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Muscle mercury and selenium in fishes and semiaquatic mammals from a selenium-deficient area

Elzbieta Kalisinska[a], Natalia Lanocha-Arendarczyk[a], Danuta Kosik-Bogacka[a,*], Halina Budis[b], Bogumila Pilarczyk[c], Agnieszka Tomza-Marciniak[c], Joanna Podlasinska[d], Lukasz Cieslik[e], Marcin Popiolek[f], Agnieszka Pirog[g], Ewa Jedrzejewska[h]

[a] Department of Biology and Medical Parasitology, Pomeranian Medical University, in Szczecin, Poland
[b] Department of Health Education, University of Szczecin, Poland
[c] Chair of Animal Reproduction Biotechnology and Environmental Hygiene, West Pomeranian University of Technology in Szczecin, Poland
[d] Department of Environmental Management and Protection, Western Pomeranian University of Technology,in Szczecin, Poland
[e] Warta Mouth National Park, Poland
[f] Department of Parasitology, Institute of Genetics and Microbiology, University of Wroclaw, Poland
[g] Department of Invertebrate Systematics and Ecology, Institute of Biology, Wroclaw University of Environmental and Life Sciences, Poland
[h] Ecoexpert Sp. z o.o., Poland

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ABSTRACT

The aim of this study was to investigate and compare total mercury (Hg), selenium (Se), and Se:Hg molar ratios in fish muscles (phytophages n=3; benthophages n=32; predators n=5) and semiaquatic carnivores, including piscivores (the European otter n=8, the feral American mink n=7) and the omnivorous raccoon (n=37) from a riverine European ecosystem in a Se-deficient area. The Hg concentration in fish reached 0.337 μg/g dry weight, dw (0.084 μg/g wet weight, ww). We found significant differences among Hg levels in tested vertebrate groups (predators vs benthophages: 0.893 vs 0.281 μg/g; piscivores vs omnivores: 6.085 vs 0.566 μg/g dw). Fish groups did not differ in Se concentrations, with a mean value of 0.653 μg/g dw. Significant differences were revealed between Se levels in piscivorous and omnivorous carnivores (0.360 vs 0.786 μg/g dw, respectively). Fish Se:Hg molar ratio values were > 2.2. Benthophages had higher the ratio than predators but similar to phytophages. Among carnivores, piscivores had much lower the ratio than raccoon (0.14 vs 3.75) but raccoon and fish medians did not significantly differ. We found almost two times higher Se levels in fish and raccoons compared to piscivores, possibly resulting from lower fish Se digestibility by piscivores in contrast to higher absorption of plant Se by many fish and omnivorous raccoons. Considering that a tissue Se:Hg molar ratio < 1 may be connected with a Hg toxicity potential increase, we assume that piscivores in Se-deficient area are in worse situation and more exposed to Hg than fish and omnivores.

1. Introduction

Mercury (Hg) in the environment can be of natural or anthropogenic origin. It is highly toxic heavy metal with high volatility. It is estimated that only 19% of deposited Hg in the European Union (EU), with an annual average of 138.5 t between 2005 and 2011, originate from local sources (Chen et al., 2014). Since the 1990s, Poland and Germany with coal-based energetics have emitted the largest amounts of Hg within the EU. Between 1990 and 2012, emissions from these two countries have declined and as a consequence, annual atmospheric Hg input has decreased by 70%, from around 32–10 t (EEA, 2014). In inland aquatic environments, major sources of Hg are the bedrock, atmospheric deposition, and effluent discharged into surface waters. Locally, the latter two sources can lead to Hg intoxication in fish and other organisms. In water sediments, biotransformation of inorganic mercury (InHg) through microorganisms results in the formation of methylmercury, MeHg (AMAP/UNEP, 2013). Although all Hg forms are toxic for warm-blooded vertebrates, MeHg is particularly dangerous because of its high bioavailability. It is almost completely absorbed (> 90%) upon ingestion and is highly neurotoxic. All Hg species are subjected to the bioaccumulation but MeHg additionally biomagnification in aquatic food chains to varying degrees, depending on Hg amounts and forms. Methylmercury predominates in fish muscles (> 80% of total Hg, THg), and its concentration is significantly correlated

* Correspondence to: Department of Biology and Medical Parasitology, Pomeranian Medical University, Powstancow Wielkopolskich 72, 70–111 Szczecin, in Szczecin, Poland.
E-mail address: kodan@pum.edu.pl (D. Kosik-Bogacka).

