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CONTENT OF CD IN WATER, SEDIMENT, AQUATIC PLANTS AND MUSCULATURE OF CARP FROM SURFACE WATERBODIES IN STARA ZAGORA REGION, BULGARIA

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Abstract

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Cd is released in considerable amounts through industrial effluents into soil, surface and ground water systems. These excessive amounts of cadmium releasing into the environment reach toxic levels and cause damage to the flora and fauna of aquatic ecosystems. This study was carried out in order to survey and assess the levels of Cd in the water, sediment, aquatic plants and carp from different surface waterbodies in Stara Zagora Region, Bulgaria. International standards of ISO and BSS for sample preparation of water, sediment, aquatic plants and musculature of carp analyze were used. Concentration of Cd in the analyzed samples was determined by atomic adsorption spectrometry. Monitoring points at which was conducted the research are located in a region with a high degree of anthropogenic impact. Despite this fact, the concentrations of cadmium in all water samples tested were well below requirements defined by Directive 2008/105/EO and Directive 2013/39/EO. The concentrations of Cd were highest in sediment samples from Bedechka River (0.33 $mg.kg^{-1}$), Tunja River, Nikolaevo Town (0.31 $mg.kg^{-1}$) and Sazliika River (0.26 $mg.kg^{-1}$); in the aquatic plants from the Tunja River, Nikolaevo Town (1.89 $mg.kg^{-1}$). Concentrations of cadmium in musculature of carp of the all studied points were significantly lower than established norms. Quantities of cadmium were not accumulated in the muscles of the fish test species probably due to their accumulation in organs with active metabolism (liver).

Key words: aquatic plants, assessment, cadmium, carp, musculature, sediment, water
Abbreviations: MCA – Maximum Allowable Concentration; YAV – *Yearly Average Value*

Introduction

Aquatic ecosystem is the final recipient of almost everything including heavy metals. This metals which cannot be degraded, continuously being deposited and included in water, sediment and aquatic organisms (Linnik and Zubenko, 2000), thus causing heavy metal pollution in waterbodies. Most of the heavy metals become associated with particles in sediment, but a small quantity becomes dissolved in the water and can spread widely in the food chains (Khadr, 2005). Metal ions can be concentrated in aquatic organisms to a level that affect their physiological state. These hydrobionts

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used for food by humans may endanger their health. Heavy metals in aquatic organisms are influenced by many external factors such as seasonal variations, pH, hardness of water, concentration and composition of particulate matter (Mgbemena and Obodo, 2011; Adefemi, 2013).

Cd is released in considerable amounts through industrial effluents into soil, surface and ground water systems. These excessive amounts of cadmium releasing into the environment reach toxic levels and cause damage to the flora and fauna of aquatic ecosystems (Pappas et al., 2010). Cadmium ions bind to the cell membranes hindering transport processes through the cell wall (Boran and Altınok, 2010). The presence of heavy metals of natural or anthropogenic origin in sediments of aquatic system represents one of the most important environmental problems (Ridgway and Shimmield, 2002). Since sediments integrate contaminants concentration over time, providing a long-term picture of influence of different factors on aquatic system (Kljaković-Gaspić et al., 2008). Such as surface sediment samples are also used as environmental indicators to reflect the current quality of aquatic systems for many pollutants. For heavy metal Cd was found that deactivated proteins, denature enzymes, and disturb cell functions (Hall, 2002). Aquatic plants have the potential to accumulate metals in their tissues. The accumulation of the metals in plants was increased when the exposure time and metal concentration is increased. Cd causes decreases in glutathione peroxidase activity, catalase activity, glutathione content and total antioxidant capacity level and can lead to oxidative damage in liver and kidney of carp (Almeida et al., 2001; Bedii and Kenan, 2005; Kim et al., 2011).

