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ARTICLE

Effects of a decade of selenium emission reductions on mercury accumulation in aquatic biota in the Sudbury region of Ontario

Mija Aždajić, Nelson Belzile, John M. Gunn, Jules M. Blais, and Alexandre J. Poulain

Abstract: Control of smelting emissions in the Sudbury (Ontario, Canada) area has dramatically decreased the amount of selenium (Se) deposited onto the surrounding landscape. Historically, Se emissions in Sudbury correlated with lower total mercury (Hg) and methylmercury levels (MeHg) in tissues of zooplankton, amphipods (*Hyalella azteca*), mayflies (*Stenonema femoratum*), and young-of-the-year perch (*Perca flavescens*). In 2017, ten years following emission reductions, we evaluated whether changes in Se deposition affected total Hg and MeHg burden in lake biota. We show that total Se concentrations in the water of the majority of lakes have increased despite decreases in Se depositions, most likely due to the long residence time of Se in the watershed and the water column. As a result, Se in water continues to correlate with lower total Hg and MeHg accumulation in tissues of zooplankton, amphipods, mayflies, and perch. These results suggest that Se continues to exhibit a protective effect on Hg accumulation in biota, even years after emissions have greatly decreased. We expect this work to inform efforts aiming at long-term recovery of aquatic environments affected by smelter emissions and aid in designing remediation strategies involving Se additions.

Résumé : Le contrôle des émissions de fonderie dans la région de Sudbury (Ontario, Canada) s'est traduit par une réduction drastique de la quantité de sélénium (Se) déposé dans le paysage environnant. Historiquement, les émissions de Se à Sudbury étaient corrélées à des concentrations réduites de mercure total (Hg) et de méthylmercure (MeHg) dans les tissus de zooplancton, d'amphipodes (*Hyalella azteca*), d'heptagénies rousses (*Stenonema femoratum*) et des perchaudes (*Perca flavescens*) de l'année. En 2017, dix ans après les réductions des émissions, nous avons examiné si les changements de la quantité de Se déposée affectaient la charge de Hg total et de MeHg dans le biote des lacs. Nous montrons que les concentrations de Se total dans l'eau de la plupart des lacs ont augmenté, malgré des baisses du dépôt de Se, vraisemblablement en raison du long temps de séjour du Se dans le bassin versant et la colonne d'eau. Par conséquent, le Se dans l'eau continue d'être corrélé à une accumulation plus faible de Hg total et de MeHg dans les tissus de zooplancton, d'amphipodes, d'heptagénies et de perchaudes. Ces résultats donnent à penser que le Se continue d'avoir un effet protecteur contre l'accumulation de Hg dans le biote, même des années après des réductions substantielles des émissions. Nous prévoyons que ces travaux soutiendront les efforts visant au rétablissement à long terme des milieux aquatiques touchés par les émissions de fonderie et aideront à concevoir des stratégies de remise en état comprenant l'ajout de Se. [Traduit par la Rédaction]

Introduction

The metal mining and smelting industry in Sudbury, Ontario, Canada, has been operating for more than 130 years (Saarinen 2013), extracting primarily nickel and copper, but also large quantities of silver, gold, cobalt, and platinum group elements from the rich local ore body (Freedman and Hutchinson 1980). Although highly profitable over much of this period, the Sudbury smelters have severely impacted the local aquatic and terrestrial environments through extensive atmospheric deposition of sulfate and metals. Several studies have shown the impact of metal smelting on soil, vegetation (Mailman et al. 2006; Turner and Rudd 1983; Wang et al. 2014), water quality (Freedman and Hutchinson 1980), and biota (Gorham and Gordon 1960). Fortunately, Sudbury is also a great example of environmental reclamation that started in the 1970s (Conroy et al. 1976). One of the most famous efforts was the liming performed to counteract the acidification of the city's lakes and soils (Boerchers et al. 2016; Gunn 1995; Saarinen 2013). Furthermore, reduction of emissions oc-

curred through the use of more efficient smelting techniques, periods of reduced production, and stricter emission regulations (Boerchers et al. 2016; Winterhaider 1983).

Particulate matter emitted from smelters contained large quantities of nickel, copper, and iron, but also considerable levels of selenium (Se) because Sudbury's nickel and copper sulfidic ores are rich in Se, which can replace sulfur in mineral structures (Gorham and Gordon 1960; Nriagu and Wong 1983; Nriagu et al. 1982). As a result, lakes closer to the smelter exhibit total Se ranging from 2.9 to 5.1 nmol·L^{-1} (Hawley and Nichol 1959; Nriagu and Wong 1983), levels well above most Ontario lakes that typically range from 0.63 to 1.3 nmol·L^{-1} (Nriagu and Wong 1983). The decreasing total Se observed in lake water with increasing distance from the smelter sites provides a unique opportunity to investigate the response of aquatic biota to Se (Beatty and Russo 2014; Sharma et al. 2015).

Se is an essential micronutrient in most animals (Belzile et al. 2006; Chen et al. 2001), usually present as selenocysteine (Ullah

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et al. 2019) and generally acquired through their diet (Burk 2002); however, it can also become toxic in certain concentrations. Although inorganic species of Se such as selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) are present in the aquatic environment, organic species are thought to be the most bioavailable for uptake by periphyton, macrophytes (Lemly 2002; Lemly and Smith 1987; Ullah et al. 2019), and fish (Besser et al. 1989). Se can be an essential or toxic element, depending on concentrations and speciation; however, the concentration range at which Se is beneficial to fish is very narrow (Besser et al. 1993). Because of this narrow range and its persistent and bioaccumulative nature in freshwater biota, there has been discussion on the concentration thresholds in the aquatic environment (Hamilton 2004). Owing to this narrow range, it is important to ensure that Se in the lakes does not reach toxic levels.

