, suggesting the prevention and reduction of potential pollution and anthropogenic influences. In a similar vein, new conservation guidelines pertaining to the biological and ecological diversity of the lakes under study from the protected region can be created. The lakes are permanently occupied; they never empty. Many fish, frog, and aquatic plant species have habitats in the water of these lakes. Additionally, several dozen unique birds that only found their habitat and food on these lakes reside in the lakes of the Tisa protected region, which are the subject of this paper's study. On these lakes, certain species of swans and ducks breed.

2. Materials and methods

2.1. Study area and sampling

Samples were collected from lakes situated in the protected area of Tisa from Sighetu Marmatiei (samples L1SM-L6SM), Sasaru (samples L1S-L4S), and Campulung la Tisa (samples L1CT-L3CT). Similarly, surface water samples were collected from Tisa River from three different areas/localities: near Sighetu Marmatiei (sample Tisa SM), Sarasau (sample Tisa S) and Campulung (sample Tisa CT). All lakes are relatively new (formed in the last 50 years) and formed as a result of excavations in order to extract the sand necessary for construction, so they are at least 5 m depth. Lakes were never dried, having a permanent residence time. They are populated by diverse fish species, which is why fishing is practiced. Likewise, these lakes became habitats for birds (ducks, swans, etc.) and frogs. All aquatic habitats in the protected area of Tisa were inventoried, the conservation potential of these habitats for aquatic species was analyzed, and a monitoring protocol to cover all habitats throughout the year was established. The soil types in the studied area were identified by soil profiles that were placed in parallel directions and arranged transversely across the width of the protected area. The slight differences in level materialize by separating the meadow area from the terrace areas of the river. The pedogenetic horizons and the relationships between the parent material and the basic properties of the soil were identified.

The sample campaign was organized in every month of 2022. The distribution of studied lakes in relation to the Tisa River is shown in Fig. 1. They are situated at 150 m away from Tisa. The protected area is marked in brown. Tisa River separates Romania from Ukraine, therefore this study has an international interest.

The sampling was performed according to procedural standards (SR ISO 5667-23:2011; SR ISO 5667-3:2013). Some of the physical-chemical parameters were determined *in-situ* with the help of portable equipment.

Clean high-density polyethylene bottles were used for the sample conservation, after rinsing with each sample. Sampling was performed manually by plunging the bottle into the water source at 10 cm depth and allowing it to fill without air. Samples destined for the major and trace elements analysis were acidified with 65% HNO₃ (supplied by Merck, Germany) until pH 1–2, in order to prevent precipitation and retention on the walls of the vessels. All samples were preserved by refrigeration in thermal boxes and protected from the sunlight. Samples were instantly transported to the laboratory for analysis within 24 h.

2.2. Chemical analysis

The chemistry of lake and river samples (16 samples collected monthly in 2022) was determined by analyzing 8 physico-chemical

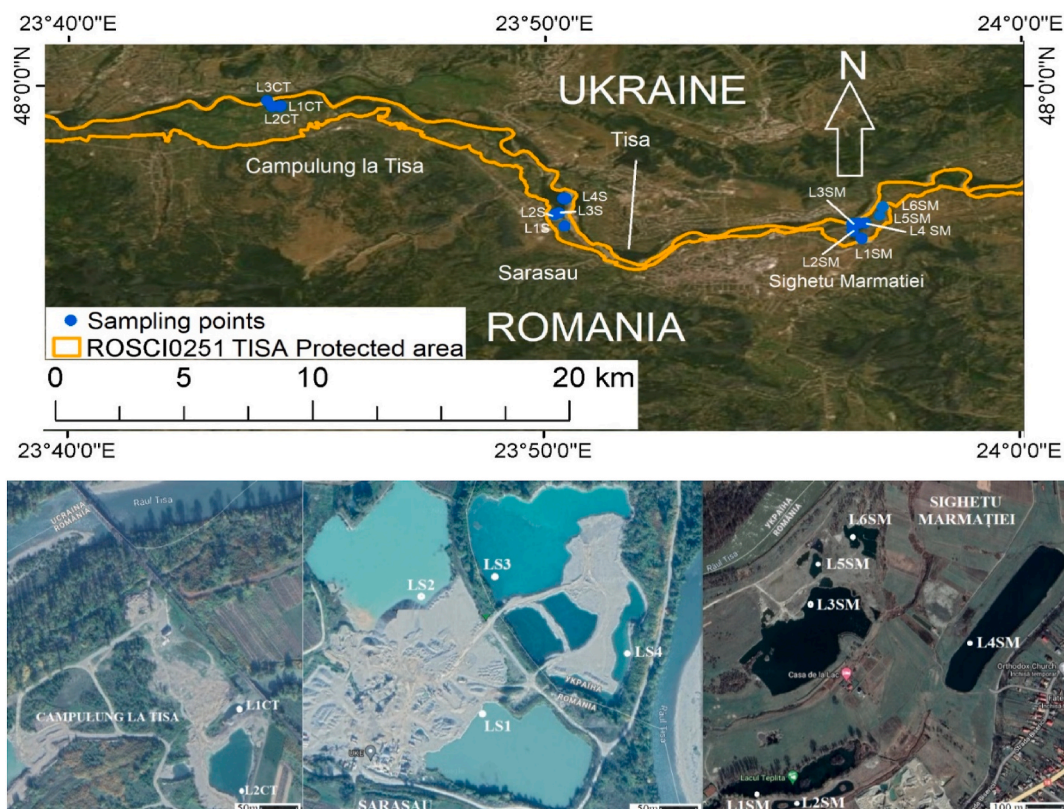


Fig. 1. Localization of the sampling points and Tisa River in the Tisa Superiora protected area.

indicators (pH, electrical conductivity- EC, total hardness- H_t , total dissolved solids- TDS, turbidity- T, oxidation-reduction potential- ORP and dissolve oxygen- DO), 16 nutrients (CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- , PO_4^{3-} , NO_3^- , NH_4^+ , NO_2^- , Ca, Mg, Na, K, Al, Li, Sr and Ba), and 13 heavy metals (Mo, Sr, Rb, Ga, Ti, As, Cr, Cu, Fe, Mn, Ni, Zn, Pb).

pH, EC and anions were determined according to SR ISO 10523/2012, SR EN 27888-1997, ISO 9297-2001 and STAS 3265-86 by using a portable equipment (Hach Lange SL1000) and a spectrophotometer (PerkinElmer Lambda 25). The content of NO_3^- , NH_4^+ , NO_2^- was analyzed with the help of a portable equipment (Hach Lange HQ40d), following SR ISO 7890-3/2000 for NO_3^- , SR ISO 7150-1/2001 for NH_4^+ and SR ISO 6777/2002 for NO_2^- . The total hardness, HCO_3^{2-} and CO_3^{2-} were determined according to SR ISO 6059-2008 and the American Public Health Association APHA (1999). Turbidity and TDS were analyzed SR EN ISO 7027/2001 using a turbidimeter (WTW, Germany) and a gravimetric method. The oxygen saturation, the dissolved oxygen and ORP were determined by following SR EN ISO 5814:2013 and SR ISO 10523/2012.

