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Low concentrations of selenium in stream food webs of eastern Canada

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ABSTRACT

Herbivorous and predatory invertebrates and two species of fish (brook trout and blacknose dace) were collected from 49 streams in New Brunswick, Canada to determine whether concentrations of selenium (Se) in the biota were affected by a point source (a coal-fired power plant), and stream water chemistry (pH, sulphate, conductivity, and total organic carbon), and to determine the trophic transfer of Se through these food webs. Total Se concentrations in the biota were generally low (0.2 to 4.8 $\mu g\ g^{-1}$ dry weight) across sites and there was no relationship between distance from the coal-fired power plant and Se concentrations in invertebrates or fishes. Water chemistry was an equally poor predictor of Se concentrations in invertebrates and fish. Trophic position (determined using $\delta^{15}N$) was a significant predictor of Se concentrations in only five of the stream food webs, and two of these had negative slopes, indicating little or no trophic magnification across most systems; many fishes had lower concentrations than their invertebrate prey and trophic transfer was higher at sites with low invertebrate Se concentrations. Variability in Se concentrations in fishes was explained more by site of capture than microhabitat use within the site (as measured with $\delta^{13}C$), suggesting among-site differences in geological sources of Se. Because concentrations were below known toxicity thresholds for fish and other consumers, these results suggest that Se is not an environmental issue in New Brunswick streams that do not receive direct inputs from mining activities.

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1. Introduction

Selenium (Se) is an essential element with a narrow range of concentrations in the body of an animal above and below which negative health effects may occur (Hamilton, 2004). While Se becomes elevated in freshwaters as a result of human activities such as coal combustion and metal smelting (Nriagu, 1989; Belzile et al., 2006), some aquatic environments have naturally high Se concentrations because of the local geology (Presser et al., 1994). Much of the recent debate over Se effects, emission control and mitigation revolves around questions of the most appropriate matrix with which to set guidelines; using concentrations in water, sediment, and lower-trophic-level biota to assess Se risk for consumers (e.g. fish) is only appropriate if these concentrations can make accurate predictions further up the food chain where toxic effects might occur (Hamilton, 2004; Simmons and Wallschlager, 2005; Stewart et al., 2010). Therefore, reliable estimations of the trophic transfer of Se in food webs from both contaminated and uncontaminated environments are needed (Stewart et al., 2010).

Many contaminants, including metals, increase with increasing trophic level in a food chain (Thomann, 1989), leading to the highest concentrations in top predators and potential for toxic effects in these organisms. While some metals such as mercury (Hg, mainly as methylmercury) are well known to increase with trophic level in aquatic systems (Kidd et al., 1995; Jarman et al., 1996; Campbell et al., 2005), others such as lead actually decrease with increasing trophic level in the food web (e.g. Jarman et al., 1996). Results for Se, meanwhile, have been equivocal (Wang, 2002), with some studies reporting increases with trophic level (Barwick and Maher, 2003; Orr et al., 2006; Stewart et al., 2004; Muscatello et al., 2008) and others showing no predictable trend (Campbell et al., 2005; Jarman et al., 1996; Hillwalker et al., 2006). DeForest et al. (2007) summarized data from several lab trials and showed that trophic transfer factors (ratios of concentrations in consumers compared to that of their diet) for whole-body Se rarely exceed 1 for both fish and invertebrates, and that the uptake from food was highest when concentrations in the diet were lowest. When uptake from the diet varies as a function of dietary concentration, this is referred to as a "trophic transfer function" (TTF, Stewart et al., 2010). Defining the TTF for Se is necessary to guide accurate ecological risk assessments for this element (Stewart et al., 2010). The trophic transfer of Se in stream food webs has never been systematically measured, and most studies of Se in lotic systems focus on heavily contaminated sites (Reash et al., 2006; Wayland and Crosley, 2006). For these reasons, it is not well understood whether trophic position or prey selection is an important

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predictor of Se concentrations in stream biota and whether other biotic and abiotic factors affect levels of this metalloid in fish and their prey in these systems.

Biogeochemical processes in lentic environments, including thermal stratification, anoxia in the hypolimnion, and high organic C content of sediments, are thought to result in higher Se exposure for consumers compared to those in lotic environments (Simmons and Wallschlager, 2005; Hillwalker et al., 2006; Orr et al., 2006). All of these conditions in lentic habitats are believed to enhance the transformation of selenate and selenite to Se^0 and organic Se species which more readily enter the food chain (Simmons and Wallschlager, 2005). In addition, other chemical characteristics of the system are known to affect the bioavailability of Se; as examples, high sulphate concentrations reduce the bioconcentration of Se in lab-reared organisms (Hansen et al., 1993; Ogle and Knight, 1996), while higher concentrations of Se have been measured in biota from rivers with higher pH and conductivity (Saiki et al., 1993). This suggests that even in the absence of point sources of Se, water quality could influence Se in stream consumers, particularly in lentic microhabitats within the river network.

