Evaluation of environmental impact and risk in Prut River using five indicators (CBO₅, CCO-Cr, SO₄²⁻, NO₂⁻, NO₃⁻)

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Abstract
Prut River is very important for sustaining the biodiversity and economical activities in its area for Romania, Ukraine and Republic of Moldova. Anthropogenic activities are present everywhere especially near a big water flow because they need a close water resource. The major problems remain the impact and a possible risk produced as a negative result in these activities (agriculture close to river, wastewater from the cities, animal farms, industry and others).

In case of Prut River, there were constructed matrices for evaluation of environmental impact and risk using five different indicators (CBO₅, CCO-Cr, SO₄²⁻, NO₂⁻ and NO₃⁻) during different months (September, October, November and December 2013). The sampling sites were fixed between Costesti-Stanca and Giurgiulesti that covered a large area of study. The impacts and risks were analyzed according to each indicator and as total ones. The resulted values were integrated in different classes for impact - EI (B-environmental impact which does not cross the maximum admitted value; C-environmental impact that creates slight disturbance of the organisms; D-environmental impact that creates high disturbance of the organisms) and risk – ER (A-insignificant risks; B-minor risks = monitoring it is not required; C-medium risks = monitoring is very required). The conclusions suggested that the impact is different according to each analyzed indicator and to sampling period. The highest peak was recorded between the sampling stations Leuseni and Leova.

Keywords: Environmental impact, Risk, Prut River, Indicators, Anthropogenic activities

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Introduction
Prut River is very important for sustaining the biodiversity and economical activities in its area. Anthropogenic activities are present everywhere especially near a big water flow because they need a close water resource. The major problems remain the impact and a possible risk produced as a negative result in these activities (agriculture close to river, wastewater from the cities, animal farms, industry and others). The aim of the study was the evaluation of environmental impact and risk using five different indicators (CBO$_5$, CCO-Cr, SO$_4^{2-}$, NO$_2^-$ and NO$_3^-$) during different months (September, October, November and December 2013).

Materials and methods
The raw data were provided by The Fifth Report, September-December 2013 issued by the Institute of Zoology, Academy of Science, Republic of Moldova, which is partner in the Project: Resources pilot center for cross-border preservation of the aquatic biodiversity of Prut River MIS ETC 1150.

In order to measure the environmental impact and risk we used the method developed by Robu and Macoveanu (2010). This method allows the measurements of impact and risk using specific indicators which are characterizing the water quality, the anthropogenic activities and the importance of water resource in biodiversity preservation and economical activities. The specific indicators that characterize the water quality in this study were: CBO$_5$, CCO-Cr, SO$_4^{2-}$, NO$_2^-$ and NO$_3^-$. The time interval for sampling and analysis of the samples started in September 2013 and ended in December 2013. This provided a 4 months interval for impact and risk monitoring. The sampling sites were: Costesti-Stanca, Braniste, Sculeni, Leuseni, Leova, Cahul, Cislita-Prut, Giurgiulesti, localized in same order from North to South of Prut River.

The environmental impact and risk were calculated for each month of monitoring. The first step of the method was to establish the importance degree of the analyzed environmental element (in this case was the surface water from Prut River) on a scale between 0 – 1 (Robu and Macoveanu, 2010); this measurement depends on the expert’s experience. The next step was the analyses of the quality for each specific indicator (CBO$_5$, CCO-Cr, SO$_4^{2-}$, NO$_2^-$ and NO$_3^-$) using a specific formula: $Q = \frac{\text{Maximum accepted concentration by law for the specific indicator}}{\text{Measured concentration in the samples for the specific indicator}}$ (Robu and Macoveanu, 2010).