An inductively coupled plasma mass spectrometer (PerkinElmer NexION 300S) was used for analyzing the metal content, following SR EN IS 15586-2004. After sampling, waters were filtered through 0.45 μm acetate cellulose filters and acidified with 65% HNO_3 .

In order to assure the quality of results, equipment was calibrated with standard solutions. All methods were verified by analyzing traceable, NIST Certipur standards, triplicates and blanks. The recovery was ranging between 87% and 111%.

2.3. Calculation of heavy metal pollution indices

Two heavy metal pollution indices (HPI- Heavy metal Pollution Index and HEI- Heavy metal Evaluation Index) were applied in order to evaluate the potential pollution status of the studied waters (samples 1–15).

2.3.1. HPI- heavy metal pollution index

Horton in 1965, proposed the concept of this index, which is based on the assessment of the weightage of the used heavy metals and maximum allowable concentrations (MACs) [27]. In the present study, MACs established in the 98/83 European Directive (1998) were used. HPI is calculated with the help of the following equations Eqs. (1) and (2) [27,28].

$$HPI = \frac{\sum_{i=1}^{i=n} (W_i \times Q_i)}{\sum_{i=1}^{i=n} W_i} \quad \text{Eq. 1}$$

$$Q_i = \sum_{i=1}^n 100 \times \frac{M_i - I_i}{G_i - I_i} \quad \text{Eq. 2}$$

Q_i and W_i are the subindex and the weightage of each measured heavy metal, while G_i , M_i and I_i are the guideline value, the measured content and the ideal value of each heavy metal [27,28]. By applying the HPI, the degree of pollution with heavy metals is defined. After calculating the HPI, three ranges of scores are obtained. Each range defines a pollution degree, for example if HPI is lower than 15, samples are characterized by a low pollution level, if HPI is higher than 15 and lower than 30, samples have a medium pollution degree, and if HPI scores are higher than 30, samples are classified into a high level of pollution [6,27].

2.3.2. HEI- heavy metal evaluation index

The HEI is also used for assessing the pollution degree caused by heavy metals, based on guidelines and the content of heavy metals determined in the studied water samples. HEI is calculated with the help of equation Eq. (3):

$$HEI = \sum_{i=1}^n \frac{C_i}{S_i} \quad \text{Eq. 3}$$

C_i , S_i and n are the monitored concentration of heavy metal, the guideline value established by International or National Regulation, and the total number of studied elements [29]. According to the HEI scores, three pollution degrees are indicated: low ($HEI < 10$), medium ($10 < HEI < 20$), and high pollution ($HEI > 20$).

2.4. Water typology

For the determination of water typology several plots are used, such as Gibbs, TIS (Total Ionic Salinity) and Piper. Generally, the diagrams are based on the major ions, pH and total dissolved solids content (TDS).

Gibbs plot establishes the relationship between the aquifer lithological characteristics and the water chemistry. It is obtained with the help of the TDS content and the $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio [30,31]. Evaporation-crystallization process, atmospheric precipitation, and water-rocks interaction are evaluated with the help of Gibbs diagram [30].

TIS (Total Ionic Salinity) plot is based on the SO_4^{2-} and $\text{Cl}^- + \text{HCO}_3^-$ concentrations. The ionic salinity of water is determined by applying the TIS plot.

Piper diagram estimates the hydrochemical data, and indicates the types of waters by analyzing the content and relation between anions (HCO_3^- , SO_4^{2-} , Cl^- , CO_3^{2-}) and cations (Na, K, Mg, Ca), analyzing the geochemical evolution of waters [1,32]. A diamond-shaped and two triangular fields are included in the diagram. The character of water is indicated by the intersection of each point which is projected into the upper field.

Diagrams were obtained with the help of GW_Chart version 1.29 and XLStat Microsoft Excel software.

Table 1
Physico-chemical composition of the water samples.

