The relationship between mercury and selenium in Baltic herring - a retrospective study

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Report nr 4:2011

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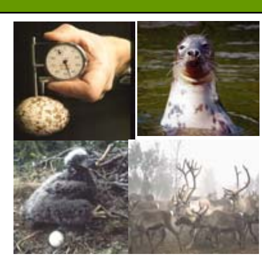

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Summary

Hg is known to affect productivity, reproduction and survival of coastal and marine animals and when deposited in aquatic ecosystems the metal can be bioaccumulated in the food web. Se is a naturally occurring essential nonmetal that is present in all cells. It has many important functions in the cell and it also stimulates the immune system. The relationship between Hg and Se has been subject to numerous studies and the majority point to a negative relationship between the two elements, showing mitigating effects of Se on Hg toxicity. However, some studies have shown no relationship between Hg and Se concentrations and others demonstrate a positive relationship between the two. Generally a large excess of Se in relation to Hg has been observed in fish. The tissue concentrations of and the relationship between Hg and Se are suggested to be dependent on a number of factors, such as the relative concentrations of the elements and their bioavailabilities. The aim of this study was to investigate the temporal trends and the relationship between Hg and Se concentrations in herring muscle at three different locations along the Swedish east coast. Further, the aim was to give recommendations to whether Se concentrations in fish in Swedish waters should be included in the SCMPMB.

Concentrations of Hg in herring muscle were generally higher than concentrations of Se. The highest Hg concentrations were found in herring muscle from Ängskärsklubb, while Landsort had the highest Se concentrations. Se concentrations in herring muscle were decreasing at Utlängan and Ängskärsklubb.

The results from this study indicate a complex relationship between Hg and Se concentrations in herring muscle, depending on the magnitude of the Hg concentration. At Hg concentrations below 40 ng/g, a negative correlation between Hg and Se was seen, while at concentrations of Hg above 40 ng/g w.w the correlation to Se was positive. The conclusion of this study is that concentrations of Se in herring from Swedish waters should be included in the SCMPMB.

1. Introduction

1.1 Background

Mercury (Hg) is a toxic element that easily transforms into different chemical forms and transports over long distances via the atmosphere. Hg has been widely used historically, for example in metal smelting and chlorine chemical plants. Cement plants are a large emitter of airborne Hg and power plants are the largest source, emitting around 50 tons of Hg pollution annually. The high toxicity and environmental hazardousness of Hg has lead to the element being banned within many commercial areas. When deposited in aquatic ecosystems the metal can be bioaccumulated in the food web (Yang et al. 2008). Hg is known to affect productivity, reproduction and survival of coastal and marine animals (WHO 1989). Since it is a heavy metal that bioaccumulates and biomagnifies through the aquatic food web, the presence and behavior of Hg in aquatic systems are of great interest and importance.

Selenium (Se) is a naturally occurring essential nonmetal that is present in all cells. It is an antioxidant, about a thousand times more active than vitamin E (Parkman and Hultberg 2002). It has many important functions in the cell and it also stimulates the immune system. A diet containing less than 0.1 ug/g Se can lead to Se deficiency for humans, but levels around 5 ug/g can cause toxic effects (Chen et al. 1980; Yang et al. 2008). Anthropogenic sources of selenium include coal burning and the mining and smelting of sulfide ores. The main commercial uses for Se today are in glassmaking and in chemicals and pigments. An important point of entry of Se into the food web is likely to be the uptake from sediments by benthic organisms or the incorporation of the element by for example phytoplankton (Parkman 2002; Kehrig and Seixas 2009). It has been shown that organisms assimilate higher concentrations of Se in their body when living in an Se rich environment, but no biomagnifications of Se along the food web has been discovered (Yang et al. 2008). Rather a decrease in Se concentrations was seen, probably due to biomass dilution. Herring and fish overall is a source of Se for marine mammals, birds and humans.

