INVESTIGATION OF HYDROCHEMICAL CHARACTERISTICS OF THE PRUT RIVER

Zubcov Elena, Biletchi Lucia, Bagrin Nina, Zubcov Natalia, Borodin Natalia, Jurminskaia Olga, Bogonin Zinaida

Institute of Zoology, Academy of Sciences of Moldova

Rezumat

În lucrare sunt prezentate rezultatele investigatiilor din 2013-2014 privind starea hidrochimică a rîului Prut în limitele Republicii Moldova. Pentru lacul de acumulare Costești-Stînca și segmentele de rîu Criva-Teţcani și Braniște-Giurgiulești au fost stabilite limitele de variaţie spaţiale și temporale ale parametrilor hidrochimici de bază (oxigenul dizolvat, $CBO_{5,}$ CCO_{Mn}, CCO_{Cr}, mineralizarea şi ionii principali, elementele biogene – azot, fosfor și siliciu) și a unor microelemente (zinc și litiu). Deși, în ansamblu, apele r.Prut întrunesc cerinţele faţă de ecosistemele acvatice multifuncţionale, capacitatea de autoepurare a rîului (CBO_5/CCO_{Cr}) de cele mai multe ori nu compensează deversarea apelor reziduale menajere și industriale neepurate direct în rîu.

Cuvinte cheie: rîul Prut, calitatea apei, mineralizare, ioni principali, elemente nutritive

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Adresa pentru corespondenţă: Zubcov Elena, Institutul de Zoologie al Academiei de Ştinţe a Moldovei, str. Academiei, 1, MD-2028, Chişinău, Republica Moldova; e-mail: ecotox@yahoo.com; tel. (+373 22) 73-75-09

Introduction

The assessment of the water quality of aquatic ecosystems from the Republic of Moldova, including the basin of the Prut River, is necessary both from theoretical and practical point of view, because it allows obtaining of new knowledge regarding a range of processes that occur in the aquatic ecosystems, e.g. production and destruction of organic matter, pollution and self-cleaning, and offers the possibility to appreciate their vulnerability. The results of these investigations are of high value for planning of activities, which are designed for the recovery of ecological situation and preservation of aquatic biodiversity, in particular, in the case of emerging situations, such as accidental pollution, floods, droughts, the role of which is indisputable in the aspect of climate change.

The difficulty of solving the environmental problems in the Lower Prut is determined by the specificity of physico-geographical conditions and intensity of anthropic impact [2, 5]. To mention that the investigation of the Lower Prut – a unique ecosystem of a great importance not only at the national, but also international level, opens new perspectives for collaboration with research institutions from Romania, Ukraine and other Danube countries. The carried out researches fit the objectives of the EU Joint Operational Programme Romania – Ukraine - Republic of Moldova 2007-2013.

Materials and methods

The investigations have been carried out during 2013-2014 and the water samples have been collected monthly from the representative sectors of the Prut River and Costesti-Stinca reservoir: stations Criva, Tetcani, Badragii Noi, Duruitoarea Noua, Costesti-Stinca, Braniste, Sculeni, Leuseni, Leova, Cahul, Cislita-Prut, Giurgiulesti.

Field samples collection and chemical analyses of water samples were performed according to established methods in hydrochemistry and hydrobiology [8].

Dissolved oxygen was determined by iodometric method, which was adapted to ISO 5813:1993; this method includes the fixation of samples directly in the field.

Content of hydrocarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions or alkalinity was determined by titration classical method, which also corresponds to ISO 9963-1:1994 and 9963-2:1994. Chlorides were investigated by silvermetric titration method in accordance with ISO 9297:1989. Sulphate ion concentration (SO_4^{2-}) was determined by gravimetric method using barium chloride according to ISO 9280:1990. Determination of calcium and magnesium total content or water hardness, as well as of calcium ions was carried out by complexometric EDTA-titrimetric method (ISO 6059:1989 and 6058:1984). Content of magnesium ions (Mg^{2+}) was calculated as the difference between hardness values and content of calcium ions. In the case of sodium and potassium ions, the method of Semenov (1977) [8] was used, but some samples were analysed by atomic absorption method - ISO 9964-2:1993.