The next step was to express the units of importance (0–1) for each specific indicator for the sampling area; it also depends on expert’s experience. The final formula of the environmental impact measurement is: Environmental impact = Units of importance/$Q$ (Robu and Macoveanu, 2010). The values were classified on a scale (<100 - >1000) based on the method proposed by Rojanschii (1997) named “Indices of global
pollution”, in different impact classes (Robu and Macoveanu, 2010). After the calculation of the each environmental impact of specific indicator for all months and sampling sites there was calculated a total environmental impact where all of these indicators were combined.

The environmental risk was calculated with a formula based on the environmental impact: Environmental risk = Environmental impact/Probability of producing an impact. The probability was analyzed for each specific indicator and sampling site (Robu and Macoveanu, 2010). The Probability units are evaluated on scale from 0 to 1 and they depend on expert’s experience (Robu and Macoveanu, 2010). Analysis and interpretation of the raw data were proceeded with OriginPro 8 and Microsoft Office Excel 2007 software.

**Results and discussions**

**Environmental impact and risk of nitrite and nitrate (NO$_2^-$ and NO$_3^-$)**

These compounds are present in waters as ions, compounds that are involved in the nitrogen cycle. The main source of nitrite and nitrate in water is the wastewater untreated properly, agriculture (inorganic nitrogenous fertilizers), and oxidation of nitrogenous waste in human and animal excreta (World Health Organization, 2011). Nitrate concentrations have increased step by step in many European countries in the last 20-50 years, and in some countries they have almost doubled. According to USEPA (1997) the naturally levels (depending of some conditions) are for nitrite 0.3 mg L$^{-1}$, and for nitrate 4 – 9 mg L$^{-1}$.
In the present study, the impact of nitrite (Figure 1.) was different for each month of monitoring. The impacts were framed for September and October within class B (environment under anthropogenic pressure below the maximum limit admitted by law), with A risk class (not significant risk) and B risk class (minor risks, the monitoring is not required) for sites Leuseni and Leova. The nitrite environmental impact decreased in November, it was framed within A class (environment not affected by the anthropogenic activities) excepting sites Leuseni and Leova situated in class B. In December, the impacts and risks were framed within the lowest class A, with no significant impact.

The environmental impact for nitrate (NO$_3^-$) was classified in all four months in class A (Figure 2.), excepting site Leova in September and November (class B). The risk was framed within class A, not significant.
Figure 2: Nitrate (NO$_3$\textsuperscript{-}) environmental impact (EI) and environmental risk (ER)

Environmental impact and risk of sulfate (SO$_4$\textsuperscript{2-})

Sulfates naturally occur in numerous minerals, including barite (BaSO$_4$), epsomite (MgSO$_4$·7H$_2$O) and gypsum (CaSO$_4$·2H$_2$O) (Greenwood et al., 1984; World Health organization, 2004). Sulfates and sulfuric acid are used in the production of fertilizers, chemicals, fungicides, insecticides and other products. Aluminum sulfate is a component used as sedimentation agent in the treatment of drinking-water (McGuire et al., 1984). The sulfates may occur in Prut River from many sources, natural and anthropogenic.

Agriculture is the major activity near Prut area; the chemicals based on sulfates used for increasing the soil productivity are causing disturbance to the environment. For example, according to a study published in 2007, the values of sulfate concentration in Dambovita River water were 31-94mg L$^{-1}$; this classified the water in Quality class I (80mg L$^{-1}$) and Quality class II (150mg L$^{-1}$)– limits according to the Order MAPM no. 1146/27.03.2002 (Mitranescu et al., 2007).

The total impact of this indicator (Figure 3) was framed within class D (environment under high anthropogenic pressure–
disturbance for organisms) during September, November and December, with minor risks. The impact for December was framed within class E (environment under extremely anthropogenic pressure – very dangerous for the organisms) but the risk was minor. The areas with the highest impacts (class E) were Leuseni and Leova during the all months but in October, it was also the case for sites Cahul, Cislita-Prut, and Giurgiulesti.

