KOROS RIVER BASIN WATER QUALITY ASSESSMENT

Fodor Alexandrina*, Petrehele Anda Ioana Gratiela*, Cupşa Diana*, Petruş Adriana*, Jakabné Sándor Zsuzsanna, Györéné Cseres Ildikó**, Vilmos Józsa**, Bogar Gáborné**, Györe Károly**, Bíró Janka** , Gyöngyössiné Papp Zsuzsanna****

* University of Oradea, Oradea, University Street, no.1, 410087, Romania, afodor@uoradea.ro
**Institute For Fisheries, Aquaculture And Irrigation, Szarvas, Anna-liget 8 , Hungary

Abstract

The aim of the study is the survey of some several chemical and physical parameters (ammonium, nitrites, nitrates, phosphates, temperature, pH, alkalinity, conductivity, hardness, chlorides, dissolved oxygen, CCOMn,) in the aquatic environment on along the Crişuri Rivers Basin around border between Romania and Hungary (Barcău, Crişul Alb, Crişul Negru and Crişul Repede Rivers). The necessity of this study appeared due to: the long tradition in mining activities in the area on Crişul Negru River, the long tradition in oil extraction and exploitation activities in the area on Barcău and other industrial activity's and agricultural and household activity's, that could be a source of ecosystems contamination. The survey was undertaken during August 2011 period and will be resumed in march-may 2012 period. A total number of 23 water samples were taken in the sampling sites establish after an anthropologic analysis of the studied rivers hydrological basin. The sampling sites were generally establishing downstream and upper stream of the major cities and water cleaning stations in the studied area.

Key words chemical water quality parameters survey

INTRODUCTION

In Romania, most of the water sources are surface waters (lakes and rivers). The process of providing safe drinking water has relied on the protection of water sources, the application of the specific treatment technologies and the protection and maintaining quality in the distribution system [Vântu V. and all, 2002]. Drinking water must have a quality that promotes and protects public health, the safe water expressing the accordance to the maximum admissible limits of the relevant water parameters for human health [Barabaş B., 2009; Gavrilescu E., 2003]. Industry and agriculture are considered as having the greatest impact on the quality and quantity of water and an overwhelming majority of Europeans think that climate change will have an impact on the water resources [Dumitrache F., E. Diacu, 2010; Gurzau A. E. and all, 2010].

The Crişuri Rivers (Hungarian: Körös) are cross the Romanian - Hungarian border at several points and the main basin might found in Romania (figure 1). The Crişuri Rivers falls into Tisza River basin which is the second important river of Hungary. Thus water pollutions might affect bought countries especially around of the borderland. For these reasons, the results of this study might give beneficial knowledge's to both countries.

Barcău River (Hungarian: Berettyó) rises in the northern Apuseni Mountains, in the village of Sag in Bihor County. The River flows in Hungary into Crişul Repede. It has a length of 34 Km, during his ongoing cross: West Hills, West Plain and major cities of Suplacul de Barcău, Marghita and Berettyóújfalu.

Crişul Repede River (Hungarian Sebes-Körös) is a river in Bihor County, Crişana, Romania and in south-eastern Hungary (Körösvidek). The Crişul Repede River runs through the city of Oradea, the capital of Bihor County. It flows into the Körös River near Gyomaendrőd, in Hungary.

The **Crişul Negru River** (Hungarian Fekete-Körös) is a river in Western Romania (Transylvania) and South-Eastern Hungary (Békés County). The river starts at the junction of headwaters Crişul Poienii and Crişul Băiței in the Western Apuseni Mountains. It flows through the town's Ştei and Beiuş in Romania. One its tributaries are the small Roşia River. Crossing the border of Hungary the river, now called Fekete-Körös, joins the Fehér-Körös a few kilometres north from Gyula to form the Körös River. **The Crişul Alb River** (Hungarian Fehér-Körös) is a river in western Romania in the historical region of Transylvania and South-Eastern Hungary (Békés County). Its source is in the Southern Apuseni Mountains. It flows through the towns Brad, Ineu, Chişineu Criş in Romania, and Gyula in Hungary. Crossing the border of Hungary, the river, now called Fehér-Körös, joins the Fekete-Körös a few kilometres north from Gyula to form the **Körös River**, 195 km long, in eastern Hungary. It is formed at the confluence of the rivers Fehér-Körös and Fekete-Körös near Gyula. The Sebes-Körös flows into the river Körös near Gyomaendrőd. All these rivers have their source in the Apuseni Mountains, in Romania. The Körös flows into the Tisza River near Csongrád.[www.wikipedia.ro]

Fig.1. Crişuri (Körös) River HU-RO Hydrographic Basin
[Andrisca S.G., 2011]

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use,

such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish.
The sampling sites were established in May 2011 in a field campaign in Romania and Hungary after an anthropogenic analysis of the rivers hydrological basin taken in study. Generally were establish sampling sites down and upper stream of the major cities and water cleaning stations in the studied area (figure 2).

