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MONITORING OF CADMIUM (Cd) IN TROTUŞ HYDROGRAPHIC BASIN

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INTRODUCTION

Trotuş's hydrographic basin is by location, geographical variety, area, number of tributaries, etc., a region of outstanding scientific interest and great attention from researchers. With an area of 4456 kmp and an average altitude of 706 m, it represents the area on which this Trotuş River, along with all its tributaries, feeds from rainwater and underground sources.

In the mountain area there are left tributaries of Valea Rece, Asau; on the right: Sulta, Ciobanuş, Uz, Dofteana, Slănic. In the sub-Carpathian area, Trotuş confluates with three rivers that have their springs in the mountain area: Oituz, Casin, Tazlau. Among the tributaries of the most important Trotus are Uz (S = 443 kmp, L = 45 km), Slanic (S = 126 km^2, L = 28 km), Oituz (S = 332 km^2, L = 59.5 km) L = 4.5 km), Tazlau (S = 10.93 km^2, L = 85.3 km).

Cadmium, a gray metallic transition metal, is found in surface and deep water as a result of subterranean infiltration of various wastes and is a major danger to human health, and is particularly damaging. Cadmium is a very toxic heavy metal that is dangerous even when exposed to very low doses.

A very large amount of cadmium is released into the environment, about 25,000 tonnes per year. Approximately half of this amount of cadmium is released into rivers, altered rocks and in the air, through forest fires and volcanic eruptions, and the rest is released because of human activities (cadmium is found in fertilizers with polyphosphates and pesticides, so it gets through the soil in the environment). Exposure to cadmium due to the environment can occur by eating basic foods, especially seeds, cereals and leaf vegetables, which rapidly absorb cadmium that occurs naturally or by contamination of soils with domestic sludge, fertilizers and polluted water.

Taking into account the importance of water in the human society (industry, agriculture, population health, etc.), it is essential to know the state of purity and pollutant loading of water. Recently, heavy metal pollution has attracted attention because of the particularly complex problem of this phenomenon, since most heavy metals are not found in water-soluble form or, if they really exist, the chemical species in question are complexed with organic ligands or inorganic compounds, which radically influences their toxicity.

MATERIAL AND METHODS

The data from each year was collected and an annual average for Cd was calculated. 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. For fixing the samples was used super-pure nitric acid (HNO_3) to keep the low pH and for preventing the precipitation of metal ions at high pH value.

The readings were made directly on the machine to a calibration curve. For determination of Cd, the SR EN ISO 15586:2004 method was used with modifications for suitability to the matrix type analyzed. Each determination was performed in three repetitions. The detection limit for Cd was 0.05 µg/l.

Cd concentrations were monitored in two steps.

The first stage took place during the years 2010-2012 on the Trotuş River, the control sections: Adjud, upstream Tg. Ocna, downstream Darmanesti, Ghimes - Faget and Vranceni; River Urmenis, section Comanesti; the Tazlăul Sărat River, the sections upstream Bolătău and Tescani; the Tazlau River, the Helegiu section; Slănic River, upstream section Slănic Moldova and downstream Slănic Moldova; Plopu Brook, upstream Lac Poiana Uzului; the Oituz River, the upstream section of Onesti; the Izvor Alb River, the upstream section of Lake Poiana Uzului; the Ciobănuş River, the Ciobănuş-Ciobănuş section; Caşin River, upstream Oneşti section and Asau River, Asau section (Table 1).

The second stage was carried out during the period 2013-2015, only on the Trotuş river in three sections: Adjud, downstream Dărmăneşti, Ghimeş - Făget and Vrânceni and Uz river in three sections: upstream Lake Poiana Uzului, downstream Lake Poiana Uzului, Lake Poiana Uzului (Table 2).

RESULTS AND DISCUSSIONS

In the monitoring period 2010-2012 (Table 1), there are exceedances of the CMA of Cd (maximum admissible value in surface waters = 0.45µg / l) only in the Uz River, the upstream Lac Poiana Uzului control section in 2010 (0.842 (0.478 µg / l) and in the Izvor Alb River, control section of upstream Lake Poiana Uzinei in 2010 (0.77 µg / l). These three exceedances could also be due to accidental leakage of pollutants. In the remaining control sections, over the entire monitoring period, there were no exceedances of the limits stipulated in GD 351/2005.

In the monitoring period (2013 to 2015), on the Trotuş, and Uz rivers, were not recorded concentration over the limit of Cd in any of the control sections studied (table 2), all concentrations detected being within the permissible limits according to the Water Framework Directive 2000/60/CEE or under the detection limits.

This situation is due to the fact that some of the industrial units in Valea Trotuşului have reduced their activity, while others, potentially producing pollutants (Dărmăneşti refinery, SC Carom SA), have completely ceased their activity. Urban wastewater treatment plants have entered rehabilitation, refurbishment and optimization programs for sewage treatment, which has led to an improvement in the quality of the Trotuş waters.

