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Tadeusz P. ŻARSKI[1], Henryka ŻARSKA[1] , Miroslav SAMEK[2],
Katerina KOVAROVA[2] and Teresa MAJDECKA[1]

COMPARISON OF MERCURY CONTAMINATION IN BRED AND WILD CARPS (*Cyprinus carpio* Linnaeus 1758) CAUGHT IN AN OXBOW LAKE OF THE VISTULA RIVER

PORÓWNANIE SKAŻENIA RTĘCIĄ KARPI (*Cyprinus carpio* Linnaeus 1758) HODOWLANYCH I DZIKICH POCHODZĄCYCH ZE STARORZECZA WISŁY

Abstract: Presence in meat of the fish of the toxic substances motivates to the undertaking of investigations can the scale of the wholesome threat for the man (angler), which he stood from the right of hunting of the fish oneself the final link in the chain trophic of water ecosystem in this also in the process of the accumulation of heavy metals. The comparison of the degree of the contamination was the generally basic aim of investigations carps mercury and the settlement, what influence on her postponing, and every he goes for this, what there is the threat toxicological for angler fishing the fish of the same species in natural reservoir or animal pond. They made up the material to investigations carps gain over from two various water environments after 10 of every one the clatter in seasons 2004–2006 years. The content of mercury in taken tests was studied use the automatic analyzer of the traces of the mercury of AMA 254 in support about the method of the *absorption of atomic spectrometry* (AAS). The degree of the mercury contamination studied ponds carps was low and many the times lower than admissible norms of hygienic. Carps coming from the old flood water of the Vistula river contain in their tissues and organs the larger quantities of mercury, what to result from the larger dirt of waters of the Vistula in this heavy metal. The average concentration the mercury in the carps studied group wild it was twice lower than admissible hygienic norms.

Keywords: breeding carps, wilds carps, contamination, mercury

The element mercury (Hg) and its compounds have no known normal metabolic function. Their presence in the cells of living organisms represents contamination from natural and anthropogenic sources; all such contamination must be regarded as undesirable and potentially hazardous.

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[1] Department of Biology of Animal Environment, Warsaw University of Life Sciences – SGGW, ul. S. Ciszewskiego 8, 02–786 Warszawa, Poland, phone: +48 22 593 66 10, email: tadeusz_zarski@sggw.pl

[2] Department of Trade and Finances, Czech University of Life Sciences (CULS), Kamýcká 961/129, 165 00 Praha 6-Suchdol, Czech Republic, phone: +420 22 438 23 77, email: kovarovak@pev.czu.cz

Mercury is a naturally occurring metal, a useful chemical in some products, and a potential health risk. Mercury exists in several forms – the types people are usually exposed to are methylmercury and elemental mercury. Elemental mercury at room temperature is a shiny, silver-white liquid, which can produce a harmful odorless vapor. Methylmercury, an organic compound, can build up in the bodies of long-living, predatory fish. To keep mercury out of the fish we eat, it's important to take mercury-containing product to a hazardous waste facility for disposal [1].

Inorganic mercury washed into water bodies is converted to an organic form, methylmercury, by the action of microbes. Mercury contaminated plankton is eaten by small fish and increasingly large fish feed on them. Higher rates of methylation are found in acidified waterbodies (low pH), and sulfates from acid rain may also accelerate methylation. There is some indication that smaller, warmer, more eutrophic bodies have higher rates of methylation. Methylmercury is the element's most toxic form; it not only accumulates in the aquatic food chain but tends to concentrate strongly as it is passed upward in the food chain. Thus methylmercury concentrations in predator fish can be a million times higher than those of the surrounding water. Mercury binds strongly with sulfhydryl groups. The sulfhydryl groups within cysteine function to form "cross-links" or disulfide bridges between two cysteines. These cross-links are what give proteins three-dimensional structure. When mercury binds to the sulfhydryl groups, the disulfide bonds are broken and the protein loses its structure and is rendered non-functional.. It has many potential target sites during embryogenesis; phenylmercury and methyl-mercury compounds are among the strongest known inhibitors of cell division. Organomercury compounds, especially methylmercury, cross placental barriers and can enter mammals by way of the respiratory tract, gastrointestinal tract, skin, or mucous membranes. When compared with inorganic mercury compounds, organomercurials are more completely absorbed, are more soluble in organic solvents and lipids, pass more readily through biological membranes, and are slower to be excreted [1, 2].