The interaction between mercury (Hg) and Se has been the focus of several studies, as Se can affect the mobility, bioavailability, and toxicity of Hg in aquatic ecosystems (Hoffman 2003). In particular, Se has been shown to have an antagonistic effect on Hg bioaccumulation in freshwater environments (Bjerregaard et al. 2011; Chapman et al. 2016; Nuutinen and Kukkonen 1998). In the Sudbury area, Belzile et al. (2006) showed that total Se in Sudbury lake water was inversely related with total Hg and MeHg concentrations in four different freshwater components: zooplankton, amphipods (*Hyalella azteca*), mayflies (*Stenonema femoratum*), and young-of-the-year perch (*Perca flavescens*). Other studies have shown similar inverse relationships between Se in lake water and total Hg in fish tissue (Belzile et al. 2009) and MeHg in young walleye (Chen et al. 2001) both in Sudbury and elsewhere (Yang et al. 2008).

Although the inhibitory effect of Se on Hg bioaccumulation is well known, there is no clear consensus on the mechanism involved. Earlier studies suggest that Se affects both Hg mobility and bioavailability. Inorganic Hg can form low solubility complexes with Se (Bjerregaard et al. 2011; Paulsson and Lundbergh 1991; Peterson et al. 2009; Southworth et al. 2000; Turner and Rudd 1983), which can (*i*) decrease the bioavailability of Hg to be methylated by microbes (Melnick et al. 2010; Truong et al. 2014), (*ii*) decrease the bioaccumulation of Hg in organisms (Wang et al. 2016), and (*iii*) increase the elimination rates of Hg from the organism (Chapman et al. 2016). In addition, selenide's (Se^{2-} or HSe^-) strong binding affinity with MeHg (Bjerregaard et al. 2011) can (*i*) promote mercury demethylation and (*ii*) prevent MeHg from binding to proteins while increasing its excretion from the cell (Sugiura et al. 1978).

Owing to Hg and MeHg toxicity to wildlife and humans (Yang et al. 2008), Se additions to lakes have been proposed as a remediation strategy to reduce Hg accumulation (Kidd and Batchelar 2011). However, to the best of our knowledge, there have not been any studies assessing the long-term effects of varying Se deposition on total Hg and MeHg accumulation in freshwater biota. Such data would aid in evaluating the feasibility of Se-based remediation strategies.

Over the past ten years, Se emissions in Sudbury have substantially decreased mostly because of a decrease in emissions from the Copper Cliff smelter, which was the largest smelter site in Sudbury (Saarinen 2013). We hypothesized that changes in Se emissions in Sudbury will alter Hg accumulation in biota and predicted that a decrease in emissions would lead to an increase in Hg and MeHg in biota. In this study, we examined (*i*) how total Se has changed in the water of lakes in the Sudbury area following an 85% decrease in emissions and (*ii*) whether total Se, total Hg, and MeHg concentrations in aquatic biota have changed 15 years after a similar study was conducted (Belzile et al. 2006).

Materials and methods

We compared the July 2002 sampling results reported in Belzile et al. (2006) with new biota and unfiltered surface water samples collected in July 2017 and 2018. Complete information of the lake water chemistry and physical characteristics are available in online Supplementary material, Table S2[1].

Lake selection

All 11 lakes from the original 2002 survey by Belzile et al. (2006) were resampled for both water chemistry and biota in July 2017. The lakes ranged from 8 to 65 km from the smelters (Fig. 1). In 2017, two samples (Lohi and Long lakes) had very high total Se; therefore, a complete set of water samples were collected and analyzed again in 2018 for total Se and total Hg. All data are shown in Table S2[1].

Biological sample collection

Four different food web components were collected: zooplankton, amphipods (*Hyalella azteca*), mayflies (*Stenonema femoratum*), and young-of-the-year perch (*Perca flavescens*). All samples were collected from the same area within the lake. Zooplankton were collected using an 80 μm net, then sorted with a mesh between 200 and 1000 μm. Amphipods were collected with a kick net and picked by hand. Mayflies were picked by hand from the underside of stones. Yellow perch were collected with seine netting. All samples were frozen after sampling, freeze-dried, homogenized with mortar and pestle, and kept in a dry and dark place until analysis.