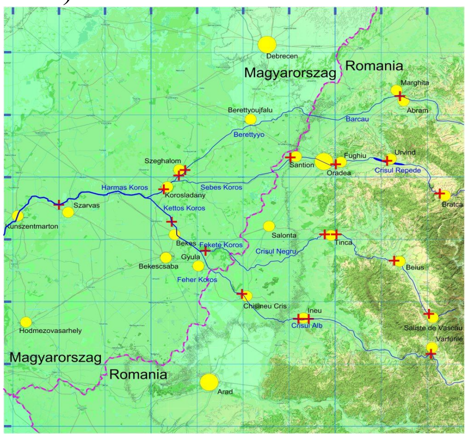

Fig.2. Sampling sites establish in the Cris (Körös) River Hydrographic Basin

MATERIAL AND METHODS

Basic chemical analysis (temperature, pH, conductivity, dissolved oxygen, CCOMn, Alkalinity, Total hardness, Chlorides, Ammonium, Nitrites, Nitrates and Phosphates) were determined by standard methods [STAS 6324-61; EN 27888-1997; EN 25 814 ISO/1999; SR EN ISO 8467-2001; STAS 6364-78; STAS 3026-76; STAS 3026-76; ISO 9297/2001; STAS 8683-70; STAS 89001-71; STAS 89001-7111-19,21] to evaluate the quality of the water.

RESULTS AND DISSCUTION

The temperature is an important physical parameter, a reference parameter for the variation of environment physico-chemical characteristics. The variation of the water`s surface temperature depends on the air temperature, while the deep water temperature remains constant. The temperature was determined in accordance with STAS 6324-61. The measured values of the temperature (figure 3) are less than 22-25°C, for surface water used to obtain the drinking water, just like it is stipulated in decision 100/07.02.2002.

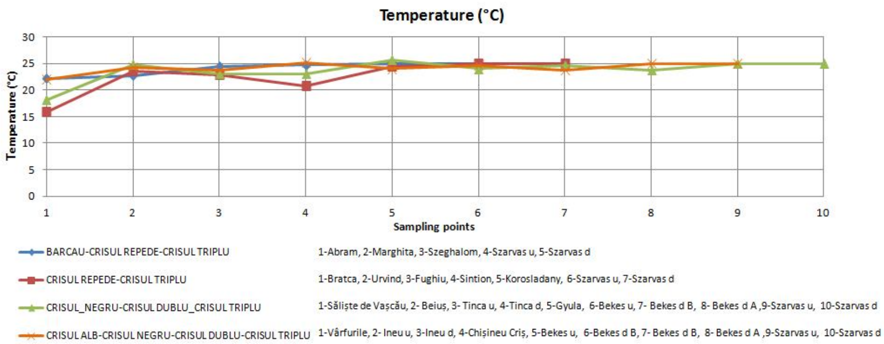

Fig. 3. The temperature measured in situ in the sampling points (August 2011)

pH, the concentration of hydrogen ions in water is an important factor for determining the reaction ability of water, its aggressiveness, but also the properties of water to form a favourable environment for development of different organisms, etc. The next water parameters (pH, acidity or alkalinity) have not the same values and their determining methods are different. Increased alkalinity or acidity is not accompanied by corresponding changes in pH due to buffering capacity, available especially natural waters. The main buffer system of natural waters is dissolved carbonic acid and carbonate system, for which the pH is between 6,5 to 8,5 values. Moreover the buffering capacity of pH is very important as for the balance of the aqueous phase, as for the interface with materials suspended sediments respectively [Lupea A.X. et all 2008]. Determination of pH was made according to Norm ISO 10523/1997. The obtained values are presented in figure 4.

