# THE IMPACT OF Cd, Pb AND Hg CONTENT IN BOTTOM SEDIMENTS OF WATER DAM TO CONTENT OF HEAVY METALS OF COMMON CARP (*CYPRINUS CARPIO*) TISSUES

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## ABSTRACT

Fish meat is delicious food which complies with the requirements of rational nutrition. Fishes are a huge source of the nutrients that are not in other food. In the terms of healthy eating, fishes should be a part of well-balanced diet. The meat is easily digestible food because of the structure of proteins with simply structure and contain negligible amounts of worse digestible fiber protein, compared to the meat of warm blooded animals. The meat contains the essential amino acids too. Scientific studies shown that people who eat fishes at least a bit for once a week is the risk of heart disease and stroke significantly lower. According to the principles of good nutrition should be fishes and fish products part in the diet from 2 to 3 times a week. Aim of our work was the analysis of bottom sediments in the water reservoir Kolíňany. We obtained information about the content of Cd, Pb and Hg and monitored heavy metals in the different parts of carp body.

The cadmium content was smaller than the maximum available amount specified by government regulations in fish meat, on the other hand the hygienic limit for Cd in selected parts of fish body such as the skin, gills and fins was exceeded by 2.9 to 6.6 times. The lead content was smaller than the hygienic limit in fish meat, but in skin, gills and fins was the content of heavy metal by 1.31 to 2.64 times higher than the maximum available amount. Fish skin, gills and fins are among the non-consumed parts of fish body. The mercury content in fish meat was also smaller than hygienic limit. The mercury content was the highest in the muscles (0.0544 mg/kg) and the lowest in the gonads (0.0058 mg/kg). The obtained results of the content of Cd, Pb and Hg in the carp body confirm that the fishes and their muscles are suitable food for human consumption.

**Keywords**: cadmium, lead, mercury, sediment, carp

## 1. Introduction

The concentration of toxic and risk elements in the environment has increased due to human's activities in last few decades. It caused the transfer of those elements into the food chain. It is important to monitor their inputs into the environment, especially in the areas with highly developed industry (Tomaš *et al.*, 2009).

The metals are in the surface as well as in ground water. Many of them are essential for life in a trace amount, but higher concentrations may prove negative. Hygienic problem involves metals with toxic properties, whose rank among the major inorganic contaminants of water and soil. (Toth *et al*, 2006; Tomas *et al, 2009*).

Mainly lead, cadmium and mercury are in the waters. The one of the major negative properties of these metals is their ability to accumulate in the sediment. In particular, mercury has a huge capacity to accumulate in the aquatic organisms. Bottom sediments could be a suitable indicator of contamination of surface waters by lead and cadmium (Cibulka *et al*, 1991).

The meal of indigenous people of Greenland (Inuits) consist of the products of the animals. It consists of fish and marine mammals, which means that it is full of proteins, lipids and cholesterol. It seemed almost incomprehensible why Eskimos do not suffer from cardiovascular diseases and their blood are levels are significantly lower cholesterol levels compared to the Europeans after consuming of large amounts of fatty meats.

Fish meat is an important part of human nutrition due to the low content of fat and high content of proteins and minerals, as well as the optimal ratio of unsaturated fatty acids. Habánová (2005) reported that consumption of fish and fish products has decreased in comparison with 2002 by 0.2 kg and 4.2 kg, compared with the recommended amount is lower by 1.8 kg. This represents almost an half compared to the other EU citizens. For example, the inhabitants of northern states, such as Norway, Finland and Sweden could boast of 60 kg of fish consumed per person during the year. Longevity, good health and slimness are known to the Japanese, who eat 90 kg of fish meat during the year (Andreji *et al* 2006).

Carp ranks among medium-time living to long-time living fish; some individuals can even live 20 - 30 years. The weight of carp in free waters is 2 - 6 kg, but relatively frequent are also catching over 10 kg (Sedlár *et al*, 1987).

## 2. Material and methods

In this case study exemplars of common carp (*Cyprinus carpio*), the samples were collected in November 2013 during fishing from the pond Kolíňany (Nitra district, river basin of Žitava, South-West part of Slovakia).

