The effect of selenium on mercury assimilation by freshwater organisms

Nelson Belzile, Yu-Wei Chen, John M. Gunn, Jian Tong, Yves Alarie, Tania Delonchamp, and Chun-Yan Lang

Abstract: In this study, we showed that selenium (Se) deposition from metal smelters in Sudbury, Ontario, greatly reduces the bioassimilation of mercury (Hg) by aquatic biota throughout the food web. Concentrations of total and methyl mercury in tissues of zooplankton, mayflies (*Stenonema femoratum*), amphipods (*Hyalella azteca*), and young-of-the-year perch (*Perca flavescens*) were positively correlated with increasing distance from Sudbury smelters and inversely correlated with Se concentrations in lake water. Although concentrations of total Hg and total Se in tissues showed weak or no correlation in most of the studied aquatic species, methyl mercury and total Se showed much clearer inverse trends. Similar to the results of our previous study of muscle tissue from adult perch and walleye (*Sander vitreus*), these findings suggest that Se plays an important role in limiting the whole-body assimilation of Hg at lower levels of the aquatic food chain. High Se concentrations may force a preferential assimilation of the element over Hg through a competitive adsorption on binding sites. They may also restrict the solubility and availability of Hg to aquatic organisms or reduce the methylation of this metal in lakes.

Résumé : Nous montrons dans cette étude que la déposition de sélénium (Se) provenant des hauts fourneaux de Sudbury en Ontario réduit grandement l'assimilation du mercure (Hg) par le biote aquatique tout au long de la chaîne alimentaire. Les concentrations en Hg total et méthylmercure dans les tissus de zooplancton, éphémères (*Stenonema femoratum)*, amphipodes (*Hyalella azteca)* et jeunes perchaudes (*Perca flavescens*) de l'année ont pu être directement corrélées avec la distance qui les sépare des hauts fourneaux de Sudbury et inversement corrélées avec les concentrations de Se dans l'eau de lac. Alors que les concentrations en Hg total et Se total dans les tissus ne montrent que des corrélations faibles ou nulles entre elles chez la plupart des organismes étudiés, le méthylmercure et le Se total montrent des relations inverses beaucoup plus claires. De façon similaire aux résultats de notre étude précédente sur les tissus musculaires de perchaudes et de dorés (*Sander vitreus*) adultes, ces données laissent croire que le Se joue un rôle important en limitant l'assimilation intégrale du Hg aux niveaux inférieurs de la chaîne alimentaire aquatique. Les fortes concentrations de Se pourraient conduire à une assimilation préférentielle de cet élément sur celle du Hg à travers une adsorption compétitive sur des sites de liaison. Elles pourraient aussi restreindre la solubilité et la disponibilité du mercure chez les organismes aquatiques ou réduire la méthylation de ce métal dans les lacs.

Introduction

There is an abundant literature describing interactions between selenium (Se) and mercury (Hg) in living organisms. A report by Pařízek and Oštádalová (1967) was one of the first to identify the protective effect of Se on laboratory rats from kidney intoxication by Hg. Since then, many studies have reported interactions or relationships between Se and Hg in various types of organisms in the laboratory using terrestrial (e.g., Gailer et al. 2000) or aquatic species (e.g., Bjerregaard and Christensen 1993) or even cells or bacteria (e.g., Frisk et al. 2003) and in the field (e.g., Dietz et al. 2000; Chen et al. 2001). A literature review by Cuvin-Aralar and Furness (1991) presented several possible mechanisms of protection, including a redistribution or excretion of Hg in the presence of Se, a competition for binding sites between

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both elements, the formation of Hg–Se complexes, the conversion of toxic forms to less toxic forms of Hg, and the prevention of oxidative damage from Hg by Se through an increased activity of glutathione peroxidase. Among those mechanisms, the formation of an inorganic and (or) protein Hg–Se complex is proposed and frequently supported by analytical evidences derived by traditional chromatographic techniques (Burk et al. 1974; Iwata et al. 1981; Ping et al. 1986), high-performance liquid chromatography (HPLC) combined with inductively coupled plasma-mass spectrometry (ICP-MS; Yoneda and Suzuki 1997*a*, 1997*b*; Sasakura and Suzuki 1998), microscopy (Christensen et al. 1989), or X-ray techniques (Carmichael and Fowler 1980; Lindh and Johansson 1987; Gailer et al. 2000). These complexes are generally found in storage organs such as liver and kidney and even in hair for humans (Soares de Campos et al. 2002). Under high Hg concentrations, a 1:1 molar ratio of Se:Hg is found in tissues (liver) of marine mammals (Koeman et al. 1973, 1975; Dietz et al. 2000), and it has been suggested that methyl mercury (MeHg) could be detoxified by a chemical mechanism involving Se through the formation of metallothioneins and insoluble tienmannite, HgSe (Palmisano et al. 1995; Chen et al. 2002; Ikemoto et al. 2004). However, it seems that the detoxification mechanism could only take place when threshold values of Hg or Se exposure are exceeded in humans (Hansen 1988), other mammals (Hansen et al. 1981; Palmisano et al. 1995; Hoekstra et al. 2003), or birds (Kim et al. 1996). Palmisano et al. (1995) found that co-accumulation of Se and Hg could only occur in dolphin liver above a Hg level of 100 $\mu g \cdot g^{-1}$ wet weight. Similarly, it was suggested that the storage of a Hg–Se complex can only take place at higher molar ratios of Se:Hg (Hansen 1988).