Nutrients ($N\text{-}NH_4^+$, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, mineral P) were investigated by using classical spectrometric methods, which complies to a range of standards: ISO 7150-1:1984, ISO 6777:1984, ISO 7890-3:1988, ISO 6878:2004, and trace metals were investigated by using mass spectrometer ICAP-6000.

Result and discussion

Oxygen is one of the most important gases, being permanently present in the natural waters. Its regime determines to a large extent the chemical and biological state of the water body. The deficiency of dissolved oxygen is registered more often in water bodies with a high content of pollutant organic compounds and in eutrophic one.

Investigations have revealed that the content of dissolved oxygen in water was relatively satisfactory for hydrobiont development, its concentration ranging within 5.23 (Giurgiulesti, summer of 2014) and 13.4 mg/l (Leova – Giurgiulesti sector, December 2014), or from 59.6 to 94.6 % of saturation at a water temperature of 0.8 – 27.2°C. In summers of 2013-2014 the content of dissolved oxygen was lower in comparison with other seasons, although, as rule, in rivers the lowest values of dissolved oxygen are registered in winters, when the ice prevents the penetration of oxygen from atmosphere. Also in the warm period of the years the content of dissolved oxygen decreased along the river.

The values of biochemical consumption of oxygen (CBO_5) varied within 1.0 (Costesti-Stinca, lower sector, September 2013) and 3.7 mgO_2/l (Giurgiulesti, February 2014), (Fig. 1). Thus, according to the *Regulation on environment quality requirements for the surface waters (*hereinafter *Regulation)* [1], the values of dissolved oxygen and those of CBO_5 indicated the classes of water quality I-II (very good – good), with a single exception for dissolved oxygen: in Mai-June 2014 on Leuseni - Giurgiulesti sector its concentration exceeded 5.5mg/l, what corresponds to the class of water quality III (moderately polluted).

The determination of CBO_5 is used to assess the content of biochemically oxidable organic substances, and this parameter is taken into consideration as an integral indicator of water pollution. The values of CBO_5 in surface waters are usually within 0.5-4 mgO_2/l and are subject to seasonal and daily fluctuations [9].

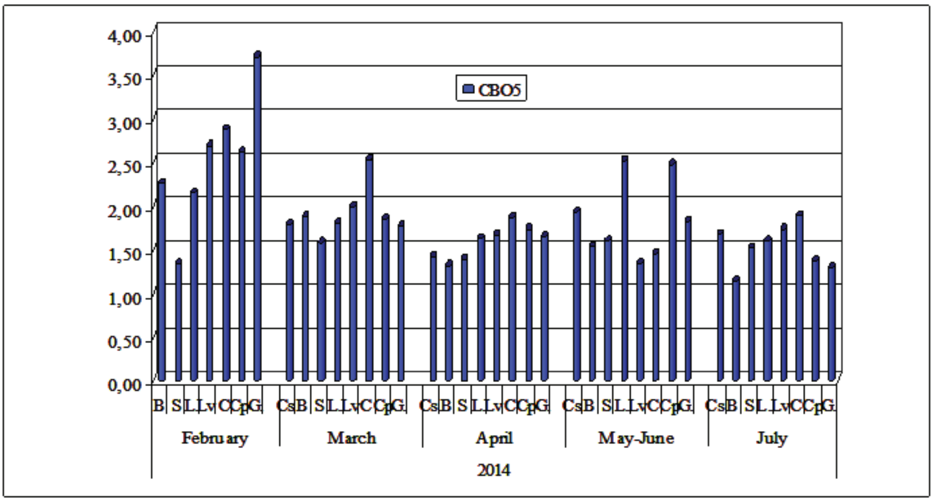

Figure 1. Dynamics of the biochemical consumption of oxygen (CBO_5, mgO_2/l) in the waters of the Prut River and Costesti-Stinca reservoir, February-July of 2014 (hereinafter*: Cs- Costesti-Stinca reservoir, lower sector, B- Braniste, S- Sculeni, L-Leuseni, Lv- Leova, C-Cahul, Cp - Cislita-Prut, G- Giurgiulesti)*

