Factors Affecting Water Strider (Hemiptera: Gerridae) Mercury Concentrations in Lotic Systems

Timothy D. Jardine†*, Karen A. Kidd†, Richard A. Cunjak‡§, and Paul A. Arp§

†Canadian Rivers Institute and Department of Biology, University of New Brunswick, Saint John, New Brunswick E2L 4L5

‡Canadian Rivers Institute and Department of Biology,

§Faculty of Forestry and Environmental Management, University of New Brunswick, Fredericton, New Brunswick E3B 5A3

(*24 September 2008; Accepted 12 January 2009*)

*To whom correspondence may be addressed (t.jardine@griffith.edu.au).

The current address of T.D. Jardine is Australian Rivers Institute, Griffith University, Nathan, Brisbane, QLD, Australia 411.

Abstract--Water striders (Hemiptera: Gerridae) have been considered as a potential sentinel for mercury (Hg) contamination of freshwater ecosystems, yet little is known about factors that control Hg concentrations in this invertebrate. Striders were collected from 80 streams and rivers in New Brunswick, Canada in August and September of 2004 through 2007 to assess the influence of factors such as diet, water chemistry and proximity to point sources on Hg concentrations in this organism. Higher than average Hg concentrations were observed in the southwest and Grand Lake regions of the province, the latter being the location of a coal-fired power plant that is a source of Hg (~100 kg annually) with elevated Hg concentrations in the lichen Old Man's Beard (*Usnea* spp.) in its immediate vicinity. Across all streams, pH and total organic carbon of water were relatively weak predictors of strider Hg concentrations. Female striders that were larger in body size than males had significantly lower Hg concentrations within sites, suggestive of growth dilution. There was no relationship between percent aquatic carbon in the diet and Hg concentrations in striders. For those striders feeding solely on terrestrial carbon, Hg concentrations were higher in animals occupying a higher trophic level. Mercury concentrations were highly variable in striders collected monthly over two growing seasons, suggesting short-term changes in Hg availability. These measurements highlight the importance of considering both deposition and post-depositional processes in assessing Hg bioaccumulation in this species. They also suggest striders may be more appropriate as a terrestrial rather than an aquatic Hg sentinel, underscoring the importance of understanding the origin of food for organisms used in contaminant studies.

Key words--Sentinel, Power plant, *Usnea*, Growth dilution, Trophic level

Introduction

Mercury (Hg) contamination of freshwater ecosystems remains a major problem in industrialized nations, with deposition from natural and anthropogenic sources and subsequent methylation leading to high Hg concentrations in fishes [1]. Human and wildlife health concerns surrounding consumption of Hg-contaminated fishes requires considerable research and monitoring efforts by government agencies [2] and losses of Hg-contaminated products (mainly fish and marine mammals) are estimated at billions of dollars globally [3].

Environmental sentinels hold great promise in providing efficient and ecologically relevant information on the regional and global distribution of contaminants [4]. Ideal characteristics of sentinel species include wide distribution, limited home range, well-known life history, moderate to high abundance, and simple taxonomic identification [4]. The predaceous water strider (Hemiptera: Gerridae) meets many of these criteria. One species, *Aquarius remigis* Say, is common and abundant on the surface film of streams and rivers across North America [5], has a home range that is restricted to approximately 100 m [6], and has Hg concentrations that have been correlated with those in small brook trout *Salvelinus fontinalis*, an important recreational fish species [7].

Despite an improved understanding of the Hg cycle over the past 40 years, several fundamental questions remain about the effect and extent of point source emissions on the surrounding environment, and the relative importance of atmospheric deposition compared with other abiotic and biotic processes such as water chemistry and food web characteristics. While mathematical models predict that reduced emissions from point sources such as coal-fired power plants will result in reductions in animal tissue concentrations [8] and certain studies have shown such concentration declines after emissions reductions [8,9], these decreases may not always be achieved due to complexities associated with water chemistry and biology [10]. Given the logistic issues surrounding the collection and analysis of fish samples for Hg on a broad geographic scale, water striders are envisioned as a rapid means of assessing spatial patterns in Hg bioaccumulation in lotic food webs [7]. Specifically, herein water striders were sampled in order to identify potential

Hg Hotspots and Areas of Concern, as have been reported previously for Northeastern North America [8].

The present study examined spatial variability and potential factors that influence Hg concentrations in water striders. First, preliminary sampling was conducted on a broad geographic scale in New Brunswick, Canada to assess the variation in strider Hg concentrations across the landscape. A study was then designed to assess spatial patterns in Hg deposition relative to a coal-fired power plant in New Brunswick, Canada, and determine if Hg concentrations in water striders reflect local deposition [11]. Lichen (*Usnea* spp., Old Man's Beard) were used as a second sentinel species since they are indicators of heavy metal contamination via atmospheric deposition [12]. A variety of other factors was examined as possible determinants of water strider Hg concentrations. For example, increased acidity [13] and dissolved organic matter content [14] of water, changes in growth and activity rates [15,16], and differences in feeding ecology [17] can all modulate Hg concentrations in aquatic biota. Differences in growth patterns among water strider species and sexes within sites were also examined to explain possible differences in Hg concentrations across sites. Mercury data from all sites were also compared with previously reported [18] stable isotope ratios of carbon ($^{13}C/^{12}C$ or $\delta^{13}C$) and nitrogen ($^{15}N/^{14}N$ or $\delta^{15}N$) as indicators of food source pathway (aquatic vs terrestrial) and trophic level, respectively, to assess the effects of feeding ecology on Hg concentrations in striders. Finally, seasonal and inter-annual changes in Hg concentrations were measured at four index sites sampled bi-weekly over two growing seasons. All of these measurements were done to assess the utility of water striders as environmental Hg sentinels, and determine the relative importance of atmospheric deposition and in-stream processes in affecting Hg concentrations in this organism.