Some recent studies have also tried to relate the inhibitory effects of Se on Hg toxicity to specific enzymatic activities (El-Demerdash 2001; Farina et al. 2003). A significant decrease was observed in the protein content of brain and liver of rats and in several enzymes in brain, liver, plasma, and serum in response to Hg treatment. The action of Se was positive in alleviating the toxic effects of Hg on different enzymes (El-Demerdash 2001). The formation of an inactive ternary complex of the thiol-Hg-Se type to prevent the inhibition of δ-aminolevulinate dehydratase was proposed by Farina et al. (2003).

In freshwater environments, the bioaccumulation of Hg by biota was retarded by elevated concentrations of Se in water of experimental ecosystems (Rudd et al. 1980; Turner and Rudd 1983; Turner and Swick 1983) and Se-treated lakes (Paulsson and Lundberg 1989). Similarly, Hg concentrations in largemouth bass (*Micropterus salmoides*) increased significantly after the elimination of Se-rich discharges to a quarry pond (Southworth et al. 1994, 2000). In a previous study (Chen et al. 2001), we reported significant inverse relationships between total concentrations of Hg and Se in muscle tissues from yellow perch (*Perca flavescens*) and walleye (*Sander vitreus*) from the Sudbury area. There are, however, very few studies on Se–Hg antagonistic effects done on biological species at the lower level of the aquatic food chain partly because of the analytical challenges in working with small sample sizes and trace elements. Other researchers have reported that the protective action of Se against Hg toxicity is not obvious in invertebrates (Pelletier 1986; Patel et al. 1988; Wang et al. 2004).

In this study, we complete our investigation on Se–Hg interactions in the aquatic food web with organisms positioned at lower levels of the food chain in Sudbury lakes near the large source of Se emissions. We use the results to suggest possible mechanisms for the observed inverse relationships between concentrations of MeHg and Se in tissues.

Materials and methods

Sampling and sample preparation

Test organisms consisted of three primary consumers (pelagic crustacean zooplankton, the mayfly *Stenonema femoratum* (Ephemeroptera), and the amphipod *Hyalella azteca* (Crustacea, Amphipoda)) and two secondary consumers (the water beetle *Graphoderus liberus* (Coleoptera) and young-of-the-year (YOY) *Perca flavescens* collected in lakes that are situated 5–65 km from the Sudbury metal smelters. The study lakes exhibit a moderate range of limnological and chemical characteristics and were selected to avoid high confounding gradients in chemical variable such as dissolved organic carbon or pH that could affect Hg assimilation (Table 1).

Mayflies were hand picked from shallow rocky shorelines. Amphipods were collected with dip nets and sorted under a dissecting scope. Zooplankton specimens were collected at mid-lake using small Wisconsin nets and then passed through sieves to retain the fraction between 250 and 1000 μm. Zooplankton samples were not sorted to species but rather represent composites of the size and species encountered in the pelagic zone of these boreal shield lakes. YOY perch were collected in littoral zones using seine nets. All perch were <40 days old. Larvae of *Graphoderus liberus* (Coleoptera) were collected at three different growth stages from only one lake (Swan Lake) to study Se and Hg assimilation. In this lake, a total of 1092, 100, and 204 individuals of *G. liberus* were hand picked at each consecutive growth stage. Organisms were collected between the end of May and the beginning of July 2002, carefully rinsed in double distilled water, and kept frozen until digestion and analysis. Mayflies and amphipods were depurated for 24 h in fresh water before being frozen. Samples were then freeze-dried, ground, and kept ready for digestion and analysis.

Analyses

For the determination of total Hg and total Se in tissues, a microwave digestion was performed in a mixture of HNO_3 and H_2O_2. Total Se and Hg were determined by hydride generation atomic fluorescence spectrometry (model PSA 10.055 Millenium Excalibur; PS Analytical, Orpington, Kent, UK) and by cold vapour atomic fluorescence spectrometry (model Tekran Mercury Analyzer 2600; Tekran Inc., Toronto, Ontario), respectively. The determination of MeHg in tissues was preformed according to the method developed by Liang et al. (1996) with slight modifications. Briefly, dry samples were digested with 2.0 mL of 25% (*w*/*v*) KOH–methanol solution in a Teflon vial at 85 °C for 3 h. The back extraction was performed on acidified digests with 6.0 mL

Table 1. Limnological and chemical characteristics of the studied lakes.

Lake	Latitude (°N)	Longitude (°W)	Distance from smelters (km)	Surface area (ha)	Mean depth (m)	pH	DOC ($mg \cdot L^{-1}$)	Ca ($mmol \cdot L^{-1}$)	Mg ($mmol \cdot L^{-1}$)	[Hg] ($pmol \cdot L^{-1}$)	[Se] ($nmol \cdot L^{-1}$)
Long (Lo)	46°22′	81°05′	8	792	7.2	7.0	4.1	0.19	0.11	12.6	1.8
Lohi (Li)	46°23′	81°02′	8	41	6.2	6.2	3.4	0.10	0.05	10.9	2.1
Swan (Sw)	46°22′	81°04′	9	5.8	2.8	5.7	2.8	0.08	0.02	10.9	1.9
Bethel (Be)	46°28′	80°57′	10	31	2.7	8.1	7.7	0.32	0.22	6.5	2.1
McFarlane (Mc)	46°25′	80°59′	11	166	7.3	7.4	4.6	0.35	0.19	10.2	2.5
Ramsey (Ra)	46°28′	80°57′	12	795	9.2	7.4	3.5	0.33	0.18	12.3	2.9
Nelson (Ne)	46°43′	81°05′	28	309	11.1	6.6	2.0	0.06	0.03	9.3	1.5
Windy (Wi)	46°35′	81°26′	32	1129	10.7	6.5	2.8	0.08	0.05	16.5	1.4
Geneva (Ga)	46°45′	81°33′	50	356	6.3	6.8	4.2	0.10	0.02	13.5	0.8
George (Ge)	46°01′	81°24′	52	189	16.4	6.3	2.2	0.04	0.02	10.4	0.9
Halfway (Ha)	46°53′	81° 38′	65	247	8.0	6.9	4.4	0.11	0.06	16.0	0.5

