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REGULAR ARTICLE

CADMIUM, LEAD AND MERCURY CONTENTS IN FISHES – CASE STUDY

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ABSTRACT

Fish meat is a perfect foodstuff which is up to standard of rational nourishment. It is source of healthy and good digestible material rich on proteins, minerals and vitamins. Fish muscles especially back and lateral muscles are the most important parts of fish organism consumed for escellent chemical composition. Proteins in fish meat are rich on high aminoacids content. The content of fish fat is usually low with the high proportion of unsaturated fatty acids. Also minerals and B, A and D vitamins are very important components of this foodstuff. According to rational nourishment the fish meat should be consumed minimal 2 times weekly. Our research was focused on analysis of bottomn sediments in water reservoir Kolinany from the aspect of Cd, Hg and Pb contents, the determination of observed heavy metal contents in different parts of carp body and the evaluation of hygienic status and suitability of fish meat for the human consumption. Our results have confirmed the hygienic wholesomeness of bottom sediments in water reservoir Kolinany. The Cd, Pb and Hg contents in sediments represent no risk of their input into the fish organisms. The Cd content in fish meat was lower than maximal available amount given by legislative norms, but in selected parts of fish organism such as skin, gills and fins the Cd hygienic limit is 2.9 – 6.6 times exceeded. The Pb content in fish meat was under the hygienic limit, however in skin, gills and fins the content of this heavy metal was 1.31- 2.64 higher than maximal legislative given value. Fish skin, gills and fins belong to the non cosumed parts of fish body by people. The Hg content in fish meat was also lower than hygienc limit. The highest Hg content was observed in fish muscles (0.0544 $mg.kg^{-1}$) and the lowest one in fish gonads (0.0058 $mg.kg^{-1}$). The results of Cd, Pb and Hg content determination in carp body confirmed that fish muscles belong to suitable foodstuffs for the human consumption.

Keywords: cadmium, lead, mercury, fish, carp, food hygiene

INTRODUCTION

While in last decades the concentration of various toxic and risky elements in environment has increased due to man's activities, it has caused the transfer of mentioned elements into food chain. Substantial issue is to monitor their entries into environment, especially in areas with highly developed industry (**Toman et al., 2003**).

Almost all of metals occur naturally in surface and also in ground waters. Many of them are essential for life in trace amounts, but in higher concentrations could act negatively. Hygienically serious issue includes metals with toxic properties that rank among the most substantial inorganic contaminants of waters and soil (**Dercová et al., 2005**).

Mainly lead, cadmium and mercury rank among toxic metals occurring in waters. One of the significant negative properties of these metals is their ability to cumulate in sediments. Especially mercury has great ability to accumulate in aquatic organisms. Mercury passes from water into bottom sediments in flowing waters and dams, where it accumulates mostly in the form of sulfhide. Content of mercury in bottom sediments is in relation to level of burden of key locality, but also to character of sediment. Bottom sediments could be as suitable indicators of contamination of surface waters by lead and cadmium. Samples of sediment with bulk of mud and organic parts have in most cases higher content of mercury in comparison to sample of sandy character (**Cibulka et al., 1991**).

Remarkable cumulating ability of sediments poses a source of eventual contamination of fish meat by risky elements. The importance representation of fish in our diet has been proved by so-called Eskimo paradox. Diet of original inhabitants of Greenland – Eskimos has consisted only from products of animal kingdom. It comprises of fish and marine mammals, what means that it is very rich in animal proteins, lipids and cholesterol. It seemed almost incomprehensible why the Greenland Eskimos do not suffer from cardio-vascular diseases and in their blood there are significantly lower levels of cholesterol in comparison to Europeans after consumption of huge amount fatty meat. The secret is in character of the present lipid alone consisting from scarce unsaturated fatty acids of so-called n-3 families.

While neither human organism nor animals can produce these essential lipids, their intake is dependent on food. Contrary, marine plankton produce them in high amounts, and due to this fact fish, cetaceans and seals forming the lowest issues of marine food chain contain in their bodies high concentration of these beneficial substances. Freshwater fish also contain them, but in lower amounts. Content of lipid in individual fish varies in relation to species, but substantial is the fact that we need not to be afraid of it at all due to its exceptional ability to protect our blood vessels against sclerosis – atherosclerosis (**Syptáková, 2006**). Fish meat is recommended food in the human nutrition due to low content of fat and high content of proteins and mineral substances as well as optimal ratio of unsaturated fatty acids. **Habánová (2005)** reported that fish and fish products consumption has declined in comparison with 2002 by 0.2 kg to 4.2 kg and in comparison to recommended dose is lower by 1.8 kg. This represents almost half a decline in comparison to other EU inhabitants. For instance, the inhabitants of northern states, such as Norway, Finland and Sweden could boast with even 60 kilograms of consumed fish per one person during the year. Longevity, good health state as well as slimness are remarkable by Japanese who eat 90 kg of fish meat during the year (**Demešová, 2008**).