Characteristics of water pond Kolinany:
Number of fishing ground: 2-4890-1-2
Description: Water area of pond near Kolíňany and brook Bocegaj from estuary to streams.
Acreage (ha): 10
Organization: SPP (Agricultural enterprise)
Range: according to rules
Purpose: breeding
Type of permission: none
Character: carp waters (Fishing ground REVÍR VN KOLÍŇANY)

Bottom sediments have been collected in November 2013 with probe and sampling rod during the period of fish catching, when the water from dam have been drained. It was collected 5 samples of sediment from water pond according to Law No. 188/2004 Collection of Laws about application of sewage sludges and bottom sediments into soil and about completing of Law No. 223/2001. The samples of bottom sediment were subsequently analysed at the department of Chemistry of FBFS SUA in Nitra. The samples were dried in oven at 105 º C and analysed for the determination of Cd, Pb and Hg content. The end of the determination of risk elements (Cd, Pb, Hg) in the bottom sediment and parts of carp bodies (samples of tissues were obtained by section – muscle, skin, gill and fin in amount of 2–3 g) was carried out by extract of aqua regia to determine the total concentration of monitored heavy metals (Cd, Pb). The mineralization of samples was prepared by 10 $cm^3$ of aqua regia (2.5 $cm^3$ $HNO_3$ and 7.5 $cm^3$ HCl, *Merck*, Germany) using microwave digestion unit Mars X-press 5 (*CEM Corp*., USA) in PTFE vessels. The determination of heavy metal content was performed by Varian AA240Z (*Varian*, Australia) atomic absorption spectrometer with Zeeman background correction. The graphite furnace technique was used for the determination of Cd and Pb.

The Hg content was determined by automatic mercury analyser AMA 254. AMA 254 was used for the determination of mercury content in sediment as well as in common carp tissues. The total mercury content was determined in homogenized samples (0.005-0.01 g) using a cold-vapour AAS analyser AMA 254 (*Altec*, Czech Republic) with a detection limit of 0.5 ng/g. Mean differences between duplicates were up to 5% (Svoboda *et al*., 2006). All statistical analyses were carried out by statistical software Statistica 12.0 *(Statsoft,* USA). We used Pearson correlation coefficients at significance level of $p<0.05$ (weak statistical significance) and $p<0.001$ (very strong statistical significance) to compare the impact of monitored parameters between them. The obtained data about the concentration of heavy metals have been compared with the limit values enacted by legislative norm in Slovak republic. The results of monitored metals are presented as wet weight, the results of bottom sediment are presented as dry weight (DW) and wet weight (WW) too. All obtained data are shown in mg/kg and compared with Food Codex and sediment´s law of the Slovak Republic.

## 3. Results and disscussion

The contents of monitored risk elements in bottom sediment were evaluated in according to Law No. 188/2003 Collection of Laws about application of sewage sludge and bottom sediments into soil and completing of Law No. 223/2001 Collection of Laws about wastes and changes and completing of some laws as amended of later Acts.

In Appendix No. 3 of mentioned Law are reported the limit values for content of risky elements in bottom sediment (Tab.1):

**Table 1:** Limit values of risk compounds concentrations in bottom sediments

| | | | |
|---|---|---|---|
| Arsenic | 20 mg/kg | Nickel | 300 mg/kg |
| Cadmium | 10 mg/kg | Lead | 750 mg/kg |
| Chromium | 1 000 mg/kg | Zinc | 2 500 mg/kg |
| Cupper | 1 000 mg/kg | PAU | 6.0 mg/kg |
| Mercury | 10 mg/kg | PCB | 0.8 mg/kg |

The results of chemical analyses of bottom sediment are reported in Table 2 and Table 3. The results of chemical composition of sediment point to the high content of organic compounds of substrate. It was confirmed by high content of humus (2.61 - 4.48 %) as well as high content of organic carbon (1.51- 2.60 %).