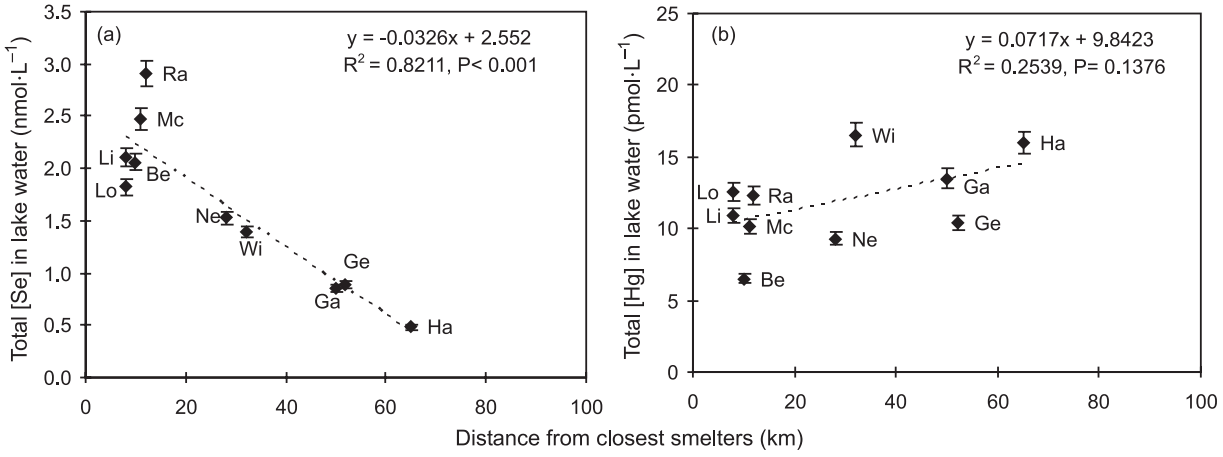
Note: DOC, dissolved organic carbon.

Table 2. Quality of analytical results.

	Total Se			Total Hg			MeHg		
CRM	Certified value	Our results	Relative error (%)	Certified value	Our results	Relative error (%)	Certified value	Our results	Relative error (%)
DORM-2 ($\mu g \cdot g^{-1}$)	1.40±0.09	1.38±0.10	1.4	4.64±0.26	4.59±0.34	1.1	4.47±0.32	4.31±0.34	3.6
TORT-2 ($\mu g \cdot g^{-1}$)	5.63±0.67	5.59±0.46	0.7	0.27±0.06	0.29±0.05	7.4	0.152±0.013	0.142±0.017	6.6
ORMS-2 ($ng \cdot L^{-1}$)	—	—	—	30.6±2.3	32.2±2.1	5.2	—	—	—

Note: DORM-2, TORT-2, and ORMS-2 are certified reference materials (CRM) from the National Research Council of Canada.

Fig. 1. Concentrations of total dissolved selenium (Se) (*a*) and mercury (Hg) (*b*) as a function of distance of sampled lakes from the closest Sudbury smelters. Lake abbreviations are as follows: Long, Lo; Lohi, Li; Swan, Sw; Bethel, Be; McFarlane, Mc; Ramsey, Ra; Nelson, Ne; Windy, Wi; Geneva, Ga; George, Ge; Halfway, Ha.



of CH_2Cl_2. The extracted MeHg in CH_2Cl_2 was collected and the ethylation step followed. MeHg (in the form of methyl ethyl mercury after ethylation) collected on the Tenax tube was analyzed by gas chromatography – cold-vapor atomic fluorescence spectrometry. The analytical quality was controlled by using the certified reference materials (CRM) DORM-2 and TORT-2 from the National Research Council of Canada at a frequency of one CRM control, a triplicate digestion, and a standard spike recovery for every 10 digested tissue samples (Table 2). The relative error on total Se and total Hg measurements in tissues was 5%–7%; it was 8%–12% for MeHg. Water samples were collected in acid-cleaned glass bottles opened below the lake surface, with all required precautions to limit contamination according to US Environmental Protection Agency method 1631. Total Se and Hg in lake water were determined by the same analytical techniques previously mentioned (Chen et al. 2001), and the quality of analysis for Hg was controlled by

Table 3. Concentrations of Se, Hg, and percentage of Hg as MeHg in tissues of aquatic organisms expressed on a dry weight basis.

