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Antagonistic effect of selenium on mercury assimilation by fish populations near Sudbury metal smelters?

Abstract—In this study, the concentrations of Se and Hg were determined in perch (*Perca flavescens*) and walleye *(Stizosedion vitreum)* muscle from nine lakes that varied in distance (4–204 km) from the metal smelters of Sudbury, Canada. Significant inverse relationships between Se and Hg in perch ($r^2 = 0.79$, $P < 0.05$) and walleye tissue ($r^2 = 0.97$, $P < 0.01$) were detected, which suggests a strong antagonistic effect of Se on Hg assimilation by these fish species. Concentration of Hg decreased exponentially with an increase of Se in fish muscle. Total dissolved Se concentrations of lake water declined with distance from smelters and were correlated to Se in perch ($r^2 = 0.75$, $P < 0.05$) and walleye ($r^2 = 0.95$, $P < 0.01$). Hg concentrations in the fish from lakes near the smelter were well below average values in fish in boreal shield lakes of this region.

In 1967, Parízek and Ostádalová discovered that an injection of selenite greatly reduced the mortality for rats intoxicated with a high concentration of mercuric chloride. This finding triggered a considerable research interest in the toxicology and detoxification of mercury by selenium. In later studies, Koeman et al. (1973), Kosta et al. (1975), and Luten et al. (1980) measured a 1:1 molar ratio between Hg and Se in various biological organs such as liver of marine mammals and perch and thyroid, pituitary, kidney, and brain of miners. Fang (1977) observed that a treatment with sodium selenite modified the tissue distribution, subcellular binding, and soluble protein binding of Hg in rats. Although these facts suggest that biological assimilation of mercury could be affected by the presence of selenium in the environment, field studies on this subject remain scarce, and the information is often controversial. Although some studies reported no correlation between the two elements in the muscles of fresh water (Cappon and Smith 1981) or marine (Lyle 1986; Barghigiani et al. 1991) fish species, another study revealed a negative correlation between Se and Hg in perch muscles from 11 Swedish lakes (Paulsson and Lundberg 1991).

The objective of the present study was to investigate the Se-Hg antagonistic effect by using perch and walleye living in lakes characterized by different Se concentrations. The Sudbury region is an ideal location for this study. Mining and smelting activities have been in operation for more than a century. One direct consequence has been the elevated concentrations of a wide variety of metals in water and sediment of the lakes in this area. With the average concentration of Se in the Cu-Ni ores ranging from 20 to 80 mg g^{-1} (Schwarcz 1973), a 1977 study estimated that 50 tonnes of Se was dispersed annually through atmospheric emissions and showed that concentrations of Se in lakes around Sudbury were significantly higher than those located in remote areas (Nriagu and Wong 1983). Fish living in these lakes have therefore been exposed to various concentrations of Se for many years, and the possible Se-Hg interactions identified in this area could be considered to reflect the natural conditions in these lakes.

Sampling—The lakes selected in the study are situated from 4–204 km from the metal smelters and exhibit a wide range of limnological and chemical characteristics (Table 1). Two fish species with different feeding habits were used for tissue analysis. Yellow perch (*Perca flavescens*) feeds mainly on zooplankton and benthic invertebrates, and walleye (*Stizosedion vitreum*) is a piscivore and a dominant predator. Fish sampling was conducted in June–July 1996 and between April and October 1997. A total of 9–20 fish of various size classes were collected from each lake, and samples of skeletal muscle tissue were dissected, frozen (−20°C), then freeze-dried and ground into a fine powder.

