Speciation of Dissolved Ferrous and Ferric Iron in Catamarasti Lake, Botosani (Romania)

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Abstract*. The aquatic chemistry of iron involves many environmental aspects because dissolved iron is present as ferrous and ferric ion and the equilibrium between these two forms depends on many natural or antropogenic factors. This paper aims to provide a brief introduction to chemistry of iron in an oligotrophic lake, a new topic in this domain. A number of 28 sampling were taken from Cătămărăşti Lake, Botoşani (Romania). The main physico-chemical properties showed that the acidity, dissolved oxygen, electrical conductivity and saturation satisfied the water quality criteria for this ecosystem. The results for dissolved iron species indicated that there is no strictly correlation with the variation of oxygen content. Thus, for the samples from NE shore, the contents of ferrous iron are bigger than of ferric iron, for the samples from SW shore the contents are almost equal, because of the low contents of oxygen. For the samples from the middle and from downstream of the lake, the contents of ferric iron are bigger than of ferrous iron, due to the oxygen content recorded.*

Keywords*: ferrous iron, ferric iron, Cătămărăşti Lake, Romania*

1. Introduction

Generally, trace metals in the environmental components are present in small concentrations, but they have a great impact on biological life because they are involved in different chemical forms. Iron (Fe) is a micronutrient for all organisms and it is involved in numerous metabolic processes, like an essential element [1]. In the Earth's crust, iron is the fourth abundant chemical element, after oxygen, silicon and aluminium, its abundance being approx. 5% [2, 3]. Nativ iron is very rare, even if it is present in many places. Most iron minerals are very dispersed in natural systems (soil, water, atmosphere) and the iron concentration varies considerably. Its concentration is proportionally to the low solubility of minerals and is ranking from 10^{-11}M in ocean water to 10^{-6} M in river water [1, 4].

In aqueous environments, speciation of iron involves species such as Fe(II) (ferrous iron), Fe(III) (ferric iron), organic/inorganic iron complex, colloidal iron and particulate matter with iron [4]. The most common species of iron in water are goethite, lepidocrocite and hematite, while the composition of amorphous solid phase is not clear, because the transformation of minerals into crystalline forms is very slow process [5]. Iron is an important biological and geochemical trace element in the coastal area, with an important role in river transportation of matter [1]. The mobility of iron in surface water has gained large attention, with the accurate determination of the cation, because iron is an environmental monitor. The determination of iron species in natural water is a challenge because of its low concentration or its slow biodisponibility and consequently, the techniques for iron determination have evolved in the last decades. It has been shown that not only low concentrations but also low bio-availability of iron may limit the biological life of surface waters [6]. Nowadays, many analytical methods had been developed for determining iron concentrations.

In soils, iron speciation is governed by some minerals, like iron sulphides (pyrite, pyrrhotite, marcasite) or iron oxy-hydroxides (ferrihydrite, goethite, hematite, lepidocrocite), which influence the biogeochemistry of soils [7]. It is well known, that iron is a major component of many soil-forming parental materials and consequently, primary or secondary Fe-minerals are well represented in most soils [8]. Because most iron minerals are coloured, its presence in solid phase is a measure of pedogenetic processes, like podzolisation or gleysation [9]. However, few informations still exist about iron

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speciation in specific environments, such as sediments, streams or lake waters, where iron concentration limits a compositional characterization [10]. Nowadays, as a consequence of the importance of Fe-minerals in soils, sediments and waters, its identification in geologic materials remains a target of researchers in the field, even if the knowledges about the multiple forms of iron are still limited. The complexity of Fe speciation is questionable on how to interpret iron chemical aspects and what environmental parameters control its chemical behaviour.

This study aims to determine iron species concentrations in Cătămărăști Lake, Botoşani County and its surroundings, an oligotrophic lake, in the northeastern part of Romania. The paper affords the basic elements for a better understanding of the chemistry principles which control lake water and illustrates the use of the theory to explain observed characteristics of Cătămărăști Lake.

