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NATURAL REMEDIATION OF THE MAIN EFFLUENTS OF TROTUȘ RIVER AFFECTED BY HEAVY METALS POLLUTION

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Abstract

The hydrographic basin of Trotuș River is a region with an important impact for science because of the geographic variety and here are important constructions on watercourses that have an important ecological impact. The purpose of this paper is to highlight the natural remediation related to heavy metals (Cd, Pb, Hg, and Ni) pollution of the main tributaries of the Trotuș River from Bacău County in 2010-2015. From the year 2010 to 2015 the presence of heavy metals was monitored from Trotuș River and its main tributaries and for monitoring purposes the hydrologic basin was divided into nine sections: Trotuș River, Asău River, Ciobănuș River, Izvorul Alb River, Plopu creek, Slănic River, Tazlău River, Tazlăul Sărat River, Uz River.
The data set from each year was collected and, following the internal procedure, an annual average for Cd, Ni, Pb, and Hg was calculated. There were some exceedances of acceptable concentrations of Cd and Pb during the monitoring period 2010-2012 as a result of the existence of pollution sources upstream sections of the study area. In 2012 it appears that the concentrations of heavy metals have started to decrease. In the next years, 2013 to 2015, in all monitoring sections, the concentrations of these metals were within the permissible limits or below the detection limit of the analysis device. Throughout the study periods, there were not exceeding concentration of Hg and Ni in any monitoring section. This decrease in heavy metal pollution is primarily due to basic management measures applied to these watercourses.

Key words: H.B. of Trotuș River; monitoring of H.M. pollution; priority hazardous H.M.; water self-purification process

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1. Introduction

Heavy metal pollution over the last decade has caused some serious concerns for the environment (Florescu et al., 2011a; Gămăneci and Căpățînă, 2011; Jacob et al., 2018; Matache et al., 2018). The presence of heavy metals in waters, especially in rivers, is a major issue, because these substances work directly on the ecological status and this is a consequence due to industrial discharge of mining, smelting, tanneries, battery manufacturing, metallurgical, municipal waste generation, fertilizers and pesticide applications etc. with a higher incidence in developing countries (Panahandeh et al., 2018; Popescu, 2010; Pugazhendhi et al., 2017).

Heavy metals that can be observed in water streams can cause serious health issues, such as stomach cramps, vomiting, skin irritations, nausea, accumulative poisoning, anemia, brain damage, cancer etc. But to effective and safe removal of heavy

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metals ions from flowing waters is a difficult task (Shanmugaprakash et al., 2018; Zaharia, 2017).

Knowledge of heavy metals action on ecosystems is particularly important for the implementation of effective measures to reduce pollution and achieving a good state of water body quality (Gheorghe and Prisecaru, 2010; Mălăcea and Gruia, 1965). The natural remediation can happen through biological processes. Bioremediation is a complex biological process, where microbes are able to reduce the bioavailability of heavy metals by the production of organic and inorganic acids, reduction, oxidation and production of complexing agents. After millions of years of evolution, microorganisms are crucial to nutrient recycling in water ecosystems, especially if they can survive and grow under various extreme conditions of pH, temperature and even at a toxic concentration so they are able to remediate heavy metal pollution (Arivalagan et al., 2014; Jacob et al., 2018; Mathimani and Pugazhendhi, 2018; Teymouri et al., 2017).

Trotuş River (Fig. 1) is a right tributary of the Siret River and it has a length of 162 km and springs from Ciuc Mts from an altitude of 1.360 m and passes through the peaks of Tarcău, Gosman and Berzuntului (Prisecaru et al, 2006; Woitke et al, 2003). With an area of 4.456 km and an average altitude of 706 m, the Trotuş hydrographical basin is fed from rainwater and underground sources. The average flow rate at the Trotuş River spill is 36.0 mc/s (Florescu et al., 2011a; Prisecaru et al, 2006). In the past, the industrial units of Trotuş Valley and the old urban wastewater had a major implication in environmental pollution (Florescu et al., 2011). And there is evidence that priority substances and priority hazardous may be present in the long term in the aquatic environment. Due to industrial activities which have taken place in the past in the studied area, polluting substances have been spread into the water. In the wastewater, bacteria are more resistant and are considered to be an eco-friendly biosorbent (Pugazhendhi et al., 2017), in this context, biosorption has evolved as a viable alternative for the removal of heavy metals and based on the results, predictive models are made (Dhanarani et al., 2016; Karthik et al., 2017; Shanmugaprakash et al., 2018). But in 2004-2005, in the hydrographic basin of Trotuş River was an amount of accidental pollution caused by the floods that affected the oil pipelines in the area. In 2006, as a result of the measures taken by the industrial units and local councils, the pollution of the Trotuş River was substantially reduced (Florescu et al., 2011a; Popa, 2005; Prisecaru et al, 2006).