The relationship between Hg and Se has been subject to numerous studies (Lourdes et al. 1991; Parkman and Hultberg 2002; Chen et al. 2001; Jin et al 2006; Yang et al 2008). The majority of the papers point to a negative relationship between the two elements (Paulsson & Lundbergh 1991; Chen et al. 2001; Jin et al. 2006), showing mitigating effects of Se on Hg toxicity (Beijer and Jernelov 1978; Cuvin-Aralar and Furness 1991). Studies have shown that intake of Se can repress the toxic effects of high Hg levels (Paulsson 1991; Chen et al. 2001). Further, Se has been shown to reduce Hg bioavailability and trophic transfer in aquatic ecosystems (Southworth et al. 2000; Kehrig and Seixas 2009). Studies have emphasized Se treatment of waters as a means of decreasing the Hg content in fish (Turner and Swick 1983; Paulsson 1991). Possible pathways leading to biological Hg-Se antagonism are for example formation of MeHg-Se compounds (methyl Hg - the most toxic form of Hg) or formation of inorganic Hg-Se compounds (Kehrig and Seixas 2009; Khan 2009). The possible formation of a non toxic Hg-Se complex seems to be the most accepted mechanism to explain the antagonism of Se on Hg toxicity (Yang et al. 2008).

However, the relationship between Hg and Se is controversial. Some studies have shown no relationship between Hg and Se concentrations in fish muscle (Cappon & Smith 1981; Lyle 1986; Barghigiani et al. 1991; Plessi et al. 2001) and others demonstrate a positive relationship between Hg and Se in fish muscle (Koeman et al. 1973; Kehrig and Seixas 2009). Generally a large excess of Se in relation to Hg has been observed in fish (Kehrig and Seixas 2009). The tissue concentrations of and the relationship between Hg and Se are suggested to be dependent on the relative concentrations of the elements and their bioavailabilities, the animals size and dietary habits and the physical, as well as the chemical characteristics of the system they inhabit (Parkman 2002; Kehrig and Seixas 2009).

This study investigates the temporal trends and the relationship between Hg and Se concentrations in herring muscle at three different locations along the Swedish east coast, Ängskärsklubb, Utlängan and Landsort. Hg concentrations at Ängskärsklubb are relatively high and fluctuating over time, while concentrations at Utlängan and Landsort generally are lower (Swedish Contaminant Monitoring Programme in Marine Biota (SCMPMB), 2010). Data on Se levels are scarce, as Se is not one of the mandatory contaminants that should be analyzed and reported within the OSPARCOM and the HELCOM conventions. Jin et al. (2006) point out that field studies on the Se-Hg interaction in freshwater fish are relatively deficient, and that the data collected from these studies often are controversial.

1.2 Aim of the study

The aim of the present study was to investigate the relationship between Hg and Se in muscle of Baltic herring. Time trends of Hg concentrations are generally better known than trends of Se. By comparing concentrations of Se and Hg over time from three locations with different Hg levels, the possibility to discover potential time trends and positive or negative relationships between the two elements is high. Based on the findings, the aim of the study was to give recommendations to whether Se concentrations in fish in Swedish waters should be included in the SCMPMB.

2. Method

2.1 Hg and Se analysis

Herring from the environmental specimen bank at the Swedish Museum of Natural History was used to investigate the relationship between Hg and Se. From the location at Landsort, data on Se and Hg levels was already available. Data on Hg concentrations for Ängskärsklubb and Utlängan already existed within the SCMPMB. However, to avoid differences between laboratories, samples from Ängskärsklubb and Utlängan were analyzed again, for both Hg and Se at ALS Scandinavia. The time series stretched from 1979 to 2010 for Ängskärsklubb, from 1980 to 2009 for Utlängan, and from 1981 to 2006 for Landsort. 0.2 g skinless herring muscle from 12 individuals from each year and location was pooled (total 2.4 g/pool, 58 pools) and sent to ALS Scandinavia for Hg and Se analysis. The samples were dissolved in closed containers with HNO_3 + H_2O_2 in a microwave. Analysis was conducted according to EPA-methods (modified) 200.7 (ICP-AES) and 200.8 (ICP-SFMS). The results were reported in ng/g wet weight.

2.2 Statistical analysis

For statistical analysis R version 2.12.1 (2010-12-16) was used, mainly linear regressions.