Also, other indirect indicators of the content of easily degradable organic compounds (CCO_{Mn}, mgO_2/l) and of more persistent organic compounds (CCO_{Cr}, mgO_2/l), which, in fact, are determined via the volume of oxygen used for mineralization of this compounds, were used. It was revealed that according to the values of CCO_{Mn} the water referred to the classes of quality I-III, but according to the values of CCO_{Cr} - to the classes of quality III-IV (Fig.2-3). There was found a medium correlation between CCO_{Mn} and CCO_{Cr}, which proved a low intensity of self-cleaning processes (Fig.2-3).

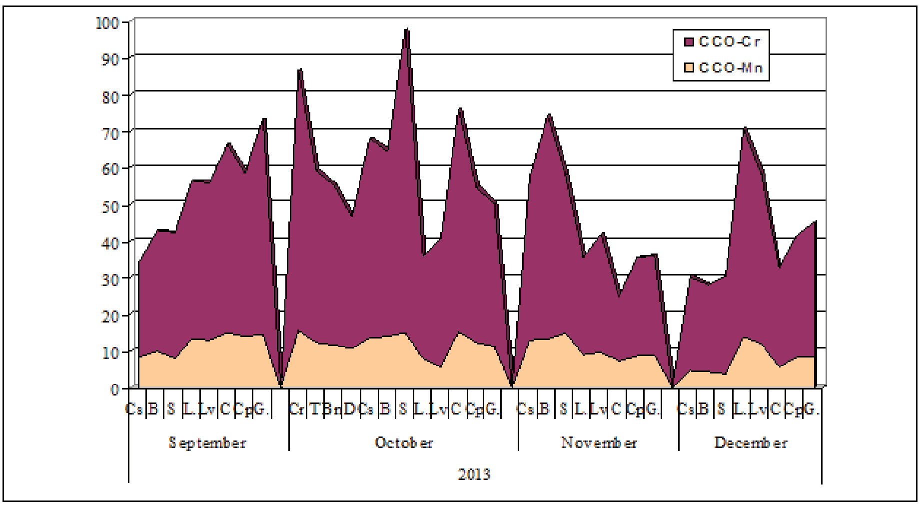

Figure 2. Dynamics of the chemical consumption of oxygen by manganese (CCO_{Mn}, mgO_2/l) and chromium (CCO_{Cr}, mgO_2/l) in the waters of the Prut River and Costesti-Stinca reservoir, September - December of 2013 (hereinafter: *Cr- Criva,T- Tetcani, Bn-Badragii Noi, D- Duruitoarea Noua)*

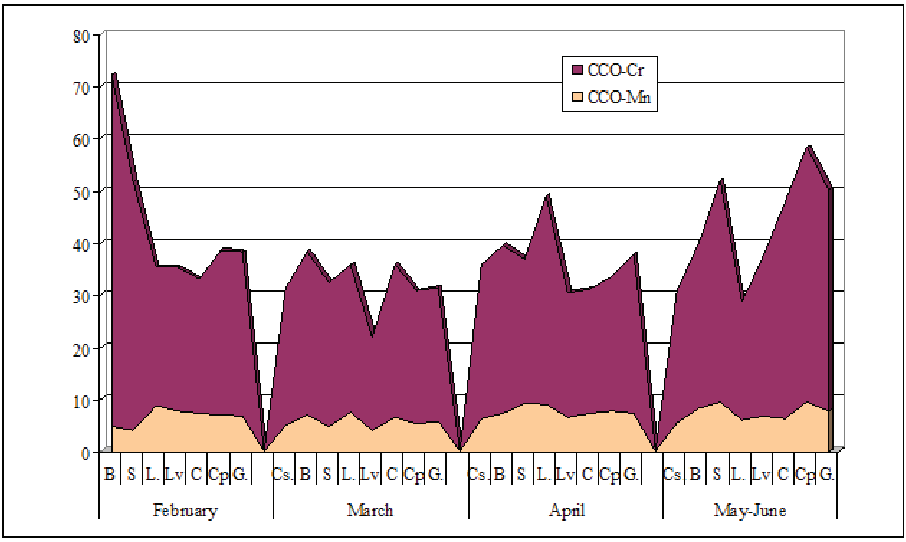

Figure 3. Dynamics of the chemical consumption of oxygen by manganese (CCO_{Mn}, mgO_2/l) and chromium (CCO_{Cr}, mgO_2/l) in the waters of the Prut River and Costesti-Stinca reservoir, February-June of 2014