2. Materials and methods

The amount of iron from surface lakes is low, due to the hydrolysis of Fe(III), a process that generates the major inorganic iron colloids in oxic waters. Because of these low inputs, most of the iron is taken up by the organisms of the lake for biological regeneration. A study of the hydrolysis species of iron ($Fe(OH)_2^+$, $Fe(OH)_3^0$ or $Fe(OH)_4^-$) was realized by Gelting-Nystrom (2004) [11]. Most of the iron present in Cătămărăști Lake comes from the interaction between the mineral substrate with the water and not from the interaction with the atmospheric air.

Cătămărăști Lake (an oligotrophic lake) is located on Sitna River, near to Mihai Eminescu village, Botoşani County, Romania. The location of the lake is presented in Figure 1. With an area of 270 ha, length is 540 m, height 14.5 m, Cătămărăști Lake has a useful volum of 7.5 mil. cubic meters of water, being included in the second class of surface water quality [12].
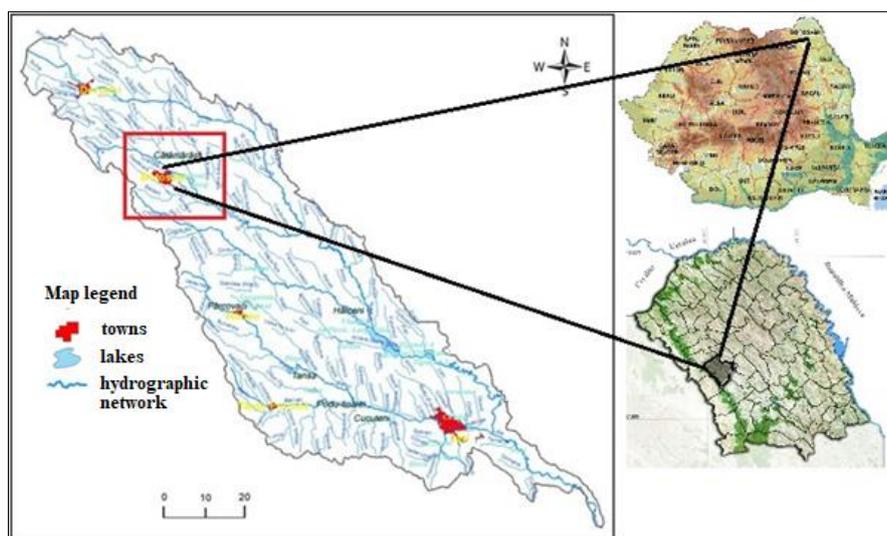

Figure 1. Map of the studied area, with the position of
Cătămărăști Lake (Botoşani County, Romania)

Consequently, iron in Cătămărăști Lake water has complicated chemistry, being present in two major oxidation states, namely ferrous and ferric iron, besides numerous colloids and hydrolysis species. Divalent iron is stable in reduced conditions, oxygen-free environments (in sediments, deep waters, groundwaters), while trivalent iron is stable in oxygen-rich and pH-neutral environments [11]. Ferrous iron predominates in soluble form (Fe^{2+}_{aq}), but also like precipitate ($Fe(OH)_2$), while ferric iron exists in numerous complex and ionizable forms, but also like precipitate ($Fe(OH)_3$). The iron speciation and its bio-availability are given by the chemical processes between these two major species and the physico-chemical conditions of lake water [13]. In order to evaluate the iron content of Cătămărăști Lake, a number of 28 samples of water (November 2014) were taken from four sections: NE shore (samples

from 1 to 10), SW shore (samples from 11 to 20), middle of the lake (samples from 21 to 26) and the bottom emptying of the dam-downstream (samples 27, 28) (Figure 2).