**Table 2:** Chemical composition of bottom sediment

| Sample no. | Content by MELICH III, mg/kg | | | | $C_{ox}$ | Humus |
|---|---|---|---|---|---|---|
| | Ca | Mg | K | P | % | % |
| 1 | 10300 | 316 | 131.0 | 1.836 | 2.07 | 3.57 |
| 2 | 8088 | 360 | 153.5 | 23.49 | 2.60 | 4.48 |
| 3 | 4908 | 270 | 125.0 | 196.91 | 1.51 | 2.65 |
| 4 | 10744 | 414 | 118.5 | 41.40 | 1.51 | 2.61 |
| 5 | 22020 | 522 | 159.5 | 25.08 | 2.14 | 3.69 |

**Table 3:** Content of risk elements in bottom sediment

| Sample No. | pH $H_2O$ | pH KCl | *Aqua regia extract* mg/kg | | AMA 254 mg/kg |
|---|---|---|---|---|---|
| | | | Cd | Pb | Hg |
| 1 | 8.33 | 8.05 | 2.54 | 12.0 | 0.025276 |
| 2 | 8.16 | 7.58 | 2.12 | 14.8 | 0.028402 |
| 3 | 7.77 | 7.65 | 2.60 | 17.2 | 0.077120 |
| 4 | 8.22 | 7.58 | 2.82 | 14.6 | 0.025618 |
| 5 | 8.22 | 7.82 | 3.10 | 30.2 | 0.032079 |
| Average content | 8.14 | 7.73 | 2.63 | 17.7 | 0.037699 |
| Limit value | | | 10 | 750 | 10 |

The content of monitored risk elements in bottom sediment and their comparison with legislative norm is shown in Table 3. The results of our analyses show that the limit values for the content of cadmium, lead and mercury of substrate were not exceeded.

The pH value of bottom sediment is neutral to weakly alkali (pH/KCl) in the range of 7.58-8.05 and average value is 7.73. The environment of substrate that is from neutral to weakly alkali is an important factor which indicates the danger of sediment, while according to many authors (Andreji *et al*, 2009; Tomáš *et al*, 2009; Hecl and Danielovič 2004) in neutral to weakly alkali environment are monitored risk elements in unavailable forms, bound to organic matter and residual fraction and occur in insoluble forms, which means that they do not get to waters, they are not available for aquatic plants and thus pose a small risk of their potential entry into fish organism.
The cadmium content in sediment was 2.636 mg/kg. It is 23.6 % of the limit value content (10 mg/kg). This content was under limit value and did not pose a real risk of its entry into biosphere and do not threat the state of environment. The lead and mercury content in sediment were deeply below limit values. The lead content was 2.3 % in comparison to limit value and mercury content only 0.38 % of limit value.

The content of risk elements does not constitute the assumption of increasing their transmission into fish organism, although all of the risk elements are characterized by their ability to accumulate in animal tissues. This accumulation is in direct proportion to the age of the fishes, which means that if the organism has been exposed to the risk compounds in the environment for long time, their content in organism will be higher.

From the point of view of risk elements, we can conclude that monitored dam is safe for the production of healthy and safe food - fishes. However, it is important to monitor this state regularly, because it is set out in part monitoring system: Contaminants in food and feed, subsystem: Monitoring of wild animals and fishes. The content of heavy metals of fish tissues are shown in Table 4.

**Table 4:** Contents of Cd, Pb and Hg of analyzed tissues of common carp (n = 4)

| | | **muscle** | **skin** | **gill** | **fin** |
|---|---|---|---|---|---|
| Cd | mean ± SD | 0.06 ± 0.04 | 0.28 ± 0.28 | 0.30 ± 0.05 | 0.67 ± 0.14 |
| | range | 0.02 - 0.13 | 0.07 - 0.76 | 0.26 - 0.38 | 0.52 - 0.84 |
| Pb | mean ± SD | 0.24 ± 0.14 | 1.31 ± 1.44 | 1.64 ± 0.31 | 2.65 ± 0.34 |
| | range | 0.09 - 0.48 | 0.24 - 3.79 | 1.40 - 2.16 | 2.29 - 3.18 |
| Hg | mean ± SD | 0.05 ± 0.02 | 0.01 ± 0.02 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| | range | 0.03 - 0.07 | 0.00 - 0.05 | 0.01 - 0.01 | 0.00 - 0.01 |