Sites of stationary combustion such as coal-fired power plants can emit large quantities of Se and Hg to the environment (Lemly, 2004). In the Sudbury region of Ontario, Canada, lakes that are near to metal smelters have high aqueous concentrations of Se (Nriagu and Wong, 1983) and low concentrations of Hg in biota (Belzile et al., 2006). At these sites, there are also inverse relationships between Hg and Se in fish tissues, with Se high and Hg low at sites near the smelter (Chen et al., 2001). Some have suggested that the presence of Se could limit Hg assimilation or increase demethylation (Iwata et al., 1982; Cuvin-Aralar and Furness, 1991); however, there are no recent evaluations of such processes in nature. Our previous studies in New Brunswick, Canada found that Hg concentrations of water striders (Hemiptera: Gerridae) in the immediate vicinity of a coal-fired power plant were lower than those at intermediate distances (Jardine et al., 2009), prompting us to examine whether Hg may be offset by high Se levels at sites closest to the point source. The power plant is also a source of sulphur dioxide (Meng et al., 1995; Jardine et al., 2009) and Se is known to co-accumulate in high S coal beds (Yudovich and Ketris, 2006) such as those used by this plant (Zhao et al., 1997).

There were four main questions to be answered in this study: 1) Does selenium increase with trophic level in New Brunswick stream food webs? 2) Are Se concentrations in invertebrates and fishes related to their proximity to the coal-fired power plant? 3) Does water chemistry (i.e. pH, conductivity, and sulphate concentration) predict Se in biota? and 4) Is there a relationship between concentrations of Se and concentrations of Hg in invertebrates and fishes? To answer these questions, we analysed Se in tissue samples (invertebrates and fish that had been previously analysed for Hg) that were collected from streams at varying distances from a coal-fired power plant, with a wide range in water chemistries, and used stable nitrogen isotopes (Kidd et al., 1995; Campbell et al., 2005) to quantify trophic enrichment of selenium.

2. Methods

2.1. Sample collection

Samples were collected at a total of 49 sites in New Brunswick, Canada in August and September 2006 and 2007. These stream sites were spread broadly across the province with most distant sites located more than 300 km apart, and the sites were forested 1st to 5th order streams that were located at varying distances from a coal-fired power plant (NB Power, Minto, NB) (for more details on site locations, see Jardine et al., 2009). Taxa collected varied across sites, and included a mixture of primary consumers (Pteronarcyidae, Hydropsychidae, and freshwater mussels), predatory invertebrates

(Gomphidae, Aeshnidae, Gerridae, Cordulegastridae, Megaloptera, and Perlidae) and two fishes (brook trout *Salvelinus fontinalis* and blacknose dace *Rhinichthys atratulus*). Water quality samples ($n = 1$ per site) were taken in polyethylene bottles at the same time as biotic collections were made. These samples were taken mid-stream in flowing water approximately 10 cm below the surface. A suite of measurements was made on each sample but analyses here focus on pH, sulphate, conductivity and total organic carbon (TOC). Biotic samples were collected with D-frame kick nets (invertebrates) and backpack electrofishing (fish), placed on ice and frozen upon return to the lab. Fish white muscle was removed from above the lateral line and invertebrates were analysed whole. Samples were freeze-dried for a minimum of 48 h and ground to a homogenate for analysis.

2.2. Analyses

A total of 279 samples were analysed for selenium, with between 5 and 12 samples per stream (Table 1). Analyses were conducted following methods outlined in Chen et al. (2001) and Belzile et al. (2006). The samples were digested with a microwave oven system (Milestone Ethos 1600 URM, HPR 1000/10, Bergamo, Italy) with a $HNO_3:H_2O_2$ of 8:2. The digestion program consisted of 5 consecutive steps: 1) room temperature to 90 °C in 5 min, 2) 90 to 150 °C in 10 min, 3) 150 to 210 °C in 5 min, 4) holding at 210 °C for 10 min, and 5) venting to cool down for 15 min. The total Se was determined with hydride generation atomic fluorescence spectrometry (PSA 10.055 Millenium Excalibur; PA Analytical, Orpington Kent, UK). The Limit of Detection (LOD) of the technique for total Se is 0.05 μg g^{-1} dry weight, and the Limit of Quantitation (LOQ) is 0.2 μg g^{-1} dry weight. All measurements are presented as μg g^{-1} total Se dry weight and all error terms are 1 S.D. Quality control was measured by analysing a certified reference material (DORM-2, Se = 1.40 ± 0.09 μg g^{-1}) which was found to have Se = 1.43 ± 0.13 μg g^{-1} ($n = 16$). Blanks were at or below the LOD and therefore samples were not blank corrected.

For the analysis of stable isotopes ($n = 279$), ~0.2 mg of dry tissue was loaded into tin cups and combusted in a Carlo Erba NC2500 Elemental Analyzer. Resultant CO_2 and N_2 gases were delivered via continuous flow to a Finnigan Delta XP mass spectrometer. Delta values are calculated according to $R_{sample}/R_{standard} * 1000$ where R is the ratio $^{15}N/^{14}N$ or $^{13}C/^{12}C$ and the standard is atmospheric N_2 or Peedee Belemnite carbonate, respectively. A commercially available standard routinely analysed in the lab that was calibrated against IAEA standards (acetanilide, Elemental Microanalysis Ltd., Okehampton, U. K., $\delta^{15}N = -1.2 \pm 0.2$‰, $\delta^{13}C = -33.2 \pm 0.2$‰, $n = 44$) and sample repeats (average $\delta^{15}N$ difference = 0.2 ± 0.2‰; average $\delta^{13}C$ difference = 0.2 ± 0.1‰, $n = 14$) were used to monitor the quality of the data. For total Hg data ($n = 278$), ~10 mg of dry sample was combusted in a Direct Mercury Analyzer, with DORM-2 and TORT-2 used as the CRMs (DORM-2 certified total Hg = 4.64 ± 0.26 μg g^{-1}, our analyses total Hg = 4.35 ± 0.14 μg g^{-1}, $n = 47$; TORT-2 certified total Hg = 0.27 ± 0.06 μg g^{-1}, our analyses total Hg = 0.28 ± 0.01 μg g^{-1}, $n = 27$). For methyl Hg data ($n = 41$), samples were analysed by GC–Mass Spectrometry following extraction using techniques described in Al-Reasi et al. (2007). DORM-2 was used as the CRM (certified methyl Hg = 4.47 ± 0.32 μg g^{-1}, our analyses methyl Hg = 4.21 ± 0.48 μg g^{-1}, $n = 21$).