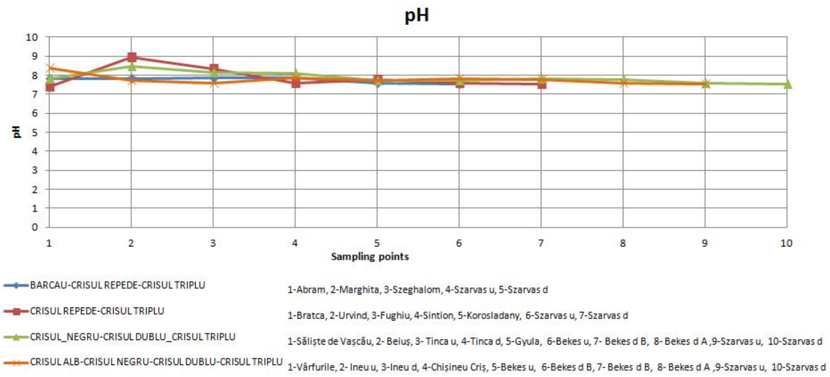

Fig. 4. The pH measured in situ in the sampling points (August 2011)

All the samples are in I category of quality, except samples from Urvind and Fughiu on the Crisul Repede River, where the water can be classified in the II and III category of quality, according to decision 100/7.02.2002, for surface water used to obtain drinking water.

The electrical conductivity of water depends on the ions nature, their concentration, the equilibriums that occur between soluble and insoluble species, chemical and biochemical redox processes, temperature and the amount of suspension. Natural water contains dissolved substances, which can be different depending on their source. The electrical conductivity of water is an indicator of the degree of mineralization of water [Lupea A.X. et all 2008]. Conductivity determination was made according to EN 27888-1997. The obtained values are presented in figure 5.

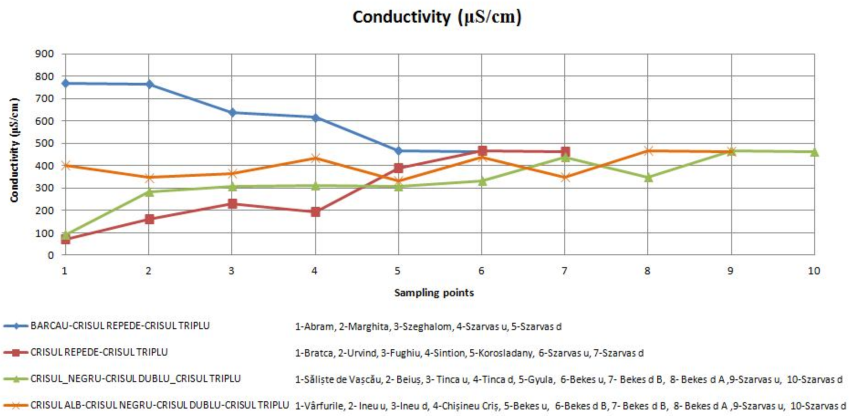

Fig. 4. The conductivity measured in situ in the sampling points (August 2011)

The obtain values are under the admissible limits (1000 µS/cm) surface water used for drinking water, in agreement with Decision 100/7.02.2002.

Dissolved Oxygen

All waters in contact with atmospheric air contain dissolved oxygen. The oxygen solubility in water depends on pressure, temperature, water temperature and salinity. The Oxygen content of river water is due to absorption of atmospheric oxygen in surface water by slow diffusion or vigorous contact at water-air interface showing a particular importance in this respect. This transfer is seriously disturbed by the presence of pollutants such as detergents and hydrocarbons. Dissolved oxygen (DO) is the most important parameter of water quality in rivers and lakes, because oxygen is vital to aquatic ecosystem [Lupea A.X. et all 2008]. Determination of oxygen dissolved in water effectuated with the analysis standard method EN 25 814 ISO/1999.

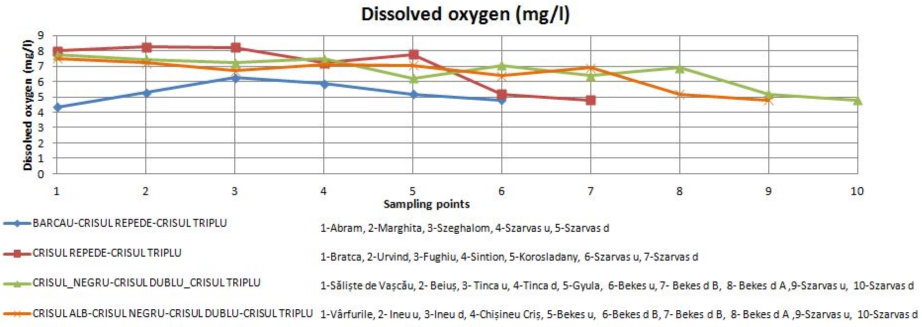

Fig. 5. The dissolved oxygen measured in situ in the sampling points (August 2011)