Figure 2. Location of water sampling for Cătămărăşti Lake
(Botoşani, Romania)

Sampling was performed by boat, both on the edge and on the middle of the lake, 10-20 cm below the water surface, at distance of approx. 100 m (on the edge) and 200 m (on the middle) respectively, between samples. The last two samples (27 and 28) were taken downstream. The sampling activity was carried out in 500 mL polyethylene bottles, which were washed twice with double-distilled water and were completely filled with water, in order to avoid the oxidation process. The samples were kept at low temperature until the analysis time. The main physico-chemical parameters were measured during the sampling, using a Multiparameter Water Quality Sonde YSI 6920 V2 (UK): pH, dissolved oxygen ($mg \cdot L^{-1}$), saturation (%), temperature (°C), conductivity ($\mu S \cdot cm^{-1}$). Chemical analysis of iron contents was carried out in the laboratory, with 1,10-phenanthroline monohydrate (form Sigma-Aldrich, Germany), using a Spectronic 301 spectrophotometer (Electronics India) [14, 15]. For the determination of Fe (II) in samples, it was used 1,10-phenanthroline (0.1% aqueous solution), to form a red-orange complex, with a maximum absorbance at 540 nm (each sample was done in duplicate). The interfering effect of Fe (III) was suppressed by masking with complexones. Further on, ferric iron in water was first reduced with hydroxylamine hydrochloride, 10% aqueous solution (Sigma-Aldrich, Germany) to ferrous iron and total iron content was determined with also 1,10-phenanthroline. The content of Fe (III) was determined by the difference between total iron and ferrous iron.

3. Results and discussions

In order to reach a better view on the physico-chemical parameters, the results of water quality from Cătămărăşti Lake are discussed below. The values of minimum, maximum, average and standard deviation of parameters are presented in Table 1. The obtained values for chemical parameters are in the acceptable levels in Romania.

Table 1. Statistical summary of water quality data for
physico-chemical parameters

Parameter	Min.	Max.	Average	Std. deviation
pH	8.51	8.80	8.59	0.050
Temperature (°C)	7.66	7.96	7.80	0.070
Dissolved oxygen ($mg \cdot L^{-1}$)	10.79	11.93	11.19	0.269
Saturation (%)	90.70	100.8	94.17	2.334
Electrical conductivity ($\mu S \cdot cm^{-1}$)	420	452	424.81	7.076

Surface water acidification caused by acidic deposition or anthropogenic activities influenced the biological life of lakes, therefore, *p*H is an important parameter for understanding the surface lake geochemistry [16]. The *p*H scale ranges from 0 to 14, with a neutrality point at *p*H=7: samples with a *p*H value below 7 are considered acidic, while samples with *p*H above 7 are alkaline [17]. The water can be acidic or alkaline in *p*H, depending on the layers of rock it comes in contact with: the limestone or dolomite layers in the soil can neutralize the acid and the water is alkaline (*p*H 7 - 8 or more) [17]. Surface water acidification can influence the solubility of chemical constituents (nutrients, heavy metals) or aquatic life of animals or plants [17].

GIS software can be used to generate a spatial distribution of parameters, using Kernel interpolation to calculate the density of features around each analyzed point. The variation of *p*H level (Figure 3) ranged from 8.51 to 8.61 (with an average of 8.56) on the NE shore, from 8.58 to 8.61 (with an average of 8.59) on the SW shore of Cătămărăști Lake, while on the middle of the lake, the variation of the acidity ranged from 8.58 to 8.63.
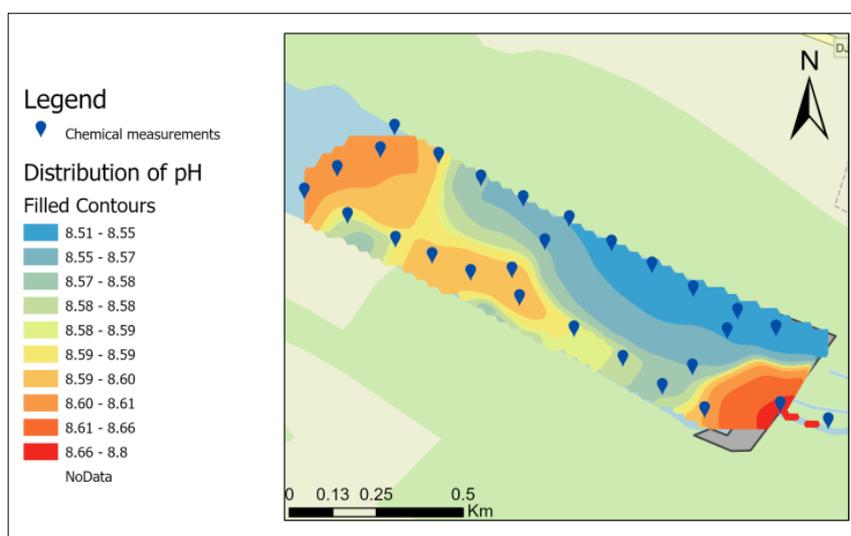