A wide range of adverse health effects have been observed in humans following methylmercury exposure, the severity largely depending on the magnitude of the dose and the duration of exposure. The predominant health affects in humans are associated with the impaired functions of the central and peripheral nervous systems. For example, elevated methylmercury exposure in a fetus or young child can cause a decrease in I.Q., delays in walking and talking, lack of coordination, blindness, and seizures. In adults, excessive methylmercury exposure can lead to personality changes, tremors, changes in vision, deafness, loss of muscle coordination and sensation, memory loss, intellectual impairment, and, in very extreme cases, even death [1–4].

Mercury is present in surface waters in both inorganic and organic forms; the latter mainly as methylmercury. This compound easily enters the aquatic food chains. Predatory fish as the last link in this chain may concentrate in their tissues 1–10 million times more mercury than that present in water [1–3]. It is assumed that 90–100 % of mercury in adult fish is bound with methyl group. Combined with sulfhydryl (-SH) groups in proteins mercury occurs mainly in fish muscles. It enters fish organism in three ways: through gills, skin and alimentary tract [1, 3, 5].

Boiling, frying or any other way of thermal processing does not decrease mercury content in fish. On the contrary, its concentration increases proportionally to the loss of water during preparation. Mercury from protein structures is not removable during these processes.

From among all types of food in human diet most contaminated with mercury are fish, crustaceans and other *frutti di mare* in which mercury concentration may be 10^3–10^4 times higher than in vegetables, fruits, meat, eggs or milk [1, 2].

Mercury poisoning has usually been associated with large ocean fish, such as shark, swordfish, king mackerel, tilefish or tuna. But the freshwater fish most likely to contain harmful amounts of mercury include smallmouth bass, walleye, largemouth bass, lake trout and pike. Freshwater fish are more likely to be contaminated than ocean fish. A report from the *Environmental Protection Agency* (EPA), showed that virtually every fresh-water fish sample tested from lakes across the United States was contaminated with mercury. About 55 % samples of freshwater fish contained mercury levels that exceeded EPA's "safe" limit for women who eat fish twice a week, particularly those in their child-bearing years and 76 % of the fish sampled contained mercury levels that exceeded the EPA's safe limit for children under age three who eat fish twice a week. [2, 3].

Studies on mercury content in the tissues of fish from the middle course of the Vistula River carried out since the beginning of the 1990's indicate systematic decrease of mercury concentration [6]. This is true for all heavy metals delivered to the Baltic Sea with river waters in the years 1995–2007. For example, the annual load of chromium decreased from 48.7 to 15.6 Mg, that of lead – from 124.7 to 68.9 Mg [7]. The load of mercury varied, however, from 9 $Mg \cdot yr^{-1}$ in 1995 to 0.6 $Mg \cdot yr^{-1}$ in 2004 to increase again in 2007 to 17.8 $Mg \cdot yr^{-1}$ [7]. The total lack of the measurements of the rigors of heavy metals in the measuring point in Kiezmark on Vistula River, and also in some rivers of near Baltic Sea makes impossible the realization of the comparative analysis in the relation till next years after 2007 [7, 8].

At present, there are nearly 1.5 million active anglers in Poland including 600 thousand members of the Polish Angling Association and their families. Specialists estimate that anglers catch annually 40–50 thousand Mg of fish which makes c. 35–80 kg of fish per person. Angling means not only fish catching but also nature protection and tourist development of the region. And finally, health aspect should also be mentioned since economic and technological development may be detrimental to human health. The presence of contaminants in fish justifies the studies undertaken to estimate the degree of health risk for angler who, by catching fish, becomes top predator in the food chain of aquatic ecosystem and thus participates in the process of heavy metal accumulation. The aim of this study was to compare fish contamination by mercury and toxicological risk posed to an angler catching fish of the same species in the natural water body and in fish pond.