Figure 3: Sulfate ($\text{SO}_4^{2-}$) environmental impact (EI) and environmental risk (ER)

Environmental impact and risk of biochemical oxygen consumption ($\text{CBO}_3$) and chemical oxygen consumption ($\text{CCO-Cr}$)

The biochemical oxygen consumption ($\text{CBO}_3$) was another indicator used in our study. The concentration of this indicator analyzed in other studies was for Dambovita River 3 – 42 mg O$_2$ L$^{-1}$; these concentrations classified the water in II (5 mg O$_2$ L$^{-1}$) and Quality class IV (>25 mg O$_2$ L$^{-1}$) - limits according to Order MAPM no. 1146/ 27.03.2002 (Mitranescu et al., 2007). In Danube River, near CELROM, the concentrations were 1.37–1.83mg O$_2$ L$^{-1}$ that classified the water quality in Class I (3mg O$_2$ L$^{-1}$)– limit values of water quality according to the Order MAPM no. 1146/2002 (Andrița, 2012).
The environmental impact of this indicator was framed for all months of the study (Figure 4) within class B (environment under anthropogenic pressure below the maximum limit admitted by law). This was analyzed for each sampling site and the results showed the highest impact during October at the sites Badragii Noi, Leova and Leuseni – class C (environment under anthropogenic slight pressure that creates slight disturbance of the organisms). It decreased in December. The risk was the highest in October and it was fitted in C class (medium risks, monitoring is very required) for sites Leuseni, Leova and Cahul. It decreased in December, but for site Leova remained in the class C. The rest of the risks were minor at the other sampling sites.

The chemical oxygen consumption (CCO-Cr) was the last indicator used in our study. The report published in 2004 showed in Danube River, near CELROM, concentrations of this indicator of 9.77–11.96 mg O$_2$ L$^{-1}$; according to this, the water quality was classified in Quality Class I (10 mg O$_2$ L$^{-1}$) and Quality Class II (25 mg O$_2$ L$^{-1}$) – limit values of water quality according to the Order MAPM no. 1146/2002 (Andrița, 2012). The water of wells from the hydrographic basin of Bega
River had the concentrations 39.6 - 86.2 mg O₂ L⁻¹ (Copacean et al., 2011).

The environmental impact of this indicator (Figure 5) was framed within the highest class–E class with high levels of risks (C, D, E). These results were not sufficient to draw a conclusion. It is obvious that there is a problem downstream of site Costesti-Stanca and the risk is increasing. The highest values are for October followed by a decreasing in November and December. Further investigations are required, assuming these results, using comparisons for different years and the dynamics of the organisms at these sites. The values of this indicator were integrated with the others to calculate the total environmental impact and risk.

**Total environmental impact and risk for all five indicators**

The environmental impact and risk were discussed for each indicator. These were different according to month and sampling site. These differences can be correlated with the anthropogenic activities around precipitations and biological cycle specific to this type of ecosystems.

These aspects can be outlined in October (Figure 6) when the impact was classified in class D (environment under high anthropogenic pressure – disturbance for organisms) which it decreasing to C class
in December (environment under anthropogenic slight pressure that creates slight disturbance of the organisms). It was observed a seasonality of the environmental impact correlated with different factors. The environmental risk suggested the monitoring in the future of the sites Sculeni, Leova, Leuseni and Cahul, field investigation to find possible pollution sources and to draw plans of management. Data suggested that the other sites, downstream the areas with the highest risk, are not affected and the river has a high capacity of self-cleaning.

This study explained the variations of the environmental impact upon Prut River during different months, directly depending on different aspects including environmental conditions and dynamics.

There were identified the areas that require an intensive monitoring and field investigations to search the main sources of pollution and which produce high environmental impact. These areas are: Sculeni, Leuseni, Leova and Cahul.

Figure 6: Total environmental impact (EI) and total environmental risk (ER) for all five indicators
In the future, this kind of study will be necessary to show the implementation of the management projects of biodiversity preservation and economic development in the Prut River area.

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References