3. Results and discussion

Concentrations and changes over time for Hg and Se are first presented per location and then the relationship between Hg and Se is discussed.

3.1 Hg and Se concentrations

Herring at Ängskärsklubb had the highest Hg concentrations, ranging between 16 and 222 ng/g fresh w.w. (Figure 1a). The concentrations fluctuated over time, which corresponds well to the time series in the SCMPMB, 2010. Further, Hg concentrations at Ängskärsklubb were showing a significant downward trend. Concentrations of Se were higher than Hg concentrations, which also have been noticed in earlier studies (Plessi et al. 2001; Kaneko and Ralston 2007; Kehrig and Seixas 2009). Se concentrations in herring muscle at Ängskärsklubb were decreasing significantly over time.

Concentrations of Hg in herring at Utlängan were generally lower than concentrations at Ängskärsklubb, not exceeding the limit in children's food by SNFA (50 ng/g fresh wt.). In the late nineties Hg concentrations started to fluctuate and a significant increasing time trend was observed (Figure 1b). Se concentrations decreased significantly in a similar way as in herring from Ängskärsklubb. The concentrations of Se were higher than the concentration of Hg.

Concentrations of Hg in herring at Landsort fluctuated over time, ranging between 14 and 58 ng/g fresh w.w. (Figure 1c). The Se concentrations were considerably higher at Landsort than at the other two investigated locations. No statistically significant time trends regarding Hg and Se concentrations were found for Landsort.

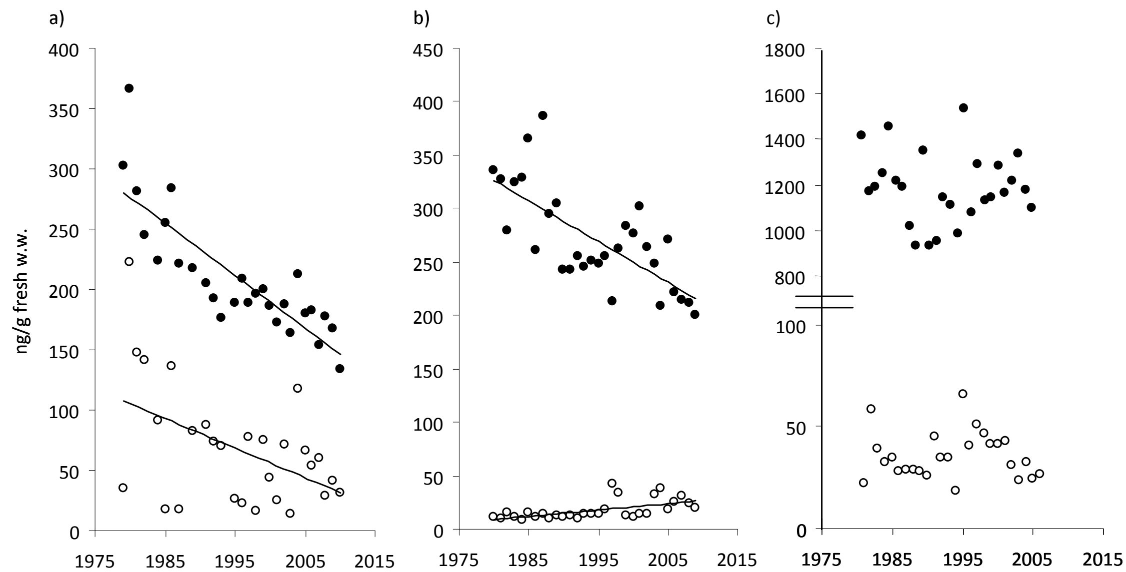

Figure 1. Concentrations of Hg (o) and Se (•) in herring muscle over time from a) Ängskärsklubb (Hg, $p<0.01$, $R^2=0.23$; Se, $p<0.0001$, $R^2=0.70$), b) Utlängan (Hg, $p<0.001$, $R^2=0.33$; Se, $p<0.0001$, $R^2=0.51$) and c) Landsort.