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

MATERIAL AND METHODS

For this study exemplars of common carp (*Cyprinus carpio*) were obtained in November 2010 during pond fishing from the fish pond Kolíňany (Nitra district, Žitava River watershed).

The area of cadastre of village Kolíňany is located in the south-west Slovakia in Nitriansky region. Village Kolíňany is situated approximately 10 km north-east from district, regional town Nitra.

Characteristics of water dam Kolíňany:

Number of fishing ground: 2-4890-1-2

Description: Water area of dam near Kolíňany and brook Bocegaj from estuary to streams.

Acreage (ha): 10

Organization: Školský poľnohospodársky podnik (Agricultural enterprise)

District: Nitra

Range: according to rules

Purpose: breeding

Type of permission: none

User: SPU Nitra

Character: carp waters (Fishing ground REVÍR VN KOLÍŇANY, [s.a.])

Bottom sediments were collected on 20th November 2010 with probe and sampling rod in period of fish catching, when the water from dam is drained. From water dam Kolíňany 5 samples of sediment were collected 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 Collection of laws about wastes and about change and completing some laws as amended of later Acts. Collected samples of bottom sediment were subsequently analysed at Department of Chemistry od FBFS SUA in Nitra. Each samples was dried in oven at 105 º C. Dry sediment was analysed for content of Cd, Pb and Ni by AAS method. Content of Hg was determined by advanced mercury analyser AMA 254. Analyser AMA 254 was used for determination of mercury content in sediment. Analyser AMA 254 (Altec, ČR) is single-purpose atomic absorption spectrometer, developed and produced in Czech Republic. It is used for assessment of total content of mercury in solid and also in liquid samples without previous amendments of samples.

Samples of tissues were obtained by section – muscle, hepatopancreas, kidney, gonads (eggs and milt), skin, gill and fin in amount of 2–3 g. Samples of bottom sediments were collected by soil pit from the depth of 0.0-0.1 m in amount of cca 1 kg per sample from the different part of pond, including inflow and outlet. For analysis, each tissue sample was dissolved in a solution of nitric acid p.a. (HNO_3:H_2O = 2:1); sediment sample in solution of acids (HF-HNO_3-$HClO_4$) and analyzed for presence of Cd, Pb by the atomic absorption spectrophotometer (AAS) Varian Duo 240FS and 240Z and Hg by AMA 254. Values of monitored metals are presented on a wet weight basis; values of bottom sediment in dry weight (DW) and wet weight (WW), all in mg.kg^{-1} and compared with Codex Alimentarius and sediment´s law valid in the Slovak Republic.

RESULTS AND DISCUSSION

Determined contents of monitored risky 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 the limit values for content of risky elements in bottom sediment are reported as following (tab.1):

Table 1 Limit values concentrations of risky compounds in bottom sediments

Arsenic	20 mg.kg^{-1}	Nickel	300 mg.kg^{-1}
Cadmium	**10 mg.kg^{-1}**	**Lead**	**750 mg.kg^{-1}**
Chromium	1 000 mg.kg^{-1}	Zinc	2 500 mg.kg^{-1}
Cupper	1 000 mg.kg^{-1}	PAU	6.0 mg.kg^{-1}
Mercury	**10 mg.kg^{-1}**	PCB	0.8 mg.kg^{-1}

The chemical analyses of taken bottom sediment with VN in Kolíňany are reported in tables 2 and 3. The results of chemical composition of sediment showed high content of organic compounds in substrate, what was confirmed also 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^{-1}**				**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

Content of macro-elements assessed by method Melich III showed high accumulation of calcium, magnesium and potassium and low content of phosphorus in sediment. Mentioned findings are the consequence of very good cumulating ability of clay minerals that are able to absorb and bind chemical elements into their structures (**Zaujec, 1999**).

Elevated content of these elements is the casual consequence of long-term intensive agricultural activity in vicinity of dam (**Tóth et al., 2006**), intensive breeding program of kept fish as well as long- term accumulation of sediment at the bottom of dam.