Material and methods

Carps (*Cyprinus carpio* Linnaeus 1758) for this study were obtained from two aquatic habitats (10 individuals from each) in the years 2004–2006. Fish were caught in an oxbow lake near Czerwinsk on Vistula (most common in Europe full scaled carps) and in ponds of the Fishery Station SGGW in Jaktorow (mirror carp). Before sampling tissues and organs of these fishes were weighed and measured. Caught fish had a mass between 500 and 1430 g and length between 27 and 39 cm. Samples of upper muscles, gills, hepato-pancreas, middle intestine, kidneys, gonads and scales were taken from each fish and kept deep frozen until analyses.

The content of mercury was determined using atomic absorption spectrophotometry with the computer controlled automatic mercury analyzer AMA 254 made by Altec (CR). The method consists in the measurement of absorption spectrum of a lamp with cathode made of mercury. Sensitivity is 0.01 ngHg $\cdot$ kg^{-1} and measurement range 0.05–600 ng. Maximum mass of the sample should not exceed 300 mg. The entire analytical procedure was validated by analyzing reference material No. 422 Cod Muscle (lyophilised) samples at the beginning and end of each set of tissue samples.

Concentration of mercury is given in mg $\cdot$ kg^{-1} of the tissue mass. Each measurement was triplicated and results are given as means. The apparatus was calibrated with the solution of polarographically pure mercury in 2 % HNO_3. Arithmetic mean, standard deviation, minimum and maximum values were calculated and results were statistically processed using the computer program Statgraphic 4 .

Results and discussion

The highest concentrations of mercury (mean 0.2548 mg $\cdot$ kg^{-1}) were found in muscles of wild full scaled carps. The concentration in muscles of bred mirror carps was nearly three times lower (0.0775 mg $\cdot$ kg^{-1}). However, maximum concentration of 0.5247 mg $\cdot$ kg^{-1} found in the largest wild carp exceeded the maximum tolerable limit of mercury established at 0.5 mg $\cdot$ kg^{-1} for bottom feeding fish [9]. It is particularly alarming since the biomass of wild carps was twice lower than the biomass of bred carps. Having in mind that the growth rate of wild carp is nearly two times slower one may assume that analyzed fishes could be of the same age. Higher concentrations of mercury were also noted in other tissues and organs of wild carp as compared with bred carp (Tables 1 and 2).

Table 1

Concentration of mercury in tissues and organs of wild carp (*C. carpio*) from the Vistula River oxbow lake [mg $\cdot$ kg^{-1}]

Parameter	Mass [g]	Length [cm]	Scales	Gills	Hepato-pancreas	Kidney	Gonads	Muscles
Mean	670	29.6	0.0084	0.0185	0.0536	0.0762	0.0217	0.2548
Standard deviation	190.8	2.72	0.0039	0.0095	0.0418	0.0317	0.0127	0.1810
Minimum	500	25	0.0038	0.0019	0.0122	0.0351	0.0187	0.1472
Maximum	980	35	0.0152	0.0394	0.1162	0.1126	0.0217	0.6247

Table 2

Concentration of mercury in tissues and organs of bred carp (*C. carpio*) from ponds in the Fishery Station SGGW in Jaktorow [$mg \cdot kg^{-1}$]

Parameter	Mass [g]	Length [cm]	Scales	Gills	Hepato-pancreas	Kidney	Gonads	Muscles
Mean	1268	36.4	0.0122	0.0098*	0.0197**	0.0294*	0.0088*	0.0775**
Standard deviation	131.3	2.02	0.0039	0.0019	0.0044	0.0138	0.0026	0.0121
Minimum	1080	34	0.0068	0.0078	0.0134	0.0198	0.0060	0.0593
Maximum	1430	39	0.0191	0.0156	0.0230	0.2334	0.0157	0.1019

Explanations: differences in the concentration of mercury between two groups of carps significant at * $p < 0.05$, ** $p < 0.01$.