The hydrographic basin of Trotuș River is a region of scientific importance because of the geographic variety and important construction on watercourses with important ecological impact (Bibire et al., 2016; Florescu et al., 2011b). The uncontrolled anthropic intervention is present and continues to affect the natural water ecosystem. Each action involved in changing the environment has many consequences (Florescu et al., 2011b; Woitke et al., 2003). Therefore, is required to realize detailed studies looking for the impact of toxic pollutants, like heavy metals on river basins by monitoring the quality of the hydrographic network (Florescu et al., 2011b; Malaney et al., 1959; Reza and Singh, 2010). Studies published so far have not focused on monitoring the water quality in terms of heavy metal pollution on Trotuș River effluents (Bibire et al., 2016; Prisecaru et al, 2006).

The purpose of this study was to evaluate the levels of four heavy metals according to Directive 39/2013 / EU of the European Parliament and of the Council, heavy metals investigated can be found on the list of supervision in the field of water policy as priority substances (Pb and its compounds, Ni and its compounds) and priority hazardous (Cd and its compounds, Hg and its derivatives) for the aquatic environment of the main effluents of Trotuș River from Bacău County in years 2010-2015.

2. Materials and methods

From 2010 to 2015 the presence of heavy metals and their compounds (Cd, Pb, Hg, Ni) was monitored from Trotuş River and its main effluents mainly by water authorities from North-East Region. For monitoring purposes, the hydrologic basin was divided into nine sections: Trotuş River, Asău River, Ciobănuş River, Izvorul Alb River, Plopu creek, Slănic River, Tazlău River, Tazlăul Sărat River, Uz River and lake (Table. 1).

The samplings were collect in Polypropylene sampling containers (PP), ethylene propylene fluorinated (FEP) or polyethylene (PE). Containers for sampling must not contain metals and not to determine the loss of metals by adsorption or diffusion. Sample storage is done immediately after sampling, by addition of 0.5 mL of concentrated nitric acid with d = 1.40 mg / mL per 100 mL sample, to obtain a pH <2. To the preservation of the water samples with high alkalinity, it may be necessary to add a surplus of acid. It is important to add enough acid to the sample in order to avoid losses of elements by the effects of adsorption. For all aqueous samples, a blank sample is prepared and analyzed under the same conditions as the sample. The data from each year was collected and an annual average for Cd, Ni, Pb, and Hg was calculated. In Table 2 we present the values above the limit for the studied heavy metals. And to establish the working parameters, the analysis of samples was performed with an atomic absorption spectrophotometer (AAS) Zenit 700, with flame and automatic graphite oven, computerized with transversal heating, deuterium lamp for background correction and hollow cathode lamps.