The ratio between CBO_5 and CCO_{Cr}, or so called self-cleaning coefficient, is another indicator, which allows judging on the trends of degradation of organic matter in the water environment. As rule, it is widely applied in the case of treatment of waste waters (treatment plants), but can be applied also in the investigation of natural waters.

In regard to the Prut River, low values of self-cleaning coefficient were ascertained: in September-December 2013 in about 70% of cases the ratio CBO_5/CCO_{Cr} was lower than 0.06 (Fig. 4) and in about 50% - in February-June 2014.

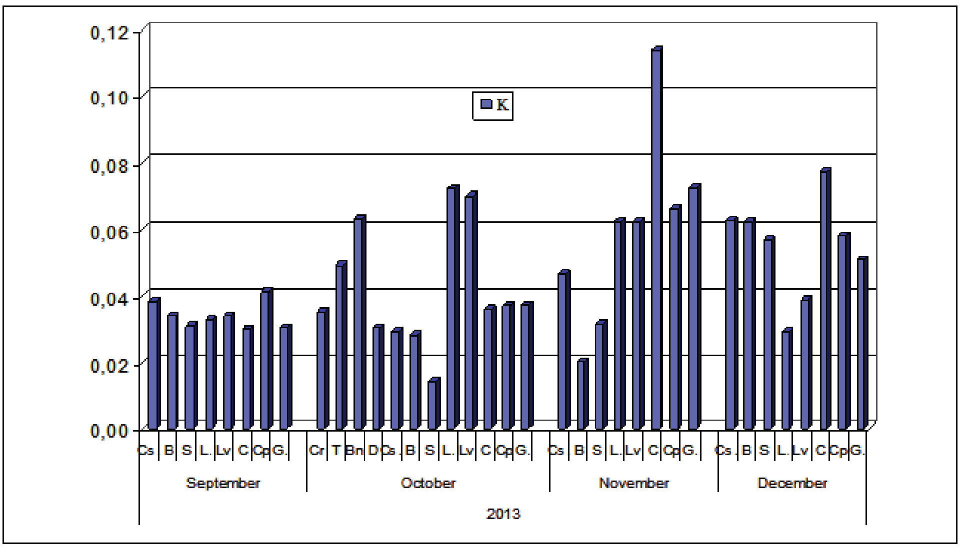

Figure 4. Dynamics of self-cleaning capacity of waters (CBO_5/CCO_{Cr}) in the Prut River and Costesti-Stinca reservoir, September - December of 2013

The quantity of suspensions in the Prut River varied in a quite large diapason - from 1.2 mg/l to 222.4 mg/l. The highest concentrations of suspensions were found in the Prut River on the Leuseni-Cahul sector (149-222 mg/l) in May of 2014. The dynamics of suspensions in the Prut River is highly dependent on its right tributary – Bahlui River, which provokes the increase of their content by ten times in the Prut River on the Leuseni - Cislita-Prut sector.

At Giurgiulesti station, in the zone of small water speed, the most of suspensions are stored in silts. It is important to note that the increase of suspension content up to 80-100 mg/l provokes the suppression of development of planktonic organisms in the Prut River.

Mineralization and main ions. During September of 2013 - June of 2014 the mineralization of investigated waters oscillated between 359 mg/l (Costesti-Stinca, lower sector, June 2014) and 702 mg/l (Leova, October 2013), having and obvious tendency to increase along the Prut River.

In most cases, the water of the Prut River referred to the hydrogen carbonate class, group of calcium, type II, accordingly to classification of Alekin [7], but in September of 2013 on the sector Leuseni - Leova, in October-November on sector Leova - Giurgiulesti, and in March of 2014 at Cislita-Prut station the class of water changed: from the hydrogen carbonate class, group of calcium, type II to the hydrogen carbonate class, group of sodium and sulfate class group of sodium type II (Fig.5-6).