The lowest mercury concentrations were found in gonads of fish from both races. This regularity was also noted in breams from the Vistula River and was explained by the protection of reproductive organs from genotoxic and teratogenic effect of mercury [6].

Carps caught in the oxbow lake of the Vistula River basin and analyzed within this study were relatively small as compared with the size carp may achieve in the wild. Since contamination with mercury increases linearly with fish weight and age, one may expect that larger individuals contain more mercury which eventually would exceed the tolerable threshold concentration.

This does not concern fish from fish farms which allow anglers to use their ponds for that form of recreation. To intensify carp production in cultures fish are given concentrated food composed of seeds of legume and cereal plants and granulated proteins. Moreover, ponds are usually filled with water of controlled quality. Taking all this into account, and relatively short (2–3 years) productive cycle in bred carps, significant contamination by mercury is less probable in this case.

The literature suggests that in our study, mean Hg concentration are lower than those reported for carp (0.70 $mg \cdot kg^{-1}$) in the Nitra River in Slovakia [10]. In contrast, mean Hg levels in carp muscles in the present study are higher than those described for Ya-Er Lake in China (0.08 $mg \cdot kg^{-1}$) [11].

Fish is an important part of healthy diet. It is a good protein source that is low in saturated fats and high in beneficial omega-3 fatty acid and other nutrients. Fish consumption decreased the risk of cardiovascular disease. Other reported benefits of fish consumption include a decrease in some cancers and protection against declines of brain function [1, 3, 4] Our results of the fish tissue analysis indicate that bred carp and carp from the oxbow lake in the Vistula are generally low in mercury concentration and do not require meal limit advice.

Conclusions

1. The degree of contamination by mercury in bred carp is many times lower than the acceptable hygienic standard.

2. Carps from the oxbow lake in the Vistula valley contain more mercury in their tissues and organs, probably because of higher concentration of this metal in river waters.

3. Mean concentration of mercury in the group of wild carps was two times lower than the acceptable hygienic standard.

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[1] Katedra Biologii Środowiska Zwierząt
Szkoła Główna Gospodarstwa Wiejskiego w Warszawie
[2] Katedra Handlu i Finansów
Czeski Uniwersytet Rolniczy w Pradze

Abstrakt: Obecność w mięsie ryb substancji skażeniowych uzasadnia podjęcie badań mogących ustalić skalę zagrożenia zdrowotnego dla człowieka (wędkarza), który z racji łowienia ryb stał się końcowym ogniwem w łańcuchu troficznym ekosystemu wodnego w tym również w procesie kumulacji metali ciężkich. Generalnie podstawowym celem badań było porównanie stopnia skażenia rtęcią karpi i ustalenie, jaki wpływ na jej odkładanie, a co za tym idzie, jakie jest zagrożenie toksykologiczne dla wędkarza łowiącego ryby tego samego gatunku w akwenie naturalnym lub stawie hodowlanym. Materiał do badań stanowiły karpie pozyskane z dwóch różnych środowisk wodnych po 10 stuk z każdego w sezonach 2004–2006 Zawartość rtęci w pobranych próbkach badano przy użyciu automatycznego analizatora śladów rtęci AMA 254, wykorzystując metodę spektrometrii absorpcji atomowej (AAS) Stopień skażenia rtęcią badanych karpi hodowlanych był niski i wielokrotnie niższy od dopuszczalnych norm higienicznych. Karpie pochodzące ze starorzecza Wisły zawierają w swych tkankach i narządach większe ilości rtęci, co może wynikać z większego zanieczyszczenia wód wiślanych tym metalem ciężkim. Średnie stężenie rtęci w badanej grupie karpi dzikich było dwukrotnie niższe od dopuszczalnych norm higienicznych.

Słowa kluczowe: karpie hodowlane, karpie dzikie, skażenie, rtęć