Sample treatment and analysis—A precise 0.1-g sample of dried fish muscle tissue was weighed and digested with 1.0 ml 30% H_2O_2 (AG) and 2.5 ml of concentrated HNO_3 (trace metal grade) at room temperature overnight, microwave-digested 10 times for 1 min at 720 W, and then made up to 10.00 ml with double-distilled water. The quality of digestion and analysis was controlled by use of two certified reference materials (CRM), DORM-2 (Dogfish Muscles) and TORT-2 (Lobster Hepatopancreas) at a frequency of one CRM digestion per 10 digested sample (relative error <8% for both Hg and Se). One triplicate digestion was carried out for both fish species of each lake throughout all analyses (relative standard deviation <5% and <6% for Hg and Se, respectively). Total Se and Hg in fish tissues were determined by use of graphite furnace atomic absorption spectrometry and cold vapor–atomic fluorescence spectrometry, respectively. Instrumental variations were <3% and <4% for Hg and Se. High-density polyethylene bottles were used to collect water for Se determination. They were first thoroughly washed with hot detergent water and 10% HNO_3, then soaked in hot 20% HNO_3 overnight, and finally rinsed with double-distilled water. The samples were filtered, subdivided, and acidified with suprapure HNO_3. For total dissolved Se, the filtered samples were subjected to a 5-h ultraviolet radiation exposure. The samples were then stored in acid-boiled Teflon vials in a freezer. Total dissolved Se was determined by hydride generation atomic fluorescence spectrometry. For the determination of total dissolved Hg in water samples, the analytical procedure, including container cleaning and sample pretreatment, was performed strictly according to method 1631 approved by the US Environmental Protection Agency. Total dissolved Hg was measured by use of cold vapor atomic fluorescence spectrometry and gold amalgamation. The whole process was completed in <4 d

Table 1. Limnological and chemical characteristics of the studied lakes listed in order of distance from the smelters.

Lake	Latitude	Longitude	Distance from Sudbury (km)	Lake surface area ($\times 10^6$ m^2)	pH	Total dissolved Cu (uM)	Total dissolved Ni (uM)	Total dissolved Ca (mM)	Total dissolved Mg (mM)	SO_4^{2-} (mM)	Total dissolved Se (nM)	Total dissolved Hg (pM)
Ramsey (Ra)	46°28′N	80°57′W	4	7.95	7.7	0.22	1.57	0.38	0.19	0.22	7.74	105
Hannah (Ha)	46°26′N	81°02′W	4	0.27	7.2	0.44	2.39	0.26	0.15	0.22	9.21	72
Laurentian (Lu)	46°27′N	80°57′W	8	1.57	6.5	0.24	0.95	0.09	0.06	0.07	5.29	190
Whitson (Wh)	46°28′N	80°58′W	10	4.88	6.7	0.27	2.39	0.18	0.08	0.19	5.97	157
Vermilion (Ve)	46°31′N	81°23′W	31	11.25	7.5	0.08	0.31	0.24	0.09	0.15	1.45	23
Geneva (Ge)	46°45′N	81°33′W	47	3.56	6.7	0.02	0.03	0.06	0.03	0.06	1.22	21
Michiwakenda (Mi)	47°38′N	81°13′W	127	3.02	7.2	0.04	0.02	0.23	0.07	0.05	1.11	17
Long (Lo)	47°55′N	80°15′W	162	7.43	7.7	0.12	0.01	0.51	0.34	0.04	1.20	13
Larder (La)	48°05′N	80°57′W	204	37.04	8.0	0.24	0.74	0.34	0.18	0.19	1.67	187

after sample collection. The detection limits were at 2 ng L^{-1} and 0.05 ng L^{-1} for Se and Hg, respectively. Other metals and sulfate were measured by inductively coupled plasma-mass spectrometry and ion chromatography, respectively.

Data treatment—Table 2 presents general information on fish samples collected for this study. A positive relationship between the concentration of Hg in muscle tissue and fish fork length was usually observed for most lakes especially for walleye samples, but because of the relatively small sample sizes and the limited size range sampled in any particular lake, no clear relationships could be observed between body size and Se. The average concentration of both Se and Hg in tissue for a common fork length range was therefore used in the data analysis. A size range of 100–150 mm was used

Table 2. Data on fish fork lengths and total concentrations of Se and Hg in fish muscle tissue from the different lakes.