Sample	Parameters															
	pH	EC (μ S/ cm)	DO (mg/ L)	SO (%)	ORP (mV)	NO ₂ (mg/ L)	NO ₃ (mg/ L)	NH ₄ ⁺ (mg/ L)	Cl ⁻ (mg/ L)	SO ₄ ²⁻ (mg/ L)	PO ₄ ³⁻ (mg/ L)	T (NTU)	Ht (G°)	At (mg/L CaCO ₃)	HCO ₃ ⁻ (mg/ L)	TDS (mg/ L)
Tisa SM	8.19 ± 0.52	213 ± 19	10.8 ± 1.1	98 ± 12	222 ± 24	0.012 ± 0.003	0.40 ± 0.11	0.110 ± 0.025	14.2 ± 1.8	11.1 ± 1.7	0.01 ± 0.01	10.90 ± 0.14	6.6 ± 0.8	102 ± 12	124 ± 14	102 ± 11
L1 SM	7.61 ± 0.41	394 ± 33	9.4 ± 0.8	90 ± 10	179 ± 19	0.016 ± 0.005	1.61 ± 0.42	0.232 ± 0.039	30.2 ± 3.8	9.2 ± 0.7	0.01 ± 0.01	0.74 ± 0.09	11.9 ± 1.4	270 ± 30	329 ± 35	203 ± 23
L2 SM	7.71 ± 0.39	442 ± 33	6.2 ± 0.5	60 ± 8	175 ± 17	0.011 ± 0.004	0.46 ± 0.16	0.309 ± 0.051	40.9 ± 4.6	20.3 ± 3.2	0.02 ± 0.01	3.04 ± 0.27	13.1 ± 1.6	202 ± 22	246 ± 27	205 ± 21
L3 SM	7.45 ± 0.33	277 ± 23	4.0 ± 0.3	40 ± 5	227 ± 25	0.007 ± 0.002	0.38 ± 0.12	0.242 ± 0.044	26.6 ± 3.4	8.3 ± 0.8	0.01 ± 0.01	1.57 ± 0.19	12.4 ± 1.4	200 ± 19	244 ± 25	173 ± 19
L4 SM	7.98 ± 0.48	319 ± 36	12.6 ± 0.9	121 ± 13	178 ± 19	0.005 ± 0.001	0.67 ± 0.19	0.130 ± 0.019	31.2 ± 3.8	7.6 ± 0.6	0.01 ± 0.01	1.07 ± 0.13	9.4 ± 1.0	146 ± 17	178 ± 19	144 ± 16
L5 SM	7.69 ± 0.43	393 ± 38	4.3 ± 0.4	41 ± 4	214 ± 23	0.002 ± 0.001	0.17 ± 0.06	0.553 ± 0.078	27.0 ± 3.2	8.8 ± 0.9	0.14 ± 0.04	5.25 ± 0.63	13.9 ± 1.9	190 ± 22	232 ± 26	176 ± 20
L6 SM	7.27 ± 0.33	1052 ± 89	2.1 ± 0.3	20 ± 2	208 ± 19	0.001 ± 0.001	0.48 ± 0.11	22.13 ± 0.38	24.1 ± 2.9	51.0 ± 6.8	0.84 ± 0.17	47.50 ± 0.56	19.7 ± 2.1	536 ± 61	654 ± 71	420 ± 45
Tisa S	8.45 ± 0.53	269 ± 22	11.6 ± 1.4	108 ± 13	258 ± 23	0.120 ± 0.023	0.04 ± 0.01	0.167 ± 0.035	27.5 ± 3.3	19.1 ± 2.7	0.09 ± 0.02	9.27 ± 0.14	7.0 ± 0.9	105 ± 14	128 ± 14	110 ± 14
L1 S	8.11 ± 0.48	307 ± 30	9.3 ± 1.2	92 ± 11	263 ± 28	0.007 ± 0.002	0.14 ± 0.03	0.176 ± 0.019	29.4 ± 4.2	12.0 ± 1.8	0.02 ± 0.01	2.65 ± 0.35	8.7 ± 1.1	127 ± 17	155 ± 18	136 ± 16
L2 S	8.19 ± 0.49	365 ± 37	11.1 ± 1.3	108 ± 12	256 ± 26	0.006 ± 0.001	0.30 ± 0.11	0.155 ± 0.024	34.6 ± 4.9	15.9 ± 2.6	0.07 ± 0.02	12.90 ± 1.56	9.1 ± 1.0	148 ± 21	181 ± 21	153 ± 20
L3 S	8.28 ± 0.59	258 ± 24	10.8 ± 1.1	104 ± 10	254 ± 24	0.020 ± 0.008	0.24 ± 0.08	0.147 ± 0.018	13.7 ± 1.2	7.1 ± 0.8	0.03 ± 0.01	3.80 ± 0.42	7.1 ± 0.8	105 ± 13	128 ± 15	86 ± 10
L4 S	7.69 ± 0.37	345 ± 33	2.4 ± 0.2	37 ± 8	261 ± 27	0.001 ± 0.001	0.13 ± 0.04	0.140 ± 0.015	23.2 ± 2.6	9.6 ± 11.4	0.01 ± 0.01	1.57 ± 0.18	9.4 ± 1.2	444 ± 50	542 ± 57	311 ± 33
Tisa CT	8.06 ± 0.48	397 ± 38	9.8 ± 0.8	96 ± 11	251 ± 23	0.010 ± 0.004	58.5 ± 3.2	1.450 ± 0.244	35.6 ± 4.3	105 ± 18	0.10 ± 0.02	12.32 ± 1.56	10.7 ± 1.3	187 ± 25	228 ± 24	312 ± 35
L1 CT	7.29 ± 0.33	771 ± 76	6.5 ± 0.6	63 ± 7	228 ± 19	0.002 ± 0.001	0.16 ± 0.03	0.139 ± 0.027	28.6 ± 3.7	32.0 ± 4.6	0.01 ± 0.01	0.68 ± 0.08	18.2 ± 1.9	345 ± 36	421 ± 47	274 ± 29
L2 CT	7.51 ± 0.37	751 ± 73	6.1 ± 0.5	58 ± 8	234 ± 24	0.024 ± 0.011	0.65 ± 0.22	0.172 ± 0.029	27.4 ± 3.2	28.1 ± 3.4	0.01 ± 0.01	2.38 ± 0.27	20.7 ± 2.3	355 ± 42	433 ± 49	276 ± 31
L3 CT	7.62 ± 0.48	605 ± 62	8.2 ± 0.8	86 ± 11	545 ± 58	0.005 ± 0.001	0.87 ± 0.31	0.675 ± 0.089	27.0 ± 3.7	17 ± 2.4	0.02 ± 0.01	2.71 ± 0.32	16.7 ± 1.8	266 ± 28	325 ± 35	218 ± 23
98/83/EC Council Directive	6.5–9.5	2500	-	-	-	0.5	50	0.5	250	250	0.4	<5	>5	-	-	-

3. Results and discussions

3.1. General quality description

In Table 1, the physico-chemical composition of studied water samples is indicated. The mean value of electrical conductivity (EC) ranged between 213 and 1052 $\mu\text{S}/\text{cm}$. A high value of EC (L6 SM) indicates pollution with free CO_2 and also high amounts of dissolved solids [1,33]. EC represents a useful water quality parameter, used in describing the salinity level, and determining the content of dissolved minerals in water [34]. The pH decreases as the water temperature increases, leading to potential negative effects on the aquatic flora and fauna [16]. This indicator is important because it affects the survival of aquatic life [35].

The dissolved oxygen ranged between 2.1 and 13 mg/L. This indicator gives data regarding the microorganism activity, photosynthesis process, nutrients availability, and similarly it indicates the pollution level [34]. Dissolved oxygen varies with different factors, such as the hydrogeochemical, microbiological, physico-chemical processes, air pressure, light, water temperature, salinity, the presence of organic substances, aquatic flora (algae), and nutrients availability [18,34]. A high dissolved oxygen content, low EC, alkalinity, and turbidity, all contribute to the growth of biotic organisms [34]. However, a rise of the algae population as well as in the levels of phosphate, ammonia, and other chemicals favor and trigger the eutrophication process, which lowers the dissolved oxygen content [18]. The exhaustion of the dissolved oxygen from a water body reduces sulfate to sulfide and nitrate to nitrite, which increases the amount of ferrous [34]. This indicator is also significant, due to the susceptibility of preservation and self-purification of aquatic life [18].

Turbidity ranged between 0.68 and 48 NTU, slightly varying per month and areas and maximum in the spring season [36]. A water with high turbidity could cause health issues and it is associated with the presence of plankton, algae, silt, clay, divided inorganic and organic matter [16,18,34]. Turbidity interferes with an adequate process of disinfection of water, due to the smell and taste that will alter and nestling microorganisms, and pathogens [16,18].

Nitrate and ammonium exceed the MACs in samples Tisa CT, L5 SM, L6 SM and L3CT, but generally are lower than 2.0 mg/L NO_3^- and 0.4 mg/L NH_4^+ . Sources of nitrate could be related to the natural and anthropogenic activities, such as the use of pesticides and fertilizers in the agricultural practices [33,37]. Nitrates convert to nitrites and are startup factors of the eutrophication process [18]. The high level of NH_4^+ in sample L6SM are attributed to the practice of agricultural activities. After oxidation, NH_4^+ converts to NO_3^- and NO_2^- in the presence of Nitrobacter and Nitrosomonas organisms [38]. Similarly, the presence in considerable amounts of NH_4^+ indicates a fresh pollution status giving the fact that NH_4^+ is the first product of decomposition of organic matter (NH_4^+ as a plant nutrient, accelerates eutrophication [38]). Waters are characterized by low amount of NO_2^- (lower than 0.12 mg/L). Sources of NO_2^- are represented by the presence of organic matter, after soil leaches into the water body, the use of manure and chemical fertilizers in agricultural practices, organic waste decomposition, mineralization of animals and plants based organic matter, industrial spills, waste leakage [7,18].

The majority of samples are free of PO_4^{3-} . Sample L6 SM has a mean value exceeding two times the MAC. Sources of PO_4^{3-} could be the water-soil interactions, and the presence of organic matter decomposition, suspended solids and fertilizers based on phosphorus [18,22]. High concentrations of PO_4^{3-} , which is linked to organic carbon, and NO_3^- cause the population of plants to grow rapidly, which lowers the dissolved oxygen quantity and kills the fish population [6,38]. The presence of dead fish in water harbor infections that can harm the human health in the cases when the water is used for drinking or other agricultural purposes. Poor concentrations of PO_4^{3-} can be detrimental if consumed, but high concentrations have the potential to affect the digestive tract [39].