The cadmium content of analyzed samples of common carp varied closely in hundredths or tenths of milligram. We obtained values of heavy metal content in mg/kg wet weight (w. w.) of tissues: muscle 0.02-0.13 mg/kg, skin 0.07-0.76 mg/kg, gill 0.26-0.38 mg/kg, fin 0.52-0.84 mg/kg. The highest mean value of Cd content was in fins (0.67 mg/kg w.w.), on the other hand the lowest content was in muscles (0.06 mg/kg w. w.)(Table 4). Smaller Cd contents were detected in the muscles and gills of common carp from the aquaculture ponds of Kolkata, India (Adhikari *et al*., 2009; Kulkina *et al.,* 2014). Also smaller Cd content was detected in carp muscles from two ponds in the southwestern part of Slovakia (Andreji *et al*., 2006). About 10 times higher values were measured in muscles and gill of common carp from the Menzelet Dam Lake and 50 times higher from the Sir Dam Lake, both Turkey (Erdogrul and Ates 2006). A little bit higher values of Cd content were measured in muscles of fishes from the pond of Malé Zálužie, Slovakia (Andreji *et al*., 2009). Cadmium accumulation in carp tissues was in general order: fin > gill > skin > muscle. Our results as well as analyzed carp tissues from the Menzelet Dam Lake confirmed the Cd distribution (Erdogrul and Ates, 2006).

The lead content of analyzed carp tissues varied widely in tenths of milligram but in the case of the skin, gills and fins in whole milligram. We obtained values of Pb content ± S.D. (in mg/kg w.

w.): muscle 0.09-0.48, skin 0.24-3.79, gill 1.40-2.16, fin 2.29-3.18. The highest (2.65 mg/kg) as well as lowest (0.24 mg/kg) mean Pb content were detected in fins and muscles (Table 4). Smaller Pb contents of tissues were detected in the muscles and gill of common carp from the Sir Dam Lake, Turkey (Erdogrul and Erbilir, 2007). Higher Pb contents in carp muscles were confirmed from the Isikli and Karacaören Dam Lakes, Turkey (Kalyoncu *et al*. 2011) in comparison to our results. A little bit higher Pb contents of carp muscles were measured from the three ponds of south western Slovakia (Andreji *et al*., 2006, 2009). Lead accumulation in carp tissues was in general order: fin > gill > skin > muscle. Similar results of Pb distribution in different carp tissues were obtained from Svitava Lake, Bosnia and Herzegovina (Has-Schön *et al*., 2008).

In study by Bervoets *et al* (2009) the Pb concentration in caro tissues was recorded as follows: gill > intestine > hepatopancreas > kidney = muscle. Tolerable limit (0.2 mg/kg w.w.) for the Pb concentration in muscle was exceeded in 2 samples.

The mercury content of carp tissues varied very closely in hundredths of milligram. Measured values ranged between 0.00-0.07 mg/kg w. w. We obtained values of Hg content ± S.D. (in mg/kg w. w.): muscle 0.05 ± 0.02, skin 0.01 ± 0.02, gills 0.01 ± 0.00, fins 0.01 ±0.00. The highest Hg content was detected in muscles and the lowest in gonads, gills and fins. Similar values of Hg content in the carp muscles are presented by Zlabek *et al*. (2006) from the five south Bohemian ponds. In comparison to our results, lower values of Hg content in different carp tissues were measured from the 10 Bohemian and Moravian ponds (Čelechovská *et al*., 2007). Mercury accumulation in carp tissues was in general order: muscle > skin ≈ fin ≈ gill. Similar results for the Hg content and its distribution in different carp tissues are published by Čelechovská *et al*. (2007) from the 10 Bohemian and Moravian ponds.

Also comparable values of Hg tissue concentration decreasing in common carp from the Svitava Lake were measured except the gill, where the highest value was detected, in comparison to our results (Has-Schön *et al*., 2008). Tolerable limit for Hg content in fish muscle (0.5 mg/kg w.w.) was not exceed.

## 4. Conclusion

The aim of this case study was to provide information that influence the content of risk elements in biotic and abiotic components of the environment. Thus, we can conclude:

- analysis of bottom sediments indicate the state of health safety of this component of the environment which directly threats the health state of fishes in the reservoir Kolíňany,
- the cadmium, lead and mercury content do not pose a real risk of entry into fish organism,
- the cadmium content in fish meat is lower than the maximum available amount (MAA), but its content is higher than MAA in some parts of fish body,
- the lead content in fish meat is smaller than hygienic limit, but higher accumulation was observed in skin, gills and fins that are non-consumable parts of fish body,
- the mercury content does not exceed MAA in fish body,
- the accumulation of risk elements in monitored parts of fish body is in general order:
    - Cd accumulation in carp tissues: fin > gill > skin > muscle
    - Pb accumulation in carp tissues: fin > gill > skin > muscle
    - Hg accumulation in carp tissues: muscle > skin ≈ fin ≈ gill
- analysis of the fish bodies in the case of the contents of Cd, Pb and Hg shows that the fish muscles are suitable for consumption and fulfill all hygienic limits for those elements.