Fish	*N*	Fork length (mm)	Element	Median concentration of *N* samples: nmol g^{-1} dry wt	Median concentration of *N* samples: mg kg^{-1} wet wt	Average concentration for selected samples (*n*): nmol g^{-1} dry wt	Average concentration for selected samples (*n*): mg kg^{-1} wet wt
Perch						100–150 mm	
Hannah (Ha)	19	103–178	Se	288	4.55	286 ± 24 (13)	4.52 ± 0.38
			Hg	0.09	0.0036	0.112 ± 0.050 (13)	0.0045 ± 0.0020
Ramsey (Ra)	20	97–203	Se	121	1.91	112 ± 14 (4)	1.77 ± 0.22
			Hg	0.39	0.0157	0.32 ± 0.05 (4)	0.0129 ± 0.0020
Laurentian (Lu)	13	85–137	Se	80	1.26	85 ± 25 (9)	1.34 ± 0.39
			Hg	0.52	0.0209	0.52 ± 0.17 (9)	0.0209 ± 0.068
Vermilion (Ve)	14	79–214	Se	52	0.82	47 ± 16 (7)	0.74 ± 0.25
			Hg	3.55	0.1426	3.43 ± 0.40 (7)	0.1378 ± 0.061
Whitson (Wh)	13	85–109	Se	124	1.96	131 ± 19 (12)	2.07 ± 0.30
			Hg	0.57	0.0229	0.56 ± 0.10 (12)	0.0225 ± 0.0040
Geneva (Ge)	10	71–115	Se	36	0.57	54 ± 2 (2)	0.85 ± 0.03
			Hg	1.02	0.0410	1.35 ± 0.31 (2)	0.0542 ± 0.0124
Michiwakenda (Mi)	9	91–220	Se	15	0.24	17 ± 3 (4)	027 ± 0.05
			Hg	1.87	0.0763	1.27 ± 0.44 (4)	0.0510 ± 0.0177
Walleye						300–350 mm	
Ramsey (Ra)	20	171–384	Se	84	1.33	83 ± 4 (6)	1.31 ± 0.06
			Hg	0.53	0.0213	0.49 ± 0.05 (6)	0.020 ± 0.002
Whitson (Wh)	14	180–539	Se	61	0.96	73 ± 5 (4)	1.15 ± 0.08
			Hg	1.14	0.0458	0.66 ± 0.13 (4)	0.027 ± 0.005
Vermilion (Ve)	19	168–631	Se	34	0.54	35 ± 7 (6)	0.55 ± 0.11
			Hg	7.69	0.3088	7.34 ± 1.60 (6)	0.295 ± 0.064
Michiwakenda (Mi)	18	177–541	Se	16	0.25	19 ± 1 (4)	0.30 ± 0.02
			Hg	6.69	0.2687	9.72 ± 1.93 (4)	0.390 ± 0.078
Long (Lo)	18	217–440	Se	11	0.17	12 ± 2 (5)	0.19 ± 0.03
			Hg	21.30	0.8554	35.7 ± 9.9 (5)	1.434 ± 0.398
Larder (La)	15	245–738	Se	29	0.46	27 ± 1 (3)	0.43 ± 0.02
			Hg	15.32	0.6153	6.97 ± 1.71 (3)	0.280 ± 0.069

N = total number of samples; *n* = number of samples in the corresponding range.

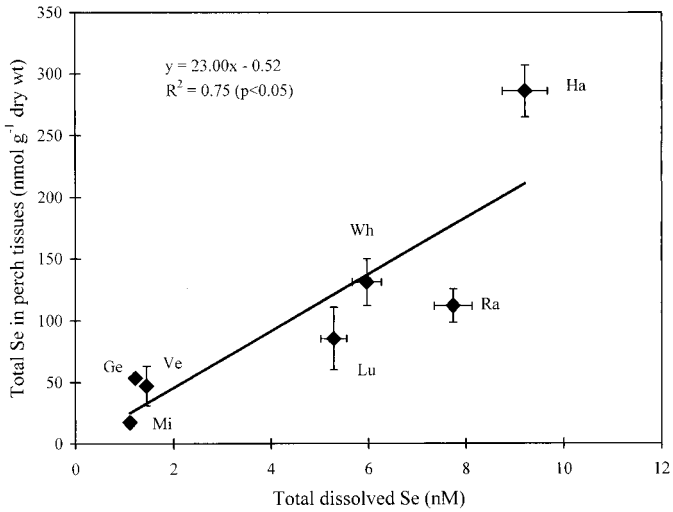

Fig. 1. Relationship between total selenium concentrations in perch muscle and total dissolved selenium concentrations in the study lakes (abbreviations are given in Table 1).