	Zooplankton			Amphipod (*Hyalella azteca*)			Mayfly (*Stenonema femoratum*)			YOY perch (*Perca flavescens*)		
Lake	Se-total ($nmol \cdot g^{-1}$)	Hg-total ($pmol \cdot g^{-1}$)	MeHg (%)	Se-total ($nmol \cdot g^{-1}$)	Hg-total ($pmol \cdot g^{-1}$)	MeHg (%)	Se-total ($nmol \cdot g^{-1}$)	Hg-total ($pmol \cdot g^{-1}$)	MeHg (%)	Se-total ($nmol \cdot g^{-1}$)	Hg-total ($pmol \cdot g^{-1}$)	MeHg (%)
Long (Lo)	56	145	19	30	41	41	88	65	15	79.5	403	32
Lohi (Li)	129	184	31	—	—	—	132	130	16	—	—	—
Bethel (Be)	46	85	49	20	47	45	—	—	—	39.1	191	74
McFarlane (Mc)	48	95	36	21	55	40	69	50	19	68.4	294	78
Ramsey (Ra)	63	135	23	35	39	56	99	100	18	96.8	293	61
Nelson (Ne)	86	150	30	76	135	13	155	145	17	135.2	340	56
Windy (Wi)	80	281	27	17	116	47	90	105	48	76.7	543	79
Geneva (Ga)	29	284	30	26	141	30	71	198	25	41.8	543	71
George (Ge)	70	364	37	—	—	—	102	239	17	—	—	—
Halfway (Ha)	22	398	54	12	174	54	56	419	16	34.5	1221	41
Average			34			41			22			62

Note: Average concentrations of Se, Hg, and percentage of Hg as MeHg in *Graphoderus liberus* collected in Swan Lake only were 94 $nmol \cdot g^{-1}$, 164 $pmol \cdot g^{-1}$ (dry weight), and 48%, respectively. Relative errors on all Se and Hg determinations were at 5%–7% and at 8%–12% for MeHg. YOY, young-of-the-year.

using the certified standard ORMS-2 from the National Research Council of Canada (Table 2). MeHg was not determined in lake waters.

Statistical treatment

Relationships between variables were examined using bivariate scatterplots. When a possible linear relationship was indicated, a simple regression model was tested using Microsoft Excel (Microsoft Corporation, Redmond, Washington). When bivariate plots appeared to be nonlinear, nonlinear regression models with least-squares were tested using the same program. Test of difference between slopes was done using the analysis of covariance (ANCOVA) and comparison between taxonomic groups and primary and secondary consumers using the analysis of variance (ANOVA).