2.3. Statistics

All statistical analyses were performed with NCSS software (Kaysville, UT). To reduce non-normality and heteroscedasticity, all Se and Hg data were log-transformed prior to analysis. Pearson correlations were used to determine if Se concentrations were inversely correlated with total and methyl Hg concentrations as has been observed previously (Chen et al., 2001). For these comparisons, concentrations were converted to molar concentrations (in nmol/g)

Table 1
Selenium concentrations in invertebrates and fishes and best-fit regressions relating total Se to $\delta^{15}N$ in streams in New Brunswick, Canada. Slopes significantly different from zero ($p<0.05$, asterisks) with positive slopes are indicative of trophic enrichment.

Site name	Lat	Long	n	Se inverts	Se fish	Slope	r^2	P
Albright's Corner Brook	46.01	66.18	6	1.2 ± 0.2^a	1.2 ± 0.1^x	<0.001	<0.001	0.995
Black River	45.33	65.78	11	$2.4 \pm 1.2^{a,b,c,d}$	$2.6 \pm 0.4^{x,y}$	0.260	0.347	0.057
Burpee Millstream	45.98	66.38	7	$1.2 \pm 0.6^{a,b,c,d}$	1.1 ± 0.1^y	0.072	0.118	0.452
Blue Rock Brook	46.38	66.07	5	$2.1 \pm 0.8^{a,e}$	1.7 ± 0.2^x	−0.148	0.200	0.450
Catamaran Brook-Middle Reach	46.86	66.19	7	0.9 ± 0.1^a	$1.5 \pm 0.3^{x,y}$	0.160	0.557	0.054
Coal Creek	46.12	65.81	5	3.5 ± 1.9^f	1.5 ± 0.4^y	−0.760	0.469	0.202
Clark Brook	46.06	65.54	10	0.9 ± 0.2^a	$1.0 \pm 0.1^{x,y}$	0.032	0.095	0.387
Corbett Brook	45.92	66.64	12	$1.0 \pm 0.4^{a,b,c,d}$	$1.5 \pm 0.6^{x,y}$	0.149	0.383	0.032*
Cow Pasture Brook	45.95	66.23	6	1.3 ± 0.2^a	1.0 ± 0.3^x	−0.870	0.474	0.130
Chockpish River	46.57	64.75	5	0.9 ± 0.1^a	1.1 ± 0.2^x	0.070	0.523	0.167
Caraquet River	47.71	65.15	5	0.9 ± 0.3^a	1.0 ± 0.3^x	−0.018	0.012	0.862
Cains River Downstream	46.54	65.84	5	1.6^g	$0.9 \pm 0.1^{x,y}$	−0.140	0.716	0.070
Cumberland Stream	46.04	65.87	8	$1.4 \pm 0.7^{a,b,c,f}$	1.4 ± 0.3^y	0.026	0.005	0.872
English Brook	46.43	66.60	6	1.1 ± 0.2^a	1.3 ± 0.5^y	0.068	0.122	0.496
Fulton Brook	46.06	66.14	5	1.2 ± 0.1^a	1.2 ± 0.2^x	−0.005	0.004	0.924
Gosnell Brook	46.19	66.10	6	$1.3 \pm 0.2^{a,h}$	1.3 ± 0.2^x	−0.020	0.060	0.641
Hutchinson Brook	46.19	65.83	6	$1.2 \pm 0.7^{a,b}$	1.2 ± 0.2^y	0.085	0.126	0.490
Kelly's Brook	45.94	65.78	7	$1.5 \pm 0.7^{a,b,i}$	1.0 ± 0.1^y	−0.174	0.266	0.236
Muzroll Brook Tributary	46.50	66.07	5	$0.9 \pm 0.1^{a,e,i}$	0.6^x	−0.072	0.246	0.395
McKenzie Brook	46.22	66.53	8	$1.3 \pm 0.7^{a,b,c}$	0.9 ± 0.2^y	−0.283	0.524	0.042*
McLeod Brook	45.73	65.36	6	1.0 ± 0.2^a	0.8 ± 0.1^x	−0.014	0.030	0.743
Newcastle Creek Tributary	46.14	66.12	5	1.5 ± 0.2^a	1.9 ± 0.4^x	0.118	0.467	0.203
Newcastle Creek Upstream	46.14	66.09	5	1.2 ± 0.1^a	1.6 ± 0.1^y	0.142	0.806	0.039*
Otter Brook	46.88	66.04	5	$2.0 \pm 0.5^{a,e}$	1.3 ± 0.1^x	−0.238	0.868	0.021*
Parks Brook	45.46	66.35	9	$1.9 \pm 0.8^{a,b,c,d,f}$	2.0 ± 0.2^y	0.130	0.129	0.342
Renous River @ Red Bridge Road	46.81	65.87	5	$1.3 \pm 0.7^{a,f}$	1.0 ± 0.2^y	−0.132	0.184	0.471
Restigouche Straight Reach	47.46	67.75	5	1.2 ± 0.4^a	1.0 ± 0.2^x	−0.059	0.153	0.516
Southeast Upsalquitch	47.54	66.50	5	1.4 ± 0.1^a	1.4 ± 0.1^x	<0.001	<0.001	0.999
South Branch Mill Brook	45.78	65.88	10	$1.2 \pm 0.2^{a,c,j}$	$1.6 \pm 0.4^{x,y}$	0.124	0.278	0.117
Smith Forks	46.96	66.58	5	$2.2 \pm 0.3^{a,g}$	0.8 ± 0.9^y	−0.406	0.761	0.054
Stratton Brook	46.19	65.75	5	1.1 ± 0.2^a	1.2 ± 0.3^x	0.055	0.128	0.555
Stickney Brook	46.38	67.57	5	0.7 ± 0.2^a	0.8 ± 0.2^y	−0.008	0.008	0.886
Six Mile Brook	46.48	65.83	5	0.9 ± 0.2^a	0.8 ± 0.2^y	−0.131	0.526	0.166
Starkey Brook	45.91	65.82	5	1.2 ± 0.1^a	1.3 ± 0.1^y	0.005	0.012	0.862
Trout Brook Tobique	46.78	67.51	7	$0.8 \pm 0.1^{a,c}$	0.7 ± 0.1^y	−0.044	0.220	0.288
Upper Libbie's Brook	46.89	66.39	5	1.9 ± 0.3^a	1.9 ± 0.4^x	0.019	0.012	0.858
Weldon Creek	45.89	64.72	7	$1.3 \pm 0.5^{a,b,c,d}$	1.6 ± 0.1^y	0.162	0.662	0.026*
Waweig River	45.25	67.14	6	$1.7 \pm 0.6^{a,d}$	2.1 ± 0.6^y	0.176	0.545	0.094
Young's Cove Brook	46.00	65.94	5	1.2 ± 0.2^a	1.2 ± 0.3^y	0.056	0.140	0.536