Extraction and metals analysis

Total Hg for yellow perch, amphipods, and mayflies were analyzed using a Nippon MA-3000 Hg analyser with a method detection limit of 0.002 ng; zooplankton samples were analysed using Tekran-2600 with a method detection limit of 0.02 ng·kg⁻¹. MeHg in biota was analysed using gas chromatography – cold vapor atomic fluorescence spectrometry (GC-CVAFS) with a limit of detection of 2.67×10^{-5} ng·L⁻¹ (digestion solution). Total Se in biota was analysed using inductively coupled plasma mass spectrometry (ICP-MS) with a detection limit of 10 ng·L⁻¹ (digestion solution).
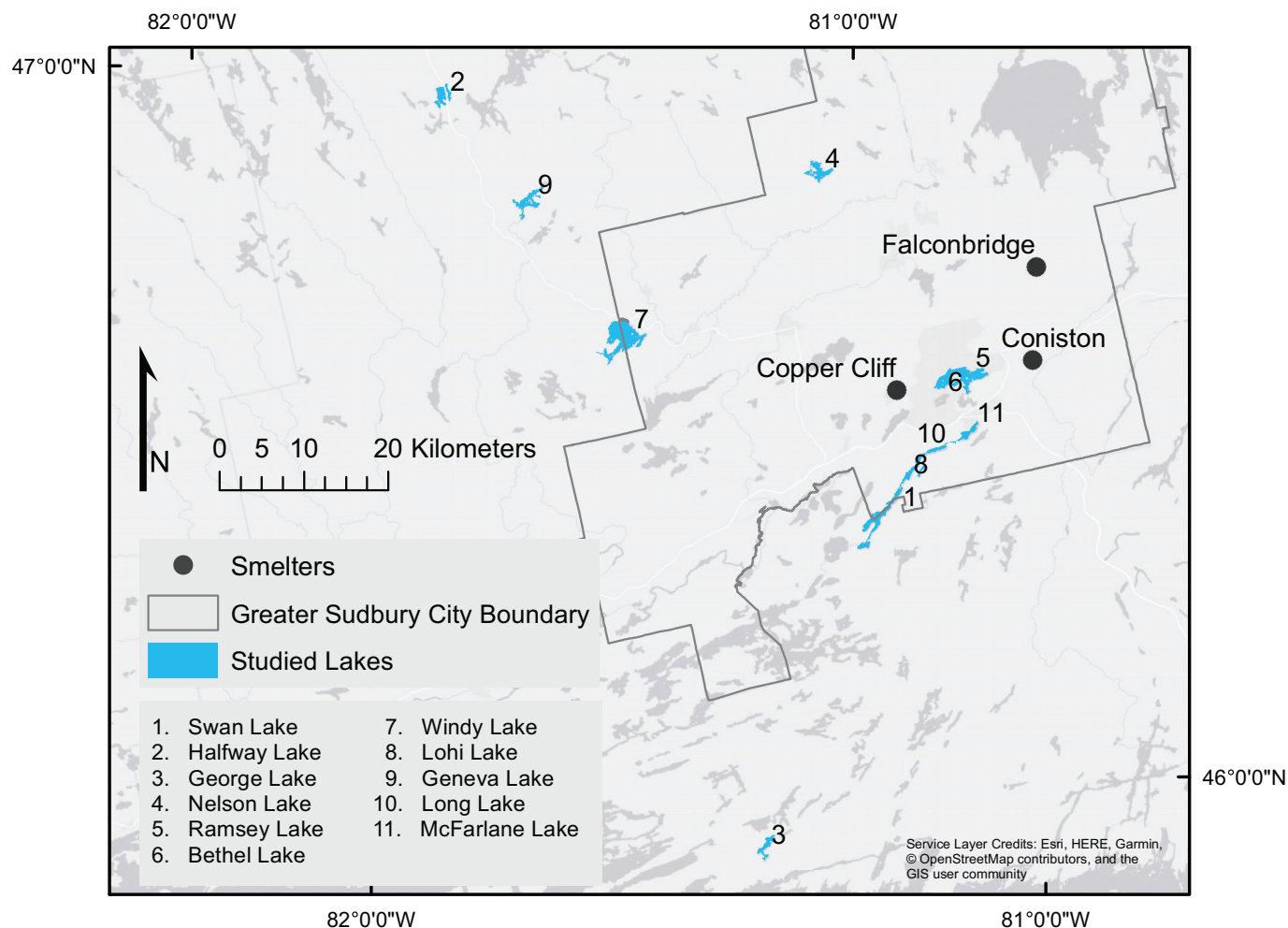
Extraction and analysis methods were maintained as similar as possible between the two study periods. Table 1 provides a summary and a comparison of techniques used in our study and that of Belzile et al. (2006). The quality of analysis between the two samplings was verified using the following certified reference materials: DORM2, DORM4, TORT2, IAEA407, and DOLT5. All five reference materials, in duplicate, were used in each extraction and analysed with the samples. The relative error on measurement was 0%–14.8% for total Hg, 0%–10.9% for MeHg, and 5.7%–21.5% for Se (Table S2).[1]

Statistical analyses

All statistical analyses were done in the program R. Simple linear regression models and analyses of covariance (ANCOVA) were used to test the relationships between variables. Model assumptions (i.e., linearity, heteroscedasticity, and normality of residuals) were tested using formal tests, and dependent variables were transformed accordingly. In certain instances, the relationship between variables was visually assessed, and it was decided that a nonlinear relationship was more suitable. ANCOVAs were used to test the difference in concentrations between years with distance from smelter stack being the covariate. This statistical analysis was chosen to address issues of spatial autocorrelation along the distance gradient when comparing sampling years.

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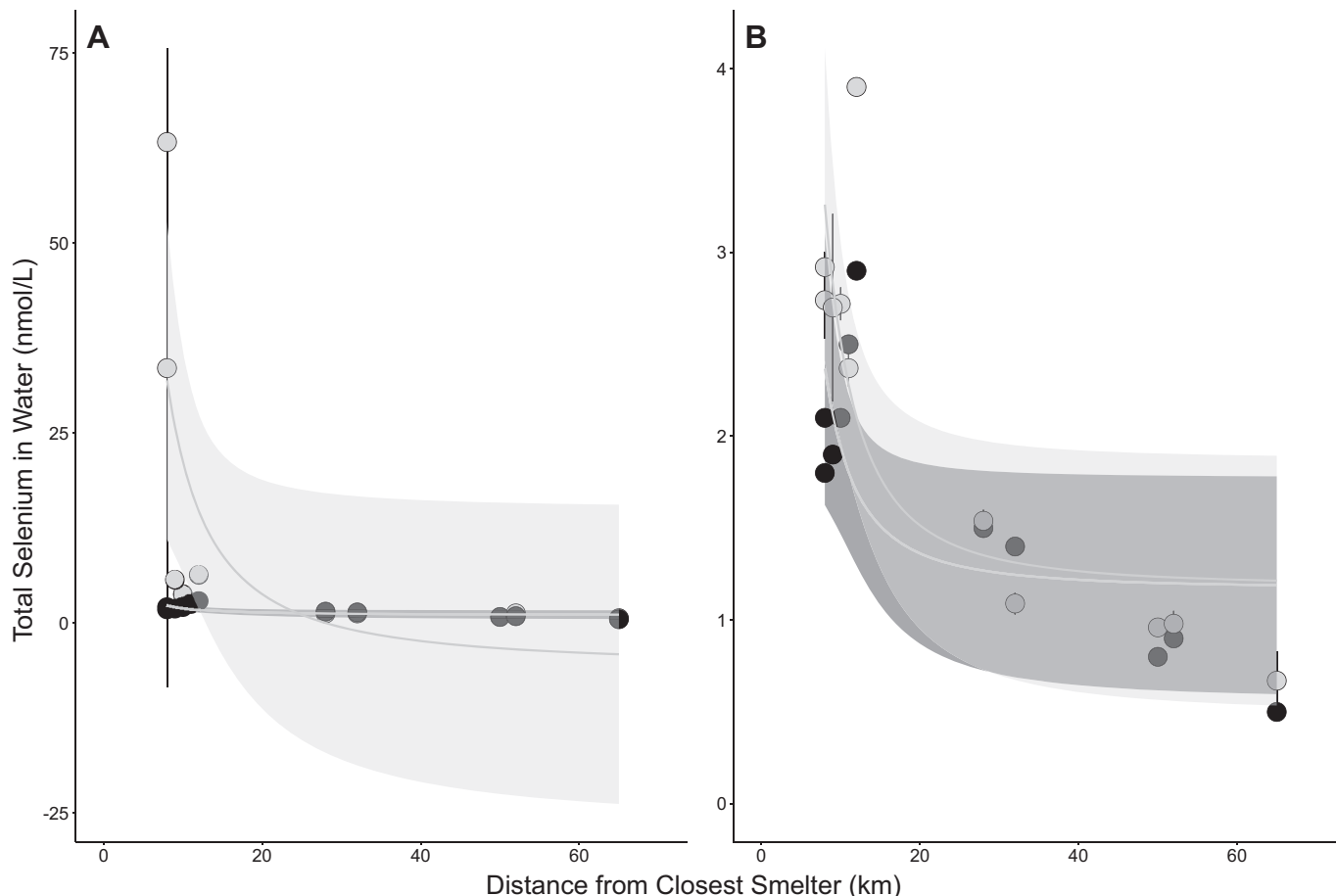Can. J. Fish. Aquat. Sci. Vol. 77, 2020