The total hardness (H_t) ranged between 6.6 and 20.7 German degrees. H_t is given by the amount of SO_4^{2-} , Ca, Mg, CO_3^{2-} , HCO_3^- . The

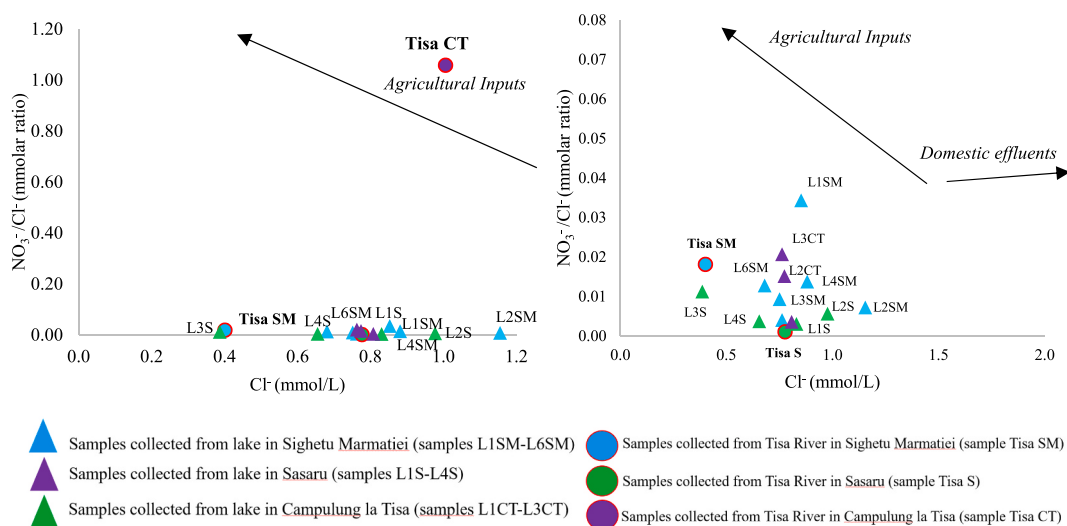


Fig. 2. The correlations between $\text{NO}_3^-/\text{Cl}^-$ and Cl^- applied for the lake samples.

Table 2
The annual median of metals in water samples and guidelines according to 98/83/EC Council Directive.

Sample	Parameters																			
	Na (mg/L)	Ca (mg/ L)	Mg (mg/ L)	K (mg/ L)	Fe (µg/L)	As (µg/ L)	Cr (µg/ L)	Cu (µg/ L)	Ni (µg/ L)	Mn (µg/L)	Pb (µg/ L)	Zn (µg/ L)	Ba (µg/L)	Mo (µg/ L)	Sr (µg/ L)	Ga (µg/ L)	Li (µg/ L)	Al (µg/ L)	Ti (µg/ L)	Rb (µg/ L)
Tisa SM	4.85 ± 0.58	2.41 ±	5.76 ±	1.63 ±	740 ± 68	1.1 ±	1.9 ± 0.2	13.3 ± 1.5	24.6 ± 2.7	31.4 ± 2.9	1.3 ±	155.2 ± 16.1	36.0 ± 4.2	1.6 ±	0.1 ±	13.0 ± 1.5	6.8 ± 0.7	157.5 ± 16.1	5.7 ± 0.6	1.5 ± 0.1
L1 SM	0.03 ± 0.01	0.04 ±	0.09 ±	0.03 ±	100 ± 16	1.5 ±	2.9 ± 0.4	1.7 ± 0.2	4.1 ± 0.3	16.9 ± 2.1	1.8 ±	14.1 ± 1.6	56.0 ± 6.5	1.4 ±	33 ± 4	20.0 ± 2.3	4.8 ± 0.4	23.1 ± 2.6	29.8 ± 3.1	1.6 ± 0.2
L2 SM	7.25 ± 0.81	4.80 ±	6.38 ±	3.84 ±	22 ± 10	1.8 ±	12.5 ± 1.1	1.6 ± 0.3	131.9 ± 9.8	510.1 ± 49.1	1.5 ±	9.4 ± 1.6	64.5 ± 7.1	1.3 ±	274 ± 31	22.7 ± 2.5	5.0 ± 0.5	31.3 ± 3.3	32.3 ± 3.3	1.2 ± 0.1
L3 SM	5.74 ± 0.61	0.05 ±	8.39 ±	2.94 ±	127 ± 17	1.3 ±	1.8 ± 0.3	2.2 ± 0.3	4.9 ± 0.6	65.4 ± 7.1	1.6 ±	11.2 ± 1.3	70.5 ± 6.8	1.2 ±	269 ± 29	24.6 ± 3.2	6.1 ± 0.7	44.9 ± 4.6	35.5 ± 3.6	1.4 ± 0.1
L4 SM	4.50 ± 0.48	3.15 ±	6.70 ±	2.29 ±	152 ± 16	1.2 ±	1.5 ± 0.2	10.2 ± 1.3	1.5 ± 0.2	6.9 ± 0.8	1.7 ±	93.6 ± 11.1	42.3 ± 4.5	1.7 ±	200 ± 21	15.2 ± 1.8	4.6 ± 0.6	38.1 ± 4.1	22.6 ± 2.5	1.7 ± 0.1
L5 SM	5.04 ± 0.52	4.03 ±	7.37 ±	8.58 ±	889 ± 96	2.9 ±	1.4 ± 0.2	15.4 ± 2.1	2.8 ± 0.3	235.2 ± 25.1	1.8 ±	57.4 ± 6.1	127.2 ± 9.7	1.6 ±	245 ± 26	45.0 ± 5.3	4.5 ± 0.5	64.4 ± 6.8	27.6 ± 3.1	1.8 ± 0.2
L6 SM	10.07 ± 1.11	7.36 ±	0.10 ±	0.03 ±	5355 ± 98	5.9 ±	1.9 ± 0.3	7.5 ± 0.9	3.9 ± 0.5	3193 ± 295	1.7 ±	191.3 ± 18.1	92.6 ± 9.6	1.3 ±	435 ± 45	31.4 ± 3.6	7.0 ± 0.8	39.0 ± 4.3	55.1 ± 5.6	26.8 ± 2.8
Tisa S	0.16 ± 0.03	0.06 ±	0.15 ±	0.05 ±	112 ± 16	1.2 ±	1.8 ± 0.3	6.6 ± 0.8	1.7 ± 0.3	21.5 ± 3.2	1.5 ±	62.1 ± 5.9	32.5 ± 3.5	1.5 ±	0.2 ±	11.6 ± 1.4	5.9 ± 0.5	156.3 ± 15.9	1.6 ± 2.1	1.6 ± 0.2
L1 S	9.46 ± 1.05	0.12 ±	6.56 ±	1.98 ±	100 ± 13	1.3 ±	1.6 ± 0.2	2.0 ± 0.4	1.3 ± 0.1	11.9 ± 1.4	1.4 ±	14.7 ± 1.7	36.2 ± 3.9	1.5 ±	218 ± 23	13.2 ± 1.6	3.6 ± 0.5	71.8 ± 6.9	22.7 ± 2.4	1.6 ± 0.1
L2 S	0.12 ± 0.02	3.02 ±	7.41 ±	2.40 ±	199 ± 24	1.0 ±	1.3 ± 0.2	7.2 ± 0.9	1.6 ± 0.2	46.1 ± 5.0	1.5 ±	25.8 ± 3.1	42.0 ± 5.0	1.2 ±	247 ± 26	15.8 ± 1.7	11.6 ± 1.1	212.2 ± 22.3	28.2 ± 2.9	1.5 ± 0.1
L3 S	0.10 ± 0.01	1.76 ±	0.10 ±	0.02 ±	29 ± 3	1.2 ±	1.2 ± 0.1	6.2 ± 0.7	3.9 ± 0.5	12.1 ± 1.5	4.3 ±	42.4 ± 4.6	36.1 ± 4.4	1.2 ±	29 ± 3	13.1 ± 1.5	3.6 ± 0.4	125.2 ± 13.2	17.3 ± 2.1	1.6 ± 0.2