Content of monitored risky elements in bottom sediment and its comparison with legislative norm is represented in table 3. Results of our analyses revealed that the limit value was not exceeded for contents of cadmium, lead, and mercury in tested substrate.

Reaction (pH) of bottom sediment is neutral to weakly alkali (pH/KCl) in range of determined values 7.58-8.05 with average value 7.73. Neutral to weakly alkali environment of substrate is an important indicating factor of riskiness of sediment, while according to many authors (**Andreji, 2009; Tomáš, 2009; Hecl, Danielovič 2004**) in neutral to weakly alkali environment the monitored risky elements are 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.

Table 3 Content of risky elements in bottom sediment

Sample no.	**pH H_2O**	**pH KCl**	***Aqua regia extract*** **mg.kg $^{-1}$**		**AMA 254 mg.kg $^{-1}$**
			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**

Average content of cadmium in sediment was 2.636 mg.kg^{-1} that in comparison to limit value 10 mg.kg^{-1} presented 23.6 % from its content. Mentioned content was under limit value and did not pose a real risk of its entry into nearest biota in range threatening the environment. Contents of lead and mercury in sediment were deeply below limit values. Content of lead was in comparison to limit value 2.3 % and content of mercury only 0.38 %. Mentioned contents of risky elements did not provide assumption about their increased transfer into fish organism, although all risky elements are characterized with ability to accumulate in animal tissues. This accumulation is in direct proportionality to the age of fish, what means that the longer the organism is exposed to the effect of risky compound in environment, the higher will be its content in organism. From the standpoint of risky elements content we could state that monitored dam is safe from the production of healthy and safe foodstuffs – fish point of view. However, it is important to carry out regular monitoring, as it is mentioned in Partial monitoring system: Foreign matters in foodstuffs and feed, subsystem: Monitoring of wild game and fish.

The concentrations of heavy metals in the fish tissues are showed in Table 4.

Table 4 Concentrations of Cd, Pb and Hg in analyzed tissues of common carp (n = 4) from the pond of Kolíňany.

		muscle	**hepatopancreas**	**kidney**	**gonads**	**skin**	**gill**	**fin**
Cd	mean ± SD	0.06 ± 0.04	0.08 ± 0.04	0.19 ± 0.07	0.08 ± 0.01	0.28 ± 0.28	0.30 ± 0.05	0.67 ± 0.14
	range	0.02 - 0.13	0.05 - 0.14	0.07 - 0.24	0.02 - 0.13	0.07 - 0.76	0.26 - 0.38	0.52 - 0.84
Pb	mean ± SD	0.24 ± 0.14	0.25 ± 0.09	0.54 ± 0.22	0.43 ± 0.16	1.31 ± 1.44	1.64 ± 0.31	2.65 ± 0.34
	range	0.09 - 0.48	0.14 - 0.35	0.19 - 0.80	0.27 - 0.66	0.24 - 3.79	1.40 - 2.16	2.29 - 3.18
Hg	mean ± SD	0.05 ± 0.02	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.02	0.01 ± 0.00	0.01 ± 0.00
	range	0.03 - 0.07	0.01 - 0.02	0.02 - 0.04	0.00 - 0.01	0.00 - 0.05	0.01 - 0.01	0.00 - 0.01

Cadmium content in analyzed sample of common carp varied closely. Measuring data ranged in hundredths or tenths of milligram. Detected values for individual tissues ranged in mg.kg^{-1} wet weight (w. w.) as follows: muscle 0.02-0.13, hepatopancreas 0.05-0.14, kidney 0.07-0.24, gonads 0.02-0.13, skin 0.07-0.76, gill 0.26-0.38, fin 0.52-0.84. The highest mean concentration was detected in fins (0.67 mg.kg^{-1} w.w.) opposite to the muscle, where only 0.06 mg.kg^{-1} w. w. concentration was recorded (Table 4). Lower mean Cd concentrations were detected in the muscle and gills of common carp from the aquaculture ponds of Kolkata, India (**Adhikari et al., 2009**), but higher values for kidney and hepatopancreas were recorded. Also lower Cd content in carp muscle was recorded from two ponds in the southwestern Slovakia (**Andreji et al., 2006**). Approximately 10-fold higher values were measured in the muscle, hepatopancreas and gill of common carp from the Menzelet Dam Lake and nearly 50-