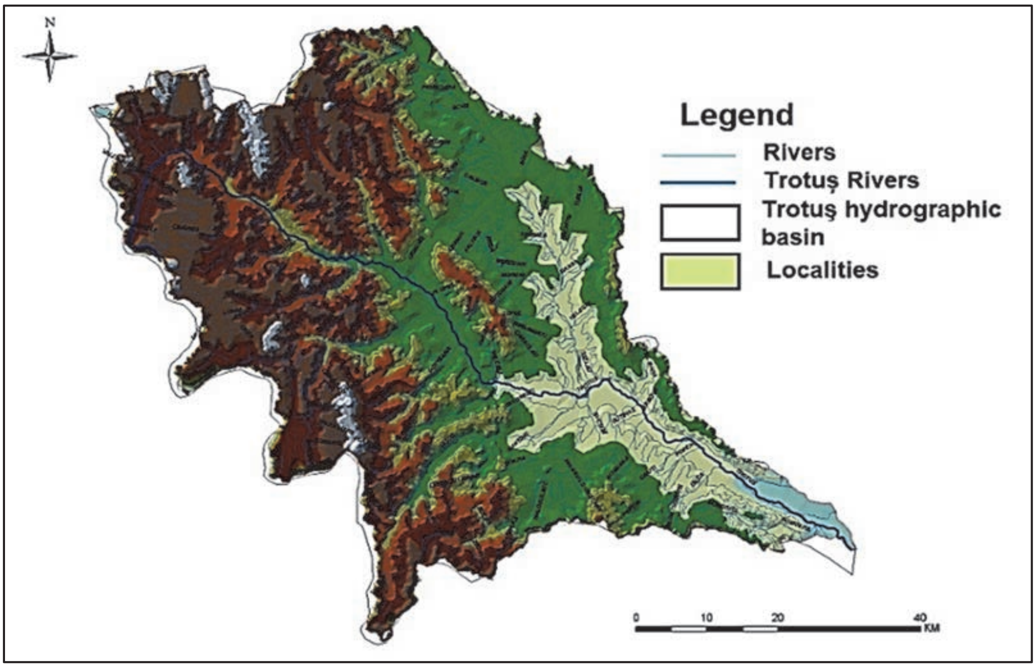

Fig. 1. The physical and geographic map of the Trotuş River Basin - a map made using the ArcMap 9.0 (ESRI)

Table. 1 The River section location with GPS coordinates

Years	*Reference River*	*River section*	*Longitude*	*Latitude*	*Reference River*	*River section*	*Longitude*	*Latitude*
2010 - 2015	**Asău**	Asău	2.640.310	4.644.320	**Tazlău**	Helegiu	2.674.373	4.634.982
	Ciobanus	Ciobanus	2.634.089	4.643.367	**Tazlău Sărat**	Amon Bolat	2.639.047	4.663.585
	Izvorul Alb	Upstream Lake Poiana Uz	2.634.361	4.631.127	**Trotuş**	Adjud	2.722.217	4.603.544
	Plopu creek	Upstream Lake Poiana Uz	2.635.334	4.630.240	**Uz**	Upstream Lake Poiana Uz	2.632.686	4.633.180
	Slănic	Upstream Slănic Moldova	2.655.354	4.624.953		lake P.Uzului	2638844	4633487

The readings were made directly on the machine to a calibration curve. For determination of Cd, Pb and Ni the SR EN ISO 15586:2004 (ISO 15586, 2004) method was used and for Hg determination, SR EN ISO 17852:2009 (ISO 17852, 2009), with modifications for suitability to the matrix type analyzed. Each determination was performed in three repetitions. The detection limits for Cd were 0.05 µg/L, for Pb 0.3 µg/L, for Hg 0.005 µg/L and for Ni 0.6 µg/L.

3. Results and discussion

In all the monitoring period (2010 to 2015), was observed on the rivers sections Trotuş, Asău, Tazlău, and Tazlău Sărat the heavy metal concentration. Even if in these sections of the river, in the past have been industrial activities, however, pollution has not been so strong, and in consequence, the heavy metals studied did not exceed the normal values (Cd - 0.08 µg/L, Pb - 7.2 µg/L, Hg - 0.025 µg/L, Ni – 20 µg/L in Trotuş, Asău, Tazlău and Tazlău Sărat Rivers) as is seen in this graph (Fig. 2).

In the year 2010 were registered some values over the limit on: Ciobănuş River section for Cd = 0.298 µg/L; Izvorul Alb River section for Cd = 0.77 µg/L and Pb = 8.31 µg/L; Plopu Creek for Cd = 0.416 µg/L and Pb = 5.55 µg/L; Slănic River for Cd = 0.375 µg/L; Uz River for Cd = 0.842 µg/L and Pb = 9.01 µg/L and in the Lake only for Cd = 0.37 µg/L (Fig. 3). The biggest value registed for Cd was 0.842 µg/L in Uz River and for Pb 9.01 µg/L in the same section of Uz River followed by 8.31 µg/L in Izvorul Alb River section.