(continued on next page)

Table 2 (continued)

Sample	Parameters																			
	Na (mg/L)	Ca (mg/ L)	Mg (mg/ L)	K (mg/ L)	Fe (μ g/L)	As (μ g/ L)	Cr (μ g/ L)	Cu (μ g/ L)	Ni (μ g/ L)	Mn (μ g/L)	Pb (μ g/ L)	Zn (μ g/ L)	Ba (μ g/L)	Mo (μ g/ L)	Sr (μ g/ L)	Ga (μ g/ L)	Li (μ g/ L)	Al (μ g/ L)	Ti (μ g/ L)	Rb (μ g/ L)
L4 S	9.03 \pm 0.95	0.11 \pm 0.02	0.14 \pm 0.03	2.06 \pm 0.22	34 \pm 4	1.6 \pm 0.3	1.1 \pm \pm 0.1	2.6 \pm \pm 0.5	2.0 \pm 0.3	226.6 \pm \pm 23.1	1.8 \pm 0.3	36.4 \pm 4.1	38.5 \pm \pm 4.1	1.4 \pm 0.1	184 \pm \pm 19	14.2 \pm \pm 1.2	3.5 \pm \pm 0.4	47.8 \pm 5.8	24.4 \pm \pm 2.7	1.4 \pm \pm 0.1
Tisa CT	0.13 \pm 0.03	0.36 \pm 0.41	0.22 \pm 0.04	0.03 \pm 0.01	106 \pm \pm 11	1.3 \pm 0.1	1.6 \pm \pm 0.2	5.6 \pm \pm 0.9	1.3 \pm 0.2	16.5 \pm 1.8	1.4 \pm 0.1	42.1 \pm 4.5	135.8 \pm \pm 9.9	1.5 \pm 0.2	0.4 \pm 0.1	15.3 \pm \pm 1.6	4.9 \pm \pm 0.5	152.2 \pm \pm 15.5	0.9 \pm \pm 0.1	1.5 \pm \pm 0.1
L1 CT	0.07 \pm 0.01	5.71 \pm 0.60	0.08 \pm 0.02	0.02 \pm 0.01	112 \pm \pm 14	1.5 \pm 0.2	1.4 \pm \pm 0.2	4.6 \pm \pm 0.6	2.2 \pm 0.3	57.4 \pm 6.1	1.7 \pm 0.2	37.1 \pm 3.9	129.3 \pm \pm 8.7	1.5 \pm 0.1	401 \pm \pm 38	45.1 \pm \pm 4.6	4.5 \pm \pm 0.6	57.4 \pm 6.0	47.7 \pm \pm 5.1	1.5 \pm \pm 0.1
L2 CT	0.05 \pm 0.02	6.41 \pm 0.67	0.06 \pm 0.01	0.03 \pm 0.02	127 \pm \pm 13	1.3 \pm 0.2	1.6 \pm \pm 0.3	9.9 \pm \pm 1.1	2.0 \pm 0.4	12.5 \pm 1.1	4.0 \pm 0.7	35.9 \pm 3.7	133.1 \pm \pm 9.3	1.6 \pm 0.1	406 \pm \pm 43	46.6 \pm \pm 4.8	4.7 \pm \pm 0.5	28.1 \pm 3.2	51.5 \pm \pm 4.8	1.6 \pm \pm 0.2
L3 CT	0.06 \pm 0.01	4.32 \pm 0.46	9.47 \pm 1.12	0.02 \pm 0.01	152 \pm \pm 19	1.7 \pm 0.3	1.3 \pm \pm 0.1	4.5 \pm \pm 0.7	1.8 \pm 0.2	32.9 \pm 3.5	1.6 \pm 0.1	37.6 \pm 4.1	95.1 \pm \pm 8.8	1.3 \pm 0.1	310 \pm \pm 35	34.0 \pm \pm 3.6	4.4 \pm \pm 0.5	55.7 \pm 6.2	37.5 \pm \pm 4.5	1.6 \pm \pm 0.1
98/83/EC Council Directive	200	100	-	-	200	10	50	100	20	50	10	5000	700	-	-	-	-	200	-	-

water-rock interaction and discharge of industrial residual waters are sources of high H_t [40]. The water's alkalinity (mostly represented by carbonates and hydroxide carbonate) varied between 102 and 536 mg/L, influenced probably by the water-rock interaction [41,42]. This indicator gives the water the ability to neutralize the acid content and it is significant for the aquatic biota, protecting against fast changes in pH [41].

The SO_4^{2-} content varied between 7.1 and 105 mg/L, below the MAC. Polluted waters (domestic and industrial), interactions of water-soil and leaching of minerals are direct sources of SO_4^{2-} [1].

The average content of Cl^- ranged between 13.7 and 41 mg/L, mainly below the MAC. Natural and anthropogenic processes enrich the waters with Cl^- . The natural sources are represented by dissolution of magmatic rocks, while the applied industrial, agricultural (animal feces and urine), and household activities are the practice of anthropogenic activities responsible for the Cl^- enrichment [5, 39]. All natural sources of Cl^- in water include the use of gypsum fertilizers, wastewater treatment, and rock water interaction [32].

According to Fig. 2, there are no anthropogenic sources of Cl^- and NO_3^- , except in the case of Tisa CT sample, characterized by agricultural inputs. The agricultural inputs were indicated by the high content of NO_3^- , exceeding the MAC established by the Council Directive 98/83/EC (1998) concerning the quality of water [43].

For rest of the samples, the anions pursuit from natural sources, after the rock-water interaction, mixing with groundwater or surface water or as effect of the nitrification process.