Figure 3. Spatial distribution of *p*H values in Cătămărăști Lake, Botoşani, Romania

The maximum value of *p*H is reached by the two samples from the downstream of the lake, which was 8.70 and 8.80, respectively. The highest values of water *p*H, probably, is caused by the geological conditions, by the interaction between planktonic algae growth and the change of dissolved oxygen content in the process of eutrophication [16, 17]. The analysis showed that the *p*H variation ranged from a minimum value (8.51) to a maximum value (8.80), which satisfied the water quality criteria for the aquatic ecosystem of Cătămărăști Lake.

Dissolved oxygen is an essential component of aquatic systems since it controls biological life and water quality. Lake biota needs oxygen from the atmosphere to survive. Oxygen level depends on whether water is flowing or not and changes with depth. In all lakes, oxygen is generally low at the bottom, where water meets the lake sediment or mud and where bacteria or animals live or breathe in these places [18]. The oxygen evaluation in a water lake is measured directly in the water as $mg \cdot L^{-1}$ or as a percent of dissolved oxygen (%). The values of dissolved oxygen (Figure 4) ranged from 10.99 $mg \cdot L^{-1}$ to 11.35 $mg \cdot L^{-1}$ (with an average of 11.13 $mg \cdot L^{-1}$) on the NE shore and from 10.79 $mg \cdot L^{-1}$ to 11.31 $mg \cdot L^{-1}$ (with an average of 11.01 $mg \cdot L^{-1}$) on the SW shore of the lake.
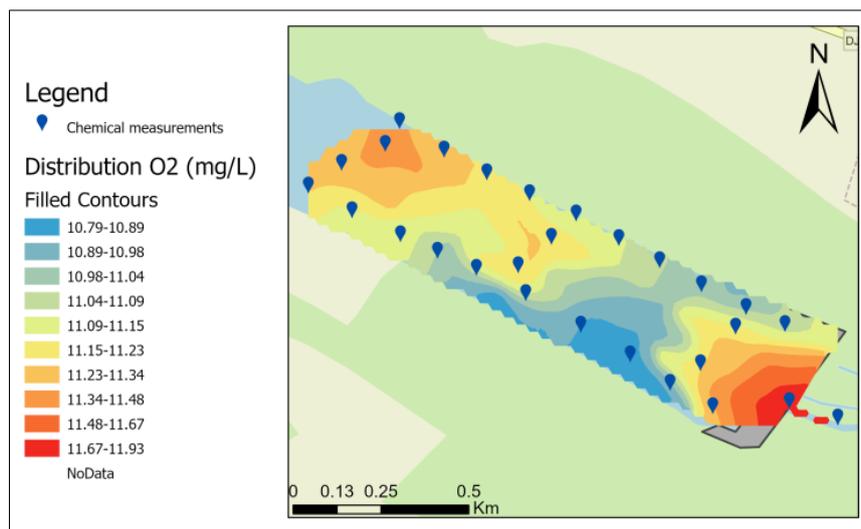
Figure 4. Spatial distribution of dissolved oxygen (mg·L^{-1}) in
Cătămărăşti Lake, Botoşani, Romania

In the middle of the lake, values ranged from 11.19 mg·L^{-1} to 11.52 mg·L^{-1} (with an average value of 11.38 mg·L^{-1}). Interesting results were obtained for the value from the downstream of the Cătămărăşti Lake, greater than the values obtained for the lake (11.93 mg·L^{-1} and 11.77 mg·L^{-1}, respectively). The modification of temperature influences total dissolved oxygen, in a way that the amount of dissolved oxygen will be greater in cooler waters than in warmer ones [16]. The measurements showed that the temperature ranged from 7.66°C to 7.97°C, while the mean value of dissolved oxygen is 11.19 mg·L^{-1}.