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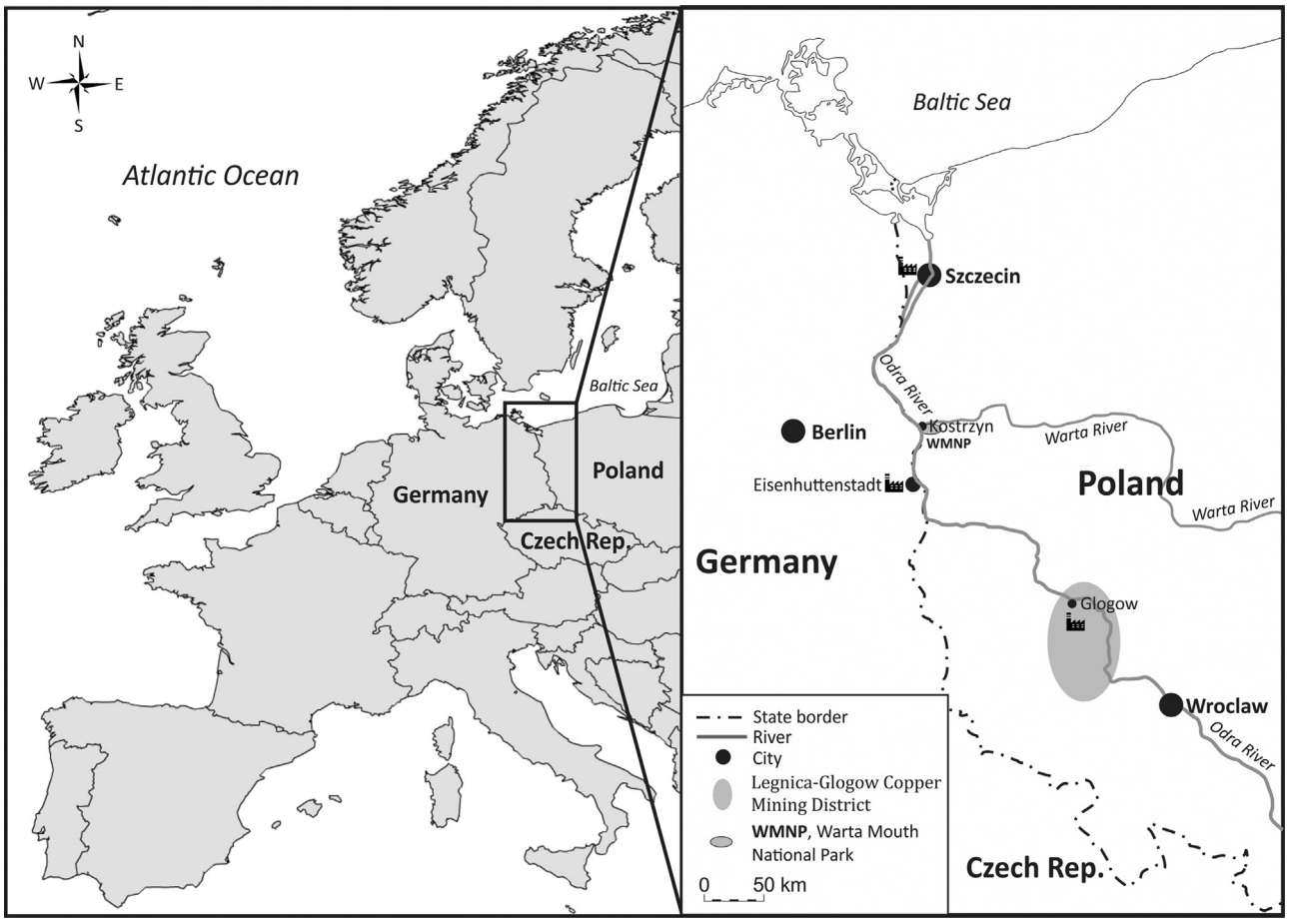