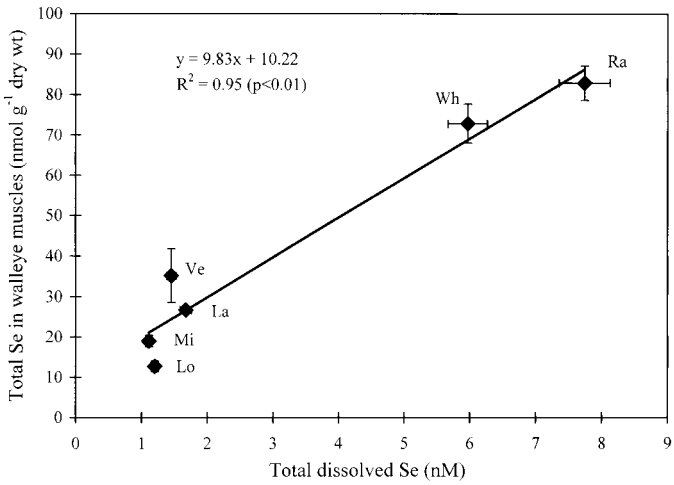

Fig. 2. Relationship between total selenium concentrations in walleye muscle and total dissolved selenium concentrations in the study lakes (abbreviations are given in Table 1).

for perch, and a range of 300–350 mm was selected for walleye. Data on the total number of fish collected, fork length distribution, median concentration of Se and Hg in all samples, as well as average concentrations for the selected size range are reported in Table 2.

The relationship between Se in fish muscle and total dissolved Se in lake water—The average concentrations of Se in perch and walleye muscle of selected ranges (Table 2) exhibited significant positive linear correlations (for perch, $r^2 = 0.75$, $P < 0.05$; for walleye, $r^2 = 0.95$, $P < 0.01$) with total dissolved Se in lake water (Figs. 1, 2). Further analyses of these data showed that the concentrations of total dissolved Se in the lakes was related to the distance to the smelters, i.e., the closer to the smelters, the higher the concentration of total dissolved Se in the lake (Table 1). Therefore, the atmospheric deposition of the metal particulates seems to be an important source of Se in these lakes. It should be mentioned that, in addition to atmospheric inputs, Whitson and Larder lakes are also affected by liquid effluents from tailings and other mining wastes in their catchment areas. Table 1 also indicates that concentrations of dissolved Hg are generally high in lakes closer to smelters.

Se-Hg relationships in fish muscle—For each lake, average concentrations of Se and Hg in muscles of perch and walleye were calculated for selected size ranges (Table 2). The concentration of Hg declined exponentially with the increase of Se concentration in the fish muscles ($r^2 = 0.79$, $P < 0.05$ for perch and $r^2 = 0.97$, $P < 0.01$ for walleye) (Figs. 3, 4). The molar Se/Hg ratios vary between 14 and 2,550 in perch and between 0.4 and 170 in walleye samples, the higher values usually corresponding to lakes close to smelters.

To facilitate the comparison with other studies in the literature, concentrations of Se and Hg are also expressed in mg kg^{-1} wet weight in Table 2. The interconversion between nmol g^{-1} dry weight and mg kg^{-1} wet weight can be expressed by these relations: for Hg, value of mg kg^{-1} wet muscle weight = value of nmol g^{-1} dry weight/24.9; for Se, value of mg kg^{-1} wet muscle weight = value of nmol g^{-1}/63.3; here, water content of 80% in fish muscle is assumed. For example, the threshold value for commercial sale in Canada of 0.5 mg Hg per kg of wet weight is equivalent to 12.45 nmol Hg per gram of dry muscle, and 22.0 nmol Se per gram of dry muscle equals 0.35 mg Se per kg of wet muscle.

