STUDY OF Pb AND Cd CONTENT OF CHEPELARE RIVER WATER

Lilko Dospatliev [1*], Dian Georgiev [2] , Diyana Dermendjieva [3], Nedyalko Katrandzhiev [4]
[1]*Department of Pharmacology, Animal Physiology and Physiological Chemistry, Faculty of Veterinary Medicine, Thracian University, Stara Zagora, Bulgaria;*
[2] *Department of Biology and Aquaculture, Zoology and Ecology Unit, Faculty of Agriculture, Trakia University – Stara Zagora*
[3]*Department of Applied Ecology and Animal Hygiene, Faculty of Agriculture, Trakia University, Stara Zagora, Bulgaria*
[4]*Department of Computer systems and technologies, Faculty of Technical sciences, University of Food Technologies, Plovdiv, Bulgaria*
lkd@abv.bg

ABSTRACT

The aim of this study is to perform an analysis of the River Chepelarska water content of Pb and Cd. Sampling was carried out during the period 2010-2013 year. Samples were taken at three places along the river from the fount to the outfall of Maritsa River. The sampling places determination was based on pollution sources at the area of Chepelare River. The sampling was performed near to the emitters approved by Plovdiv Water Agency. The analysis for the presence of heavy metals (Pb and Cd) showed that at place 1 and 2 were not exceeded concentrations of Pb according the Average annual value (AAV) of the Environmental quality standards (EQS) for 2013. At place 3 there was an amount of 0,010018 mg/dm^3 that was more than the AAV of the EQS for 2011 (0,00015 mg/dm^3). No excess of Cd was proven at place 1 compared to the AAV of the EQS for 2013. For the period 2011-2012 compared to the standard (0,00015 mg/dm^3) the amount of both heavy metals was excessive, respectively 0,00041 mg/dm^3 Pb and 0,000798 mg/dm^3 Cd. The reason was a breakthrough in tailing pod of the mining company GORUBSO-Lucky.

Key words: *Pb, Cd, content, water*

INTRODUCTION

Tracing the levels of heavy metals in water is a subject of several studies [1-5]. According to Olsvik et al. [6] the concentrations of heavy metals in water ecosystems usually change during the year. In this case the important factors to cause this are melting of the snow during spring, periods with lots of raining during the fall or dry summer. Thanks to this the levels of heavy metals can increase so much, that they adversely affect the sea dwellers, their health condition and biodiversity, causing physiological stress and even causing death.

A subject of testing in the present work are one of the most dangerous heavy metals in the nature-cadmium (Cd) and lead (Pb).

Polluting the environment and mainly the water ecosystems with cadmium (Cd), is one serious ecological problem, because its resistance, bioaccumulation potential and having no biological features. It's been found that each year 30 000 t of cadmium are released in the nature, as between 4 000 and 13 000 t comes from human action [1, 7]. According to Asagba et al. [8], the cadmium enters the water ecosystems as a result of wide anthropogenic activities - mines, paint production, plastic, ceramics, tires, batteries, industrial emissions, use of fertilizers, waste water sludge, including some natural ways (weathering of soils rich of cadmium, etc.)

According to Xu & Wang [9] and Jezierska *et al*. [10] the cadmium enters in the fish body through the gills and food. Finfish are extremely sensible to cadmium, as the different species have different tolerance to this metal[11]. Hoekstra et al. [12] found that LC50 values (48-96 h exposure) varies from 0.002 to 4.6 mg L^{-1}.

The lead is a grey-white metal, which occurs naturally in the nature in three forms: Pb, metal; Pb (II), and Pb (IV). He practically could be found everywhere on Earth, in all biological sistems and its the most disseminated from the heavy metals in the crustal. The lead usually occurs in combination with two or more other elements, with which forms lead compounds [6]. With his physical and chemical characterizations the lead is one incredibly useful and used in the different sectors of the industry metal. The lead is been used from ancient times, as some of his toxic effects were found ages ago. The biggest increase of the quantities of lead in the nature is registered in the period of 1950-2000 [6]. Nowadays the primary use of this metal is in the production of batteries, because in many countries the lead supplements in gasoline are forbidden. This contributed for sustained decline in air pollution, water pollution and soil pollution with this metal.

USEPA (2001) states the lead as the second most dangerous toxic pollutant, as the US agency for consumer protection prohibits the use of paints that contain lead yet in 1978. Because of his specific properties (low solubility) the lead penetrates in the fish organism slower. The toxic action of the lead on the aquatic organisms occurs in concentrations over 0.1 mg L^{-1} and it very much depends on their kind.

MATERIALS AND METHODS

Table 1 Parameters of ICPMS

Parameter	Value
RF generator power (kW)	1.3
Analytical lines (nm)	Pb (220.353) Cd (226.502)
Auxiliary gas flow rate(L min^{-1})	0.2
Nebulizer flow rate (L min^{-1})	0.8
Torch mode	Axial

Instrumentation

An inductively coupled plasma optical emission spectrometer (ICPMS) model Agilent 7500 was employed for the determination of the metal ions. The parameters of the instrument and emission lines of each element are shown in Table 1.

Water

Water samples were taken from each sampling sites by using 0.5-L polyethylene bottles immersed about 25 cm below the water surface. Before sampling was done, the polyethylene containers were pre-cleaned with 10% reagent grade HNO3, followed by rinsing three times with ultrapure water (18 M/cm resistivity) and dried in an oven at 70◦C for 6 h. Then, the samples were transported to laboratory in a cooler box and kept at 4◦C before their use.