In Table 2, the metal content is presented together with the maximum allowable concentrations according to the 98/83/EC Council Directive [43]. Because they are resistant to oxidation, degradation, and chemical-biological processes that convert them into less harmful components, heavy metals remain persistent in the environment. Heavy metals can pose serious risks to the environment at concentrations higher than those that are considered safe, even if many living things would benefit from certain amounts of these metals. Potential indicator of pollution is represented by the metallic bond in organic phases, sulfide, and carbonate [44]. Ni, Pb, Fe, Hg, T, Cd, Cr, Cu are among the potentially hazardous substances that are frequently discharged by thermal power plants, electroplating companies, metalworking companies, and mining operations [45]. The heavy metals once inherit in the body, do not decompose but accumulate in the soft tissues, affecting the fish health and finally the human health through the food chain [46]. It was observed that metals emitted through anthropogenic activities are associated to organic matter and Mn/Fe oxides, through chemical adsorption, complexation and ion exchange [9]. Mean values of Fe exceed the MAC (200 $\mu\text{g/L}$) in samples Tisa SM, L5SM and L6 SM, probably due to water-rocks interaction or contact with groundwater rich in Fe [46]. Fe participates in the photosynthesis process, as part of the reactive redox Fe-sulfur center and also reduces nitrogen to ammonia [20]. Mn is present in relatively high amounts (L3CT), possibly due to its geological abundance, dolomitic rocks and limestone respectively [5]. Fe levels are in the range of 22–5355 $\mu\text{g/L}$ and are mostly caused by the weathering processes of granite, gneiss, and tourmaline as well as the metal alloys industry. In the crust of the Earth, iron is one of the most prevalent metals [47]. Leaching of wastewater from discarded waste and weathering of iron-rich rocks into the aquifer system are two potential sources of iron in water resources [48]. Manganese levels were higher than the MAC in the case of lakes. Mn originates from mining, agriculture, and industrial processes such as the usage of fungicides, fertilizers, and pesticides, as well as the production of alkaline batteries and cleaning goods [49]. This is justified since Maramures County is very rich in metalliferous ores (gold, silver, manganese, copper, iron) and has a long history of mining [50]. Manea et al. [51] identified Mn as the most prevalent heavy metal the soil of Maramures County. The contamination of lakes with Mn can be anthropogenic and geogenic [52].

The highest values of Na were obtained in sample L6SM, indicating interchangeable cations between water and clay, caused by dissolution and infiltration of silica salts emitted by anthropogenic activities [53,54]. Water rich in Na is not required for irrigation due to the development of alkaline affecting the soils [4]. Na can be removed by ionic change, inverted osmosis and distillation [36]. Persons affected by cardiac and renal disorders require water with low amount of Na, consequently if used with the drinking purpose, those water sources need treatment [53]. Potassium ranged between 0.02 and 8.58 mg/L. K represents an essential element in plant

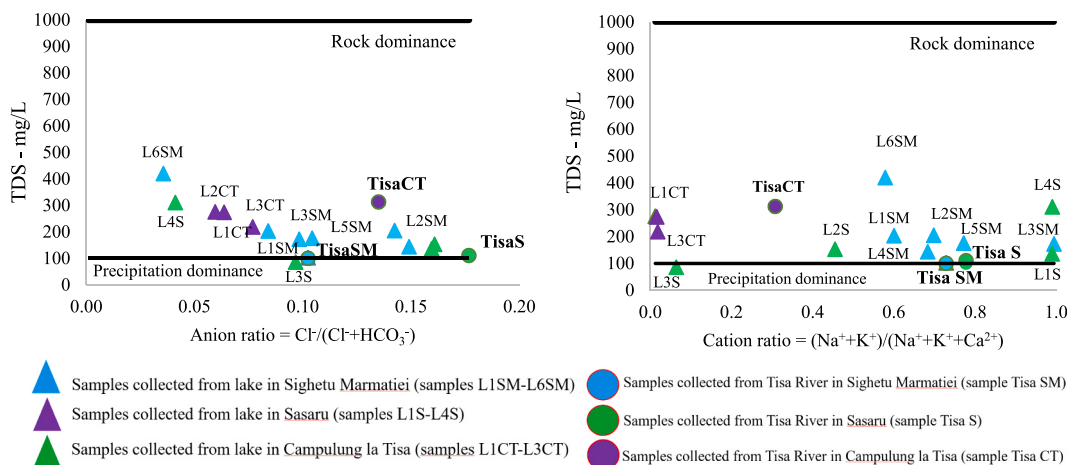


Fig. 3. Gibbs diagram applied for the lake and Tisa samples.

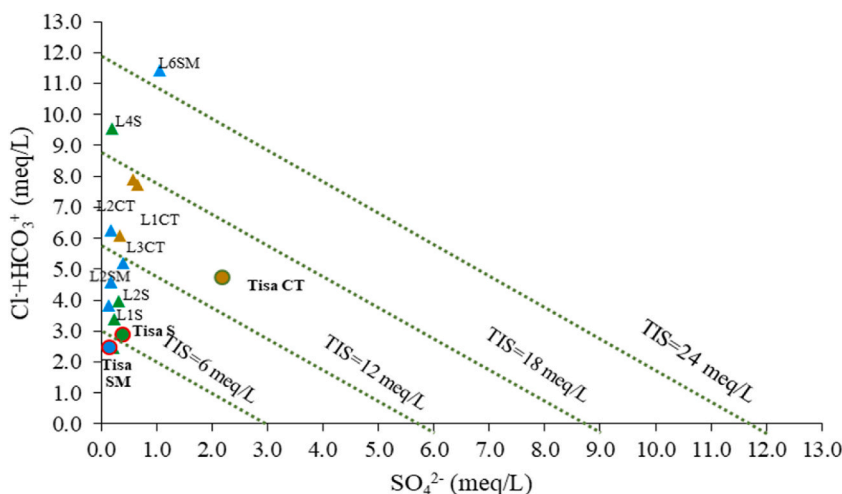


Fig. 4. TIS (total ionic salinity) diagram applied for the lake and Tisa samples.

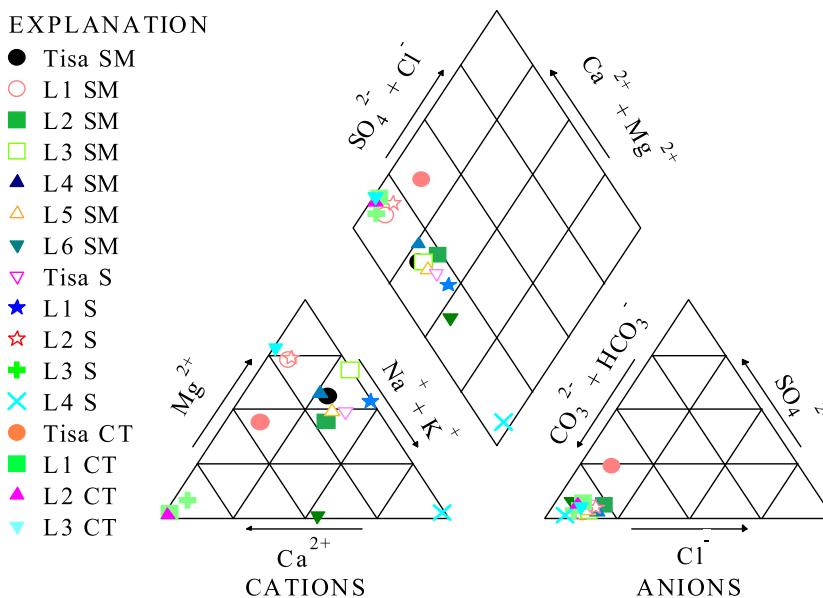


Fig. 5. Piper diagrams applied for lake and Tisa samples.

and human alimentation. The dissolution of minerals is responsible for the occurrence of K in water systems [53].