During the working period, the measurements showed variations in oxygen saturation from 90.70% to 100.80% for all the samples. Percent saturation of dissolved oxygen ranged from 92.5% to 95.6% (with an average of 93.74%) on the NE shore and from 90.7% to 95.4% (with an average value of 92.69%) on the SW shore of the lake. In the middle of the lake, the values are greater, meaning the interval ranged from 94% to 97% (with an average of 95.64%). Also, the values from the downstream of the lake were 100.80% and 99.4%, respectively.

The electrical conductivity (EC) represents the ability of an aqueous solution to conduct the electric current, depending on the concentration of dissolved salts or gases and on colloidal suspension [19]. This property is directly related to the concentration of ions from the samples, ions which come from dissolved inorganic materials (such as chlorides, sulphides or carbonates) [20]. Surface water EC measurements were nearly constant in the perimeter of Cătămărăşti Lake, with values ranging from 420 µS·cm^{-1} to 452 µS·cm^{-1} during the day. The electrical conductivity ranged from 421 µS·cm^{-1} to 432 µS·cm^{-1} (with an average of 423.6 µS·cm^{-1}) on the NE shore and from 420 µS·cm^{-1} to 425 µS·cm^{-1} (with an average of 422 µS·cm^{-1}) on the SW shore of the lake. In the middle of the lake, the values were similar, meaning they ranged from 423 µS·cm^{-1} to 426 µS·cm^{-1} (with an average of 423.8 µS·cm^{-1}). The values from the downstream of the lake respect the same rule, these were again greater than the rest of the values, 441 µS·cm^{-1} and 452 µS·cm^{-1}, respectively. The low values of conductivity can be correlated with lower water temperature during November, meaning a lower solubility of ionizable compounds or dissolved ions.

Iron has an essential role in many metabolic processes and all the biological activities in aqueous environments are affected by this element. It is not a toxic element but becomes toxic when is accumulated, especially as a free ion [21]. The problem of the toxicity of ferrous and ferric iron has not been clarified. Generally, Fe(II) is more toxic than Fe(III), because it may cause cell degeneration [22]. The ability of ferrous iron to oxidize to ferric iron is widely presented in the literature, namely for redox reactions in natural systems [13, 23]. In reducing conditions (redox potential under 0.20 V and relatively low *p*H, under 6) ferrous iron is permanently stable. As the water dissolves oxygen from the air, instability equilibrium appears between these two species and ferrous iron is oxidized to ferric iron [22].

In many natural water systems, oxygen modifies the state of Fe(II) to Fe(III). In the *p*H range 5 to 8, the total amount of ferric iron is either complex species or ferric precipitate. The speciation of iron in natural waters depends on its oxidation state, its solubility or the formation of complex combinations [11]. The ratio between Fe(II)/Fe(III) ions in waters depends on the redox state, light, *p*H and organic matter (humic acids or organic ligands) from the environment [21]. Ferrous iron is unstable in waters and is rapidly oxidized to ferric iron, process which is accelerated by microorganisms, trace metals, phosphates or oxides [21, 23]. The presence of colloidal matter or sulfate, nitrate and chloride ions may contribute to stabilizing of ferrous iron. Contrary, organic complexes of Fe(III) can be easier reduced by UV light to Fe(II) [23].

Very low concentrations of iron ions in Cătămărăşti Lake and its reactivity represent a challenge for the redox speciation measurements and therefore the ideal methods would be the *in-situ* determination of iron content, with minimal manipulation of the samples [24, 25]. Organic matter is known to be able to reduce iron (III) to iron (II) with high efficiency. Iron (II) is present in the hydrated ion form if it is not strongly bound to natural organic matter, while iron (III) has different chemistry. It has low solubility and it easily precipitates like oxides or hydroxides and presents a very high adsorption capacity due to their high surface area [13, 23, 26]. The variation of the observed oxygen content did not strictly reflect in the ferrous or ferric ions content in the Cătămărăşti Lake. The spatial distribution of dissolved iron content in the analyzed area is presented in Figure 5.