As a result of the measures taken by the industrial units and the local councils in the Trotuş catchment area and the intense activity carried out by the representatives of the Siret Water Directorate, the pollution of the Trotuş River decreased substantially during the years 2010-2015, which is also evident from the results presented in this paper.

Over the years 2015-2020, all potentially polluting units have the obligation to self-monitor waste treated wastewater, to track their waste water through production sites and treatment stages to fit within the maximum regulated limits and gradually reduce and stop evacuation of dangerous / priority hazardous substances.

Table 1. Concentrations of Cd recorded in Trotuş Basin waters during the years 2010-2012

River	River section	Metal µg/l	2010	2011	2012
TROTUŞ	Adjud	Cd	0.38	0.39	0.29
TROTUŞ	Upstream Tg. Ocna	Cd	0.4	0.42	0.38
TROTUŞ	Downstream Dărmăneşti	Cd	0.41	0.43	0.39
TROTUŞ	Ghimeş - Făget	Cd	0.41	0.4	0.41
TROTUŞ	Vrânceni	Cd	0.43	0.42	0.32
UZ	Upstream Lac Poiana Uzului	Cd	**0.842**	**0.478**	0.42
UZ	Downstream Lac Poiana Uzului	Cd	0.42	0.2	0.42
UZ	Lac Poiana Uzului	Cd	0.37	0.15	0.35
URMENIŞ	Comăneşti	Cd	0.39	0.43	0.4
TAZLĂU SĂRAT	Upstream Bolătău	Cd	0.35	0.4	0.2
TAZLĂU SĂRAT	Tescani	Cd	0.31	0.4	0.38
TAZLĂU	Helegiu	Cd	0.42	0.41	0.38
SLĂNIC	Upstream Slănic Moldova	Cd	0.375	0.2	0.45
SLĂNIC	Downstream Slănic Moldova	Cd	0.4	0.41	0.35
PLOPU CREEK	Upstream Lac Poiana Uzului	Cd	0.416	0.24	0.45
OITUZ	Upstream Oneşti	Cd	0.44	0.38	0.33
IZVOR ALB	Upstream Lac Poiana Uzului	Cd	**0.77**	0.182	0.171
CIOBĂNUŞ	Ciobănuş	Cd	0.298	0.28	0.45
CAŞIN	Upstream Oneşti	Cd	0.35	0.3	0.4
ASĂU	Asău	Cd	0.4	0.36	0.31

Table 2. Concentrations of Cd recorded in the Trotuş and Uz Rivers during the years 2013-2015

River	River section	Metal µg/l	2013	2014	2015
TROTUŞ	Adjud	Cd	0,075	0,076	0,08
TROTUŞ	Downstream Dărmăneşti	Cd	0,07	0,076	0,09
TROTUŞ	Ghimeş - Făget	Cd	0,082	0,087	0,09
TROTUŞ	Vrânceni	Cd	0,075	0,073	0,056
UZ	Upstream Lac Poiana Uzului	Cd	0,079	0,075	0,103
UZ	Downstream Lac Poiana Uzului	Cd	0,075	0,076	0,075
UZ	Lac Poiana Uzului	Cd	0,057	0,075	0,075

CONCLUSIONS

In conclusion, the Trotuş River and its main tributaries do not encounter serious problems with Cd contamination, although there have been some exceedances of acceptable concentrations during the 2010-2011 monitoring period, on the Uz River and the Izvorul Alb - upstream section Poiana Uzului Lake, as due to the existence of sources of pollution from the upstream study sections and probably having accidentally leaked pollutants.

In the following years, 2012-2015, in all monitoring sections, Cd and its compounds concentrations were within or below the detection limit of the analyzer.

Based on the results presented, it can be noticed that during the years 2010-2015 the water quality in the Trotuş Hydrographic Basin has improved, especially due to some economic agents that have reduced or closed the activity and other administrative factors that have contributed, over time, to a natural water rehabilitation.

For good water quality, it is necessary to continue the water monitoring program, and potentially polluting units have the obligation to self-monitor the treated wastewater and to analyze the waste water on production sites and treatment stages, so that to fall within the maximum regulated limits.

ABSTRACT

In the period 2010-2015 the monitoring of the incidence of Cd and its compounds in the waters of the Trotuş River and its main tributaries (Uz, Urmeniş, Tazlăul Sărat, Tazlău, Slănic, Plopu, Oituz, Izvorul Alb, Ciobănuş, Caşin, Asău) was carried out. There have been some exceedances of acceptable Cd concentrations during the 2010-2011 monitoring period, on the Uz River and the Izvorul Alb - upstream section of Lake Poiana Uzului. In the following years, 2012-2015, in all monitoring sections, Cd and its compounds concentrations were within or below the detection limit of the analyzer.

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