Ba, Li and Sr ranged between 32 and 135 $\mu\text{gBa/L}$, 3.5–11.6 $\mu\text{gLi/L}$ and 0.1–435 $\mu\text{gSr/L}$ respectively. These elements inhibit phytoplankton development. The significant amount of Li showed strong water/rock interactions [20]. The processes controlling Ba’s absorption, dispersion, and detrimental effects on species are poorly understood, contributing to the complexity of the compound’s ecological consequences. In this case, the presence of carbonate or sulfate must be considered because they tend to reduce Ba’s bioavailability [55].

The presence of Ba may be attributed to Mn-rich sedimentary rocks, volcanic rocks, alkaline igneous, and granite [56]. Geological variables, such as the makeup of the subterranean rocks, which might have higher strontium concentrations, could be the cause of the changes in Sr. Sr may replace Ca and Mg in bones, which could affect the strength and growth of the bones [57,58].

Ca ranged between 0.04 and 7.36 mg/L , obtained after CO_2 attack of calcareous rocks; calcium salts are the main cationic elements of surface water bodies [5]. Sources of Ca in water are represented by industrial wastewaters, and limestone [56]. High amounts of Mg increase the development of exchangeable Na, which could be harmful for irrigation [5]. Water in areas with acidic rocks and soils may naturally contain Al or it may be contaminated by Al salts used to clean wastewater, restore lakes, and purify drinking water [59]. Water is enriched with B and Li by the presents of colloids, granite intrusion and through the process of water-rock interaction [60]. Ga has no established MAC, although it is characterized by moderate toxicity, and plays a non-decisive role in the biological cycle [56].

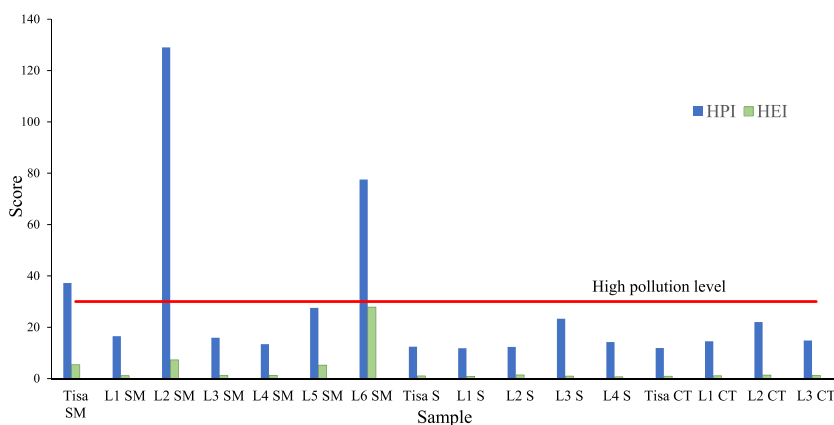


Fig. 6. HPI and HEI scores for the studied samples.

The sources of As found in sediment and water include both anthropogenic (metal processing, fossil fuels combustion, the use of fertilizers and pesticides) and natural (weathering of clay minerals, atmospheric precipitation) processes [50]. Arsenic is a tasteless, odorless, and poisonous pollutant that is frequently present in high amounts in water. Geological factors, which are frequently common in rural areas, can cause naturally existing arsenic in aquifers.

Cu is an essential nutrient for aquatic biota, it is part of the enzyme activities, related to the protein synthesis and chlorophyll occurrence [36]. Although not all Cu species are bioavailable, dissolved Cu is correlated to the sediment phase Cu. The intense occurring of industrial, agricultural and mining activities, and rock degradation increase the amount of Cu [58]. Cu is released in water after chemical reaction including bornite, chalcocite present in the natural bedrock of the aquifer [46]. Low temperatures and lack of disturbance increase the adsorption of Cu in the surface of sediments. Sources could be related to the use of herbicides and algacides based on Cu [19].

Cr ranged between 1.1 and 12.5 $\mu\text{g/L}$, varying below the MAC. Relatively high amounts could influence and inhibit the plants development [20]. In water ecosystems, Cr exists in different forms with different mobilities. Cr^{6+} is toxic and strong, while Cr^{3+} has a certain bioavailability and is weaker than Cr^{6+} [20]. Cr is commonly found in the environment in chromite and magnesiochromite ores, and also in the volcanic emission, soil, rocks, animals and vegetation [52,61].

Pb concentrations are below 10 $\mu\text{g/L}$, ranging between 1.3 and 4.3 $\mu\text{g/L}$. The transport of Pb from the catchment to the lakes was accelerated by erosion [23]. High amounts of Pb affect the assimilation and fixation of carbon, negatively affect the reaction center of phytoplankton cells and prevent the photosynthetic electron transfer processes [20]. Sources of excess of Pb in the water are mainly the wastewater discharges, indiscriminate garbage disposal, construction, vehicle exhaust, metal alloy, batteries in mechanic shops, industrial facilities, and the use of fertilizers [61,62]. Pb is much more harmful than the other heavy metals when it bioaccumulates. The main human activities that cause enrichment water sources in Pb include careless rubbish disposal, electronic device waste, and battery use in auto repair shops, air conditioning units, and industrial operations [61,62].

Within the present samples, the lowest Zn concentration is 9.4 $\mu\text{g/L}$, while the highest is 191.3 $\mu\text{g/L}$. The accumulation of Zn in sediments is considered the primary source of water enrichment in Zn [63]. The main anthropogenic sources are represented by waste-fired power plants, fertilizer in agricultural fields spin-offs from steel production [47,48,64]. When Zn concentrations increases over time, they may reach levels hazardous to species living in the sediment, especially macroinvertebrates. Mobility is mostly affected by pH, while other variables such the concentration of organic matter, phosphorus availability, redox conditions, and clay content also matter [57,59].

The most typical Ni compounds are hydrous nickel silicate (granite) and nickel ferrous limonite, frequent sources of Ni pollution include discarded batteries, power stations, the glasses and ceramic materials industry, color manufacturing companies, and trash manufacturing [52]. The water pH and depth, the presence and interaction with ultra-mafic and mafic rocks and soil are significant in the enrichments of water in Ni, as well as pigments manufacturing, Ni alloy production, and water discharge from tannery processes [57].

3.2. Water typology

Gibbs diagram indicates three distinct fields, namely evaporation, precipitation and rock-water interaction dominance areas [30]. According to Fig. 3, the majority of studied samples fall into the rock-water interaction dominance. This indicates that the chemistry of waters is related to the water-rock interaction. Sample L3S is the only sample characterized by precipitation dominance, due to the low value of the TDS, while samples Tisa SMA and Tisa S are at the edge of the two typologies.

In order to determine the salinity of waters, TIS diagram was applied and interpreted (Fig. 4). Based on the diagram, generally the total ionic salinity is below 24 meq/L, except in one sample (L6SM). Samples have a TIS ranging between 6 and 18 meq/L, while samples Tisa SM, Tisa S and L3S have a TIS below 3.0, due to the low amounts of Cl^- and HCO_3^- .