Fig. 1. Study area and the main source of its contamination.

with age, weight, and body length. Moreover, the MeHg level depends on the trophic position of fish species. Monitoring toxic Hg concentrations in biota are widely and increasingly used for assessing the chemical status of aquatic ecosystems, mainly selecting common bentophagous or predatory fish (Scheuhammer et al., 2007; Peterson et al., 2009; Schäfer et al., 2015).

Numerous ecotoxicological studies revealed the highest THg levels in liver and kidneys of terrestrial wildlife feeding on aquatic animals but both tissues account 4–6% of their body weight only (Lanszki et al., 2008). Methylmercury demethylation mostly occurs in the liver and kidneys, leading to the production of the less toxic InHg, which is excreted with feces and urine. When nephritic and hepatic THg concentrations are greater than 8–10 mg THg/kg dry weight (dw), MeHg may be well below 40–50% of THg in semiaquatic carnivores (O'Connor and Nielsen, 1981; Fortin et al., 2001). In avian and mammalian muscles demethylation of MeHg is insufficient or does not occur at all, leading to MeHg percentages of around 90% of THg (Scheuhammer et al., 2007). Skeletal muscles constitute 50–55% of carnivore bodies (Muchlinski et al., 2012) and play a greater role in MeHg transmission from the aquatic to the terrestrial environment than liver and kidneys. Determination of Hg muscle levels in fish and semiaquatic carnivore allows conclusions about contamination of e.g. riverine and riparian ecosystems. However, ecotoxicological studies of muscle Hg concentrations in fish and semiaquatic predators from the same area are rare (Chumchal et al., 2011).

In mammals and fish, an important detoxification mechanism is the antagonistic impact of selenium (Se) in relation to Hg, which is well documented for marine species, and there are various hypotheses for Se protective mechanisms. Selenium is essential element for vertebrates and in some of their proteins (selenoproteins). In comparison to bony fish birds and mammals produce less number of selenoproteins. In mammals, the difference between necessary and harmful Se amount is very small. Selenium deficiency results in muscle pathology, fetal death and reproduction deterioration. In some regions, i.e. west North America, Se is present in significant quantities in surface waters and soils, resulting in excessive Se bioaccumulation in fish, waterfowl, and grazing animals (Fordyce, 2005). In other regions, e.g. some areas of Germany, Poland, and Scandinavia Se deficiency in soils was observed, resulting in low bioavailability for mammals (Salminen, 2005; Pilarczyk et al., 2011).

Ecotoxicologists are especially interested in various relations between Se and Hg in animals. In some marine vertebrate species, the insoluble, biologically inactive forms are generated as nontoxic combinations of Se–Hg, including equimolar HgSe compound. The presence of HgSe was first demonstrated in livers, kidneys and brains, and more recently, in marine mammal muscles (Nakazawa et al., 2011). It is likely that with low Hg molar concentrations in relation to Se in organs and tissues, selenoenzyme remains active. However, when tissue Hg exceeds Se, Se tissue portions vital for antioxidant selenoenzyme production become sequestered and symptoms of Hg toxicity develop. Therefore, Hg concentration in an organism might not be the critical factor, but rather the ratio of tissue Hg and Se. Hence, Se:Hg molar ratios below one may increase Hg toxicity potentials, while molar ratios that approach or exceed one effectively may protect against Hg toxicity (Peterson et al., 2009; Zhang, 2014). Information about Se and Hg levels in freshwater fish and semiaquatic mammals is scarce (Wren, 1984; Burger and Gochfeld, 2013). In the literature no information on correlation, proportion between Se and Hg or Se:Hg molar rations in carnivore muscles has been found. Moreover, probably studies on of these elements in muscles of freshwater fish and semiaquatic mammals