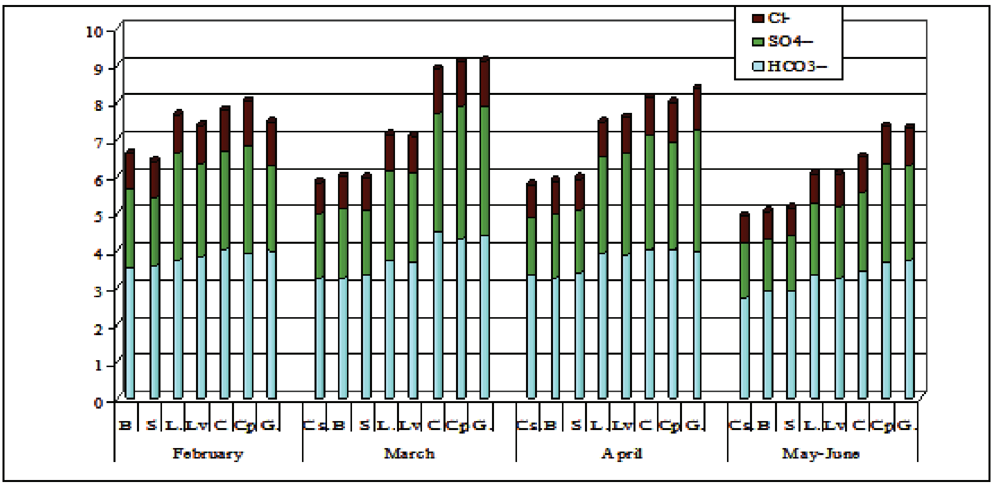

Figure 5. Dynamics of hydrogen carbonate, sulfate and chloride ions in Costesti-Stinca reservoir, and the Prut River in February-June of 2014, mg-ecv/l

It is known that the correlation between cations and anions is a basic indicator in the determining of surface water stability. The modification of water class reveals the existence of pollution or the water metamorphosis under the influence of some major factors.

The Prut waters, taking in account the composition of main ions, corresponded to the requirements on quality, which must be met by drinking water, and waters used in pisciculture and aquaculture.

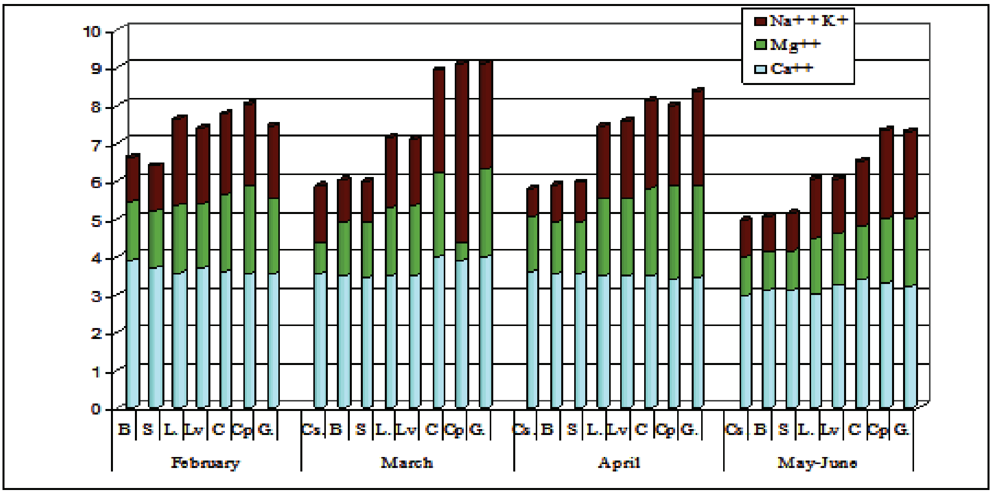

Figure 6. Dynamics of calcium, magnesium, sodium and potassium ions in Costesti-Stinca reservoir and the Prut River in February-June of 2014, mg-ecv/l

Nutrient substances. The content of nutrients is one of the most important indicators of water quality, which determines both the development of several aquatic organisms, as well as trophicity level, intensity of production-destruction processes of aquatic ecosystems. The dynamics of nitrite nitrogen and of nitrate nitrogen corresponded to waters of classes of quality I-II, of ammonium nitrogen – to classes II-III and of total nitrogen – to classes I-III. It was registered that in most of cases the concentrations of mineral nitrogen on Leuseni-Giurgiulesti sector exceed by 2-3 times those on Costesti-Sculeni sector.

