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Species differences in total mercury concentration in gulls from the Gulf of Gdansk (Southern Baltic)

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ABSTRACT

Aquatic birds occupy a high position in the trophic pyramid of the Baltic Sea. This means that they accumulate the greatest amount of harmful substances, including mercury, in their bodies. This element penetrates into their systems mainly via the alimentary canal. The amount of mercury absorbed from food depends on how badly the environment is polluted with this metal. The aim of this study was to discover the concentrations of total mercury (Hg_T) in the contour feathers, muscles, brain, lungs, liver, kidneys, heart and blood of four gull species Herring Gull (*Larus argentatus*), Common Gull (*Larus canus*), Black-headed Gull (*Larus ridibundus*) and Great Black-backed Gull (*Larus marinus*) and organic mercury (Hg_{org}) in the liver and brain of Herring Gull. The most important characteristic of the results obtained for the studied gulls was the statistically significant differences between the four species, probably resulting from their different diets-confirmed by stable-isotopes analysis ($\delta^{15}N$ and $\delta^{13}C$). A logarithmic dependence was found between Hg_T in the blood and Hg_T in the brain of the Herring Gull. The authors suggest that among gulls burdened with the greatest mercury load, it is possible that the brain is protected by higher Hg accumulation in the muscles. The percentage share of Hg_{org} in the brain and liver of the Herring Gull depended on the concentration of Hg_T in these tissues and was always higher in the brain. In none of the cases, did the mercury levels assayed in the internal gulls' tissues exceed values associated with adverse health effects.

1. Introduction

Mercury is a highly toxic metal which becomes accumulated in the environment in living organisms, and whose concentration increases with the trophic level. Despite being an element occurring naturally in the environment, as a result of anthropogenic activity its concentration in water and sediments often considerably exceeds the geochemical background [1]. Organisms situated at the top of the trophic pyramid (predatory fish, piscivorous marine mammals and birds) are exposed to the greatest influence of mercury [2]. Mercury enters into the systems of birds mainly by their food [3], and is then transported to the liver with blood, where the organic forms of mercury, particularly methylmercury (MeHg), may undergo partial demethylation [4]. In the body of a bird mercury is accumulated primarily in the feathers (only during growth), liver and kidneys. To a smaller degree mercury is also accumulated in skeletal muscles, the heart and the brain. The most effective means of mercury removal is through the growth and exchange of feathers, but it is also excreted with guano and – in the case of females – while laying eggs [5]. The concentration of mercury in the tissues and organs of birds is thus a result of accumulation and excretion, both of which are heavily influenced by environmental and biological factors (taxonomic and trophic classification, and the age and gender). Mercury, particularly in its organic form, is a highly toxic element with an ability to permeate internal barriers of the system, including the blood–brain barrier [6]. Increased mercury accumulation in the brain may impair the visual-kinetic coordination and spatial orientation in birds [7].

Mercury is introduced into the marine environment mainly through atmospheric deposition and surface run-off. The Gulf of

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Gdansk is an integral part of the Baltic Sea, which is a shallow, intercontinental sea (average depth 52 m), and the highly urbanized catchment area makes this water basin particularly exposed to the inflow of substances of anthropogenic origin, including mercury. This metal occurs in all elements of the marine environment, resulting in its entry into the trophic chain [8]. The pre-industrial background concentration was determined at 30 $\mu g\,kg^{-1}$ for Baltic sediments, however the latest studies in the Gulf of Gdansk have shown a several-fold increase in mercury concentration in sediments, reaching up to 250 $\mu g\,kg^{-1}$ [9,10]. Many researchers agree that [10–12] the increase in the concentration of this metal in the surface sediments of the Baltic Sea must therefore be attributed to human activity.

It is considered necessary all around the world to effectively monitor the level of mercury contamination of the environment [13], and it is believed that birds, owing to their position in the marine trophic chain, may be good indicators of aquatic environment contamination with this element [14]. Despite the fact that relevant literature abounds in information concerning mercury accumulation in aquatic birds, studies using gulls are widespread only in North America. In Poland, in the Southern Baltic, such studies are sparse and concern mainly Great Cormorants, Mallard Ducks and the Common Merganser [15,16].

Naturally occurring stable-isotope ratios of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) reflect the consumer's diet at the time of tissue synthesis and are commonly used to investigate trophic relationships and to understand foraging ecology of birds. $\delta^{15}N$ reflects trophic position and $\delta^{13}C$ can indicate a geographic foraging area by determining relative contributions of marine and terrestial foods to the diet. Stable isotopes are useful in ecotoxicology studies because they provide continuous variables against which mercury levels can be gauged [17].