Results and discussion

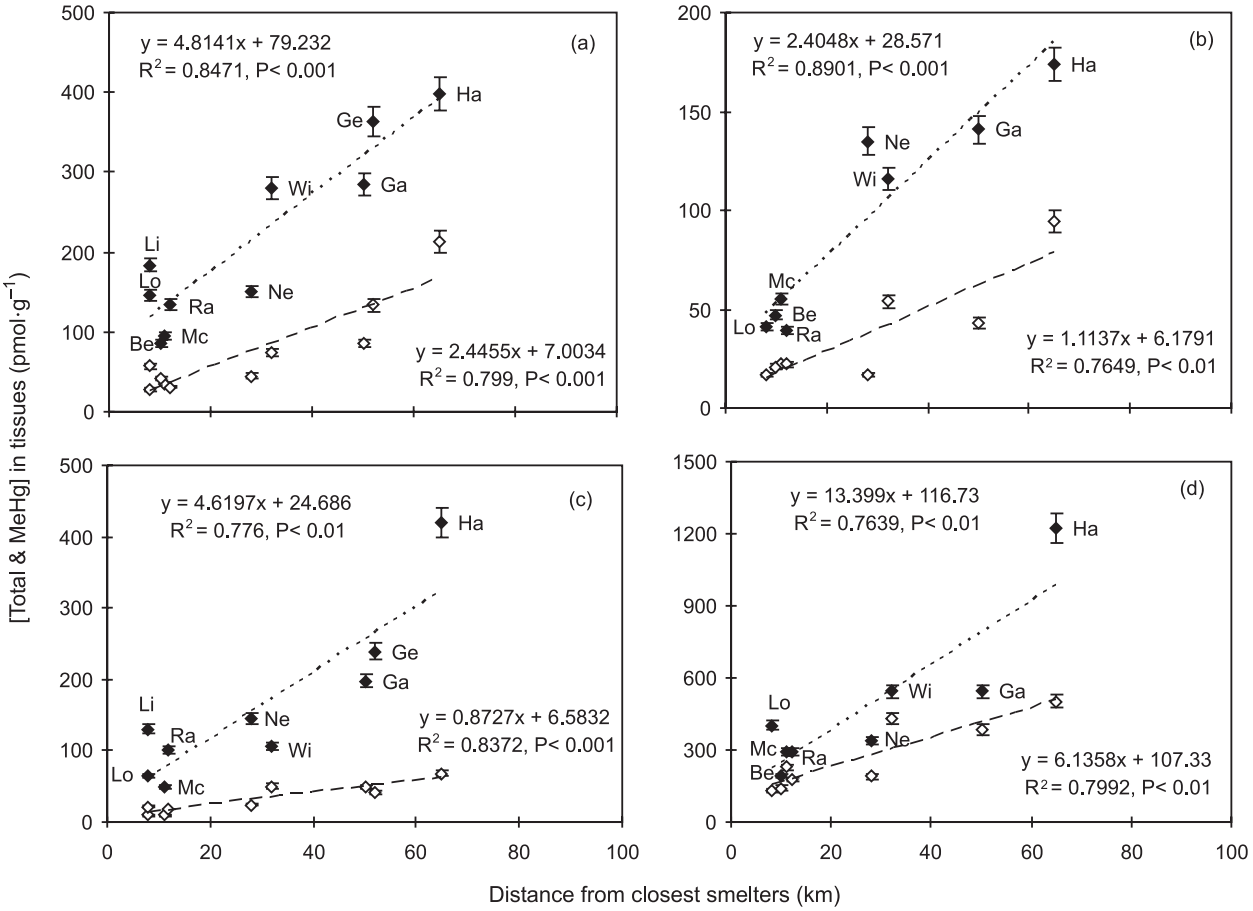
The effect of distance from smelters

Concentrations of total Se in lake water varied from 2.91 to 0.48 $nmol \cdot L^{-1}$, showing the clear effect of declining concentration with distance from the nearest smelters (Table 1). However, the concentrations of total Hg in lake water remained very low with distance from the smelters (Table 1; see also the poor regression of Fig. 1*b*). The presence of higher Se levels in lakes close to Sudbury is directly related to mining and smelting activities, and several tons of Se are released annually to the environment through atmospheric emissions (Nriagu and Wong 1983). To confirm the source of these elements, four ore samples coming from different mines of Inco Limited were analyzed for their total contents in Se and Hg using the above analytical methods. Total Se levels were more than 1000 times higher (62 ± 18 μg $Se \cdot g^{-1}$) than levels of total Hg (58 ± 22 ng $Hg \cdot g^{-1}$) in these ores. Differences in emission levels could therefore explain the different trends between total Se and total Hg in surface waters as function of distance from smelters (Fig. 1). The low level of Hg in the ore and the ubiquitous nature of Hg in the environment due to its long-range transport from a variety of other sources may in turn explain the lack of a distance effect on Hg in lake water near Sudbury.

When total Hg and MeHg concentrations (expressed on a dry weight basis; Table 3) were plotted against the distance from smelters, significant, positive linear relationships were obtained in all four studied species or taxonomic groups (Fig. 2). The difference in the two slopes (all p values <0.05 as tested by ANCOVA) suggests that the percentage of MeHg decreased in studied organisms with increasing distance from the Se source. The average percentage of MeHg in tissues increased from mayfly (22%) to zooplankton (34%), amphipod (41%), water beetle (48%), and larval perch (62%). These results could suggest a biomagnification of MeHg along the food chain. It has been shown that MeHg in muscle tissue of adult fish generally exceeds 85% of the total Hg (e.g., Bloom 1992).

In lakes that were affected more directly by Se deposition, the concentration of MeHg in tissues was significantly different between taxonomic groups (ANOVA, $p < 0.001$): mayfly and amphipod were significantly lower and larval perch were significantly higher than all others, but zooplankton and *G. liberus* were intermediate (Tukey's post hoc test).

Fig. 2. Concentrations of total mercury (Hg) (solid symbols) and methyl mercury (MeHg) (open symbols) in tissues (dry weight) of zooplankton (*a*), amphipods (*Hyalella azteca*) (*b*), mayflies (*Stenonema femoratum*) (*c*), and young-of-the year perch (*Perca flavescens*) (*d*) as a function of distance of sampled lakes from the closest Sudbury smelters. Lake abbreviations are as follows: Long, Lo; Lohi, Li; Swan, Sw; Bethel, Be; McFarlane, Mc; Ramsey, Ra; Nelson, Ne; Windy, Wi; Geneva, Ga; George, Ge; Halfway, Ha.



When the taxonomic groups were pooled into primary consumers (zooplankton, mayfly, and amphipod) or secondary consumers (*G. liberus* and YOY perch), the former had significantly lower MeHg than the latter (ANOVA, $p < 0.001$). The percentages of MeHg reported here are consistent with values reported in the literature for similar organisms (e.g., Bloom 1992; Gorski et al. 2003). However, the absolute concentrations of total Hg and MeHg in zooplankton and invertebrates were much lower in the Sudbury area than those reported by Gorski et al. (2003) in inlands lakes of Isle Royale National Park in Lake Superior (e.g., 1000 pmol total Hg·g^{-1} dry wt for bulk zooplankton compared with 130 ± 40 pmol Hg·g^{-1} in Sudbury lakes) or in insect larvae from Quebec hydroelectric reservoirs, with average concentrations up to 10 times the levels in larvae from natural lakes (Tremblay and Lucotte 1997).