It is therefore necessary to be study the content of cadmium in the water, sediment, aquatic plants and fish for a better assessment of anthropogenic impacts on aquatic ecosystems (Stancheva et al., 2010). The waterbodies in Southern Bulgaria are under high anthropogenic influence. The pollution sources in this region include a number of industrial enterprises (the biggest in the country Thermal power plants, ferrous metals plants, mechanical engineering plants, etc.) and agricultural activities (intensive agriculture, livestock production). This study was carried out in order to survey and assess the levels of Cd in the water, sediment, aquatic plants and carp from different surface waterbodies in Stara Zagora Region, Bulgaria.

Materials and Methods

Study area

In the period of the present study were investigated four waterbodies from Stara Zagora Region, South Bulgaria: Tunja River, Bedechka River, Sazliika River and Jrebchevo Dam Lake (Figure 1). Tunja River passes through the area, which is characterized by large settlements, industrial enterprises and intensive agriculture. The outflow of wastewater from these anthropogenic activities are the preconditions for quality deterioration the river waters. Bedechka River and Sazliika River are also subject to anthropogenic impacts and they are mainly used for irrigation of crops. The main directions in which are use the waters of the Jrebchevo Dam Lake are irrigation, fishing and electricity production.

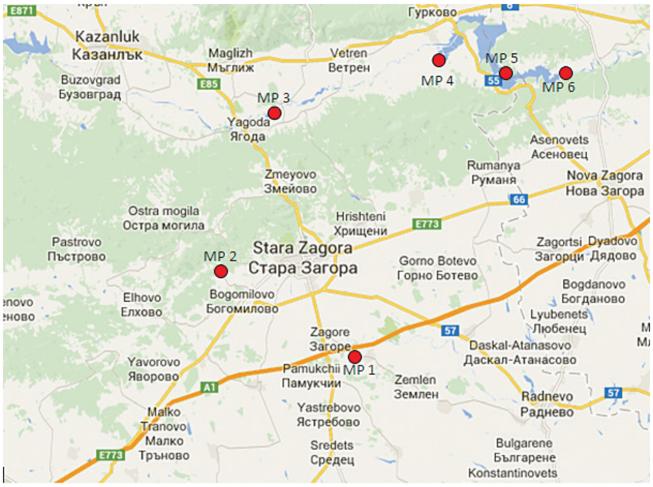

Fig. 1. Map with studied surface waterbodies and monitoring points in Stara Zagora Region, Bulgaria

Monitoring points

It was set 6 monitoring points for screening purposes in accordance with Regulation No 5/2007 and Regulation No 13/2007, as follows:

- Monitoring Point 1 (MP–1) – Bedechka River, Stara Zagora Municipality
(N42.27049° E25.37937°);
- Monitoring Point 2 (MP–2) – Sazliyska River, Stara Zagora Municipality
(N42.26914° E25.29015°);
- Monitoring Point 3 (MP–3) – Tundzha River at Yagoda village, Maglizh Municipality (N42.32740° E25.3380°);
- Monitoring Point 4 (MP–4) – Tundzha River at Jrebchevo Dam Lake, Nikolaevo Municipality (N42.38333° E25.49350°);
- Monitoring Point 5 (MP–5) – Jrebchevo Dam Lake, Nova Zagora Municipality
(N42.35346° E25.57020°);
- Monitoring Point 6 (MP–6) – Tundzha River, Banya Village, Nova Zagora Municipality
(N42.36243° E25.59466°).

Samples collected

Samples of water, sediment, aquatic plants and carp musculature from surveyed monitoring points were tested regarding the content of elements Cd.

Water

From studied waterbodies were taken 72 water samples which were collected from MP each month during one year (from November 23, 2009 to November 23, 2010) in accordance with the requirements of BS EN ISO 5667 – 1/2007. The water samples were stored in accordance with BS EN ISO 5667 – 3/2006.

Sediment

The sediment samples (6 issues), collected from studied waterbodies, were prepared, archived, stored and analyzed for the period from May to December 2010.

Aquatic plants

The total of six aquatic plants samples, collected from studied waterbodies, were prepared, archived, stored and analyzed for the period from May to December 2010.

Carp

Samples of carp musculature (18 pieces) were collected, archived and analyzed in the period from May to December 2010. Samples of musculature were taken from the annuals carps of a weight 800–1000 grams.