Letters indicate taxa: [a]*Aquarius remigis* water striders, [b]Megaloptera, [c]Perlidae, [d]Pteronarcyidae, [e]Odonata, [f]*Metrobates hesperius* water striders, [g]freshwater mussel, [h]Tipulidae, [i]Hydropsychidae, [j]Philopotamidae, [x]brook trout, and [y]blacknose dace.

using atomic weights of 78.96 and 200.59 g/mol for Se and Hg, respectively.

Our previous work showed that blacknose dace from these sites were more connected to in-stream carbon sources (% aquatic = $55.8 \pm 35.0\%$ using $\delta^{13}C$) while brook trout consumed terrestrial carbon (% aquatic = $5.1 \pm 12.9\%$; T.D. Jardine, unpublished data). Because the trophic transfer of Se in estuarine food webs is affected by the source of carbon and prey items consumed by higher-order consumers (Stewart et al., 2004), blacknose dace and their supporting food web were analysed separately from the brook trout and their food web. To evaluate patterns of trophic transfer in stream food webs, Se concentrations in dace were compared to concentrations in predatory invertebrates that rely ~50% on aquatic carbon (Perlidae stoneflies; Aeshnidae and Cordulegastridae dragonflies, *Metrobates hesperius* water striders, T.D. Jardine, unpublished data), while trout were compared to the water strider *Aquarius remigis*, a predaceous invertebrate that relies more heavily (typically ≪50% aquatic C) on terrestrial carbon in these systems (Jardine et al., 2005, 2008). Sites where we did not have data for these combinations were not included in the analysis.

We assessed the trophic transfer of Se using two methods. First, mean fish Se concentrations were regressed against corresponding predatory invertebrate Se concentrations within streams (dace against in-stream predators, trout against water striders). If the majority of the data fell above the 1:1 line, trophic enrichment was inferred because insectivorous stream fishes are approximately one

trophic level above predatory invertebrates (Anderson and Cabana, 2007). Total Hg data were also included on these plots for illustrative purposes, because Hg is known to biomagnify in streams (Chasar et al., 2009). The 2nd method used $\delta^{15}N$ to quantify the transfer of Se from prey to predator (Campbell et al., 2005). Sufficient data (minimum $n = 5$/site) were available to develop regression equations relating Se to $\delta^{15}N$ for a total of 39 sites. Each of the 39 sites had data for fish (dace only = 18 sites, trout only = 15 sites, both species = 6 sites) and predatory invertebrates, and a subset also had herbivorous invertebrates ($n = 12$ sites). Slopes significantly greater than zero at $\alpha = 0.05$ were considered indicative of trophic enrichment within sites.

Within each species of fish and for all predatory invertebrates, regression analyses were used to determine factors affecting concentrations of Se in these organisms across sites. Taxon-specific average Se concentrations within sites were regressed against water quality variables (pH, sulphate, conductivity, and TOC) and distance from the coal-fired power plant, with regressions considered significant at $\alpha = 0.05$. Sulphate, conductivity and distance from the power plant were log-transformed prior to the analysis to reduce non-normality. To assess if the variation in Se concentrations of dace was influenced by habitat use, data were split into three categories based on their $\delta^{13}C$. Algae growing in pools have isotope ratios that are enriched in ^{13}C compared to those growing in riffles (Finlay et al., 2002); thus we used $\delta^{13}C$ as an indicator of the relative use of pools and riffles by dace. There were three categories: 1) low $\delta^{13}C$ (< −30.1‰) indicative of feeding in riffles, 2) intermediate $\delta^{13}C$ (−30.1 to −26.1‰) within the

typical range of terrestrial material (-28.1 ± 0.9‰ S.D., Finlay, 2001) and 3) high $\delta^{13}C$ (>-26.1‰) indicative of feeding in pools. A one-way analysis of variance was used to test if dace from these three categories had different Se concentrations, and differences were considered significant at $\alpha = 0.05$.