Fig. 1. Map of the lakes selected for the study as well as the placement of the three smelter stacks in the greater Sudbury area. Spatial data was extrapolated from Belzile et al. (2006), the National Pollutant Release Inventory (Environment and Climate Change Canada 2017), and the Ontario Integrated Hydrology Data (Ministry of Natural Resources and Forestry 2012). [Colour online.]

Table 1. Comparison of extraction methods for total Se, total mercury, and methylmercury.

Method	July 2002 – Belzile et al. (2006)	July 2017 – present study
Total selenium	Digested with HNO_3 and H_2O_2	Digested with concentrated HNO_3 and H_2O_2
	Analyzed by HG-AFS (hydride generation atomic fluorescence spectrometry)	Analysed by ICP-MS
Total mercury	Digested in mixture of HNO_3 and H_2O_2	Digested with concentrated HNO_3 and H_2O_2 (zooplankton)
	Analyzed by CVAFS (Tekran 2600)	Tekran 2600 (zooplankton) or Nic MA-3000 mercury analyser (perch, amphipods, mayflies)
Methylmercury	Digested with 2.0 mL of 25% KOH–methanol in Teflon vial at 85 °C for 3 h	Digested with 2 mL of 6 mol·L^{-1} KOH, shaken for 4 h
	Back-extracted with 6.0 mL of CH_2Cl_2	2.0 mL of 6 mol·L^{-1} HCl adjusted to pH 3.0 with 20% HCl and 20% KOH
		Add 4 mL acidic potassium bromide and copper sulfate (3:1) and 5 mL of CH_2Cl_2, shake overnight
	CH_2Cl_2 is collected and ethylated	CH_2Cl_2 is collected into vial with 1 mL of sodium thiosulfate, shaken
	MeHg collected on Tenax tube	Sodium thiosulfate added to 3:1 mixture of acidic potassium bromide and copper sulfate and CH_2Cl_2, shaken
		CH_2Cl_2 is collected
	Analysed by GC-CVAFS	Analysed by GC-CVAFS

Fig. 2. Concentration of total Se as a function of distance from the closest smelter stack, with and without outliers. Black points represent the samples from July 2017 (A) and July 2018 (B), and the grey points represent the samples from Belzile et al. (2006). Standard deviations of analysis replicates are shown for samples from July 2017 and July 2018.

Results

Total Se, total Hg, and water quality variables differences between 2002 and 2017–2018

Results from all sampling years showed that total Se was inversely related to distance from the closest smelter (Fig. 2). The two ANCOVA models had distance as covariate and tested for effect of year on total Se; this was done for 2017 versus 2002 ($p < 0.05$, $r^2 = 0.86$, $F_{[2,17]} = 61.41$) and for 2018 versus 2002 ($p < 0.05$, $r^2 = 0.90$, $F_{[2,19]} = 91.73$).

Total Se in 2017 decreased with distance from the closest smelter (GLM model, $p = 0.046$, $r^2 = 0.38$, $F_{[1,7]} = 5.863$; Fig. 2). When comparing 2002 and 2017, there was a significant difference in the intercepts between the years ($p = 0.002$), with the July 2017 intercept being significantly higher (Fig. 2). For the 2017 samples, total Se in lake water ranged from 0.63 to 63.32 nmol·L^{-1}, with two lakes appearing as extreme outliers: Lohi (63.32 nmol·L^{-1}) and Long (33.56 nmol·L^{-1}). After excluding the Lohi and Long lake samples from the 2017 versus 2002 analysis ($p < 0.05$, $r^2 = 0.82$, $F_{[3,14]} = 28.03$), the intercepts were significantly different between the 2 years ($p < 0.05$). When the lakes were resampled again in 2018, total Se was no longer highly elevated (0.67 to 2.74 nmol·L^{-1}), and total Se remained inversely correlated with distance from the closest smelter ($p < 0.05$, $r^2 = 0.75$, $F_{[1,9]} = 31.63$). When comparing the total Se results from 2018 with those from 2002 ($p < 0.05$, $r^2 = 0.89$, $F_{[2,19]} = 31.63$), there was once again a significant difference in the intercepts ($p < 0.03$), with the 2018 intercept being higher (Fig. 2).