Analyzing samples water, sediment, aquatic plants and carp musculature was carried out in the laboratories of the Scientific – Research Center for Environment at Faculty of Agriculture, Trakia University, Stara Zagora.

The cadmium concentrations in water, sediment, aquatic plants and musculature of carp were measured by atomic absorption spectrometer (AAS) "A Analyst 800" – Perkin Elmer.

The cadmium content of surface waters was determined in graphite tube or flame (depending on the concentration of these elements), at a definite wavelength and water preservation in advance of the samples with 5 cm^3 k HNO_3 of a sample (ISO 8288, BS EN ISO 5667–3/2006). The contents of Cd in water samples were measured in $mg.l^{-1}$.

All samples of sediment and aquatic plants were lyophilized to constant weight. The dried sediment was milled and sieved repeatedly to fine powder. It was received not less than 20 grams of average representative sample. Sediment samples were decomposed by means of concentrated nitric acid and hydrochloric acid, in accordance with ISO Standard 11466. The samples were filtered and diluted to 50 ml with distilled water.

The preliminary sample preparation of samples aquatic plants and carp musculature was performed by wet combustion in a microwave oven Perkin Elmer Multiwave 3000. The obtained extracts were diluted with distilled water to 25 ml. Concentrations of cadmium in acid solutions were established of AAS in accordance with BSS ISO 11047. Quantities of the examined element in the sediment and aquatic plants are expressed as $mg.kg^{-1}$ dry weight. The cadmium content in the samples of carp musculature was expressed in $mg.kg^{-1}$ wet weight.

The device was periodically calibrated with standard chemical solutions prepared from commercially available chemicals (Merck, Germany). An air–acetylene flame and hollow cathode lamp for all samples were used. Calibration curves were prepared using dilutions of stock solutions. Each sample of water, sediment, aquatic plants and musculature of carp was measured three times and the mean values were calculated.

Quality of the studied surface water was determined by regulated average annual concentration values of cadmium in Directive 2008/105/EO and MCA in Directive 2013/39/EO. The data obtained in the analysis of sediment samples from investigated waterbodies are interpreted in accordance with Regulation № 3 from 01.08.2008 for norms for permissible content of harmful substances in the soil as there are no established norms relating to sludge.

Assessment of the cadmium content in aquatic plants samples was not done, because regulated norms for this element are not available in Bulgaria.

Samples of carp musculature are discussed according to Regulation № 31 – July of 29th 2004 and Commission regulation (EO) № 1881/2006 on the maximum permissible quantities for contaminants in food.

Statistical analysis

Statistical processing of the results was computed by the program STATISTICA using ANOVA test.

Results and Discussion

Water pollution with heavy metals leads to a radical change of the biochemical parameters and life cycles of aquatic species. Heavy metals which cannot be degraded continuously being deposited and incorporated in water, sediment and aquatic organisms, thus causing heavy metal pollution in waterbodies (Linnik and Zubenko, 2000; Ogoyi et al., 2011). This calls to make an objective assessment of the status of aquatic ecosystems requiring monitoring of the quantity heavy metals both in the water and in other units sediment, aquatic plants and fish. The bottom sediments of waterbodies reflect even temporary pollution adsorbing and decreasing their quantity in the water column.

The data obtained from analysis of the content of cadmium in the water, sediment, aquatic plants and carp musculature are shown in Figures from 2 to 5.

The data concerning the levels of Cd (Figure 2) in the waters of all the studied waterbodies are significantly lower than the standards regulated in Directive 2008 and 2013. Concentrations measured in points from 1 to 5 have a value 0.001 mg.l^{-1}, which is with 98% lower than normative requirements. In monitoring point 6 the level of Cd content is even lower than the level in the other monitoring points (1–5). This fact allows us to make conclusion that probably available quantities of cadmium have been sedimented in Jrebchevo Dam Lake. Basis for such an assertion we find and in the results for Cd content in the sediment of the studied waterbodies (Figure 3).