The low Hg concentrations in walleye in the studied lakes near the metal smelters are in sharp contrast to the results of extensive surveys of walleye in Ontario, where >70% of the lakes contain walleye that exceed the consumption guidelines for mercury (Ontario 1997). In a series of 536 samples collected in Ontario lakes, the average concentration for 300 mm walleye was 8.16 ± 4.71 nmol g^1 dry wt (0.33 ± 0.19 mg kg^{-1} wet wt), whereas the average concentration

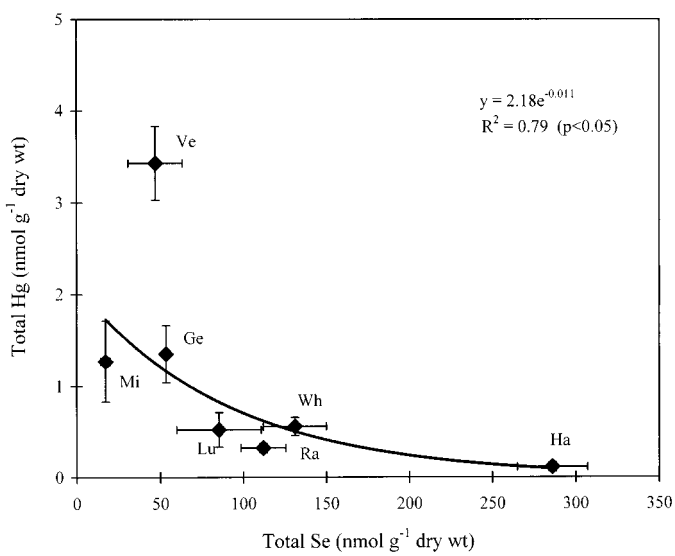

Fig. 3. Relationship between concentrations of total mercury and total selenium in perch muscle, best fitted to an exponential relationship between Se and Hg.

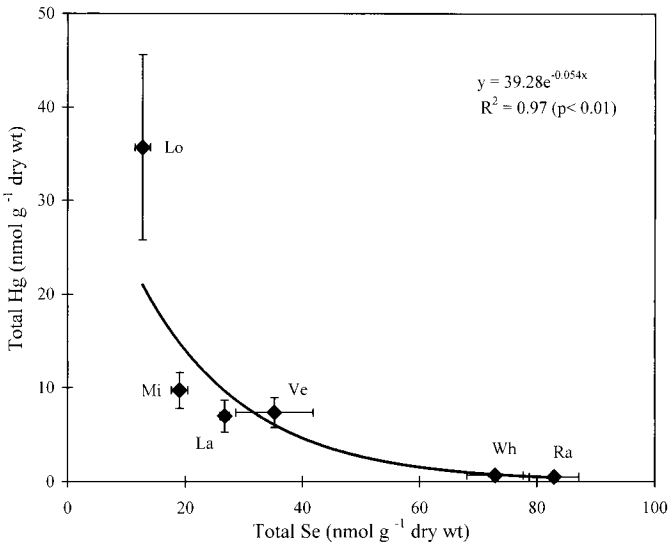

Fig. 4. Relationships between concentrations of total mercury and total selenium in walleye muscles, best fitted to an exponential relationship between Se and Hg.

for 100 mm perch was 1.64 ± 2.07 nmol g^{-1} dry wt (N = 79) or 0.07 ± 0.08 mg kg^{-1} wet wt. These two values are 11–16 times and 3–16 times higher than concentrations measured in walleye and perch of the same length collected within 20 km of the Sudbury smelters in our study. These findings are consistent with the earlier study by Wren and Stokes (1988), who reported lower Hg concentrations in Sudbury perch population. Those authors speculated that Se deposition from the smelters might have affected Hg accumulation in that species. It is also reported that accumulation of Hg is often very high in fish tissues coming from pristine remote water bodies. In a study on eight Swedish headwater lakes of a boreal forest region (Lindqvist et al. 1991), Hg concentrations of 0.9–9.9 nmol g^{-1} dry perch muscles (0.04–0.40 mg kg^{-1} wet wt) were measured, while total Hg in these lake waters ranged from 4 to 50 pM (0.8–19 ng L^{-1}), except for one lake (120 pM or 24 ng L^{-1}). Watras and Bloom (1992) found that, even in water containing very low concentrations of Hg (5.5 pM or 1.1 ng L^{-1}), 1-yr-old yellow perch could still accumulate Hg as high as 1.4 nmol g^{-1} dry wt (0.06 mg kg^{-1} wet wt). These values are much higher than those in perch collected in lakes of the Sudbury region (average 0.49 nmol g^{-1} dry muscle or 0.02 mg kg^{-1} wet wt; n = 46, fork length 8.5–22.3 cm). If an antagonistic effect exists ubiquitously in fish muscles, the unusually high concentrations of Hg observed in some remote areas might be partially due to low concentrations of Se in the lake catchments. Long-range atmospheric pollution by Hg might not be the only explanation for high Hg concentrations found in fish muscles living in some pristine lakes.