The dynamics of nutrient substances is not unequivocal and depends on a range of factors, but an evident increase of the level of nitrate ions, which form more than 50% of total mineral nitrogen, was observed from the Leuseni station along the river, excepting few cases, when the content of ammonium ions was higher: in October of 2013 – in Costesti-Stinca reservoir and the sector Braniste-Leuseni of the Prut River and in May of 2014 - at Leova station of the Prut River.

The dynamics of the total nitrogen revealed an increase along the river in September-December 2013, the highest values being recorded on Leova - Giurgiulesti sector (Fig.7). It is important to stress that in mentioned sector the content of total nitrogen increased due to the organic nitrogen.

In February – May 2014 the mineral nitrogen oscillated between 0.206 (Giurgiulesti, May) - 2.365 mgN/l (Giurgiulesti, April), and organic nitrogen – between 0.009 (Costesti-Stinca, lower sector, March) - 2.737 mgN/l (Leova, March). It was interesting that both by location and time the lowest values of total nitrogen (0.414 mgN/l) coincided with the lowest values of mineral nitrogen and the highest one (4.5 mgN/l) - with the highest values of organic nitrogen. The share of the mineral nitrogen in the content of total nitrogen was less than 50% at Sculeni station in February, at Costesti-Stinca, lower sector, Sculeni and Leova – in March and at Cislita-Prut station in May-June.

In river waters the regime of another nutritive element – phosphorus – is similar to those of nitrogen. It is worth to mention that in September of 2013 in the Prut River on

Leova-Giurgiulesti sector, and in October of 2013 at all stations, in February of 2014 in the Prut River on Braniste-Cahul sector, and in March-June of 2014 almost at all stations the concentrations of organic phosphorus were higher than those of mineral phosphorus (Fig. 8). The analyze of ratio between the mineral and organic phosphorus for entire 2013 (February-December) put in evidence that in 58% of collected water samples the organic phosphorus formed at least 50% of the total phosphorus.

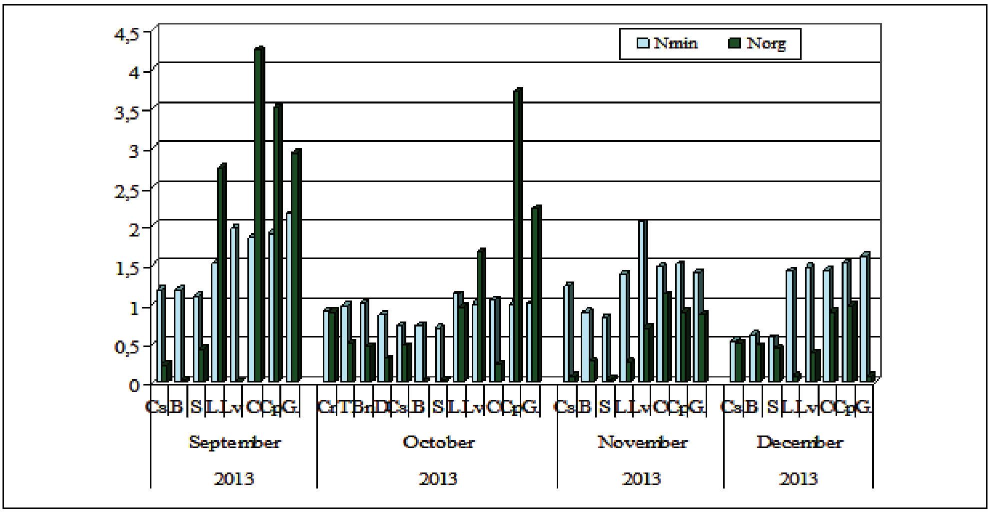

Figure 7. Dynamics of mineral (Nmin) and organic (Norg) nitrogen in Costesti-Stinca reservoir and the Prut River in September-December of 2013, mg N/l