Total Hg in water in 2018 (Table S2[1]) decreased significantly with distance from the smelters, although the relationship was weak ($p = 0.0495$, $r^2 = 0.29$, $F_{[1,9]} = 5.147$), and the effect size was small (slope (m) = 0.029 pmol·L^{-1}·km^{-1}). When comparing the two years with an ANCOVA model ($p < 0.05$, $r^2 = 0.91$, $F_{[2,18]} = 94.17$), the 2018 samples had significantly lower concentrations than the 2002 samples ($p < 0.05$, $m = -2.04$ pmol Hg·L^{-1}). Unfortunately, no total Hg data are available for lake water samples in 2017.
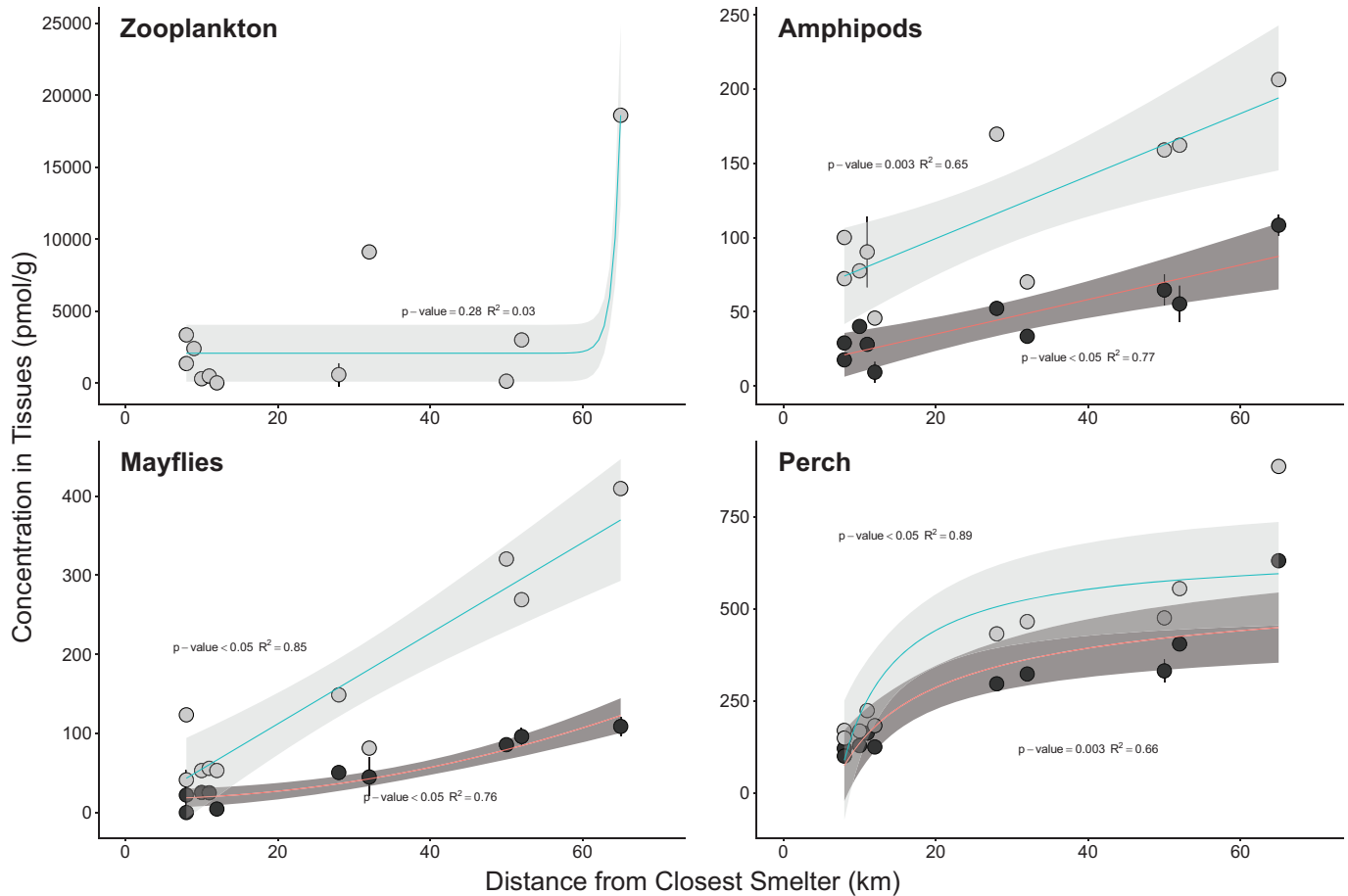
Other chemical variables from 2017 were also inversely correlated with distance from the stacks, such as sulfate ($p = 0.004$, $r^2 = 0.58$, $F_{[1,9]} = 14.62$, $m = -0.019$ mg·L^{-1}·km^{-1}), nickel ($p = 0.021$, $r^2 = 0.49$, $F_{[1,7]} = 8.753$, $m = -0.843$ µg·L^{-1}·km^{-1}), and copper ($p = 0.007$, $r^2 = 0.62$, $F_{[1,7]} = 14.25$, $m = -0.16$ µg·L^{-1}·km^{-1}); however, the effect sizes were small. Calcium decreased with distance ($p = 0.04$, $r^2 = 0.32$, $F_{[1,9]} = 5.603$) with a small effect size ($m = -0.027$ mmol·L^{-1}·km^{-1}). Environmental variables such as dissolved organic carbon, pH, nitrogen, and phosphorous were not significantly different between 2017 and 2002 sampling seasons (ANCOVA models, $p > 0.05$), nor were they significantly correlated with distance from the smelters ($p > 0.05$).

Total Se, total Hg, and MeHg in tissues in 2017

Total Hg in organisms increased with distance from the smelters (Fig. 3) for amphipods ($p = 0.003$, $r^2 = 0.65$, $F_{[1,8]} = 17.92$), mayflies ($p < 0.05$, $r^2 = 0.85$, $F_{[1,8]} = 53.45$), and perch ($p < 0.05$, $r^2 = 0.89$, $F_{[1,7]} = 66.07$). However, total Hg in zooplankton was not significantly correlated with distance from the smelters ($p > 0.05$; Fig. 3).

