Mercury and Selenium Contents of Seals from Fresh and Brackish Waters in Finland

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A strong correlation between the mercury and selenium concentrations in the livers of marine mammals has been reported by KOEMAN et al. (1973). On the other hand, a protective effect of selenium against the toxicity of both organic and inorganic mercury compounds has been observed in laboratory experiments with rats (PAŘIZEK et al. 1967, PAŘIZEK et al. 1971, STILLINGS et al. 1974, CHEN et al. 1975) and quails (GANTHER et al. 1972, STOEWSAND et al. 1974). In some wild animals living at the top of the food chain, remarkably high mercury levels are found, which makes it interesting to study their selenium contents from the point of view of environmental mercury pollution. KOEMAN et al. (1973, 1975) suggested that selenium may have a protective effect against the toxic action of mercury also in marine mammals. In order to study, whether the mercury-selenium correlation could be found also in brackish and fresh water mammals, samples of ringed seals from Finland were analysed.

The ringed seal (Phoca hispida) lives in the brackish Baltic Sea and its Gulfs. In addition to this, a small population of a ringed seal species, Phoca hispida saimensis, lives in the fresh water lake Saimaa, south-eastern Finland, as a relict from the glacial period. It is a rare, endangered species, living under special protection. Mercury levels of the ringed seals from Saimaa have been analysed before to some extent (HELMINEN et al. 1968, HENRIKSSON et al. 1969, HÄSÄNEN 1974, KARPPANEN and HENRIKSSON 1974) as well as those from the Gulf of Finland and Gulf of Bothnia (HENRIKSSON et al. 1969, HERVA and HÄSÄNEN 1972, KARPPANEN and HENRIKSSON 1974). The concentrations observed have in some cases been remarkably high, even though the animals seemed to be healthy (HENRIKSSON et al. 1969, HERVA and HÄSÄNEN 1972). High levels of chlorinated hydrocarbons have also been observed in seals from Finland (KARPPANEN and HENRIKSSON 1974, HELLE et al. 1976a, HELLE et al. 1976b), and the high PCB-levels found have been linked with the observed decrease of the reproduction of the seals (HELLE et al. 1976a, HELLE et al. 1976b).

The selenium contents of Finnish seals have not so far been analysed. In this study the selenium and mercury levels of some ringed seal samples from fresh waters and, for comparison, from brackish waters in Finland were determined by instrumental neutron activation analysis. Some fish samples were also analysed.

Bulletin of Environmental Contamination & Toxicology,
0007-4861/78/0019-0273 $1.60

MATERIALS AND METHODS

The fresh water seal samples were obtained from three ringed seals from Saimaa. All of the animals had been found dead, one had probably been illegally killed and two had been accidentally killed in fishing nets in different parts of the Saimaa water-course during the years 1974 and 1975. The brackish water seals, twelve in all, came from Simo, the northern part of the Bothnian Bay. They were caught by seal nets, mainly in October-November 1974. In both of the above mentioned areas mercury contamination of water, originating from the pulp and paper industry, may be still present, even though the mercury-containing slimicides have no more been used in Finland during the last decade (HÄSÄNEN 1974).

The samples taken from different organs of the seals were stored deep frozen, dried before analysis, and homogenized.

The selenium and total mercury contents were determined by activation analysis without prior chemical separation using the 136.0 keV photo-peak of Se-75 and 279.2 keV photo-peak of Hg-203. Se-75 also has a gamma energy at 279.6 keV, which is not resolved from the mercury peak. However, the fraction of the measured total peak at 279 keV that is due to selenium can be subtracted by using the ratio of the 136.0 keV and 279.6 keV gamma peaks of Se-75, determined from the standard selenium sample.

The methyl mercury contents were analysed by a gas chromatographic method (KAMPS et al. 1972), based on the procedure of WESTÖÖ (1966).

RESULTS AND DISCUSSION

The total mercury and selenium contents of muscle, liver, kidney and blubber were determined. The results are given in Table 1. The mercury contents found agree in general with earlier reports (HELMINEN et al. 1968, HENRIKSSON et al. 1969, HERVA and HÄSÄNEN 1972, KARPPANEN and HENRIKSSON 1974), except for the liver samples, where our results appear to be somewhat higher, the highest values being more than twice as high as the earlier ones.