fold higher from the Sir Dam Lake, both Turkey (**Erdogrul & Ates 2006**). A little higher values of the muscle Cd content are given from the pond of Malé Záluzie, Slovakia (**Andreji et al., 2009**). General order of Cd accumulation in carp tissues was:

fin > gill > skin > kidney > hepatopancreas ≈ gonads > muscle

Similar to our results, also in analyzed carp tissues from the Menzelet Dam Lake the order of Cd distribution was confirmed (**Erdogrul & Ates 2006**). Different cadmium concentration tissue decreasing was measured in the caged carp at four different aquatic sites in Flanders (Belgium), where the highest concentration in kidney and lowest in muscle were confirmed (**Bervoets et al., 2009**). Permissible limit for Cd content in the musle (0.05 mg.kg^{-1} w.w.) was exceeded in one sample.

Lead concentration in analyzed carp tissues varied widely and achieved higher values than cadmium. Recorded amounts range generally in the tenths of milligram, but in the cases of the skin, gills and fins also in whole milligram. Measured values in individual tissues were as follows (in mg.kg^{-1} w. w.): muscle 0.09-0.48, hepatopancreas 0.14-0.35, kidney 0.19-0.80, gonads 0.27-0.66, skin 0.24-3.79, gill 1.40-2.16, fin 2.29-3.18. The highest (2.65 mg.kg^{-1}) as well as lowest (0.24 mg.kg^{-1}) mean Pb concentrations likewise to cadmium, in fins and muscle were recorded (Table 4). Lower Pb tissue concentrations were detected in the muscle and gill of common carp from the Sir Dam Lake, Turkey (**Erdogrul & Erbilir 2007**). On the other hand, higher Pb concentration in carp muscle in comparison to our results was confirmed from the Isikli and Karacaören Dam Lakes, both Turkey (**Kalyoncu et al. 2011**). A little higher Pb concentrations in the carp muscle were measured from the three ponds of south western Slovakia (**Andreji et al., 2006, 2009**). General order of Cd accumulation in carp tissues was:

fin > gill > skin > kidney > gonads > hepatopancreas > muscle

Close identical results of Pb distribution in different carp tissues are presented from Svitava Lake, Bosnia and Herzegovina (**Has-Schön et al., 2008**). Resembling results in Pb distribution in carp tissues were presented by **Bervoets et al**. (2009) from the four sites of Flanders (Belgium). In their study the Pb concentration decreasing was recorded as follows: gill > intestine > hepatopancreas > kidney = muscle. Tolerable limit (0.2 mg.kg^{-1} w.w.) for the Pb concentration in muscle was exceeded in 2 samples.

Mercury content in carp tissue samples varied very closely. Estimated Hg concentration reached the values of several hundredth of milligram only and measured values in individual tissues fluctuated between 0.00-0.07 mg.kg^{-1} w. w. Recorded mean (±S.D.) Hg concentrations were as follows (in mg.kg^{-1} w. w.): muscle 0.05 ±0.02, hepatopancreas 0.01

±0.00, kidney 0.02 ±0.01, gonads 0.01 ±0.00, skin 0.01 ±0.02, gills 0.01 ±0.00, fins 0.01 ±0.00. The highest mean concentration in muscle and the lowest in gonads, gills and fins were detected. Comparable values of Hg content in the carp muscle 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 confirmed from the 10 Bohemian and Moravian ponds (**Čelechovská et al., 2007**). General order of Cd accumulation in carp tissues was: muscle > kidney > skin ≈ hepatopancreas ≈ fin ≈ gill ≈ gonads

Very similar results for the Hg content 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^{-1} w.w.) was not exceed.

CONCLUSION

The objective of this case study was to provide information about characteristics, affecting and occurrence some risky elements in biotic and abiotic environment, exactly as mentioned. On the of our findings we can conclude:

- analysis of bottom sediments shows on hygienic safety of this environmental component without direct threatening of health state of fish bred in dam Kolíňany
- content of cadmium, lead, and mercury does not pose a real risk of their increased entry into fish organism
- content of cadmium in fish meat is lower than the highest acceptable amount (HAA), but in some parts of fish its content is higher than HAA
- content of lead in fish meat is under hygienic limit, higher accumulation was observed in skin, gills and fins, what are non-consumable parts of fish
- content of mercury does not exceed HAA for its content in fish
- accumulation of risky elements in tested parts of fish is as following:
- analysis of fish from the standpoint of Cd, Pb and Hg contents showed that muscle of fish is suitable for consumption and fulfil all hygienic limits determined for these elements

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