The mechanism of interaction between these two elements in the bioassimilation processes has not yet been clarified. Many studies present a positive linear correlation between Hg and Se (Koeman et al. 1973; Kosta et al. 1975; Luten et al. 1980). From an experiment based on the addition of the ^{82}Se isotope and $HgCl_2$ in rat blood, Yoneda and Suzuki (1997) proposed the formation of an equimolar Hg-Se complex binding to selenoprotein P, which seems to support the observation of the positive linear relationship. However Figs. 3 and 4 in our study present a different correlation, which could suggest a mechanism of competition between Hg and Se in fish muscles. From the work by Paulsson and Lundbergh (1991), a very similar correlation as ours was found for nontreated 1-yr perch. However, this correlation completely disappeared after the lakes were treated by elevated concentrations of sodium selenite, although a general decrease of Hg concentrations in fish muscles was observed. This might indicate a disturbed metabolism of fish under artificially created conditions.

This remarkable discrepancy in Hg-Se relationships suggests that Hg and Se distribution and interaction in muscles could be different from those that occur in other organs that are closely connected to the blood system and require a large blood supply, such as liver, brain, and kidney. The redistribution of these two elements among tissues would also be different if the main source of Hg and Se is food, compared with water. The diffusion of aqueous metal ions through skin could cause an increase of concentrations in fish muscles, and biological elimination processes of the two elements also need to be considered.

In addition, the geochemistry of lake can play a crucial role on bioassimilation of Hg (Morel et al. 1998) and Se, because the bioavailability of these elements largely depend on their chemical speciation, which is related to pH, dissolved organic carbon, [Cl^-], temperature, seasonal variations, specific limnological conditions, etc. The relatively high concentrations of Se in waters and sediments of Sudbury area lakes might also play an inhibiting role on sulfate reducing bacteria, which, in turn, could affect the methylation of Hg in sediments (Oremland and Capone 1988). This study is a preliminary step toward understanding the complicated interactions between Se and Hg in bioassimilation processes. More systematic investigations on distributions of Hg and Se in different organs of the same species and at other levels of the food chain are therefore necessary to better understand the biochemical behaviour of these two elements.

Finally, in spite of the possible antagonistic effect between Se and Hg, one should be very careful in recommending Se as a remediating agent against mercury, because Se possesses a complex nature. Although the deficiency of this essential element at low concentrations can cause different diseases, it can show significant potential toxicity at higher concentration levels (Fergusson 1990). Lemly (1993) recently reported serious teratogenic effect of Se on freshwater fish living in a lake used as a coal power plant impoundment. His study shows that percentage of deformed fish increased exponentially with Se concentrations in fish body, although the deformities could not be unequivocally attributed to Se. The Se concentrations in fish of this lake were up to 130 times those in the reference lakes. The identified teratogenic defects include lordosis, kyphosis, scoliosis, edema, exophthalmus, cataracts, etc. Finding the threshold of Se concentration levels in different biological species and its bioaccumulation in the food chain would be the key step for using it in mercury detoxification of contaminated sites.

Our study demonstrated that the presence of Se in fish

muscles is positively correlated to the concentrations of Se in waters and that the presence of Se in fish muscles appeared to be an explanation for the limited accumulation of Hg in fish. The presence of Se in a watershed could therefore be an important factor influencing mercury bioaccumulation. We would expect similar trends in other areas of the world where sulfidic ores are mined, because Se is often associated with sulfide deposits.

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