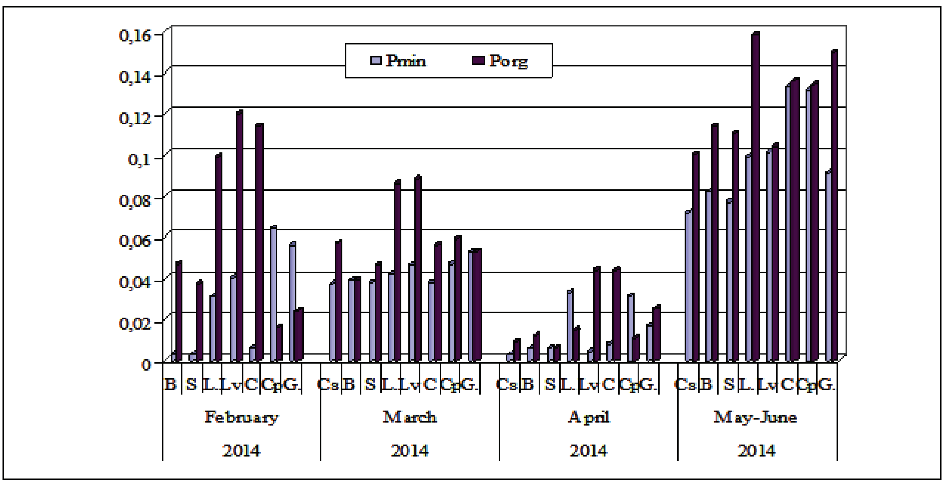

Figure 8. Dynamics of mineral (Pmin) and organic (Porg) phosphorus in Costesti-Stinca reservoir and the Prut River in February-May 2014, mg P/l

The concentrations of mineral and total phosphorus in water of the Prut River corresponded to the classes I- II of quality.

Silicon is a nutritive element, whose content is strongly related to its plancton uptake during the summer months under baseflow conditions and more exactly, to the development of *Bacillariophyta* algae or diatoms [4, 6]. Their overlapping shells or frustules, which surround the diatom protoplasm are made of polymerized, opaline silica. With the reference to our area of investigations, the concentration of silicon in the Lower Prut ranged from 1.3 (Sculeni and Cislita-Prut, April 2014) to 3.0 mgSi/l (Cahul, September 2013).

In October 2013 at Criva and Tetcani stations, situated on the Middle Prut and in the upper sector of Costesti-Stinca reservoir concentrations of silicon were much lower – 0.5-0.8 mgSi/l.

The high impact of human activity on the Prut River is proved not only by water macroelements, but also by several of microelements. As example, during November 2013-July 2014 the concentrations of dissolved zinc fitted to the class of water quality I-II in conformity with the *Regulation*, excepting the Giurgiulesti station in April of 2014, when it was higher than 30 µg/l than means the moderately polluted water (class III), (Fig.9).