The aim of the present paper was to evaluate the exposure of seabirds found around the Gulf of Gdansk. In the years 2009–2012 studies were conducted on:

- determining the concentration level of total mercury in various soft body parts of birds from the *Laridae* group and comparing the obtained results with those provided in literature from other geographic regions of the Northern Hemisphere,
- interspecies similarities and differences in total mercury distribution in various organs,
- sex and age differences in the Herring Gull.

Determination of Hg_{org} level made it possible to initiate discussion on the effectiveness of the demethylation process in the liver and the brain of the Herring Gull.

2. Materials and methods

2.1. Birds collected

In Poland all birds from the *Laridae* family are protected species under a directive by the Environmental Protection Minister (Dz.U. No. 220, Item 2237) [18]. Dead birds were collected between December 2009 and August 2012. Due to the atmospheric conditions and the species characteristics of the birds, 90% of the specimens were found during winter and summertime. Most of the dead birds were collected in Wladyslawowo ($\phi = 54^\circ 47'$, $\lambda = 18^\circ 25'$) and in the "Mewia Lacha" bird sanctuary, situated at the Vistula Estuary ($\phi = 54^\circ 21'$, $\lambda = 18^\circ 57'$). A few species came from the city beaches of the Tri-city and Hel.

Table 1
The average moisture [%] of internal organs and tissues collected from four gull species found around the Gulf of Gdansk between 2009 and 2012.

Statistics	Liver	Muscle	Kidneys	Heart	Lungs	Brain
AM ± SD	70 ± 3	72 ± 3	76 ± 2	73 ± 3	80 ± 4	79 ± 3
Min–max	65–79	68–81	71–84	65–82	71–89	69–82

2.2. Material preparation

Prior to dissection, the weight was determined with an accuracy of up to ±0.1 g, and the birds' age was assessed based on their plumage. Three age categories were set out: juvenile, immature, and mature. In the case of the Great Black-backed Gull and the Herring Gull, specimens in their first winter plumage were classed as juvenile, those in their second and third plumage were categorized as immature, and those in the fourth and final plumage were considered mature. In the case of the Black-headed Gull and the Common Gull, specimens were classed as juvenile when in the first plumage, immature in the second, and mature in the final plumage. Due to the sexual immaturity of the birds and the condition of internal organs of some of the collected specimens, the gender was determined in genetic tests through DNA amplification using the PCR method. Contour feathers were collected from the birds' breast as such feathers tend to reflect the whole-body burden, particularly for mercury [19]. The variability of mercury concentration in these feathers is not as strongly related to the molt pattern as is the case with the flight feathers (remiges and restrices) [20].

During dissection, cause of death was not investigated. Tissues and organs were collected from the carcass, including: the brain, breast muscles (further referred to as muscles), the heart, the blood, the liver, kidneys and lungs. The blood was collected from the heart, often in a congealed form, which is why its moisture is not given. Organs and tissues were rinsed in MilliQ water (17.4 Ω), and then placed in sterile, labelled ziploc bags and preserved frozen at −20 °C. The samples were homogenized with the use of a stainless steel blade. Having been lyophilized, the biological material was homogenized again in a mortar and underwent chemical analysis within a few days. During the preparation procedure, the moisture of the collected organs and tissues was measured, excluding blood (Table 1). Feathers were washed with 80% acetone, in an ultrasonic bath, then rinsed with MilliQ water and left to dry at room temperature.

2.3. Chemical analysis

The assay of total mercury concentration (Hg_T) was carried out using the atomic absorption spectroscopy method (AMA 254 mercury analyzer). Mercury was determined in measured amounts of dried biological material of the following mass: 0.1 g—muscles, heart, lungs and brain; 0.01 g—liver and kidneys; 0.03 g—feathers (accuracy: 0.0001 g). The weighed and prepared material was placed in pre-heated nickel boats, which were automatically inserted into a furnace. The samples were dried at 120 °C for 300 s and mineralized at 550 °C in 180 s. Decomposition products were transported via oxygen as a carrier gas and absorbed on a gold trap. Subsequently, following desorption in a 60 s measurement cycle, absorbancy measurement took place at a wavelength of 253.65 nm.

The method used to assay organic mercury (Hg_{org}) involved extracting organic mercury from the biological material, and then transferring it onto a hydrophobic carrier [21,22]. Lyophilized material used for the analysis was in the following amounts: brain 0.5 g, liver 1.0 g (accuracy: 0.001 g). Measurement was conducted using an AMA 254 mercury analyzer.

The precision and accuracy of the analysis method for Hg_T and Hg_{org} were measured using certified standards from the European