In 2011 it was registered some values over the limit on the same sections of the rivers and on the same metals: Ciobănuş River section for Cd = 0.28 µg/L; Izvorul Alb River section for Cd = 0.182 µg/L and Pb = 3.3 µg/L; Plopu Creek for Cd = 0.24 µg/L and Pb = 4.01 µg/L; Slănic River for Cd = 0.2 µg/L; Uz River for Cd = 0.478 µg/L and Pb = 1.68 µg/L and in the Lake only for Cd = 0.15 µg/L (Fig. 4). Compared with 2010 the values are much lower, a noticeable drop in the level of Pb was in the Uz River section from 9.01 µg/L in 2010 it remain only 1.68 µg/L in 2011, in Izvorul Alb River remain in 2011 3.3 µg/L compared with 2010 when the value was 8.31 µg/L. The high value for Pb remains in Plopu Creek 4.01 µg/L.

In 2012 remain some values over the limit for Cd = 0.171 µg/L and Pb = 0.75 µg/L they were registered in Izvorul Alb River and in Uz River section for Pb = 0.55 µg/L (Fig. 5). In the coming years, 2013, 2014 and 2015, in all sections of the river were not exceeded the yearly average values of heavy metals, all concentrations detected being within the permissible limits according to WFA 60, (2002) or under the detection limits: Cd - 0.08 µg/L, Pb - 7.2 µg/L, Hg - 0.025 µg/L, Ni – 20 µg/L in Ciobănuş, Izvorul Alb, Slănic, Uz rivers and Plopu Creek (Fig. 6).

Based on the results presented, it can be noticed that during the years 2010-2015 the water quality improved for Ciobănuş, Izvorul Alb, Slănic, Uz Rivers and Plopu Creek due to the fact that the industrial activity in the area has gradually decreased to zero after the 1990's and so there were no sources of pollution, the waters had the necessary capacity and time of gradual natural purification. Aquatic organisms, especially bacteria, they have contributed significantly in this regard, along with other vegetal and animal organisms (Mathimani and Pugazhendhi, 2018; Karthik et al. 2017) and physical factors and chemical that continued the transformation initiated by the bacteria.

Table. 2. Cd and Pb over the limit in 2010-2012

River / *Year*	*Ciobănuș River*	*Izvorul Alb River*		*Plopu Creek*		*Slănic River*	*Uz River*		*Poiana Uzului Lake*
	Cd (µg/L)	*Cd (µg/L)*	*Pb (µg/L)*	*Cd (µg/L)*	*Pb (µg/L)*	*Cd (µg/L)*	*Cd (µg/L)*	*Pb (µg/L)*	*Cd (µg/L)*
2010	0.378	0.85	15.5	0.496	12.75	0.455	0.922	16.21	0.45
2011	0.36	0.262	10.5	0.32	11.21	0.28	0.558	8.88	0.23
2012		0.251	7.95					7.75	

