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Bioaccumulation of mercury in the pelagic food chain of the Lake Baikal

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ABSTRACT

Mercury (Hg) concentrations were analyzed in the livers of Baikal seals and in plankton, zoobenthos and fish which constitute food items for the seals. Concentrations of Hg in the liver of Baikal seals were up to two orders of magnitude lower than those in seals inhabiting other lakes. The low levels of Hg are due to the low levels of the Hg in the fish from the family Comephoride, which reflect the very low concentrations of Hg in Baikal water. The development stage (pups and adults) and the sex of the seals have significant influence on their hepatic Hg concentrations. The differences between Hg accumulation in adult males, adult females and pups could be attributed to the reproductive cycle of the Baikal seals. In spite of low concentrations, Hg is characterized by high values of the concentration factor (CF) for the livers of for Baikal seals. Biomagnification factors (BMFs) suggest biomagnifications of Hg in the fish-seal trophic link.

1. Introduction

Anthropogenic factors have increased the geochemical cycling of Hg to a significant extent, on both regional and global scales. Two to three times more Hg is presently being cycled through the atmosphere and upper ocean water than before the rise of industry (Macdonald et al., 2005). The UN Environment Program "Global Mercury Assessment" reported Hg to be a growing and worldwide problem. Chemical elements, like heavy metals can be transported along the successive links of the food chain and their concentrations rise at each higher trophic level. This phenomenon is known as biomagnification. Mercury in the form of monomethyl mercury bioaccumulates and biomagnifies along marine and freshwater food chains and this leads to high levels in the top predators. Finally this can result in severe toxicological effects in aquatic top predators (Booth and Zeller, 2005; McIntyre and Beauchamp, 2007).

Several previous studies have focused on the influence of local industrial emission sources on the Hg levels in the Lake Baikal ecosystem and adjacent areas (Grachev, 1999; Koval et al., 1999). Important sources of the potential Lake Baikal pollution have been described by Ciesielski et al. (2006a). The main anthropogenic Hg sources in the vicinity of the Lake Baikal are concentrated primarily in the Irkutsk-Cheremkhovo industrial zone where Hg is used in the chemical industries such as chemical pulp and paper production. Other sources include thermal energy and power plants as well as urban activity and gold production (Koval et al., 1999).

The Lake Baikal consists of three separate basins: southern, central and northern. The distance from and occurrence of Hg pollution sources are different for each of the basins (Vetrov and Kuznetsova, 1997). Additionally, hydrothermal vents found in the sediment floor of the northeastern area of the lake could also be potential sources of natural Hg emissions (Meuleman et al., 1995). However, in spite of different atmospherics and natural sources, the levels of Hg in the Lake Baikal are very low and comparable to those in open ocean waters and even lower than the concentrations reported for other remote and unpolluted freshwater systems (Meuleman et al., 1995).

The only species of seal living exclusively in fresh water, the Baikal seal (*Phoca sibirica*), is the top predator in the Lake Baikal pelagic food chain. Marine mammals can accumulate substantial levels of organochlorine compounds and heavy metals (Das et al., 2003). This has led to speculation about the possible involvement of environmental pollutants in immunosuppression associated effects (Bennett et al., 2001; Kannan et al., 2006). Severity of lesions and high Hg levels were associated with a relatively poor health status of marine mammals from German waters of the North Sea and the Baltic Sea (Siebert et al., 1999).

Concentrations of different elements in tissues and organs of Baikal seals have been reported previously by Watanabe et al. (1996, 1998), Beim and Renzoni (2000), Ikemoto et al. (2004) and Ciesielski et al. (2006a). The relatively straightforward trophic relationships in the Lake Baikal make it a very good system for

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studying natural biogeochemical fates of Hg in a relatively unpolluted aquatic ecosystem (Gurova and Pastukhov, 1974; Yoshii et al., 1999). Such a study includes work on biological factors that influence bioaccumulation and biomagnification of Hg in low exposure conditions.

The aim of the present study was to examine trophic transfer of Hg along sequential trophic levels of the food chain of the Baikal seal, and to examine the biological importance of sex and age and spatial (geographical) distribution on the bioaccumulation of Hg. In addition, concentrations of other elements previously reported in Baikal seals (Ciesielski et al., 2006a) were included in a meta-analysis to clarify biological processes responsible for Hg accumulation in relation to other elements.

2. Experimental procedures

The sample collection and biometry for 27 individuals of Baikal seal (*P. sibirica*), fish species (*Comephorus dybowski*, *Comephorus baicalensis*, *Cottocomephorus inermis*, *Cottocomephorus grewingki*), zooplankton and zoobenthos species (*Acanthogammarus godlewskii*) have been described in detail previously (Ciesielski et al., 2006a). Seals were found dead ($n = 11$) or were obtained from local hunters (who had appropriate permission) during the official cull ($n = 16$). The location of the sampling stations is shown in Fig. 1. The mesozooplankton composition was as follows: *Epishura baicalensis* (50%), *Cyclops kolensis* (20%), *Daphnia galeata* (20%) and *Bosmina longirostris* (10%). *Macrohectopus branickii* (macrozooplankton) samples were obtained with the use of an appropriate plankton net in 2003. All samples were preserved and transported frozen at −20 °C until analysis. The age of adult seals was determined in analysis of the dentinal and cemental growth layers in the canine teeth.