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Fig. 3. Concentrations of methylmercury and total mercury in tissues with respect to distance from the closest smelter in zooplankton, amphipods, mayflies, and perch. Black points represent methylmercury concentrations, and grey points represent total mercury concentrations. Standard deviations of analysis replicates are shown for samples from July 2017. [Colour online.]

In addition, total Hg in organisms decreased with increasing total Se in water (Fig. 4) for zooplankton ($p = 0.022$, $r^2 = 0.71$, $F_{[1,4]} = 13.17$), amphipods ($p = 0.017$, $r^2 = 0.58$, $F_{[1,6]} = 10.77$), mayflies ($p = 0.007$, $r^2 = 0.68$, $F_{[1,6]} = 16.06$), and perch ($p < 0.05$, $r^2 = 0.96$, $F_{[1,5]} = 183.9$). When the two outliers (Lohi and Long lakes) were removed, a significant inverse relationship for total Hg in zooplankton ($p = 0.042$, $r^2 = 0.73$, $F_{[1,3]} = 11.63$), amphipods ($p = 0.039$, $r^2 = 0.63$, $F_{[1,4]} = 9.102$), mayflies ($p = 0.016$, $r^2 = 0.75$, $F_{[1,4]} = 16.21$), and perch ($p > 0.05$, $r^2 = 0.96$, $F_{[1,4]} = 129.1$) was observed with respect to total Se in water. Total Hg was not correlated with total Se in tissues ($p > 0.05$) of zooplankton, amphipods, mayflies, and perch (Fig. S3[1]).

MeHg in tissue samples increased with distance from smelter stacks (Fig. 3) for amphipods ($p = 0.001$, $r^2 = 0.77$, $F_{[1,7]} = 28.08$), mayflies ($p = 0.001$, $r^2 = 0.76$, $F_{[1,8]} = 29.67$), and perch ($p = 0.003$, $r^2 = 0.66$, $F_{[1,8]} = 18.31$). They decreased with respect to total Se in water for amphipods ($p < 0.05$, $r^2 = 0.89$, $F_{[1,5]} = 52.11$), mayflies ($p = 0.002$, $r^2 = 0.78$, $F_{[1,6]} = 26.28$), and perch ($p < 0.05$, $r^2 = 0.95$, $F_{[1,6]} = 144.9$) (zooplankton were excluded due to missing data). Additionally, when the two outliers (Lohi and Long lakes) were removed, MeHg was significantly inversely correlated with total Se in water for amphipods ($p = 0.008$, $r^2 = 0.91$, $F_{[1,3]} = 41.75$), mayflies ($p = 0.024$, $r^2 = 0.70$, $F_{[1,4]} = 12.49$), and perch ($p < 0.05$, $r^2 = 0.95$, $F_{[1,4]} = 98.53$). Finally, only MeHg in perch tissues significantly decreased with total Se in perch tissues ($p = 0.03$, $r^2 = 0.40$, $F_{[1,8]} = 6.92$). This is interesting because total Se in tissue samples did not significantly correlate with distance from the smelters stacks ($p > 0.05$) nor with total Se in water ($p > 0.05$; Fig. S2[1]).
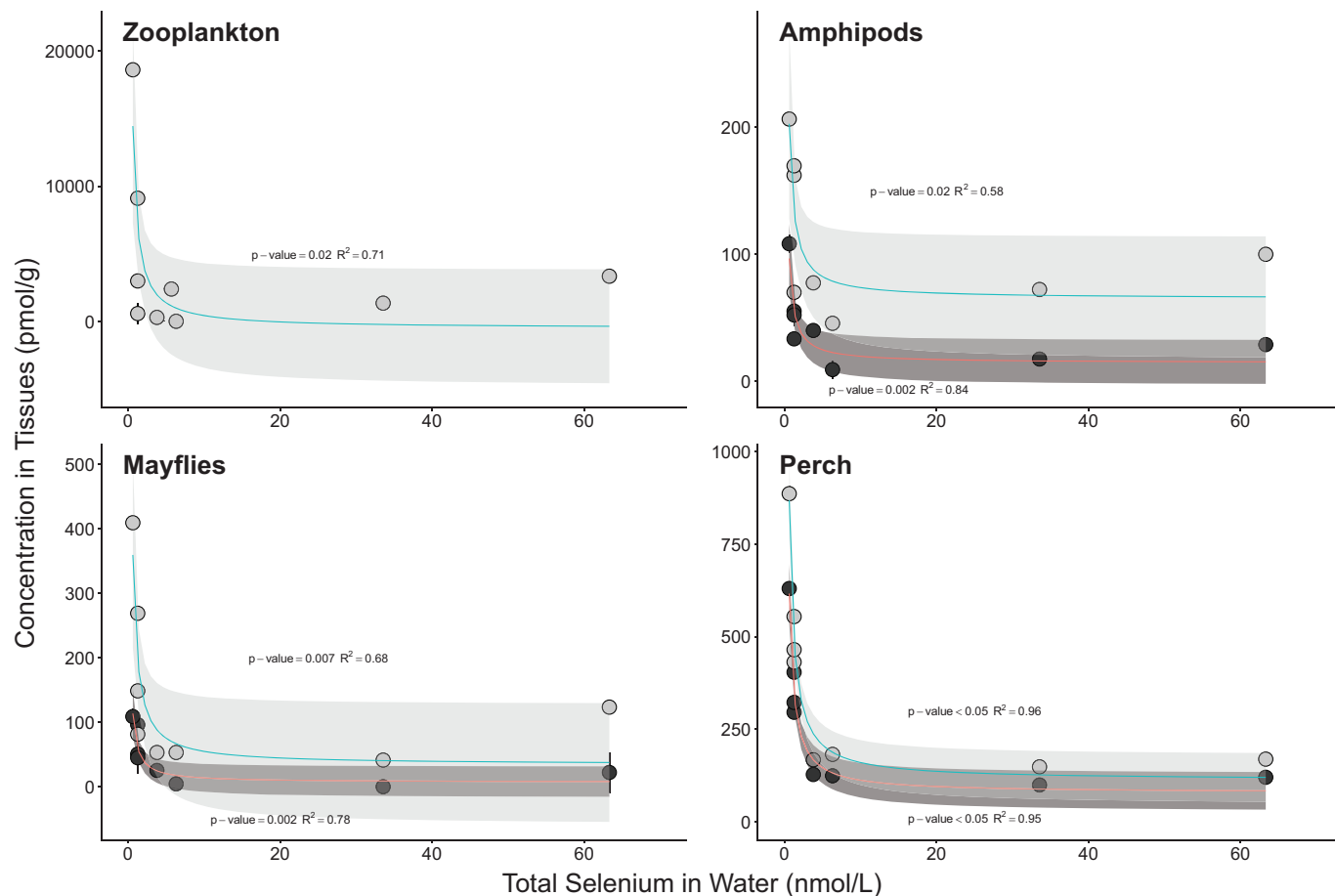
Total Se, total Hg, and MeHg in tissues between 2002 and 2017