According to Piper diagram, implemented with the help of GW_Chart v 1.29.0.0 software, similarities between the water samples

are indicated. The plot is generally dominated by CaCO_3^{2-} chemical character, except samples L6SM and L4S (Fig. 5). L6SM is included in the mixed Ca^{2+} - Na^+ - HCO_3^- typology and L4S in the Na^+ - HCO_3^- typology. In the triangular field concerning the anions amount, all samples are characterized by a $\text{CO}_3^{2-} + \text{HCO}_3^-$ chemical character. The cationic field is dominated by alkaline earth metal, Mg, exceeding the alkali metals in the majority of samples except for L3S, L1CT and L2CT (dominated by Ca) and L4S (Na + K type). Sample L3S is the only sample with precipitation dominance due to the low value of the TDS. Samples Tisa SMA and Tisa S are characterized by a mixture concerning both typologies.

3.3. HPI and HEI

Giving the presence, and the high amounts of heavy metals in the studied water samples, comparison with Regulation concerning the water quality is not sufficient. Therefore, different heavy metal pollution indices are applied with the aim of determining the overall heavy metal contamination in the water systems [65]. Applying HPI, for example, the composite influence of heavy metals on the aquatic system is indicated, categorizing the studied waters on different quality status [65,66]. In this study, HPI and HEI were calculated based on the As, Cr, Cu, Fe, Ni, Pb and Zn concentrations. The standard values (Si) for each heavy metal were used according to the 98/83/EC Council Directive concerning the quality of water. The HPI and HEI scores are indicated in Fig. 6. HPI scores ranged between 11.8 and 129. This implies that 10% of samples, especially lakes, are classified into the high pollution category. This observation is associated to the significant concentrations of As, and six times exceeded MAC related to the Ni amount. The MAC of Fe was exceeded as well up to four and twenty-six times. Samples L2SM, L6Sm and Tisa SM were characterized by high pollution level; where HPI scores ranged between 37.2 and 129. Those pollution statuses could affect the biotic life and implicitly the human health, if the water is used for irrigation of crops or used directly as drinking water sources [65,66]. Contaminated waters after ingestion could cause serious negative health issues especially in infants, children and inhabitants with diverse diseases. Further studies concerning risk assessment at heavy metal exposure need to be implemented in order to conclude the status of heavy metal pollution which characterize the studied water samples situated in a protected area.

A percentage of 40% of the studied water are characterized by a medium polluted level with the heavy metals of interest, and 50% of samples present low pollution level with the studied heavy metals. It was observed that the lowest scores were obtained for samples Tisa S, Tisa CT and L1S-L4S, L1CT-L3CT. Sample L1S was characterized by the lowest score (11.8), followed by Tisa CT (11.9), L2S (12.3) and Tisa S (12.4). Those assumption are corelated with the lower amounts of heavy metals. In other studies, conducted in Romania (Rodnei Mountains), lakes are characterized by lack of metal pollution with the HPI scores ranging from 5.2 to 28. The obtained scores are corelated to the low amounts of heavy metals, which are below the MACs [67]. HPI was calculated based on the As, Cd, Cu, Mn, Pb, Zn, Ba and Se concentrations. Different studies in India (Nainital town) and Malawi (southern part) indicated that the studied lakes are not contaminated with metals, the pollution status being determined with the help of the HPI [67,68]. In Haridwar region, Ganga River, a significant water resource for the inhabitants was characterized by the HPI scores. Based on the study results, the quality of the irrigation water and human health are vulnerable and at-risk giving metal pollution [69]. In Bangladesh, due to the intense industrial activities, more than 80% of the studied surface waters have high level of pollution with heavy metals. HPI scores exceed 1000, indicating serious contamination with heavy metals [70].

HEI scores obtained in the present study are correlated to the HPI scores, indicating three pollution levels (low, medium and high). The results were ranging between 0.7 and 28, as indicated in Fig. 6. The highest value was obtained in L6SM as well due to the high amount of As, Fe and Zn. In other and different studies from Romania (Rodnei Mountains), HEI scores ranged between 0.55 and 5.07 revealing as well a low level of pollution with heavy metals [54,71]. This tool is successfully applied in other parts of the world. In China, for example, river samples were characterized by the HEI, with scores below 2.0, as poor or slightly affected. The potential sources of heavy metal include beside natural resources, agricultural, industrial, and domestic activities, waste emissions, and traffic sources [71]. On the other hand, in Bangladesh, due to the discharge of industrial effluent, surface water presents high content of heavy metals, which imply HEI scores exceeding the threshold limits, ranging between 0.51 and 257 and characterized the samples in high pollution with heavy metals [70].

The significant constituents that contribute to the HEI and HPI values in our study are represented by the As, Fe, and Ni amounts measured in the studied water samples. Based on the potential negative impacts on the environment, and implicitly on the human health, applying restrictions concerning the use of water in household activities, and agricultural practices are mandatory. Also, further studies implying human health risk assessment at heavy metals exposure through water ingestion and dermal contact are mandatory.

4. Conclusions

In the present research, chemical characterization and mathematical models were used in order to investigate the quality and potential pollution status of lakes and Tisa River situated in the protected area of Tisa, Romania. Water-rock interactions and the influence of precipitation were determined with the help of Gibbs diagram and salinity levels lower than 40 meq/L, according to the TIS (Total Ionic Salinity) plot. The studied water samples were classified into three types (CaCO_3^{2-} , mixed Ca^{2+} - Na^+ - HCO_3^- and Na^+ - HCO_3^-), demonstrating the correlations concerning the water rock interactions identified with the help of Gibbs plot. From the perspective of chemical composition, the findings showed that the studied lakes had a medium quality, as evidenced by the high concentration of NH_4^+ in sample L6SM and the significant amounts of Al, Fe, Ni, and Mn that, in the cases of some samples, respectively, exceeded the maximum acceptable concentrations (MACs). Those high amounts of toxins may be associated with negative impact on human health generated by the use of untreated waters. Generally, the water quality was good, with the pH in normal range, adequate

electrical conductivity and high degree of oxygenation. The scores related to the heavy metal pollution indices indicated values ranging between 11.8 and 129 (HPI), and between 0.7 and 28 (HEI), respectively. HPI and HEI scores revealed three pollution categories, namely high, medium and low pollution levels with studied heavy metals (As, Cr, Cu, Fe, Ni, Pb and Zn). Results indicated that the anthropogenic pressure manifested in various forms, such as the intense agricultural activities, traffic, the area itself, gravel and sand activities, the presence construction waste. This anthropic pressure could lead to the transfer of chemicals from water to crops or fish and finally to animal and human bodies, and potentially influence and alter the human health. Further studies on this theme are in progress. Understanding the human impact on lake ecosystems is crucial for conservation and sustainable resource management, which is possibly made by this multidisciplinary study. Because it demonstrates how shepherding grazing and tourism-related activities are causing the quality of the water to deteriorate, this study is helpful to local authorities responsible for managing water resources. Some steps have already been done, such as encouraging the locals to engage in extended traditional activities (hand mowing, rational grazing, or proper cutting) in an environmentally responsible manner.

Data availability statement

Not applicable.

CRediT authorship contribution statement

Thomas Dippong: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Maria-Alexandra Resz:** Writing – review & editing, Writing – original draft, Software, Resources, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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