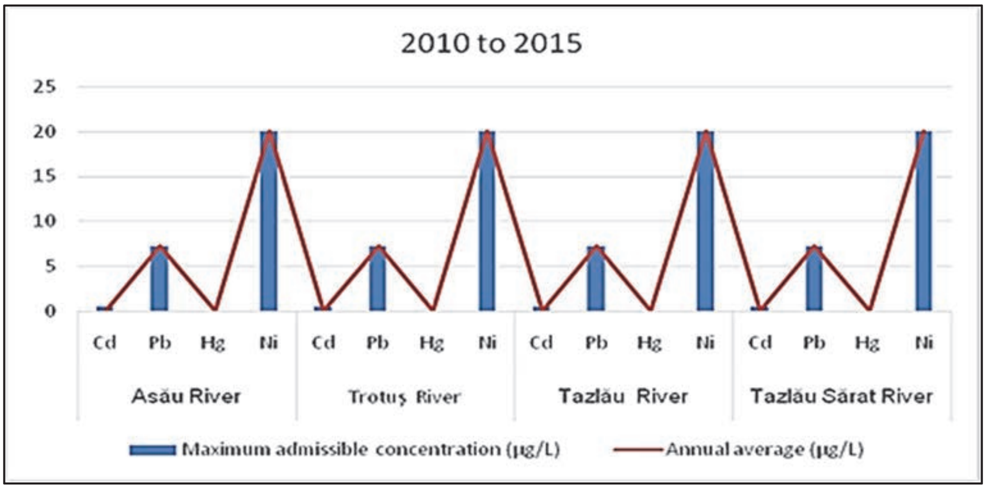

Fig. 2. Annual maximum allowable concentration for analyzed metals

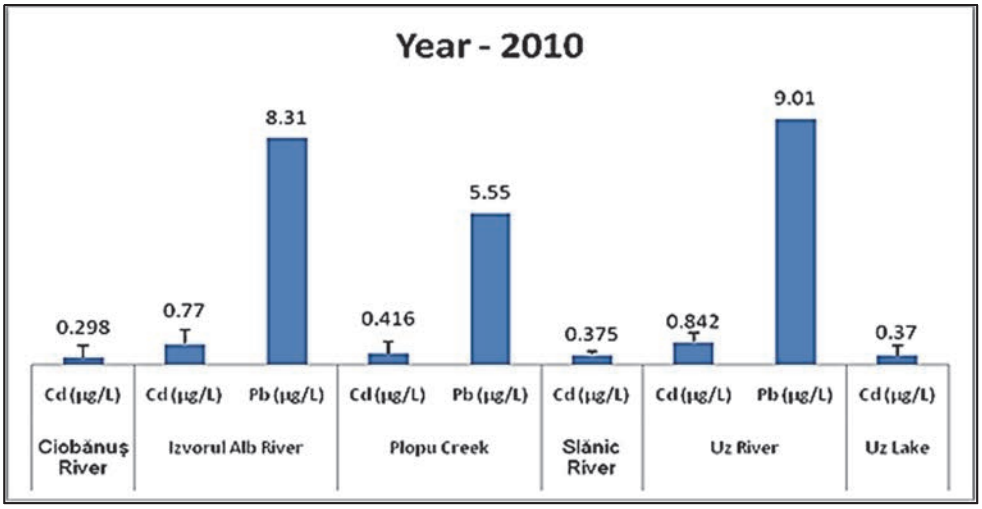

Fig. 3. Concentrations above the annual average of heavy metals analyzed in 2010

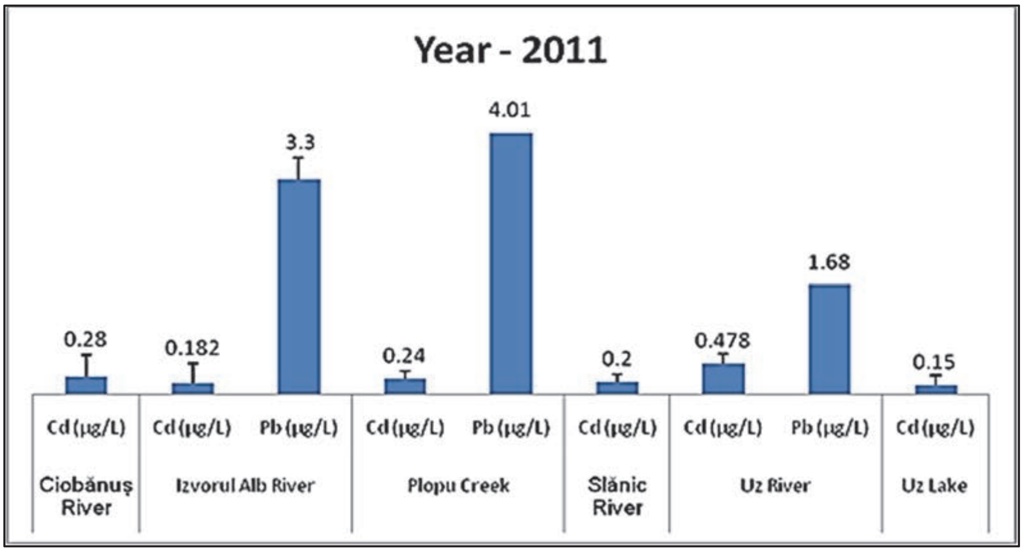

Fig. 4. Concentrations above the annual average of heavy metals analyzed in 2011

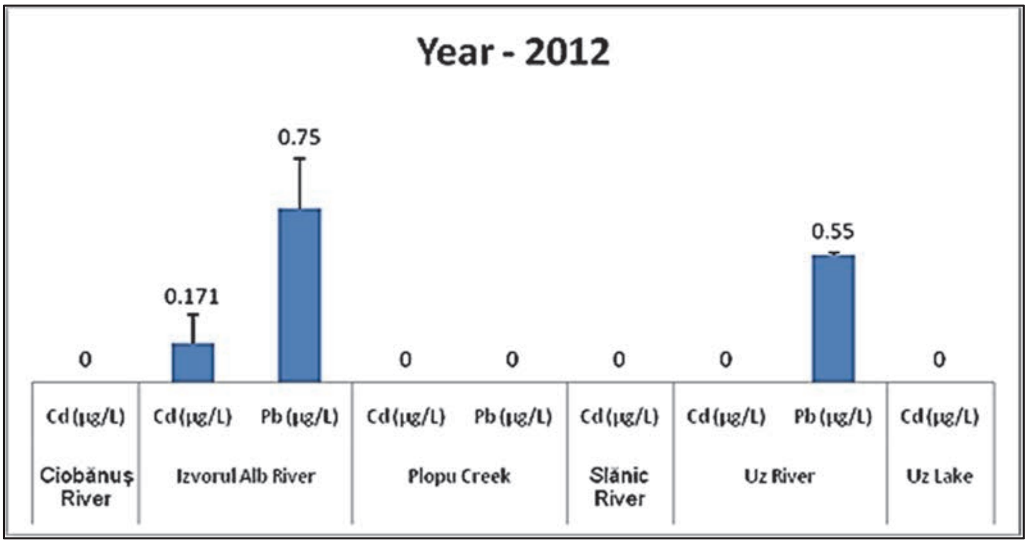

Fig. 5. Concentrations above the annual average of heavy metals analyzed in 2012

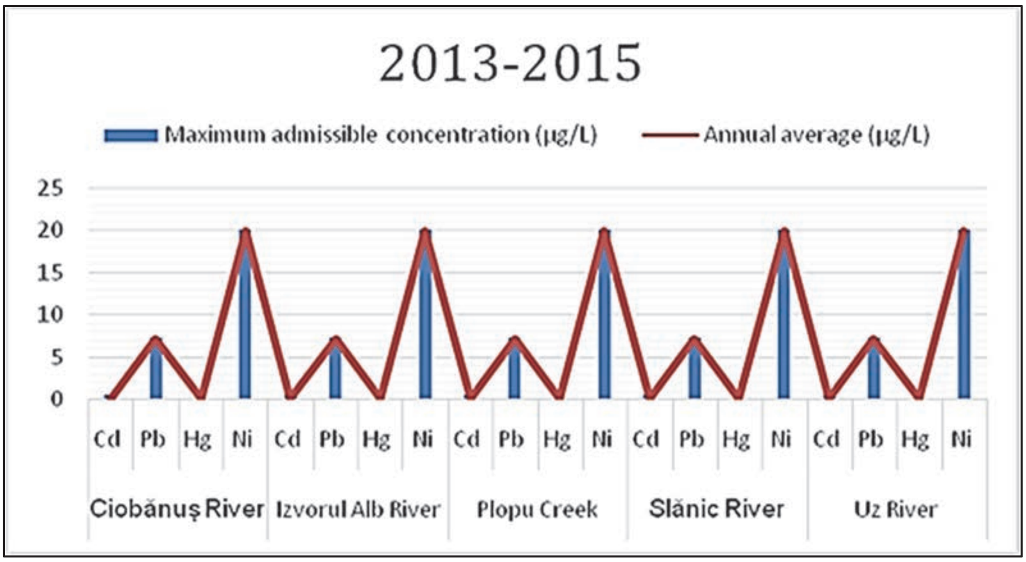

Fig. 6. Annual maximum allowable concentration for analyzed metals

Comparing with other results obtained by other authors we also found as the microorganisms can only withstand to a specific heavy metal and that different parameters (pH, temperature, etc.) play an important role in natural remediation (Arivalagan et al., 2014; Jacob et al., 2018). We think this is the reason that the pollution of the Trotus River has decreased significantly, a situation confirmed by the study made by Prisecaru et al. (2006) about the saprobic index in Trotus River, but we can also compare the distribution of quality classes on the Trotuş River in 2003 (Fig. 7) and 2006 (Fig. 8) where we can see an improvement in water quality in just three years.