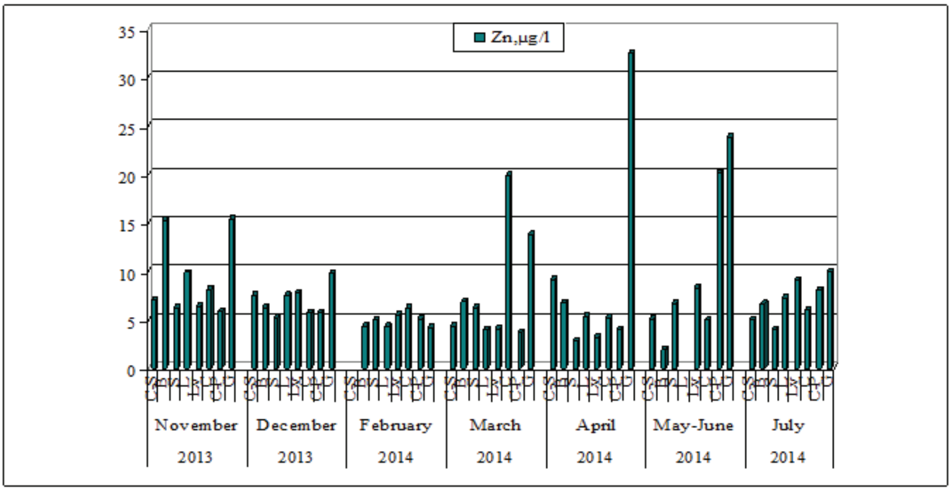

Figure 9. Dynamics of zinc in Costesti-Stinca reservoir and the Prut River in November 2013-July of 2014

But according to previously used maximum admissible concentration (MAC) of Zn for water used in pisciculture purposes – 10 µg/l [9] – in 13% of cases the water of the Prut River not satisfied the requirements for this type of water bodies.

Another element and namely lithium, an alkaline element, is generally found naturally in the aquatic and terrestrial ecosystems, but in small concentrations. According to the literature, the typical background concentrations of lithium in fresh water range 0.07 – 40 µg/l, whereas rivers generally contain around 3 µg/l [3].

For the first time the level of lithium has been investigated in the surface waters of the Republic of Moldova and the carried out researches revealed for the Prut River quite high concentration of lithium – up to 35 µg/l (Fig.10).

Moreover, in the case of lithium there is an obvious increase of its concentrations along the river. This phenomenon may be linked with the fact that lithium is not expected to bioaccumulate, it is not a dietary mineral for plants, although it does stimulate the plant growth [3].

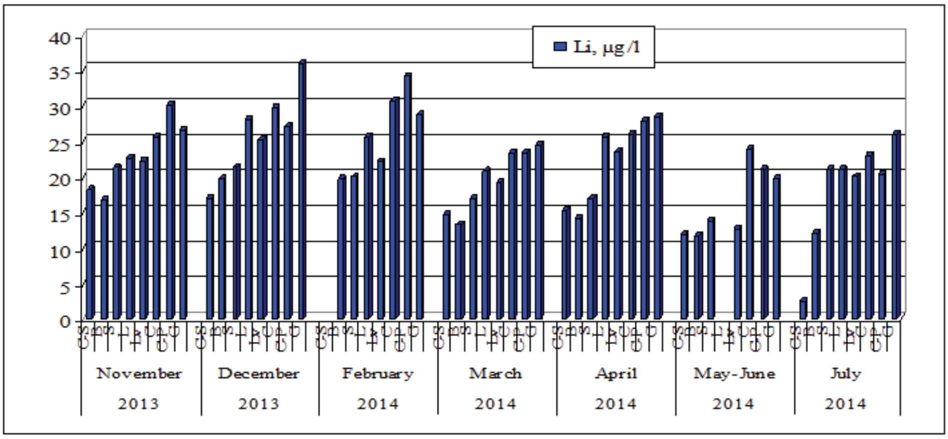

Figure 10. Dynamics of lithium in Costesti-Stinca reservoir and the Prut River in November 2013 - July 2014

Conclusions

It was preserved the classical trend of mineralization growth along the river. In most cases, the water of the Prut River referred to the hydrogen carbonate class, group of calcium, type II, accordingly to classification of Alekin, but in some of cases it was replaced by the hydrogen carbonate class, group of sodium, type II or sulfate class, group of sodium, type II.

In most cases for investigation period, the waters of the Prut River were satisfactory for hydrobionts development, but the concentrations of suspensions (in 14.7% cases – higher than 80 mg/l), nutritive elements were not always favorable for development of planktonic organism. However, in general the Prut River waters met the requirements for multifunctional aquatic ecosystems (which may serve as source of drinking water, as well as of water for irrigation, pisciculture and aquaculture).

For sustainable use of aquatic resources in the hydrographic basin of the Prut River, it is necessary to revise and restore the protection areas of the river, the Prut natural wetlands and of its tributaries, most of which are dammed by diverse hydrotechnic constructions and on the banks of which are placed numerous dumps.

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