Concentrations of Se in herring from Ängskärsklubb and Utlängan were within the same range and showed a similar statistically significant decrease over time (Table 1). Analyzes of Hg and Se concentrations in herring from Landsort was performed at SLU and ITM, respectively. Se concentrations at Landsort were higher, and showed no decrease over time. Whether this reflects geographical differences, or differences between the laboratories conducting the analyses are not known.

Table 1. Mean±SD of Hg and Se concentrations (ng/g) for Ängskärsklubb, Utlängan and Landsort.

	Ängskärsklubb	Utlängan	Landsort
Hg	67.6±49.3	17.6±9.1	35.2±11.9
Se	209.7±50.0	270.9±47.1	1184±156

3.2 The relationship between Hg and Se

The concentrations of Hg and Se in herring muscle at Ängskärsklubb were positively correlated (Figure 2a). However, at Hg concentrations below approximately 40 ng/g w.w., the correlation to Se appeared to be negative (not statistically significant). At Utlängan, Hg and Se concentrations in herring muscle were negatively correlated (Figure 2b). At Landsort, Se and Hg concentrations in herring muscle was negatively correlated, however, not statistically significant (Figure 2c).

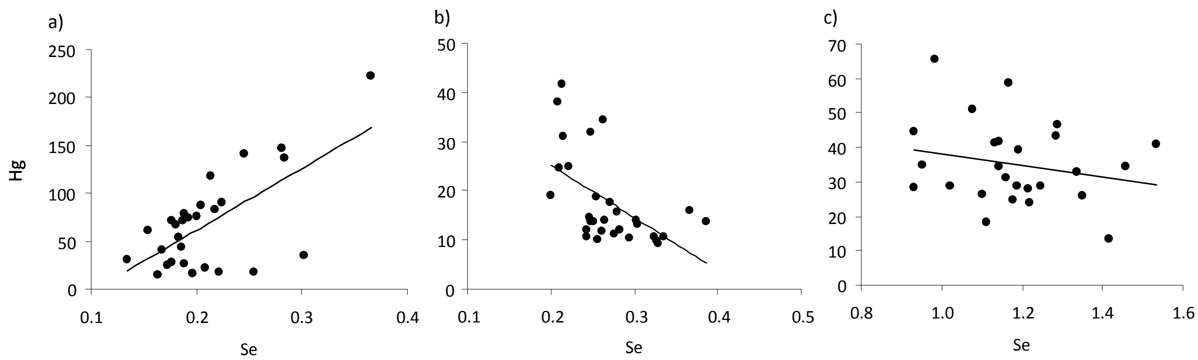

Figure 2. The relationship between Hg (ng/g) and Se (ug/g) in herring muscle at a) Ängskärsklubb ($p<0.001$, $R^2=0.43$), b) Utlängan ($p=0.001$, $R^2=0.30$) and c) Landsort (no significant trend).

The difference in Hg concentration between locations could explain the differences in the relationships between Hg and Se. The positive correlation between Hg and Se concentrations at Ängskärsklubb could be due to the much higher Hg concentrations compared to the other two locations. As described earlier, Parkman (2002) suggests that the relationship between Hg and Se is dependent on the relative concentration of the elements.

The results from this study indicate a complex relationship between Hg and Se concentrations in herring muscle, depending on the magnitude of the Hg concentration. At Hg concentrations below 40 ng/g, a negative correlation between Hg and Se was seen, while at concentrations of Hg above 40 ng/g w.w the correlation to Se was positive.

More information regarding the relationship between Hg and Se could be gained by studying concentrations in the liver. Studies have shown that in some cases of high Hg concentrations, Se is transported to the liver to mitigate the toxic effects of Hg (Kehrig and Seixas 2009).

4. Conclusions

Se levels are decreasing over time at both Ängskärsklubb and Utlängan. Se is a nutritionally essential element and the concentrations are regulated by homeostatic mechanisms, a decreasing trend over time is not expected. Because of the many risks with Se deficiency as an essential substance, and the proven mitigating effects of Se on Hg toxicity, decreasing levels of Se in the marine environment can be a potential problem to fish, marine mammals and even humans. The conclusion of this study is that concentrations of Se in herring from Swedish waters should be included in the SCMPMB.

5. Acknowledgements

The Swedish EPA for funding.

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