In terms of dissolved oxygen the framing by quality categories for the sampling sites was made according to the Norm of 10.12.2001 on surface water quality: 1) I Category (mg $O_2 \cdot L^{-1}$ = 7): Bratca, Urvind, Fughiu, Sîntion, Körösladány, Saliste Vaşcău, Beiuş, Tinca; 2) II Category (mg $O_2 \cdot L^{-1}$ = 6-7) Szeghalom,Gyula, Bekes; 3) III Category (mg $O_2 \cdot L^{-1}$ = 5-6): Marghita, Szarvas; 4) IV Category (mg $O_2 \cdot L^{-1}$ = 4-5): Abram

Chemical oxygen - Mn Method (CCO-Mn)

Chemical oxygen (CCO-Mn) was determined using the standard method SR EN ISO 8467-2001. The obtained values are presented in figure 6.

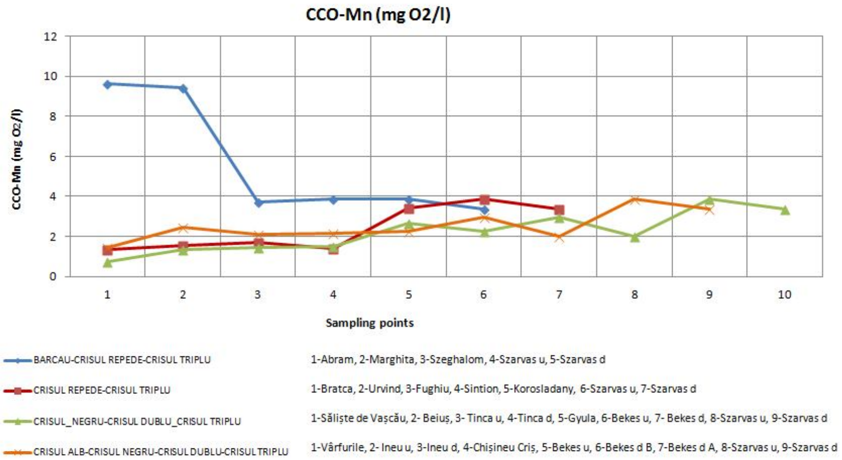

Fig. 6. The CCO-Mn measured in situ in the sampling points (August 2011)

In almost sampling points the CCO-Mn values were below 5 mg $O_2 \cdot L^{-1}$, which falls on first quality category of the surface water, with very good rating, which requires only a simple physical treatment and disinfection for drinking. Samples taken downstream and upstream of Marghita (Abram), the CCO-Mn value were below 10 mg $O_2 \cdot L^{-1}$, which falls on second quality category of surface water with good condition, that they requires physical and chemical treatments and disinfection for drinking. The lowest values of the parameter CCO-Mn were obtained only in Sălişte de Vaşcău, (1,44 mg $O_2 \cdot L^{-1}$), Bratca (0,74 mg $O_2 \cdot L^{-1}$) and Vârfurile (1,34 mg $O_2 \cdot L^{-1}$), as they are the zero sampling points of the studied rivers. CCO-Mn maximum values were obtained downstream of Marghita (9,43 mg $O_2 \cdot L^{-1}$) and upstream of Marghita (Abram), (9,65 mg $O_2 \cdot L^{-1}$), values that can be explained because in Upstream of Marghita it is an Oil exploitation site. Higher values of CCO-Mn on other rivers examined were obtained upstream of Szarvas, Hu (3,86 mg $O_2 \cdot L^{-1}$) and downstream of Szarvas (3,34 mg $O_2 \cdot L^{-1}$) Szeghalom upstream (3,71 mg $O_2 \cdot L^{-1}$) and downstream of Szeghalom (3,86 mg $O_2 \cdot L^{-1}$) and in Körösladány (3,42 mg $O_2 \cdot L^{-1}$).