The absence of clearly regulated global standards on permitted levels of Cd in sediments of a different character is a serious constraint to analyzing obtained data. As sediment plays the role of soil into waterbodies, the only document that can be reference point on the concentration of cadmium in sediment samples is Regulation № 3 of 01.08.2008 of the Bulgarian legislation. Levels of this metal in all monitored points are much below MCA referred to in this document (2 mg.kg^{-1}). It is of great significance because the sediments, serving as soil were suitable living environment for many benthic organisms.

From Figure 3 is apparent that the highest values of Cd were measured in MP1 (0.327 mg.kg^{-1}) and MP4 (0.306 mg.kg^{-1}), which is explained by the fact that these points are respectively close to the Stara Zagora Town and Nikolaevo Town. After MP4 is observed a gradual decrease in the concentration of Cd, which reaches its minimum at MP6 (0.004 mg.kg^{-1}). This result explains the low concentrations of Cd in the water taken from the latest monitoring points that are consequence of processes of sedimentation.

The accumulation of Cd in aquatic plants (Figure 4) follows the trend of the content of this metal in the sediments of the same studied points. The highest levels of cadmium were recorded in the aquatic plants from the Tunja River, Nikolaevo Town (1.89 mg.kg^{-1}). In accordance with sedi-

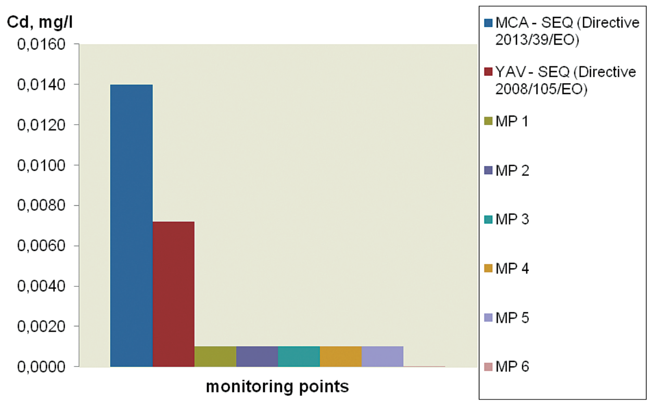

Fig. 2. Content of Cd in water of waterbodies from Stara Zagora Region, Bulgaria

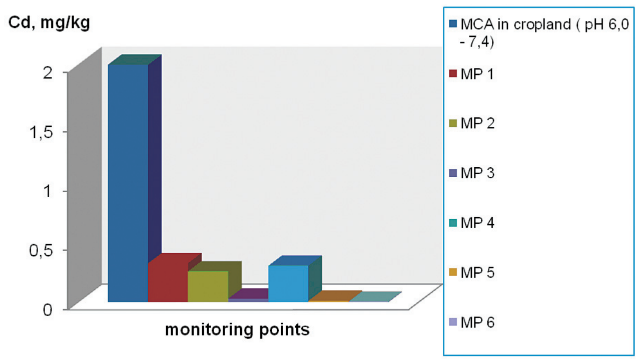

Fig. 3. Content of Cd in sediments of waterbodies from Stara Zagora Region, Bulgaria

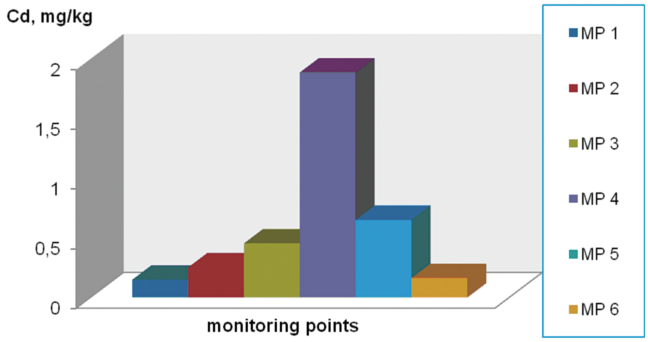

Fig. 4. Content of Cd in aquatic plants of waterbodies from Stara Zagora Region, Bulgaria