4. Conclusions

In conclusion, there were some exceedances of acceptable concentrations of Cd and Pb during the monitoring period 2010-2012 on Ciobănuş, Izvorul Alb, Plopu Creek, Slănic; Uz Rivers and Lake, but the industrial activity in the area has gradually decreased to zero after the 1990's and aquatic organisms have contributed significantly in gradual natural purification, along with other vegetal and animal organisms and physical factors and chemical that continued the transformation initiated by the bacteria that's why in 2013 to 2015, in all monitoring sections, the concentrations of these heavy metals were within the permissible limits or below the detection limit of the analysis device.

During the study period, the Hg and Ni not exceeding the limit concentration in any monitoring section. In the Trotuş River Basin, the pollution with heavy metals has been substantially reduced as can be seen in the graphs presented in this study. But it also appears from the graphs that the pollution with priority hazardous heavy metals was not critical both on Trotuş River and on his main tributaries, but for good water quality, the water monitoring program continues.

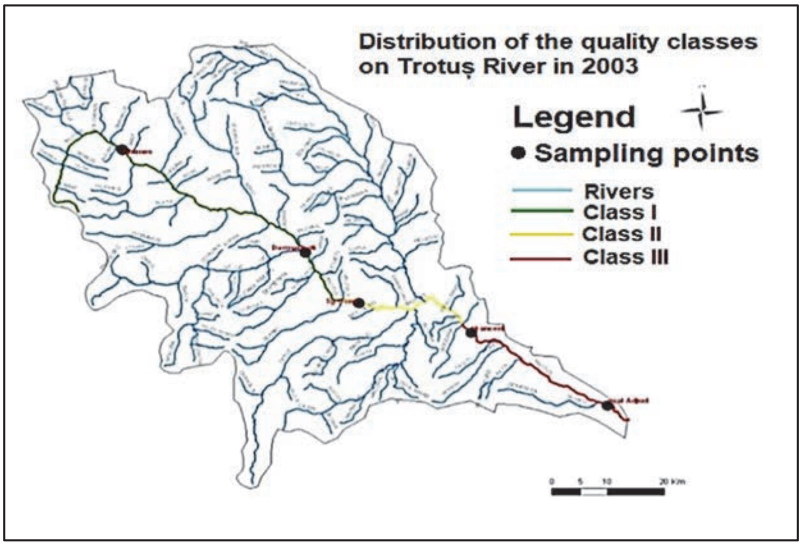

Fig. 7. The distributions of biological quality classes on the Trotus River in 2003

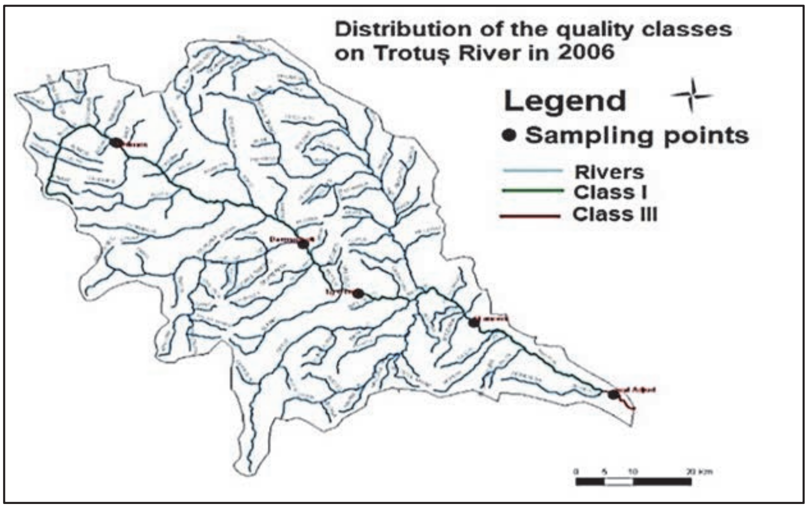

Fig. 8. The distribution of biological quality classes on the Trotus River in 2006

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