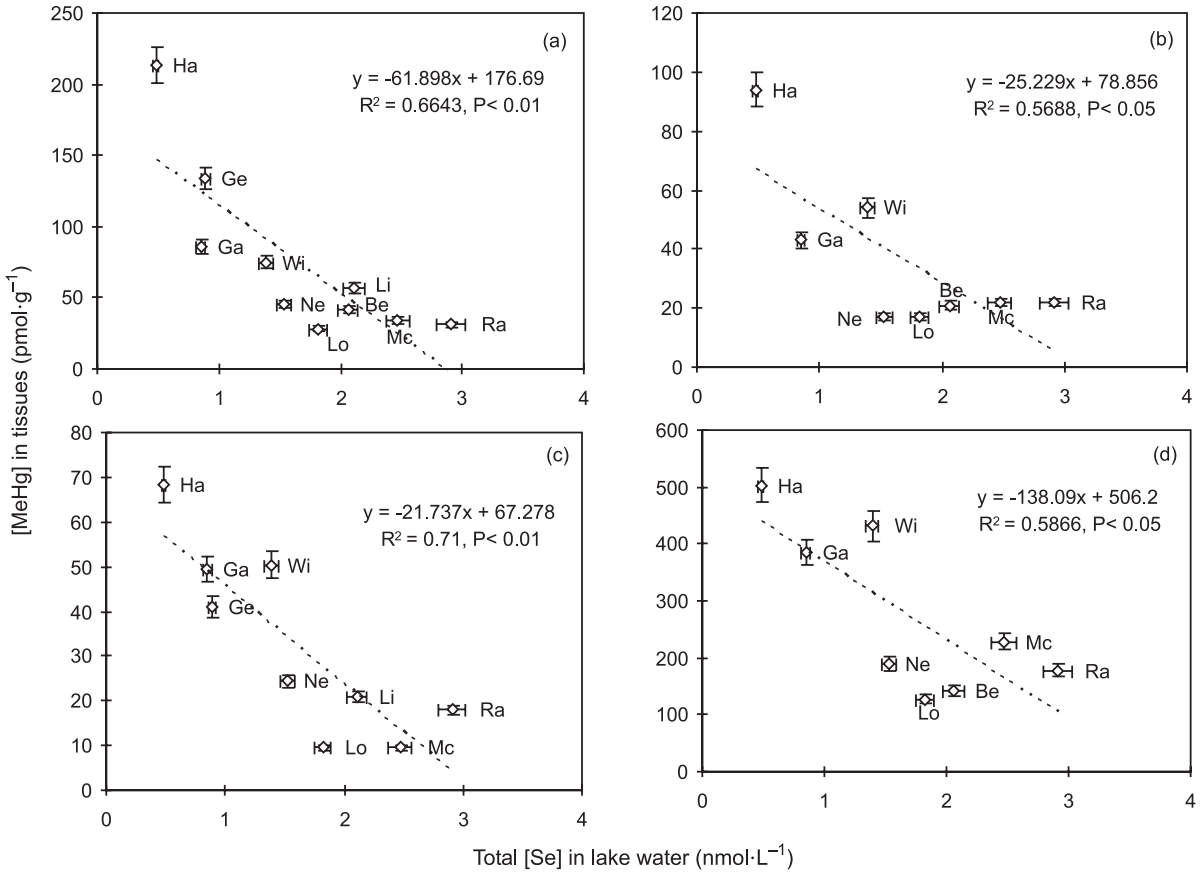
In our study, the protective effect of Se is demonstrated by the significant inverse linear regression between concentrations of MeHg in tissues and levels of total dissolved Se in lakes for all species (Fig. 3). These results suggest that Se affects the concentrations of MeHg in the studied species.

Se versus Hg and MeHg in tissues

In a previous study, we reported highly significant correlations (R^2 = 0.79–0.97) between concentrations of total Hg and total Se in adult perch and walleye muscle tissue (Chen et al. 2001). In the present study with zooplankton, mayfly, amphipod, and yearling perch, no statistically significant relationships between tissue total Hg and total Se in the whole body measurements of the four taxa were detected. Slightly stronger inverse trends were observed for MeHg (Figs. 4*b*, 4*d*, 4*f*, and 4*h*), although the relationships were not statistically significant at $p < 0.05$.

Less clear Se–Hg relations were expected when using species positioned at low levels of the food chain, especially with species such as zooplankton, which have a much shorter life-span than fish. In these taxa, the variations in bioassimilation because of lake-to-lake differences in physico-chemical characteristics such as the size of the basin, temperature, nutrients, food structure, etc. are expected to be much greater than in long-lived fish. Better correlations are obtained when using MeHg instead of total Hg presumably because MeHg concentrations more closely reflect biological assimilation, whereas total Hg concentration can reflect contribution from nonbioavailable forms: those present in incompletely depurated guts or in shells. These findings suggest that MeHg rather than total Hg is a better indicator for studies of assimilation, particularly when the concentration of Hg in a biological sample is extremely low. It should be noted that the correlation between MeHg and

Fig. 3. Concentrations of methyl mercury (MeHg) in tissues (dry weight) of zooplankton (*a*), amphipods (*Hyalella azteca*) (*b*), mayflies (*Stenonema femoratum*) (*c*), and young-of-the-year perch (*Perca flavescens*) (*d*) as a function of concentrations of total dissolved selenium (Se) in lake water. Lake abbreviations are as follows: Long, Lo; Lohi, Li; Swan, Sw; Bethel, Be; McFarlane, Mc; Ramsey, Ra; Nelson, Ne; Windy, Wi; Geneva, Ga; George, Ge; Halfway, Ha.



total Se in mayfly is poorer than that in other species. This is perhaps due to the particular nature of this species. Mayflies have relatively large amounts of hard exoskeletons that caused greater difficulties during steps of sample grinding, digestion, and MeHg extraction. The percentage of MeHg in mayfly was also the lowest (Fig. 2), consistent with a study of the mayfly *Hexagenia* sp. (Gorski et al. 2003). Se concentrations in organisms did not appear to be related to Se concentrations in lake water. This finding may be due to the fact that trace element bioaccumulation in organisms is a complex process that includes uptake of food, suspended particles, and sediment contact.

Significant inverse relationships between total Hg and MeHg and total Se were found when comparing the three larval stages of the water beetle *G. liberus* in Swan Lake (Fig. 5). Surprisingly, the concentrations of total Hg and MeHg were lower at growth stage 2 than at stages 1 and 3, while the concentration of total Se was the highest at this intermediate stage. A slightly lower proportion of MeHg was also observed (41% compared with 49% at stages 1 and 3, respectively). The results indicate that for some reason, larvae preferentially assimilated larger amounts of Se at their second growth stage, which in turn caused a lower level of MeHg and total Hg in their body. It could also be due to an unmeasured change in water quality or feeding habits during the three-stage period.