For ferrous iron and ferric iron contents, the results showed that:

- on the NE shore of the lake, values of ferrous iron (mean value 0.320 mg·L^{-1}) are bigger than the values of ferric iron (mean value 0.155 mg·L^{-1}). In this area, the concentration of ferrous iron ranged between 0.265-0.374 mg·L^{-1}, while the concentration of ferric iron ranged between 0.0604-0.229 mg·L^{-1}.

- for the samples from SW shore of the analyzed area, the first samples have more ferrous iron than ferric iron and the last samples have more ferric iron than ferrous iron. Mean values for all the samples are almost equal (0.273 mg·L^{-1} for Fe^{2+} over 0.228 mg·L^{-1} for Fe^{3+}). Ferrous iron concentration ranged between 0.229-0.326 mg·L^{-1} and ferric iron concentration ranged between 0.132-0.302 mg·L^{-1}.

- on the middle of the lake, ferric iron predominates (mean value 0.320 mg·L^{-1}) over ferrous iron (mean value 0.245 mg·L^{-1}). For Fe (II) the concentrations ranging from 0.217 mg·L^{-1} to 0.277 mg·L^{-1}, while for Fe (III) the concentrations ranging from 0.217 mg·L^{-1} to 0.422 mg·L^{-1}.
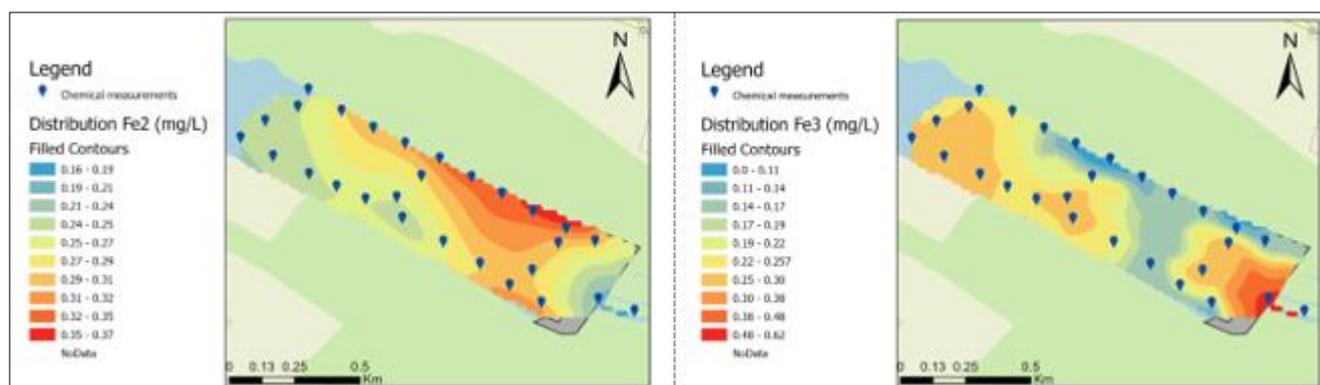

Figure 5. Spatial distribution of iron dissolved species (mg·L^{-1}) in Cătămărăşti Lake, Botoşani, Romania

- for the samples from downstream of the lake the values of ferric iron (0.598 mg·L^{-1}) are over ferrous iron content (0.187 mg·L^{-1}). The ferric ions are overall the values recorded in the lake and that is due to the oxygen content recorded downstream of the lake.

Besides other nutrients (nitrogen, phosphorus, sulfur) iron is present in surface waters from natural (rainwater, dust, vegetable matter etc.) or anthropic activities, so the total iron is influenced both by natural and anthropogenic factors, which control the iron speciation. The ferric iron can form insoluble

oxides or hydroxides and ferrous iron exist usually as iron hydroxide at low alkaline waters of Cătămărăşti Lake. Also, at low temperature (mean value 7.79°C), the oxygen solubility increased, so iron is most probably oxidized to ferric iron.

4. Conclusions

The paper determined the concentration of ferrous and ferric iron in Cătămărăşti Lake, using a standard method. The recorded concentrations of iron during the measurements were correlated with some physico-chemical properties (pH, temperature, dissolved oxygen, saturation and electrical conductivity).