The mercury and selenium contents found in the livers were by far the highest. A very strong correlation between mercury and selenium was found in the liver (Fig. 1), while little, if any, correlation can be seen in the muscle and kidney samples (Figs. 2 and 3). The correlation coefficients between the mercury and selenium contents are given in Table 2. Least squares treatment of the liver data leads to a regression of mercury on selenium

$$Hg(ppm) = (2.95 \pm 0.04)\ Se(ppm) + (-11.6 \pm 2.6)\ .$$

TABLE 1

The total mercury and selenium contents in seals from the Bothnian Bay and from Saimaa

	µg Hg/g wet wt.			µg Se/g wet wt.		
	range	mean	median	range	mean	median
BOTHNIAN BAY						
muscle (8)[x]	0.47-1.6	1.1	1.0	0.44-0.92	0.63	0.59
liver (12)	14 -300	91	62	6.1 -110	35	26
kidney (2)	2.8 -5.2	4.0		2.5 -3.3	2.9	
SAIMAA						
muscle (3)	1.3 -6.1	3.5	3.2	0.24-2.8	1.2	0.40
liver (3)	72 -510	230	100	29 -170	81	39
kidney (3)	1.9 -13	7.4	6.9	0.34-3.0	2.0	2.8
blubber (2)	0.14-0.46	0.30		0.06-0.11	0.09	

[x] number of samples

TABLE 2

The correlation coefficients between mercury and selenium contents of seal tissues

	muscle of seal	liver of seal	kidney of seal	flesh of fish
samples from the Bothnian Bay	0.252 (8)[x]	0.999 (12)		0.468 (8)
samples from Saimaa	0.940 (3)	1.000 (3)	0.864 (3)	0.948 (3)
all together	0.837 (11)	0.998 (15)	0.568 (5)	-0.573 (11)

[x] number of samples

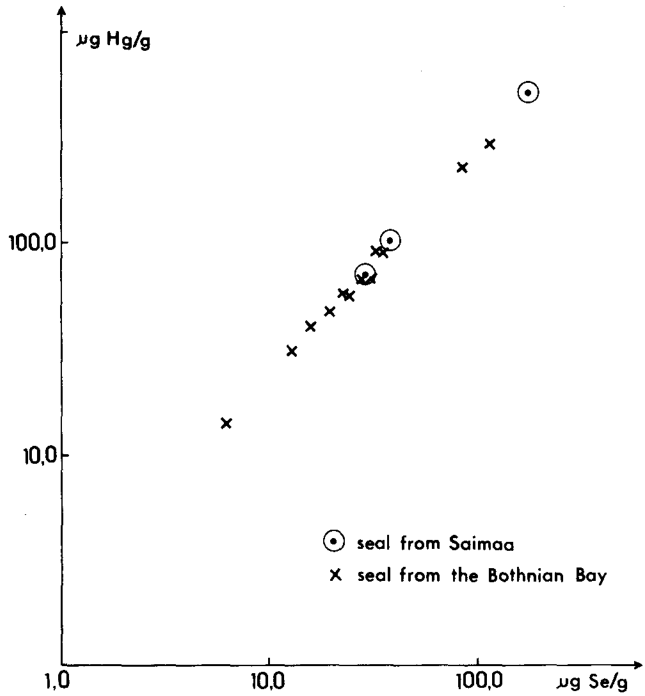

FIGURE 1. Correlation between mercury and selenium in livers of seals

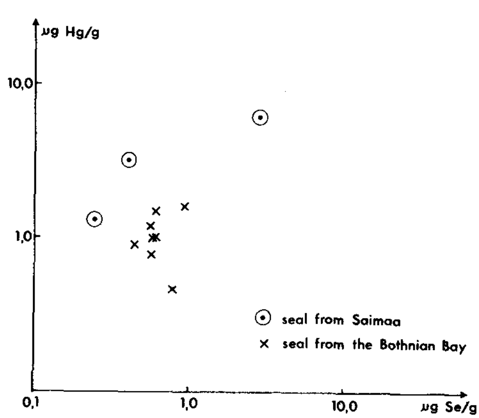

FIGURE 2. Correlation between mercury and selenium in muscles of seals

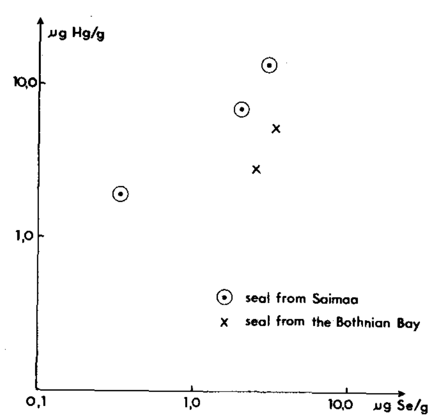

FIGURE 3. Correlation between mercury and selenium in kidneys of seals

This differs to some extent from the results of KOEMAN et al. (1975), who reported for different marine mammals the regression

$$Hg = 2.47\ Se + 12.8\ .$$

The atomic weight ratio of mercury and selenium is 2.54. Thus, on an atomic basis, the regression of mercury on selenium in our liver samples is 1,16, indicating an excess of mercury over the 1:1 ratio observed by KOEMAN et al. (1975).