The water **alkalinity** is given by the presence of bicarbonates, carbonates of alkali and alkaline - earth and their hydroxides [Lupea A.X. et all 2008]. The permanent alkalinity (P) is determined by titration of the sample with a solution of HCl in the presence of phenolphthalein (pH = 8.2). Permanent alkalinity is the free bases and alkaline carbonates. The total alkalinity (T) - this is determined by titration with HCl in the presence of methyl orange (pH=4.4). Total alkalinity is the free bases, carbonates and alkaline bicarbonate. The alkalinity of surface waters is not normal for a quality show, but her determination is particularly important for assessing the temporary hardness (carbonated).

The determination of the alkalinity was done according to STAS 6364-78.

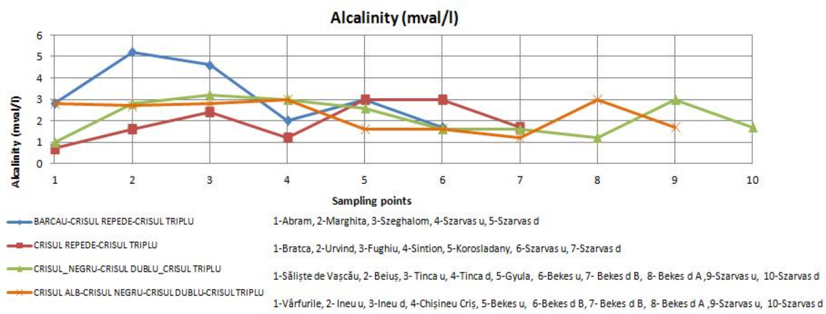

Fig. 5. The total alkalinity measured in the sampling points (August 2011)

From the alkalinity values obtained (figure 5) we can draw the following conclusions:

-in all cases permanent alkalinity is zero, which means that the alkalinity is due to bicarbonate dissolved in water.

-the highest values of alkalinity were obtained downstream of Marghita, (5,2 $mval \cdot L^{-1}$) and upstream of Szeghalom (5,2 $mval \cdot L^{-1}$).

- the lowest alkalinity values were obtained at Sălişte de Vaşcău (1,0 $mval \cdot L^{-1}$) and Bratca (0,7 $mval \cdot L^{-1}$), which were chosen like zero points on the Crişul Repede and Crişul Negru Rivers.

The Total Hardness is the total content of calcium and magnesium ions, which corresponds to the content of calcium and magnesium salts in water [Lupea A.X. et all 2008]. Determination of hardness in surface waters was made according to STAS 3026-76.

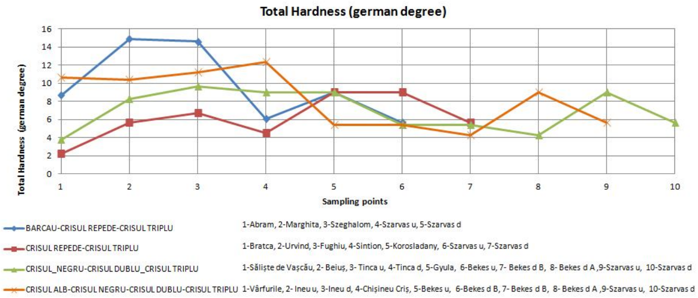

Fig. 6. The Total Hardness measured in the sampling points (August 2011)

For related results (figure 6) can be drawn the following conclusions:

- Weak Hard Water (3,8-5,6 °German) were found in: Crişul Dublu to Bekes, Hu; Crişul Repede to Sântion, Ro, Bratca, Ro; Crişul Negru to Sălişte de Vaşcău, Ro; Barcău to Abram, Ro;

-Moderately hard water (5,6-11,2 °German) were found in: Crişul Triplu to Szarvas, Hu; Barcău to Szeghalom, Hu and Marghita, Ro; Crişul Repede la Korosladany, Hu, Fughiu, Ro, Urvind, Ro; Crişul Negru to Gyula, Hu, Tinca, Ro, Beiuş, Ro; Crişul Alb to Vârfurile, Ro and Ineu, Ro;

-Very hard waters (11,2-28 °German) were found in: Crişul Alb to Chişinău Criş, Ro.

A special situation was observed in obtaining the permanent hardness values at both sampling point in Abram, RO and Marghita, RO on the Barcău River, where probably there were interference factors, which led to the increase of the obtained values for total and temporary hardness and for total alkalinity, too.

Chloride content determination was made according to ISO 9297/2001 (Mohr method).