Analytical procedures and analysis

In the laboratory, water samples for total recoverable metals were acidified with 10% HNO3 (analytical grade), then subsamples of which were filtered through a pre-weighed 0.45-μm membrane filters (Xinya membrane, Millipore), and the filterable fractions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin-Elmer, Optima 7000 DV).

Determination of the points for monitoring

The location of the point for monitoring is based on sources of pollution in the area of Chepelarska river, as the sample taking was near as possible to the emitters, confirmed by RIOSV Plovdiv:

-Point No. BG3MA00523MS0600 Chepelarska r., Bachkovo

-Point No BG3MA05213MS0590 Chepelarska r. after Asenovgrad, 1km after ГК

-Point No BG3MA05213MS0570 Chepelarska r. before the firth of Kemera.

The data is from the period of 2010-2013, as for the year of 2013 is taken data from month January to August including and they are submitted in the graphic below:

RESULTS AND DISCUSSION

In regard to the cadmium in point 1 for the 2013 according to the Standard for the Quality of the Environment, there is no excess on the annual average. For the period of 2011-2012 there is an excess of the annual average of the SQE (Standard for the Quality of the Environment) with 0.00041 mg/dm^3 and 0.000798 mg/dm^3 for an annual average of 0.00015 mg/dm^3. The pollution is probably caused by waste from GORUBSO-Laki.

In point 2 the values from 2012 and 2013 do not excess the annual average of SQE (Standard for the Quality of the Environment), there is an excess in 2011.

In point 3 for the 2013 there is an excess of the annual average of SQE (Standard for the Quality of the Environment) - 0.00193 mg/dm^3 when the annual average is 0.00015 mg/dm^3. The reason may be KCM AD, because of the presence of cadmium in their product. For the period of 2011 and 2012, there is an excess of the annual average by the (Standard for the Quality of the Environment) too with 0.0535 mg/dm^3 and 0.00367 mg/dm^3. All deviations are shown in the figure 1.

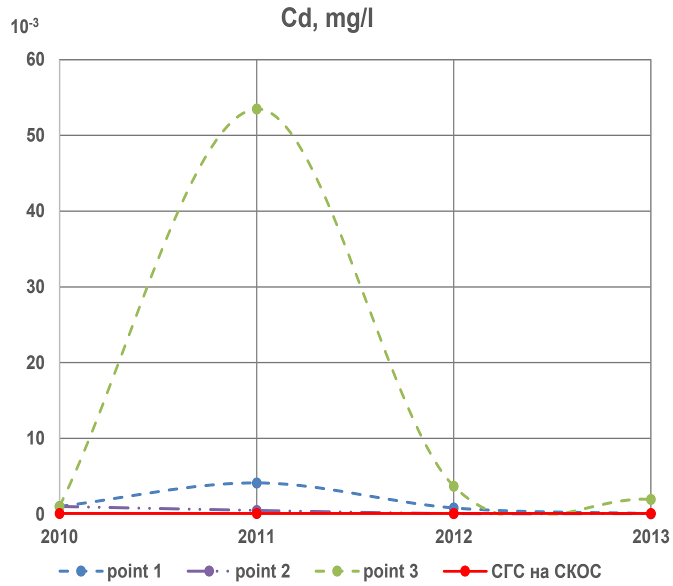

Figure 1: Annual average of the cadmium for the period 2010-2013 in points 1,2 and 3

There is no excess of the concentration of lead in point 1 and 2 by the annual average of (Standard for the Quality of the Environment), but there is one in point 3 for 2011 - 0.010018mg/dm^3 while the annual average is 0.00015 mg/dm^3. The reason to cause this expiration of the heavy metal in the water is a breakthrough from the dam into the tailing of GORUBSO-Laki. It's an ex tailing, in which were left significant deposit of tailings. All deviations are shown in the figure 2.

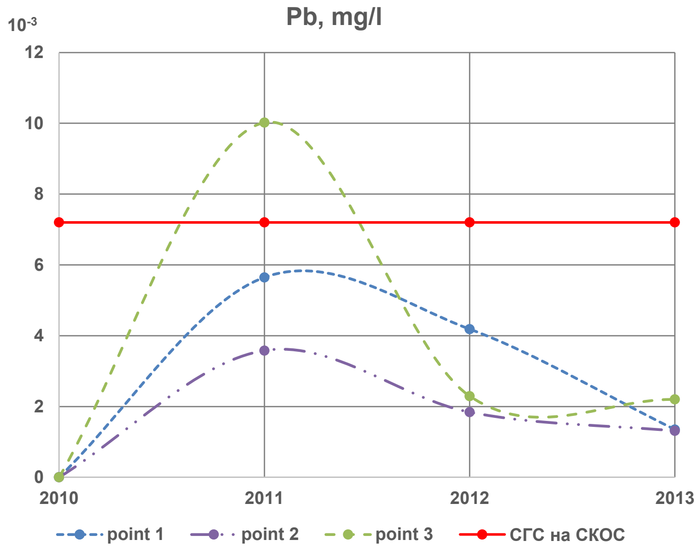

Figure 2: Annual average of the lead for the period 2010-2013 in points 1,2 and 3

CONCLUSIONS

The condition of Chepelarska river in her downstream shows that there is need for some serious improving. Legally this may be done with the help of the calculated emission load and compare it with the calculated load in the firth of Chepelarska river. After that the new emission restrictions of the waste water can be calculated.

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