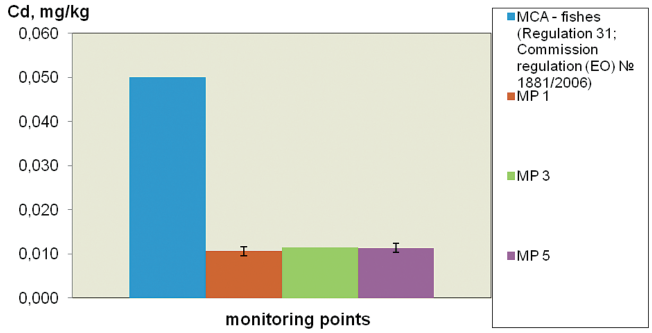

Fig. 5. Content of Cd in carp musculature of waterbodies from Stara Zagora Region, Bulgaria

ment samples the relatively low concentrations are registered in samples of aquatic plants MP6 (0.163 $mg.kg^{-1}$). The presence of Cd in the water may have a profound effect on the aquatic plants which constitute the main food source for bivalve mollusks in all their growth stages, zooplankton (rotifers, copepods, and brine shrimps) and for larval stages of some crustacean and fish species (Ogoyi et al., 2011).

Concentrations of cadmium in musculature of carp of the all studied points (Figure 5) were significantly lower than established norms. In the samples of all monitoring points were observed only traces of cadmium. Zhelyazkov et al. (2014), researching the content of heavy metals in freshwater fish from the Jrebchevo Dam Lake was found similar levels of cadmium in muscle samples. Quantities of cadmium were not accumulated in the muscles of the fish test species probably due to their accumulation in organs with active metabolism (liver) (Handy, 1992; Khoshnood et al., 2010; Djedjibegovic et al., 2012).

The data received in the analysis of water, sediment, aquatic plants and muscles of carp of the investigated monitoring points give reason to be determined ratios of Cd between them (Table 1).

Table 1

Concentration ratios of Cd sediment/water, aquatic plants/water and carp/water in the monitoring points of investigated waterbodies

points	Coefficient of Cd concentration (sediment/water), in times more	Coefficient of Cd concentration (aquatic plants/ water), in times more	Coefficient of Cd concentration (musculature of carp/water), in times more
MP 1	326.8	149	11
MP 2	259	252	
MP 3	29.1	454	11
MP 4	306	1888	
MP 5	11.4	651	11
MP 6	633.3	27 167	

In determining the ratio between the concentration of Cd in sediment and water is found that this metal is accumulated from 11.4 (Jrebchevo Dam Lake) to 633.3 (river Tunja, Banya Village) times more in sediment as compared to the water. The received data from content of Cd in aquatic plants and sediment showed accumulating to a greater degree in the aquatic plants compared to sediment. The proportion aquatic plants/water leads to the conclusion that Cd is accumulated from 149 (Bedechka River) to 27167 (Jrebchevo Dam Lake, Banya Village) times more in aquatic plants compared to water. The results of the ratio of carp musculature/water show that the accumulation in the studied points is 11 times more in musculature compared to water. The low results in the musculature of carp in studied waterbodies indicate that the accumulation of this element was probably performed to active organs such as the liver, gills and kidneys (Stewart, 1999; Jezierska and Witeska, 2006).

Conclusion

The concentrations of cadmium in all water samples tested were well below requirements defined by Derective 2008/105/EO and Directive 2013/39/EO. With the highest concentrations of Cd are characterized sediment samples from Bedechka River (0.33 $mg.kg^{-1}$), Tunja River, Nikolaevo Town (0.31 $mg.kg^{-1}$) and Sazliika River (0.26 $mg.kg^{-1}$). The highest levels of cadmium were measured in the aquatic plants from the Tunja River, Nikolaevo Town (1.89 $mg.kg^{-1}$). Concentrations of cadmium in musculature of carp of the all studied points were significantly lower than established norms. Quantities of cadmium were not accumulated in the muscles of the fish test species which is probably due to their accumulation in organs with active metabolism (liver).

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