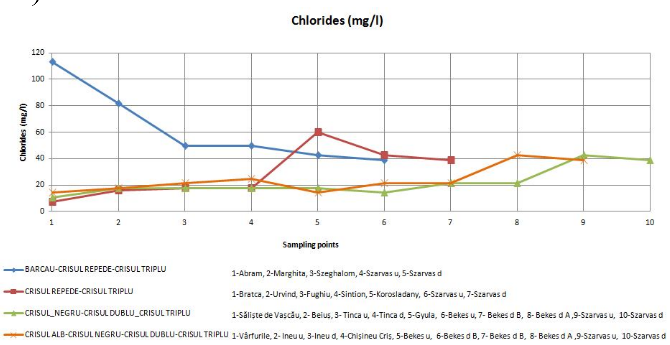

Fig. 7. The Chlorides measured in the sampling points (August 2011)

As we can see in the above graph (figure 7), the variation of the chlorides content in analyzed water samples, we can give the next conclusions: almost fall within the very good chemical status I. It is a exception at Abram sample on Barcău River, where the chloride ion concentration (13,47 mg$\cdot^{-1}$) slightly exceeds the threshold of 100 mg$\cdot$L^{-1}, which places in the water category II, indicated a good chemical status. The lower concentrations for chloride ions were recorded in Bratca (7,09 mg$\cdot$L^{-1}) and Sălişte de Vaşcău (10,64 mg$\cdot$L^{-1}). The highest values for chloride concentrations were registered in Abram (113,47 mg$\cdot$L^{-1}), Marghita (81,56 mg L) and Körösladány (60,28 mg$\cdot$L^{-1}).

Ammonium is found in very small quantities, either in free form (gas) near the decaying substances, or in the soil as ammonium salts. Ammonium toxicity, compared with the ion is much higher [Orbeci C., D. Turtoi, 2006]. Determination of ammonium is usually carried out for water having a pH between 6.5 and 8.3, by analyzing the ionic form ammonium. Standard method used was a spectrophotometric method (λ=400 nm): STAS 8683-70.

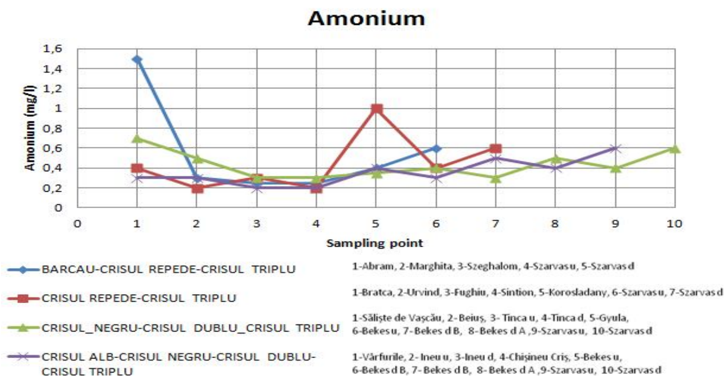

Fig. 8. The Ammonium measured in the sampling points (August 2011)

According to the ammonium content of the analysed samples (figure 8) almost fall within the very good chemical status I ($\leq$ 1 NH_4^+ mg$\cdot$L^{-1}) [Decision no. 100, 7 February 2002, Aligned 7]. There are some exceptions: Abram sample on Crişul Negru River (1,5 mg$\cdot$L^{-1} ammonium ion concentration) and Korosladany sample on Crişul Triplu (1,7 mg$\cdot$L^{-1} ammonium ion concentration), where the ammonium ion concentration exceeds the threshold of 1 mg$\cdot$L^{-1}, which places the samples in the water category II (1-1,5 mg NH_4^+ mg$\cdot$L^{-1}), indicated a good chemical status. The lower concentrations for ammonium ions were recorded in Bratca on Crişul Repede (0,25 mg$\cdot$L^{-1}) and Sintion on Crişul Repede (0,3 mg$\cdot$L^{-1}).

Nitrates (NO_3^-) is an advanced oxidation of ammonium, suggesting the presence of old pollution. Origin of nitrates may be of animal origin caused by the mineralization processes of proteins, or can be from mineral origins, waters flow over surfaces to which fertilizers have been used [Manescu

Orbeci C., D. Turtoi, 2006]. Standard method used was a spectrophotometric method (λ=410 nm) STAS 89001-71.