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## REFERENCES


1. Adhikari, S. *et al* (2009), Metal concentrations in water, sediment, and fish from sewage-fed aquaculture ponds of Kolkata, India. Environ. Monit. Assess., 159, p. 217–230.
2. Andreji, J. *et al* (2006), Heavy metals content and microbiological quality of carp muscle from two Southwestern Slovak fish farms. J. Environ. Sci. Health Part A, no. 41, p.1071 – 1088.
3. Andreji, J. *et al* (2009), Heavy metal concentration in in fish muscle and bottom sediments from the Malé Zálužie pond. Acta fytotechnica et zootechnica, vol.12, no. 1, p. 13-16.
4. Bervoets, L. (2009), Bioaccumulation of micropollutants and biomarker responses in caged carp (Cyprinus carpio). Ecotoxicology and Environmental Safety, vol. 72, p. 720 – 728.
5. Čelechovská, O. *et al* (2007), Distribution of Metals in Tissues of the Common Carp (Cyprinus carpio L.). Acta Vet. Brno, vol.76, p. S93-S100.
6. Cibulka, J. *et al*. (1991), Movement of lead , cadmium and mercury in the biosphere. Praha: Academia, 1991. 427 p. ISBN 80-200-0401-7
7. Codex Alimentarius (2011) http://www.svps.sk/legislativa/legislativa_kodex.asp.
8. Erdogrul, Ö. and Ates, D.A. (2006), Determination of cadmium and Copper in fish samples from Sir Dam Lake and Menzelet Dam Lake, Kahramanmaras¸ Turkey. Environmental monitoring and assesment, vol. 117, p.281-290.
9. Erdogrul, Ö. and Erbilir, F. (2007), Heavy Metal and Trace Elements in Various Fish Samples from Sır Dam Lake, Kahramanmaraş, Turkey. Environmental monitoring and assesment, vol. 130, p. 373 – 379.
10. Habánová, M. (2005), Nutric epidemiology. First edition, Nitra: SPU, 2005. p. 112 ISBN 80-8069-542-3
11. Has–Schon, E. *et al* (2008), Heavy metal distribution in six fish species included in human diet, inhabiting freshwaters of the nature park „Hutovo Blato" (Bosnia and Herzegovina). Archives of Environmental Contamination and Toxicology, 54, p. 75–83.
12. Hecl, J. and Danielovič, I. (2004), Heavy metal pollution level in the Zemplín region in mixtures of grass species. In Acta regionalia et environmentalica SPU Nitra, , vol. 6, no. 2, p. 42- 48, ISSN 1336-5452
13. Kalyoncu, L. *et al* (2011), Determination of heavy metals and metals levels in five fish species from I¸sıklı Dam Lake and Karacaören Dam Lake (Turkey). Environ. Monit. Assess., DOI: 10.1007/s10661-011-2112-9
14. Kulina *et al* (2014), Accumulation of heavy metals in Crayfish and fish from selected Czech reservoirs, Biomed Research International, 2014, 9 p., dx.doi.org/10.1155/2014/306103
15. Sedlár, J. *et al* (1987), Carp. Bratislava: Príroda, 1987. 192 s.
16. Tomáš, J. *et al* (2009), Monitoring of risk elements in zone of pollution Strážske area. In Czech journal of food sciences. ISSN 1212-1800, 2009, vol. 27, special issue, p. 397-400.
17. Tóth T. *et al* (2006), Antropogenic risky elements in soils from Midlle Spiš region. In Chemical Paper, Vol. 100, 2006, no. 8, p. 701-702. ISSN 0009-2770.
18. Žlábek, L. *et al* (2006), Hygienic quality of fish from ponds in the Czech Republic. Bulletin VÚRH Vodňany, 42, 3, pages: 97-100.