We tested differences in concentrations of total Se in biota between the two years using analysis of covariance (ANCOVA). Two models identified significant results; the first model ($p = 0.002$, $r^2 = 0.44$, $F_{[2,18]} = 8.84$) identified that, for zooplankton, the intercept of total Se in 2002 was lower than that in 2017 with respect to distance from the smelters ($p = 0.021$), meaning that total Se concentration in zooplankton has increased overall. The second model ($p < 0.05$, $r^2 = 0.41$, $F_{[2,15]} = 6.83$) also identified the 2002 intercept as being higher than the value for 2017 for total Se in perch, with respect to distance ($p = 0.046$); therefore, total Se also increased in the 2017 sampling. In addition, total Hg and MeHg in tissue samples were not significantly different, with respect to distance from the closest smelter, between sampling years for any of the organisms ($p > 0.05$). However, there was a significant difference in the slopes of MeHg ($p = 0.001$) in mayfly tissue samples with respect to distance from the smelters in 2002 versus 2017 (ANCOVA analysis, $p < 0.05$, $r^2 = 0.91$, $F_{[3,15]} = 61.73$; Fig. 5).

Discussion

Total Se in lake water samples was inversely related to distance from the closest smelter stacks in all years (2002, 2017, and 2018), consistent with other studies in the Sudbury area, which show the effect of metal smelting emissions on water chemistry (Ontario Ministry of the Environment 1982; Keller 1994; Nriagu and Wong 1983). Interestingly, despite almost an 85% decrease in Se emissions, total Se in lake water increased rather than decreased be-

Fig. 4. Concentrations of methylmercury and total mercury in tissues with respect to concentrations of total Se in water for zooplankton, amphipods, mayflies, and perch. Black points represent the methylmercury concentrations and grey points represent the total mercury concentrations. Standard deviations of analysis replicates are shown for samples from July 2017. [Colour online.]

tween 2002 and 2017–2018 (Fig. 2). We also noted that total Hg in water decreased between 2002 and 2018, and although these concentrations are low, they do fall within the range of concentrations shown for Ontario lakes in the last few years (Brazeau et al. 2013; Environment and Climate Change Canada 2019). However, these temporal results should be interpreted with caution as we have only compared data from 2002 and 2017–2018.

Several factors may explain why total Se did not decrease following a reduction by stack emissions. First, it has been previously shown that catchment soils near the smelters are heavily contaminated with metals, and some studies have predicted that high metal concentrations in runoff water may continue for decades or even centuries after the smelting operations have come to an end (Nriagu et al. 1998). Increased runoff of Se from soil may therefore explain the patterns we observed.
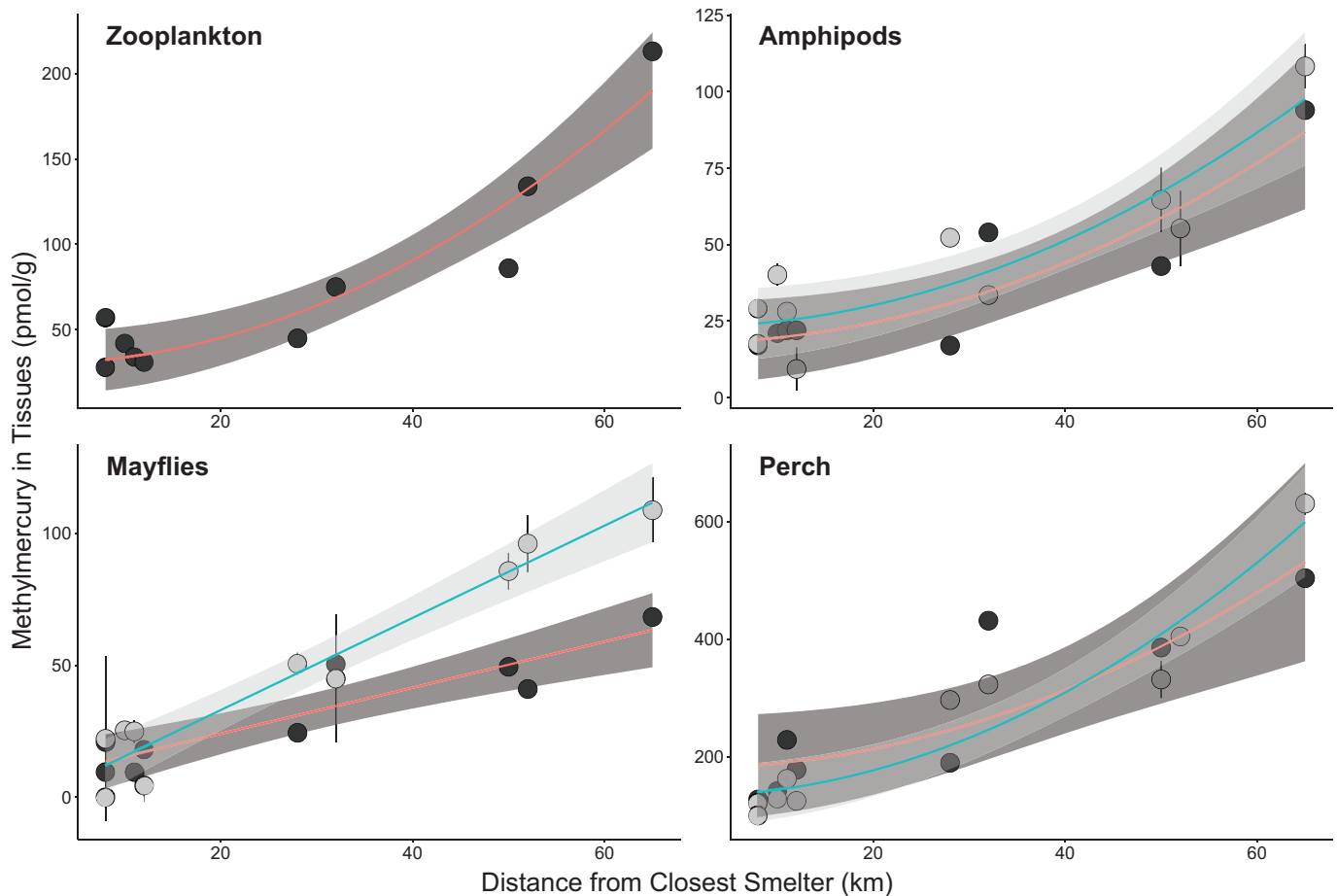
A second potential important source of Se is lake sediments. Se in sediments can be remobilized by oxidation processes, disturbance of the sediments by water turbulence or burrowing insects (Lemly 2002), decomposition of organic matter (Bowie et al. 1996), or by the desorption of Se from mineral phases (Sharma et al. 2015). Remobilization of Se from sediments has been shown to occur in two lakes near Sudbury smelters (Clearwater and McFarlane), though the authors did not state that this process could account for large quantities of Se mobilized to the water column (Belzile et al. 2000). Desorption of Se from iron or manganese oxyhydroxides in sediments occurs mostly because of changes in pH (Chapman et al. 2010); we did not observe a significant change in lake water pH