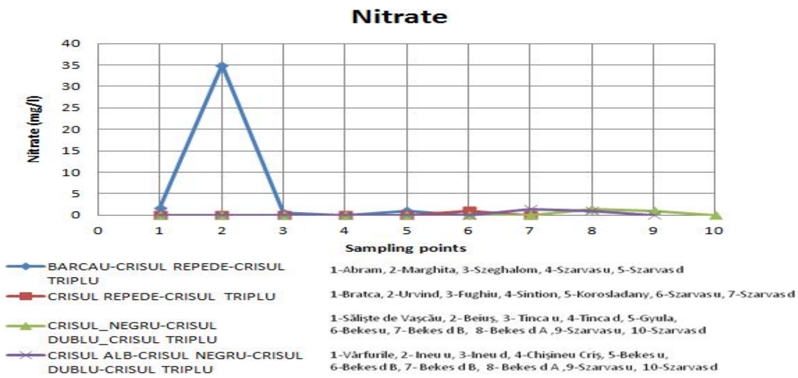

Fig. 9. The Nitrates measured in the sampling points (August 2011)

According to the nitrates content of the analysed samples (figure 9) almost fall within the very good chemical status I (NO_3^-) ≤ 50 mg·L^{-1}) [Decision no. 100, 7 February 2002, Aligned 7]. The highest values for nitrates concentrations were registered in Marghita (35mg·L^{-1}) on Barcău River.

Nitrites (NO_2^-) is the first step of ammonia oxidation. They may come from the reduction of nitrates also. Their presence in water suggests the existence of oxidation-reducing processes generators [Orbeci C., D. Turtoi, 2006]. Standard method used was a spectrophotometric method (λ=520 nm): SR ISO 3048/2/96. The method applies to nitrites concentration more than 0,5mg·L^{-1}. According to the nitrites content of the analysed samples all fall within the very good chemical status I (NO_2^- ≈ 0mg·L^{-1}) [Decision no. 100, 7 February 2002, Aligned 7].

Phosphorus found in surface waters in the following forms: dissolved inorganic phosphorus (orthophosphate, PO4-3, HPO4-2, H2PO4-); dissolved organic phosphorus (phosphorus contained in organic compounds dissolved or colloidal state, especially type particles coming from the decomposition of organic phosphorus); phosphorus organic matter (called "particular"), representing the phosphorus contained in living organisms and organic debris; inorganic phosphorus in suspension or "particular", composed generally of polyphosphates, such as hexametaphosphate or sediment (minerals containing phosphates, orthophosphates adsorbed on clays, etc.), inorganic phosphorus "nonparticular" originate from detergents; -Biotic phosphorus (contained in algae, aquatic plants, zooplankton, fish, etc.) [Orbeci C., D. Turtoi, 2006].

Standard method used was a spectrophotometric method SR EN ISO 6878/2005 (λ=600 nm).

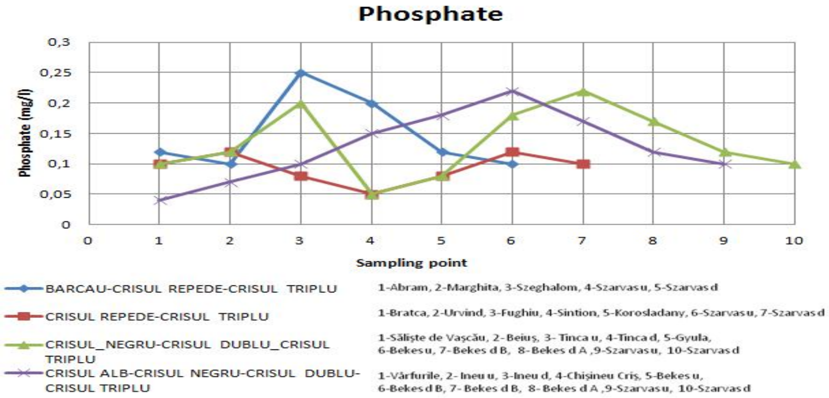

Fig. 10. The Phosphates measured in the sampling points (August 2011)