Possible mechanisms of interaction

Se and MeHg molar ratios within tissues and between tissue and water concentrations were calculated for all samples. Ranges of ratios and average values for the lakes close (<15 km) to Sudbury smelters are presented (Table 4). Ratios comparing concentrations in organisms and in water (columns 3 and 4) were calculated based on molar concentrations in wet tissue; that is, Se or MeHg concentrations in dry samples converted to those in wet tissues according to their respective water contents: 80%–85% for yearling perch, 84%–88% for amphipod and mayfly, 75%–87% for *G. liberus*, and 95%–98% for zooplankton. Ratios of Se-organism/Se-water (3rd column) and those of MeHg-organism/Hg-water (4th column) indicate a strong enrichment factor or bioconcentration of both elements in tissues compared with water, with Se ratios being much larger than Hg ratios. Higher Se-organism/Se-water ratios suggest a preferential assimilation of Se compared with total Hg in all organisms. This is expected because Se is an essential element, while Hg is not. A preferential affinity of binding sites for Se could exist and that could explain how Se plays an antagonistic role on the assimilation of MeHg in aquatic organisms. Even in lakes near the smelters where Se concentrations are high, ratios of MeHg-organism/Hg-water demonstrated the continued biomagnification of Hg in the food chain. The enrichment factors for the primary consumers

Fig. 4. Concentrations of total mercury (Hg) (left panels) and methyl mercury (MeHg) (right panels) in tissues (dry weight) of zooplankton (*a*, *b*), amphipods (*Hyalella azteca*) (*c*, *d*), mayflies (*Stenonema femoratum*) (*e*, *f*), and young-of-the-year perch (*Perca flavescens*) (*g*, *h*) as a function of concentrations of total selenium (Se) in tissues of the same organism. Lake abbreviations are as follows: Long, Lo; Lohi, Li; Swan, Sw; Bethel, Be; McFarlane, Mc; Ramsey, Ra; Nelson, Ne; Windy, Wi; Geneva, Ga; George, Ge; Halfway, Ha.