3. Results and discussion

3.1. Selenium concentrations in stream organisms

Selenium concentrations in the fishes and invertebrates ranged from 0.2 to 4.8 µg g^{-1} dw, with an overall average of 1.4 ± 0.6 µg g^{-1}. Of the 126 invertebrate samples analysed, only three were above the proposed threshold of 3.0 µg g^{-1} that could cause toxic effects in their fish and bird predators (Lemly, 1993), while none of the 153 fish samples analysed had a concentration above the biological effect threshold of 4 µg g^{-1} (Lemly, 1993). Results suggest that Se is not a hazard in these New Brunswick streams. The sites we sampled had wide geographic coverage, including some near a suspected airborne point source (coal fired generating station), and they covered the range of values for water chemistry variables known to influence Se availability. However, because we did not randomly select stream sites on a probabilistic basis to facilitate broader conclusions (Peterson et al., 2009), or target sites receiving mining effluents (Wayland and Crosley, 2006), it is possible that elevated biotic Se may exist in some locations in the province. The higher proportion of fish above the Se toxicity threshold in the northwestern United States (15%, Peterson et al., 2009) may be due to the higher Se availability in soils in that region compared to eastern Canada (e.g. Kubota et al., 1967).

There have been few measurements of Se in stream food webs, particularly from uncontaminated environments. Andrahennadi et al. (2007) reported concentrations in stream insects in the range 5–10 µg g^{-1} in coal-mine impacted reaches of Luscar Creek and the Gregg River, Alberta, Canada. In a larger survey in the same region, Wayland and Crosley (2006) reported high Se concentrations in coal-mine affected (3.7 to 11.9 µg g^{-1} dw) and reference (3.8 to 7.3 µg g^{-1} dw) streams, suggesting that background levels in the region are elevated compared with the current study. May et al. (2001) found concentrations in benthic invertebrates from 1.5 to 18.0 µg g^{-1} dw (average = 7.6) in the Republican River of the midwestern US. These higher concentrations were attributed to irrigation with Se-rich groundwater throughout the river basin. Our results, with concentrations that range from 0.2 to 3.2 µg g^{-1} in fishes and 0.3 to 4.8 µg g^{-1} in invertebrates, constitute low environmental exposures. Our values (2 to 61 nmol/g, Fig. 1) are also lower than those for invertebrates and fishes from lakes near metal smelters (20 to 150 nmol/g, Belzile et al., 2006), suggesting that coal-fired power plants may not emit quantities of Se as large as those from other emission sources. However, we have not examined Se in the nearby lake that receives aqueous fly-ash discharge from the coal-fired power plant; previous

work has shown elevated Se concentrations and toxicity to fish associated with long-term disposal of this type of waste (e.g. Belews Lake, South Carolina, Lemly, 2002).

3.2. Relationships with the coal-fired power plant

Our data showed no relationship between the proximity to the coal-fired power plant and Se concentrations in local biota. There was no relationship between Se concentrations and distance from the coal-fired power plant for dace ($r^2 < 0.01$, $p = 0.806$, $n = 29$, Fig. 1), trout ($r^2 < 0.01$, $p = 0.910$, $n = 25$, Fig. 1), water striders ($r^2 = 0.03$, $p = 0.307$, $n = 41$, data not shown) or predatory invertebrates ($r^2 < 0.01$, $p = 0.977$, $n = 14$, data not shown). This may be due to the very low amounts of Se emitted from coal burning relative to Hg and S, as concentrations of Se are approximately 2000 times lower than S in coal (Interagency Monitoring of Protected Visual Environments, 1994). This and other coal-fired power plants may also emit low levels of Se compared with that released from other point sources such as metal smelters (e.g. Sudbury ON, Belzile et al., 2006). The Sudbury metal smelters have historically been identified as being one of the world's largest Se emission sources at approximately 2 tonnes per day (Nriagu and Wong, 1983), likely much larger than that emitted from the power plant in the current study.

3.3. Trophic enrichment of Se and Hg

Concentrations of Se in consumers were neither correlated with total ($r = 0.03$, $p = 0.634$, $n = 278$) nor methyl ($r = -0.17$, $p = 0.299$, $n = 41$) Hg concentrations (Fig. 2), suggesting no effect of Hg on Se concentrations in these stream food webs. Past studies have shown negative correlations between Se and Hg (Chen et al., 2001; Burgess et al., 2005; Belzile et al., 2006), although larger datasets reveal a wide variation in the relationship between the two elements in biota, ranging from Se:Hg molar ratios below 1:1 to greater than 500:1 in marine organisms (Dietz et al., 2000). In the current study, Se:methyl Hg ranged from 0.2 (1:5) to 85.2 (for Se:total Hg, range = 0.2 to 131), and only one sample was below 1:1. Only twelve samples were below 1:1 for Se:total Hg, all of which were from blacknose dace. This indicates a general excess of Se relative to Hg in body tissues of stream consumers, and supports what has been observed in other aquatic organisms (Dietz et al., 2000), including those from other streams in North America (Peterson et al., 2009).