The details of chemical procedure for Hg determination including sample preparation, microwave digestion and final determination by atomic absorption spectrometry with cold vapor generation (CV-AAS) are given in Ciesielski et al. (2006b). The livers of the seals were lyophilised and homogenized and subsamples of around 0.6 g were subsequently weighed. Because of their high fat content, the fish samples were homogenized whole, without prior drying. The plankton and zoobenthos samples were treated in the same way. The final results were calculated as the mean of the concentrations determined for three replicate samples.

The analytical quality of the procedure was checked using reference materials such as DORM-2 (Dogfish Muscle Certified Reference Material for Trace Metals, National Research Council of Canada) and MA-B-3-TM (Fish Tissue IAEA), obtaining yields of 93.8% and 98.0% of the certified concentration, respectively. The precision expressed as the relative standard deviation (RSD) was 1.2% and 8.2%, respectively. These results were calculated by subsequent analysis (performed during the same day) of three subsamples of each of the reference material. Limit of detection ($LOD_{Hg} = 12$ ng g^{-1} w.w.) corresponds to Hg concentration (calculated from the calibration curve) of an average blank plus three times the standard deviation of the blank signal.

The concentration factor (CF) was calculated from the modified equation given by Mackey et al. (1995):

$$CF = C_x[\mu g(g\ \text{wet weight})^{-1} \Big/ C_s[\mu g(g\ \text{lake water})^{-1}]$$

where the concentration of Hg in Lake Baikal water (C_s) was taken from Meuleman et al. (1995).

The average concentration (C_x) of Hg for all age groups of Baikal seals was used to calculate CF values.

The biomagnification factor (BMF, also known as predator–prey factor PPF) was expressed as the ratio between the concentration of Hg in a predator (consumer, whole body w.b.) and the concentration of Hg in the prey (food, whole body w.b.):

$$BMF = C_{w.b.}(\text{predator})/C_{w.b.}(\text{prey})$$

The content of Hg differs considerably in various tissues and organs of vertebrates. To overcome the problem of using liver concentrations of the seals in the calculation of BMFs we used the procedure described by Strand and Jacobsen (2005). Thus, the concentration of Hg in whole body of the seals (C_{seal}) was estimated from the concentration in liver C_{liv}, and the proportion between the two factors L and P using the equation:

$$C_{seal} = C_{liv.} * L/P$$

where L is the liver weight/body weight (weights measured during dissections), and P is the ratio between the liver and total body residues of Hg in Baikal seals based on literature values. For the BMF calculation only Hg concentrations in adult seals were used. P data were obtained both from Watanabe et al. (1996) and from personal communication with authors of this publication.

Two-way analysis of variance (ANOVA) was used to test for the two qualitative biological predictors, sex (males and females), and age. The seals were grouped into one of three age groups: 1–2 months, 5–8 years and 9–15 years. In order to assess the significance of the spatial (geographical) distribution of the seals, a 'region' factor (the southern, central and northern basins of Baikal) and a qualitative predictor reflecting both maturity and the sex of the seals (seals were divided into 3 groups-pups [1–2 months], adult males [>5 years] and adult females [>5 years]) were also included. ANOVA was applied to test for the differences in Hg concentration between seals found dead and those that had been culled. The Hg concentrations obtained herein were compared to our previous results on other chemical elements for the same seals (Ciesielski et al., 2006a) in a meta-analysis using factor analysis (FA). The application of multidimensional statistical analysis (FA) allows correct interpretation of the results because of the numerous interrelationships between the elements in the data set. Mann–Whitney U test and linear correlation analysis (Pearson's *r*) were used for comparing groups and for examining associations, respectively. Statistical analyses were performed with STATISTICA 6.0 for Windows. For comparison with results on element concentrations reported in other studies, a factor of 0.3 was applied to convert the results from dry weight (d.w.) into wet weight (w.w.). This value is based on data obtained experimentally and it is in agreement with the conversion factor reported by Yang and Miyazaki (2003).

3. Results

The details of Hg concentrations in the liver samples of Baikal seal are presented in Table 1. Higher concentrations were found in adult females (5.83 ± 1.85 μg g^{-1} d.w.) than in adult males (3.92 ± 4.31 μg g^{-1} d.w.). In pups the concentrations of Hg were considerably lower (0.42 ± 0.14 μg g^{-1} d.w.). In the endemic Lake Baikal fish from the *Comephoride* family, the Hg concentrations varied from 0.041 ± 0.021 to 0.021 ± 0.007 μg g^{-1} w.w. for *C. dybowskii* ($n = 3$) and *C. baicalensis* ($n = 3$), respectively. For *C. inermis* ($n = 3$) and *Cottocomephorus grewinki* ($n = 3$) the concentrations of Hg were, in all but one sample, below the detection limits of the method applied. The only specimen with detectable Hg concentrations was the largest *C. inermis*, which had a Hg concentration of 0.013 μg g^{-1} w.w. In the invertebrate samples, the Hg concentration was 0.029 μg g^{-1} w.w. for zooplankton, 0.027 μg g^{-1} w.w. for benthic *A. godlewskii* and 0.030 ± 0.003 μg g^{-1} w.w. for *M. branickii* ($n = 3$). Bioconcentration (CF) and biomagnification (BMF) factors of the Hg in the Baikal seals are presented in Table 2. Mercury