According to the phophates content of the analysed samples (figure 10) the samples from: Vărfurile, Ineu, Chişineu Criş on Crişul Alb River, Fughiu, Sintion, Korosladany on Crişul Repede River, Sălişte de Vaşcău on Crişul Negru River and Szarvas upstream on Crişul Triplu River fall within the very good chemical status I (phosphates ≤ $0,1 mg\cdot L^{-1}$) [Decision no. 100, 7 February 2002, Aligned 7]. The samples from Beiuş, Tinca, Bekes upstream on Crişul Negru and Szarvas downstream on Crişul Triplu, where the phosphates concentration slightly exceeds the threshold of $0,1 mg\cdot L^{-1}$, which places in the water category II ($0,1$-$0,2\ mg\cdot L^{-1}$), indicated a good chemical status. The samples from Szeghalom on Crişul Repede and Bekes downstream on Crişul Negru where the phosphates concentration slightly exceeds the threshold of $0,2\ mg\cdot L^{-1}$, which places in the water category III ($0,2$-$0,4\ mg\cdot L^{-1}$), indicated a weak chemical status.

CONCLUSIONS

According to the analysed physical and chemical parameters content of the water analysed samples almost fall within the very good chemical status I [Decision no. 100, 7 February 2002, Aligned 7], except:

-samples from Urvind and Fughiu, where the water can be classified in the II and III category of quality, for pH parameter;

-samples from Szeghalom, Gyula, Bekes where the water can be classified in the II Category; Marghita, Szarvas where the water can be classified in the III Category and Abram where the water can be classified in the IV Category for dissolved oxygen parameter;

-samples taken downstream and Abram have the CCO-Mn value in the second quality category of surface water with good condition

-sample taken in Abram have the chloride ion concentration, which places it in the water category II.

-samples from: Abram and Korosladany could be place in the II category in accord with the ammonium ion concentration, this indicated a good chemical status.
-samples from Beiuş, Tinca, Bekes upstream and Szarvas downstream, where the phosphates concentration places the samples in the water category II, indicated a good chemical status.
-samples from Szeghalom and Bekes downstream where the phosphates concentration places the samples in the water category III, indicated a weak chemical status.
In all cases permanent alkalinity is zero, which means that the alkalinity is due to bicarbonate dissolved in water. Weak Hard Water (3,8-5,6 °German) were found in: Crişul Dublu to Bekes; Crişul Repede to Sântion, Bratca; Crişul Negru to Sălişte de Vaşcău, and Barcău to Abram. Moderately hard water (5,6-11,2 °german) were found in: Crişul Triplu to Szarvas; Barcău to Szeghalom, and Marghita; Crişul Repede to Korosladany, Fughiu, Urvind; Crişul Negru to Gyula, Tinca, Beiuş; Crişul Alb to Vârfurile, and Ineu. Very hard waters (11,2-28 °german) were found in: Crişul Alb to Chişinău Criş.
Acknowledgments This work was financially supported by the Cooperation Program Hungary-Romania, project HURO 0901/086/2.2.2.

REFERENCES

1. Andrisca S.G., 2011, pHD thesis "Starea de calitate a apei in bazinul hidrografic Barcau", Universitatea din Oradea
2.Barabaş B., 2009, Poluarea apelor. Sursele şi efectul poluării, Ed. Rovimed
3.Decision no. 100, 7 February 2002, Aligned 7
4.Dumitrache F., E. Diacu, 2010, Study on the Seasonal Variation of Nitrogen Nutrients, Content from Ialomita River Hydrographic Basin, Revista de chimie, 61(3), 328-332
5.EN 27888-1997
6.EN 25 814 ISO/1999
7.Gavrilescu E., 2003, Poluarea mediului acvatic, Ed. Sitech
8.Gurzau A. E., E. Popovici, A. Pintea, O. Popa, C. Pop, I. Dumitrascu, 2010, Quality of surface water sources from a central Transylvanian area as a possible problem for human security and public health, Carpathian Journal of Earth and Environmental Sciences, 5(2), 97-101
9.ISO 9297/2001
10.Lupea A.X., A. Garibeh Branic, A. Ardelean, D. Ardelean, 2008, Fundamente de chimia mediului, EDP Bucureşti
11.Orbeci C., D. Turtoi, 2006, Ed. Agir, Bucureşti
12.STAS 6324-61
13.SR EN ISO 8467-2001
14.STAS 6364-78
15.STAS 3026-76
16.STAS 3026-76
17.STAS 8683-70
18.STAS 89001-71
19.STAS 89001-71
20.Vântu V., M. Bertcea, I. Borza, I. Custe, D. Şchiopu, et all, 2002, Ecologia şi protecţias mediului, Ed. Ion Ionescu de la Brad
21.www.wikipedia.ro