The excess of Se relative to Hg occurs despite limited trophic enrichment of the former element. Concentrations of Se in predatory invertebrates were significantly related to those in fish, but there was little evidence for trophic enrichment (Fig. 3). Almost all data points fell between the 2:1 line and the 1:2 line (mean for dace and in-stream predators = 0.99 ± 0.43, $n = 12$ streams; mean for trout and water striders = 1.08 ± 0.29, $n = 23$ streams), indicating limited increase with trophic level, particularly when compared to a 1 to 7
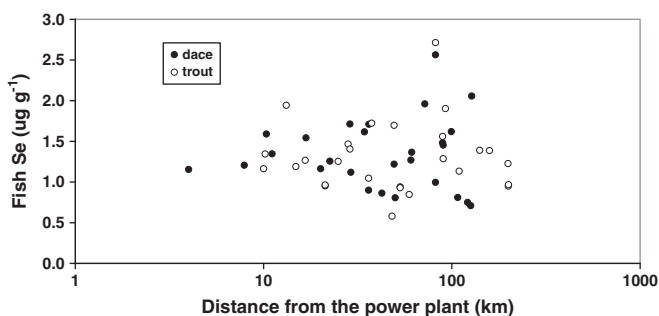

Fig. 1. Mean total Se concentrations (µg g^{-1} d.w.) in brook trout (open circles) and blacknose dace (solid circles) versus distance from a coal-fired power plant in streams in New Brunswick, Canada.
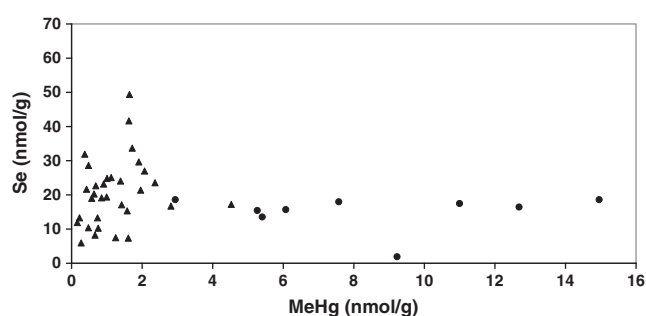

Fig. 2. Total selenium concentrations (nmol g^{-1} d.w.) versus methylmercury concentrations (nmol g^{-1} d.w.) in invertebrates (triangles) and fishes (circles) from streams in New Brunswick, Canada, sampled in August and September 2006 and 2007.
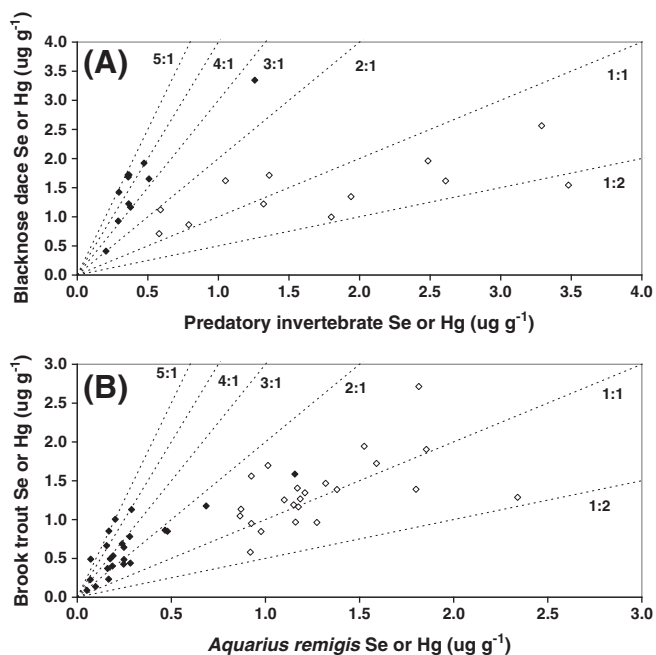
Fig. 3. Mean total Se (open diamonds) and Hg (solid diamonds) concentrations in fish versus concentrations in predatory invertebrates collected from streams in New Brunswick, Canada. (A) Blacknose dace versus predatory invertebrates (Odonata, Perlidae, *M. hesperius*); and (B) brook trout versus water striders (*Aquarius remigis*).

times increase in Hg with each increase in trophic level (DeForest et al., 2007, Fig. 3). Se-δ^{15}N slopes were significantly different from zero at only five of the 39 sites and, in two of these cases, slopes were negative (Table 1). Across all sites, slopes of these relationships averaged -0.05 ± 0.23 (range = -0.87 to 0.26), while r^2 averaged 0.31 ± 0.26 (range = <0.001 to 0.87). In contrast, using the same criteria (significant relationship between Hg and δ^{15}N) and data from the same samples, Hg trophic enrichment was observed in 32 of these 39 sites (Fig. 3; T.D. Jardine, unpublished data.). The simple explanation for this apparent paradox that Se does not exhibit trophic enrichment yet is almost always in excess of Hg (which does biomagnify) is that, on a molar basis, [Se] in lower trophic levels tend to be higher than [Hg] (Fig. 4). As such, animals lower in the food chain will always have Se in excess of Hg, while those animals at the top of food chains are slightly more likely to have Se:Hg <1 (e.g. piscivores in Peterson et al., 2009) and thus exhibit Hg toxicity because of a lack of the protective effects of Se (Ganther et al., 1972).