The results of pH measurements showed that the Cătămărăşti Lake acidity had small variations from a minimum value of 8.51 to a maximum value of 8.80, which satisfied the water quality criteria for this ecosystem. The values of dissolved oxygen ranged from 10.79 to 11.93 mg·L^{-1}, with an average of 11.19 mg·L^{-1}. These values could be correlated with the oxygen saturation and temperature measurements, which showed an intense biological life in Cătămărăşti Lake. The electrical conductivity is directly related to the concentration of ions from the samples and the measurements ranged from 420 µS·cm^{-1} to 452 µS·cm^{-1}, with a mean value of 424.79 µS·cm^{-1}, during the sampling day.

Concerning the iron species, our measurements were focused on ferrous and ferric iron from the lake, but not on the other species present in aqueous environments. The distribution of iron contents is not constant: on the NE shore the ferrous ion is dominant, on the SW shore the contents in these ions are almost equal, while on the middle of the lake there is more ferric iron than ferrous iron. The content of iron in downstream samples is over the content from the lake, due to the oxygen content recorded.

The results of research of the occurrence and the presence of iron in Cătămărăşti Lake, Botoşani will be continued in further activities of the authors.

References
1.ZHU, Y., HU, X., PAN, D., HAN, H., LIN, M., LU, Y., WANG, C., ZHU, R., Speciation Determination of Iron and its Spatila and Seasonal Distribution in Costal River, *Scientific Reports*, **8**, 2018, 2576.
2.FREY, P.A., REED, G.H., The Ubiquinty of Iron, *ACS Chem. Biol.,* **7** (9), 2012, 1477-81.
3. KRING, D.A., Composition of Earth's Continental Crust as Inferred from the Compositions of Impact Melt Sheets: *28th Lunar and Planetary Science Conference*, **28**, 1997, 763-64.
4.BREITBART, E., BELLERBY, R.J., NEILL, C.C., ARDELAN, M.V., MEYERHOFER, M., ZOLLNER, E., CROOT, P.L., RIEBESELL, U., Ocean Acidification Affects Iron Speciation in Seawater, *Biogeosciences Discuss.*, **6**, 2009, 6781-802.
5.BRYNE, R.H., KESTER, D.R., Solubility of Hydrous Ferric Oxide and Iron Speciation in Seawater, *Marine Chemistry*, **4**, 1976, 255-74.
6. SU, H., YANG, R., PIZETA, I., OMANOVIC, D., WANG, S., LI, Y., Distribution and Speciation of Dissolved Iron in Jiaozhou Bay (Yellow Sea, China), *Frontiers in Marine Science*, **3**, 2016, 99, 1-17.
7.SUNDMAN, A., KARLSSON, T., LAUDON, H., PERSSON, P., XAS Study of Iron Speciation in Soils and Waters from a Boreal Catchment, *Chemical Geology*, **364**, 2014, 9301-2.
8.SIPOS, P., CHOI, C., NEMETH, T., SZALAI, Z., POKA, T., Relationship Between Iron and Trace Metal Fraction in Soils, *Chemical Speciation and Bioavailability,* **26** (1), 2014, 21-30.
9.PRIETZEL, J., THIEME, J., EUSTERHUES, K., EICHERT, D., Iron Speciation in Soils and Soil Aggregates by Synchrotron-based X–ray Microspectroscopy (XANES, μ-XANES), *Eur. J. of Soil Science*, **58**, 2007,1027-1041.
10.SJOSTEDT, C., PERSSON, I., HESTERBERG, D., KLEJA, D. B., BORG, H., GUSTAFSSON J. P., Iron Speciation in Soft-water Lakes and Soils as Determined by EXAFS Spectroscopy and Geochemical Modelling, *Geochimica et Cosmochimica Acta,* **105**, 2013, 172-86.
11.GELTING-NYSTROM, J., Physico-chemical Speciation of Iron in the Baltic Sea, a Study in a Costal Bay, *Master of Science Thesis in Applied Geology*, 2004, Lulea University of Technology, Sweden.