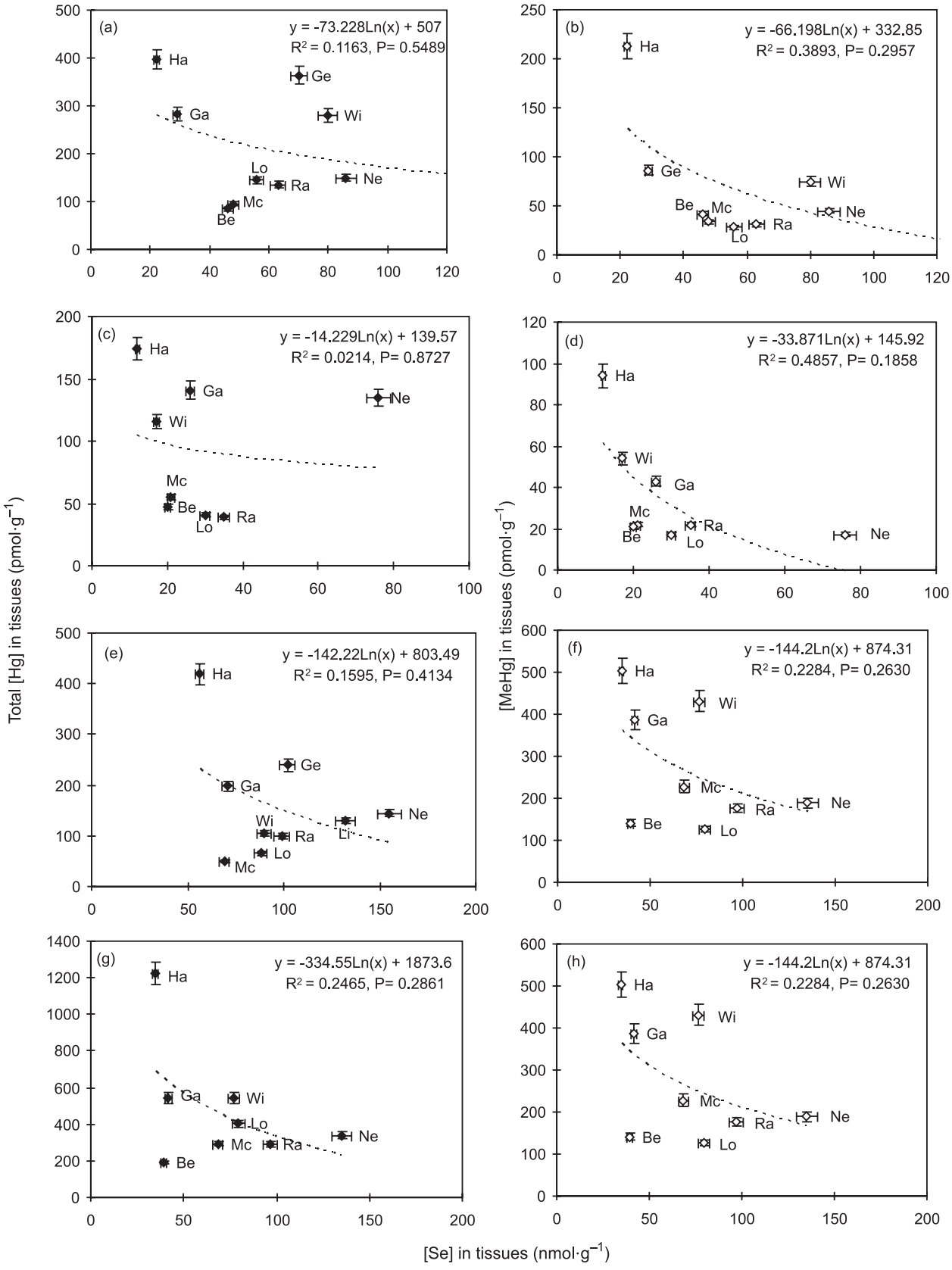


Table 4. Comparison of calculated molar ratios.

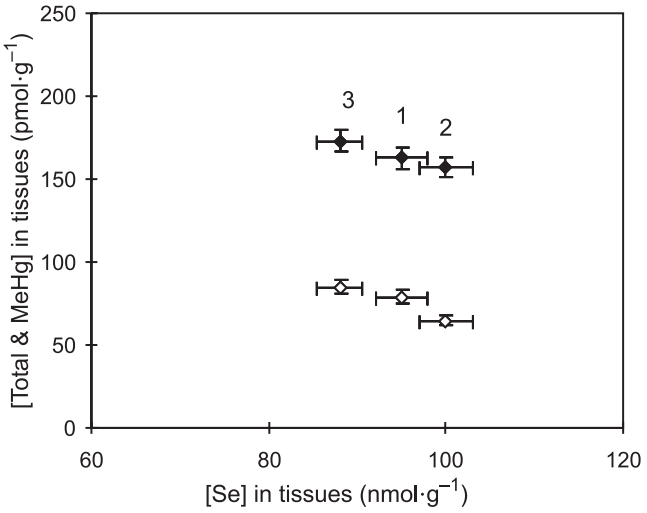
Medium	Se/MeHg	Se-organism/Se-water[a]	MeHg-organism/Hg-water[a]
Zooplankton	103–2263 (1760±485)	650–2360 (930±520)	70–400 (120±55)
Mayflies (*Hyalella azteca*)	820–9263 (7085±1620)	1020–3500 (1300±465)	100–550 (160±68)
Amphipods (*Stenonema femoratum*)	128–4471 (1316±425)	1100–6460 (1520±460)	170–760 (280±105)
YOY perch (*Perca flavescens*)	69–714 (437±175)	4150–13260 (4640±1550)	1510–4720 (2580±890)
Graphoderus liberus	(1260±250)	(8060±1410)	(1140±345)
Adult perch (*Perca flavescens*)[b]	(820±210)	(14380±2650)	(7200±1450)
Adult walleye (*Sander vitreus*)[b]	(104±44)	(5900±1460)	(11200±3620)

Note: Data are shown as a range of values for all studied lakes. All values in parentheses represent an average (±SD) for lakes that are located within 15 km of Sudbury smelters. YOY, young-of-the-year.

[a]Expressed on a wet weight basis.

[b]Estimated average ratio of Se-organism over MeHg and that of MeHg-organism over total Hg in water, assuming that 95% of measured Hg in fish muscles is MeHg.

Fig. 5. Concentrations of total mercury (Hg) (closed symbols) and methyl mercury (MeHg) (open symbols) in tissues (dry weight) of the three larval stages of *Graphoderus liberus* as a function of concentrations of total selenium (Se) in tissues of the same organism.



were at 120 for zooplankton, 160 for mayfly, and 280 for amphipods. Secondary consumers showed much larger ratios, with average values of 1140 for *G. liberus* and 2580 for YOY perch. For comparison with higher levels of the food chain, adult perch were estimated at 7200, while the top predator walleye was at 11 200, using data from Chen et al. (2001). The pattern for Se was the same, but the biomagnification of Se seemed to stop at the level of yellow perch (14 380) and actually declined at the level of walleye (5900) (Table 4). This could be due to mass dilution in larger fish. The molar ratio of Se-organism to MeHg-organism also indicates that the proportion of Se in tissues compared with that of MeHg decreased when moving upward in the food chain. It might again indicate a preferential assimilation of Se by primary consumers. This is especially noticeable in mayfly, where high ratios could reflect the feeding mechanisms of the species. *Stenonema femoratum* grazes the organic film of submerged surfaces where benthic algae and sediment particles rich in Se can be found in Sudbury lakes.

It has also been suggested that Se could reduce the methylation rate of Hg (Jackson 1991; Jin et al. 1997, 1999) and the bioaccumulation of MeHg in species living in sediments by limiting the solubility of Hg (Nuutinen and Kukkonen 1998). Se levels are indeed very high in Sudbury lake sediments and can reach several micrograms per gram (ppm) (Nriagu and Wong 1983; Belzile et al. 2000). Such high Se levels could limit the solubility and consequently the methylation of Hg as well as its bioavailability. Several earlier studies (see Introduction) also speculated that threshold values of Hg or Se must be reached before antagonistic effects or detoxification mechanisms through the formation of HgSe compounds could occur. That could further explain why the antagonistic phenomenon is more clearly observed close to Sudbury, where Se levels in lakes and sediments are very high. Additional data on Hg and Se concentrations in fish organs such as liver will help to confirm or refute this last hypothesis.

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