Although the majority of Se in consumer tissues is derived from the diet and not surrounding water (Besser et al., 1993), based on our data and those in the literature (DeForest et al., 2007) it appears as
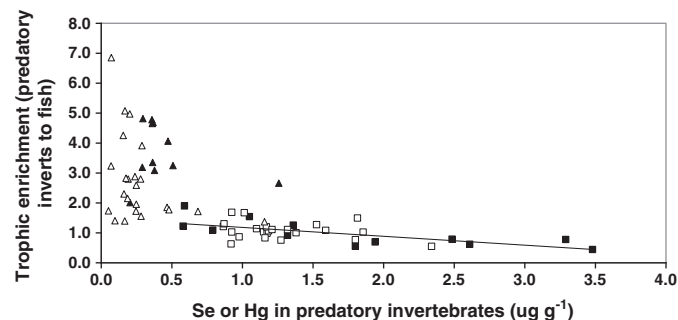

Fig. 4. Trophic enrichment as a function of Se or Hg concentration in predatory invertebrates for sites with blacknose dace and in-stream predators (Odonata, Perlidae, *M. hesperius*) (Se: solid squares; Hg: solid triangles) and brook trout and *A. remigis* (Se: open squares; Hg: open triangles).

though trophic enrichment of Se from invertebrates to fishes is a rare phenomenon. When lizards were fed with crickets that were laced with Se at a concentration of 30 µg g^{-1}, concentrations in the lizards stabilized at approximately 15 µg g^{-1}, corresponding to a TTF of 0.5 (Hopkins et al., 2005). Likewise, Hemipterans fed with Lepidopterans with varying Se concentrations resulted in a TTF of ~0.85 (Vickerman and Trumble, 2003). DeForest et al. (2007), in a literature survey, report TTFs for Se ranging from 0.1 to 1.4 for invertebrates and 0.4 to 1.3 in fishes (with a single value of 4.5). This is in contrast to Hg, that in the same review had TTFs ranging from 1 to 7 (DeForest et al., 2007) and has been shown repeatedly to increase with trophic level in stream (Chasar et al., 2009), lake (Kidd et al., 1995) and marine (Jarman et al., 1996; Campbell et al., 2005) food webs. However, the lack of clear trophic enrichment of Se in aquatic food webs does not preclude its importance as a toxic element to consumers. This is because Se can accumulate from low concentrations in water to high concentrations in low trophic level organisms, as described by an "enrichment function" (Stewart et al., 2010) and, as such, large Se exposures can occur in higher order consumers even if the transfer through trophic levels is low.

Other studies with δ^{15}N have also shown limited trophic enrichment of Se that is often dependent on the exposure route. In a marine food web there was a poor relationship between Se and δ^{15}N (slope = -0.004, $r^2 = 0.004$) in invertebrates, fishes, birds and seals (Campbell et al., 2005). Both Stewart et al. (2004) and Orr et al. (2006) found that trophic enrichment was habitat-specific and depended on the prey items being consumed. More specifically, in San Francisco Bay consumers connected to a clam-based food chain showed evidence of Se trophic enrichment, but those connected to a crustacean based food chain did not (Stewart et al., 2004). Biota from lentic sites in the Elk River, British Columbia, located downstream from coal mines showed trophic enrichment, whereas biota from reference sites and lotic exposure sites did not (Orr et al., 2006). Trophic enrichment of an element occurs when its rate of assimilation exceeds that of its elimination in consumers (Reinfelder et al., 1998; Wang, 2002). Se not only has a relatively rapid loss rate (0.01 to 0.03 day^{-1} in bivalves, 0.2 to 0.9 day^{-1} in copepods, and 0.02 to 0.09 day^{-1} in fish) but also can have a high assimilation efficiency (>50%, Wang, 2002), particularly if organo-Se species are the major dietary form. Elemental Se is less easily assimilated by higher trophic levels (Luoma et al., 1992) and parallels the lower assimilation of inorganic Hg relative to methyl Hg (Mason et al., 1996). The differences observed in Se trophic enrichment among systems may therefore reflect the balance between these two processes that are particular to the species involved and the dominant chemical species present. For example, the mysid *Neomysis mercedis* has a much more rapid Se loss rate (0.25 day^{-1}) than the bivalve *Potamocorbula amurensis* (0.025 day^{-1}), which results in much lower Se concentrations in the former than the latter taxa even though assimilation efficiencies from food are similar (>50%) (Stewart et al., 2004). These different loss rates resulted in higher concentrations in bivalves and organisms feeding further up this food chain, compared to mysids and their consumers in San Francisco Bay (Stewart et al., 2004). Unequal Se uptake rates can also occur in primary producers, as different species of phytoplankton differ by an order of magnitude in Se assimilation (Baines and Fisher, 2001). It is possible that the primary sources of carbon in streams (e.g. benthic algae and riparian trees) have a low Se assimilation efficiency, resulting in generally low concentrations in both aquatic and terrestrially dependent consumers.

Once in the food web, Se trophic transfer differed as a function of the concentration in prey. Fishes that had higher concentrations of Se in their diet (as indicated by predatory invertebrate Se concentrations) exhibited lower Se trophic enrichment (trophic enrichment = $-0.30 *$[predatory invertebrate Se] + 1.48, $r^2 = 0.36$, $p < 0.001$, Fig. 4), possibly reflecting a higher assimilation efficiency at low dietary concentrations for this essential element (Guan and Wang, 2004). This may also explain the discrepancy in trophic enrichment between Hg and Se observed here, as Hg concentrations

in predatory invertebrates were lower than those for Se and fish had correspondingly higher trophic enrichment (Fig. 4, DeForest et al., 2007).