between the two sampling years; however, this does not exclude a possible pH change in sediments, which was not measured.

Finally, the overall increase in total Se in lake water between 2002 and 2017–2018 could be attributed to the retention time of Se in water, which studies have shown to vary widely from system to system (Hesslein et al. 1980; Southworth et al. 2000). Differences in Se retention time could be influenced by the retention time of lake water itself, by differences in primary productivity, or by chemical conditions that regulate the natural cycling dynamics and sedimentation rates (Lemly and Smith 1987). Typically, lentic systems such as lakes and wetlands allow Se to stay in the water column for longer periods of time (Lemly 2002; Presser and Luoma 2010) than for lotic systems such as rivers. In lakes, the slow-moving water allows Se species to be reduced into selenite and organic selenium, which are more likely to be associated with particulates, making Se more bioavailable to biota (Besser et al. 1993; Fernández-Martínez and Charlet 2009). Se tends to have a longer residence time once it is reduced, as it can be recycled in the water column through trophic interactions preventing its deposition and burial in sediments (Bowie et al. 1996; Chapman et al. 2010; Orr et al. 2006). Additionally, Se species have very slow oxidation rates (Cutter and Bruland 1984), further increasing the residence time of more bioavailable reduced Se species in the water column (Chen et al. 2005).

Our study replicated trends observed by Belzile et al. (2006), showing that total Se is inversely correlated with the accumulation of total Hg and MeHg in zooplankton, amphipods, mayflies,

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Fig. 5. Concentrations of methylmercury in tissues with respect to distance from the closest smelter for zooplankton, amphipods, mayflies, and perch. Black points represent the results from the sampling in July 2017, and grey points represent the results from Belzile et al. (2006). Standard deviations of analysis replicates are shown for samples from July 2017. [Colour online.]

and perch. Only MeHg in perch tissue samples significantly decreased with increasing total Se in tissue samples. However, total Se in water remained the best predictor of MeHg in perch. Our results are in line with others that have shown an antagonistic effect of Se in water on total Hg and MeHg bioaccumulation in animal tissues (Chen et al. 2001; Southworth et al. 2000). In this study, we offer the first assessment of the effect of Se on Hg species accumulation over a decade after a significant reduction in Se emissions.

A reduction in Se emissions and a reduction in total Hg in water between 2002 and 2017–2018 have not resulted in overall changes in total Hg or MeHg in biota. Mayflies appear to be the only biota for which the slope describing MeHg with respect to distance from the smelters changed between July 2002 and July 2017 (Fig. 4). MeHg burden in mayflies was greater in 2017 than in 2002 for lakes located further away from the stacks, but no change occurred in lakes located closer to the emission sources. Several other variables besides total Se may have affected MeHg in primary consumers such as mayflies. Such variables include MeHg in algae (Pickhardt et al. 2002), pH (Clayden et al. 2014), DOC (Rennie et al. 2005), or feeding patterns (Tremblay et al. 1996). It is also possible that the effects of a change in Se emissions in such a historically metal-contaminated environment is first detectable in the less impacted lakes at the edge of the deposition zone. We predict that over time, with continued low emission, a response of the biota will increasingly apply to lakes closer to the emission sources.

In conclusion, our results show that a reduction in Se emissions did not translate into less total Se in lake waters and emphasize the complexity of Hg accumulation in biota under these conditions. MeHg and total Hg burden in biota continues to be correlated with the total Se in the water column, 15 years after the original findings by Belzile et al. (2006). These results are important as they can help manage long-term recovery of mining-impacted aquatic systems and can inform future remediation strategies involving Se additions.

Acknowledgements

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