12.BURUIANĂ, D., Atmopheric Precipitations, Water Discharge and Inundations in the Moldavian Plain, PhD Thesis, University "Al. I. Cuza" Iași and Université de Larraine, 2015. http://docnum.univ-lorraine.fr/public/DDOC_T_2015_0251_BURUIANA.pdf

13.BIRGHILA, S., BARONESCU, G., DUMBRAVA, A., Seasonal Variation and Speciation of Dissolved Iron in an Artificial Surface Water Body, *Ovidius University Annals of Chemistry*, **28**, 2017, 43-48.

14.HERRARA, l., AGUILLON, J.C., FEHRMANN, A., New Spectrophotometric Method for the Determination of Ferrous Iron in the Presence of Ferric Iron, *J. of Chemical Technology and Biotechnology*, **44** (3), 2007, 171-81.

15. FAULKNER, s.p., HINTZE, P.E., ASHBY, S.L., Evaluation of Colorimetric Methods for Measured Reduced (Ferrous) Iron, *Water Quality Technical Note, U.S. Army Corps of Engineerings*, **PD-02**, 1999, 1-12.

16.COCHIORCA, A., BARSAN, N., NEDEFF F.M., SANDU, I., MOSNEGUTU, E.F., PANAINTE LEHADUS, M., CHITIMUS, D., IRIMIA, O., SANDU, I.G., Surface Water Quality from a Mining Area. Case study, Groapa Burlacu Lake, Targu Ocna, Romania, *Rev. Chim,* **70**(10), 2019, 3678-80.

17.QIAO, Y., FENG, J., LIU, X., WANG, W., ZHANG, P., ZHU, L., Surface Water pH Variations and Trends in China from 2004 to 2014, *Environ. Monit. Assess*, **188**, 2016, 443.

18.PRASAD, B.S.R.V., SRINIVASU, P.D.N., SARADA VARMA, P., RAMAN, A.V., RAY, S., Dynamics of Dissolved Oxygen in relation to Saturation and Health of an Aquatic Body: A Case for Chilka Lagoo, India, *J. of Ecosystems,* 2014, art ID 526245, 1-17.

19.McNEIL, V.H., COX, M.E., Relationship between Conductivity and Analysed Composition in a large set of Natural Surface-water Samples, Queensland, Australia, *Environ. Geology*, **39** (12), 2019, 1325-33.

20. RODRIGUEZ-RODRIGUEZ M., FERNANDEZ-AYUSO A., HAYASHI M., MORAL-MARTOS, F., Using Water Temperature, Electrical Conductivity and *p*H to Characterize Surface-groundwater Relations in a Shallow Ponds System (Donana National Park, SW Spain), *Water*, **10**, 2018, 1406.

21.ARPADJAN, S., TSEKOVA, K., PETROVA, P., KNUTSSON, J., Field Sampling, Speciation and Determination of Dissolved Iron (II) and Iron (III) in Waters, *Bulgarian Chemical Communications*, **44**, 2012, 299-306.

22.MILLERO, F.J., YAO, W., AICHER, J. (1995). The Speciation of Fe(II) and Fe(III) in Natural Waters, *Marine Chemistry*, **50** (1-4), 1995, 21-39.

23. PEPPER, S.E., BORKOWSKI, M., RICHMANN, M.K., REED, D.T., Determination of Ferrous and Ferric Iron in Aqueous Biological Solutions, *Analytica Chimica Acta*, **663**, 2010, 172-177.

24.WELLS, M.L., PRICE, N.M., BRULAND, K.W., Chemistry in Seawater and its Relationship to Phytoplankton, a Workshop Report, *Marine Chemistry*, **48**, 1995, 157-182.25.

25.ROMANESCU, Gh., SANDU, I., STOLERIU, C., SANDU, I.G., Water Resources in Romania and Their Quality in the Main Lacustrine Basins, *Rev. Chim.*, **65**(3), 2014, 344-49.

26.BONTAS, B.I., MIRILA, D.C., GRITCU G., NISTOR, I.D., URECHE, D., High Pollution with Heavy Metals NATURA 2000 Protected Area in Bacau County, Eastern Romania, *Rev. Chim.,* **71**(6), 2020, 154-169.