The lack of a relationship between trophic level and total Se in our study may also be due to different Se species present in the two main trophic groups (invertebrates and fish). Organic selenides and diselenides were found to be the most common forms present in benthic insects from coal-mine impacted streams of western Canada, while biofilm contained a higher proportion of selenite and elemental Se (Andrahennadi et al., 2007); this suggests that different trophic levels in the current study could contain different Se species. If the proportion of organic Se does indeed increase with increasing food chain position, our measurement of total Se may have masked the true trophic enrichment of the organic Se species. Future studies that include Se speciation will likely illuminate some of the underlying variation in Se transfer through food webs.

3.4. Relationships with water quality

Most relationships between average Se concentrations in trout, dace, water striders or other predatory invertebrates and water quality variables were weak (Table 2). This was despite a wide range in sulphate (0.8 to 59.5 mg/L), pH (4.7 to 8.3), conductivity (19 to 502 μS), and TOC (1 to 33 mg/L) in the streams. Concentrations of Se in water striders were negatively related to stream conductivity ($r = -0.45$, $p = 0.004$), while Se in predatory invertebrates was negatively related to pH ($r = -0.49$, $p = 0.076$), although this relationship was not significant. This is in contrast to earlier work that showed strong positive correlations between Se concentrations in a variety of matrices and water chemistry (pH and conductivity, Saiki et al., 1993) and high sulphate concentrations reduced bioconcentration of Se into two invertebrates (*Daphnia magna* and *Chironomus decorus*, Hansen et al., 1993). At low sulphate concentrations and high dissolved selenate concentrations, Se concentrations in *Daphnia magna* increased considerably (Ogle and Knight, 1996). However, the Se concentrations used in those studies (Se = 50 to 500 μg/L, Ogle and Knight, 1996) were unlikely to be encountered in the streams sampled here.

One possibility for some of the unexplained variability in our data is the variation in microhabitat use of the different taxa. Animals that forage in pools likely have higher Se concentrations than those foraging in riffles of streams, similar to patterns observed previously for lentic versus lotic environments (Orr et al., 2006). The difference between these two types of systems is presumed to stem from the presence of more labile organic carbon in lentic habitats compared to lotic habitats, and higher oxygen content and flushing in lotic systems (Simmons and Wallschlager, 2005). However, in the current study there was no obvious link between $\delta^{13}C$ (as an indicator of habitat use, Finlay et al., 2002) and Se concentrations for dace (F = 2.71, df = 2, $p = 0.072$), suggesting that local geological sources and resultant effects of predatory invertebrate Se concentrations on trophic

enrichment were the primary drivers of Se availability to fishes. The $\delta^{13}C$ data, however, may also be confounded by feeding on terrestrial carbon and variability in algal $\delta^{13}C$ in pools versus riffles across sites, as dace use terrestrial C to varying degrees both within and among sites and those fish with $\delta^{13}C$ between −30.1‰ and −26.1‰ could be linked to any of the three possible sources (riffle algae, pool algae, and terrestrial detritus). Further exploration of the effect of stream microhabitat use on fish Se would likely require some telemetry and/or gut content analysis to facilitate a fuller understanding of foraging areas.

4. Conclusions

Our studies suggest that, as predicted by kinetic models (Wang, 2002), trophic enrichment of Se is a rare phenomenon in these stream food webs. Furthermore, the concentrations of Se are not a concern for fish and wildlife supported by these systems, and are consistent with previous, low Se measurements on the blood of fish-eating common loons (*Gavia immer*) in the region (Burgess et al., 2005). We found few relationships between Se in fish or invertebrates and water chemistry of the system or its proximity to a potential point source. Our data could serve as a low-selenium reference for streams in other locations that have high natural Se availability or are affected by point sources (e.g. coal mines, Wayland and Crosley, 2006), as well as furthering our understanding of the rates of trophic transfer of Se and other metals (Campbell et al., 2005). Future studies are needed to explore how different sources of carbon (autochthonous versus allochthonous) affect Se concentrations in stream-dwelling consumers, especially given the broad range of Se uptake capacities among primary producers (Baines and Fisher, 2001). This will help advance our understanding of the processes at the base of the food web that are likely to lead to high concentrations in upper-trophic-level organisms, and where management intervention at polluted sites may be necessary (Lemly, 2004).

Table 2
Relationship of selected water chemistry variables with average selenium concentrations in blacknose dace (n = 29), brook trout (n = 25), *Aquarius remigis* water striders (n = 41), and predatory invertebrates (Perlidae, Megaloptera, Odonata, n = 14) in streams in New Brunswick, Canada. Slope significantly different from zero (p < 0.05) is indicated with an asterisk.

Group	pH		Sulfate		Conductivity		Total organic carbon	
	r	p	r	p	r	p	r	p
Blacknose dace	-0.20	0.287	0.03	0.859	-0.13	0.503	-0.07	0.714
Brook trout	-0.13	0.547	-0.27	0.192	-0.22	0.281	0.01	0.979
Aquarius remigis	-0.25	0.108	-0.25	0.108	-0.45	0.004*	0.03	0.857
Predatory invertebrates	-0.49	0.076	-0.01	0.969	-0.06	0.827	0.31	0.275

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