The means of the atomic Hg-Se-ratios are higher in all the seal samples from Saimaa than in those from the Bothnian Bay (Table 3), but due to the small number of samples, the differences are not statistically significant according to the Student's t-test.

TABLE 3

Atomic Hg-Se-ratio in different seal tissues

	Seals from Saimaa		Seals from the Bothnian Bay	
	mean ± SD	number of samples	mean ± SD	number of samples
muscle	2.05 ± 1.15	3	0.68 ± 0.22	8
liver	1,063 ± 0.096	3	0.984 ± 0.072	12
kidney	1.64 ± 0.62	3	0.53 ± 0.13	2
blubber	1.76 ± 1.78	2		

According to our preliminary methyl mercury determinations the fraction of methyl mercury in the total mercury content of the seal liver is about 10 %, while in muscle as well as in the fish samples the principal part of total mercury is in the form of methyl mercury. This agrees with earlier results (WESTÖÖ 1967, KOEMAN et al. 1972, FREEMAN et al. 1975) and seems to support the conclusion that the highly toxic methyl mercury is demethylated in the liver. Selenium possibly takes part in this process, even though the underlying mechanism of the demethylation has not yet been fully elucidated (FANG 1974, OHI et al. 1976). Liver possibly collects the mercury of other tissues as far as it can do it by retaining the atomic ratio of Hg:Se around 1. In our samples from the Saimaa seals the atomic ratio Hg:Se tended to be higher than 1 (Table 3), indicating heavier mercury exposure or poor selenium availability, or both.

In order to get some information about the intake of mercury and selenium by seals via food, the mercury and selenium contents of some fish species from the Bothnian Bay and from the watercourse of Saimaa were analysed (Fig. 4 and Table 2). The atomic Hg-Se-ratio (Table 4) differs remarkably from the results presented by KOEMAN et al. (1973) which are lower, ranging between 0.008 and 0.026 if expressed as the atomic ratio. This is apparently due to the higher selenium content of marine fish. In the fish of Saimaa the mercury content of the flesh is much higher than that of other tissues, which makes the Hg-Se-ratio in the whole fish lower than in the flesh.

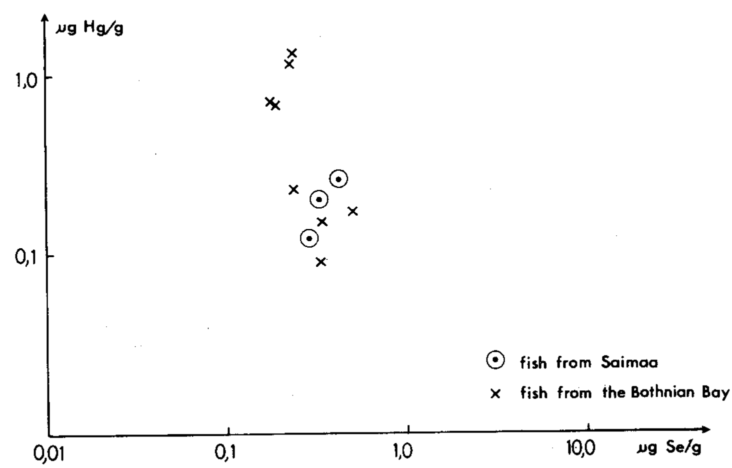

FIGURE 4. Correlation between mercury and selenium in flesh of fish

For a more detailed study about the effects of food on the mercury-selenium correlations in seals, additional knowledge of their feeding habits is needed.

ACKNOWLEDGEMENTS

We are indebted to Eero Helle, M.Sc., University of Oulu, for providing us with samples of the Bothnian Bay seals. We are also grateful for the co-operation of a number of persons in providing us with the samples of the Saimaa seals. The opportunity to use equipment at the Physics Department is also gratefully acknowledged.

TABLE 4

The total mercury and selenium content and atomic Hg-Se-ratio in fish

	MUSCLE			WHOLE FISH		
	Hg	Se	Hg:Se	Hg	Se	Hg:Se
	µg/g wet wt.	µg/g wet wt.		µg/g wet wt.	µg/g wet wt.	
SAIMAA						
roach	0.12	0.29	0.16	0.07	0.37	0.07
perch	0.20	0.33	0.24	0.22	0.50	0.17
vendace	0.26	0.43	0.24	0.19	0.50	0.15
BOTHNIAN BAY						
burbot[x]	1.0	0.21	1.8			
whitefish	0.17	0.50	0.13			
vendace	0.15	0.34	0.17			
pike	0.23	0.24	0.38			
Baltic herring	0.09	0.33	0.11			

[x] mean of four samples from a mercury polluted area

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