Methods and Materials

Water striders were collected with hand nets from a total of 80 streams in New Brunswick (NB) from 2004 to 2007. In 2004 water striders were collected from 42 randomly selected streams (**Fig. 1a**) that represented the eight recreational fishing areas designated by the provincial authority

(NB Department of Natural Resources) and the major drainage basins in the province; these data were used to establish regional patterns of Hg concentrations. These sites were generally forested first to sixth order streams and rivers with cobble/gravel bottoms. Although four species of water strider were present at some sites (*Aquarius remigis*, *Metrobates hesperius*, *Limnoporus* sp., and *Gerris comatus*), adult *A. remigis* was most common and collections focused primarily on this species. *Metrobates hesperius* was also collected at nine of the sites in 2004, but it only occurred in sympatry with *A. remigis* at one site.

In 2005, *A. remigis* was collected from 13 streams, with preliminary sampling directed at locations near two coal-fired power plants operated by NB Power in Belledune (northern NB) and Grand Lake (south-central NB) (Fig. 1a). The Grand Lake plant, burning local high S coal (S content = 6.6%, [19]) at approximately 230,000 to 430,000 metric tons per year, is a source of low-grade sulphur dioxide [20] and also emits approximately 100 kg of Hg per annum [21]. The Belledune plant releases approximately 13 kg of Hg per annum [www.ec.gc.ca/npri, 21] but the presence of two other local sources (a metal smelter emitting ~30 kg Hg per annum and a chlor-alkali plant emitting ~32 kg Hg per annum, [22]) add further amounts of Hg to the local environment.

In 2006 a bullseye design was used to select sampling sites and map Hg concentrations in water striders and *Usnea* spp., with the Grand Lake generating station at the centre of the bullseye (**Fig. 1b**). Repeat sampling of the sites within the bullseye was done in 2007, due to an operational shutdown at the station in 2006 during the months of July and August (A. Bielecki, NB Power Corporation, personal communication). A minimum of one site was chosen within each section delineated by six radii (10, 20, 30, 50, 100, >100 km) and eight compass directions, yielding a total of 60 sites per year (Fig. 1b). Water striders were collected in August/September from these sites, with *A. remigis* again being the main target species (collected at 51 sites); *M. hesperius* was also collected when present (9 sites). Old Man's Beard was randomly sampled from two to five trees per site at the same locations sampled for water striders (Fig. 1b), and pooled into a single composite for analysis, for a total sample size of 60.

In all four years, water quality samples were collected during baseflow conditions (August and September, n = 1/site). In 2004 water samples were analyzed for total Hg and total organic carbon (TOC) with a Tekran Model 2600 (U.S. Environmental Protection Agency Method 1631) and a Technicon Traacs 800 auto analyzer, respectively. In 2005, water samples were analyzed for total Hg at the Environment Canada Laboratory in Moncton, NB, by flameless atomic absorption spectrometry after oxidation to inorganic mercury by sulphuric acid, dichromate and ultraviolet photo-oxidation and reduction with stannous sulphate in hydroxylamine sulphate - sodium chloride solution. The detection limit was 0.02 μg/L. From 2005 through 2007, water samples were analyzed for pH and TOC at the NB Department of Environment Analytical Laboratory (Fredericton, NB). Due to logistic constraints associated with the collection of large volumes of water at remote sites, in 2006 and 2007 water samples were not analyzed for Hg. Also, because the pH, TOC, and Hg of water samples was not being compared among years, no trials were performed to compare data generated by the different techniques.

In 2006 and 2007, water striders from four index sites (Corbett Brook, N 45.92 W 66.64, English Brook N 46.43 W 66.60, McKenzie Brook N 46.22 W 66.53, and Parks Brook N 45.46 W 66.35) were sampled bi-weekly from May to October to assess seasonal changes in Hg concentrations. *Aquarius remigis* adults and nymphs were collected at all four sites; *M. hesperius* was only present at Parks Brook and was not included in any temporal analyses.

For the strider samples collected in both 2004 and 2005, two to three composite samples of two individuals (sexes and wet weights not determined) per composite were analyzed for total Hg from each site. In 2006 and 2007, male and female striders were analyzed separately; males are readily discernable from females by inspection of genital morphology [23]. For each site, individuals were weighed to obtain wet weights and two to seven individuals were pooled for each sex. This yielded a mean wet weight and a single composite Hg concentration for each sex at each site on a given date.

In the laboratory, water strider samples were freeze dried for a minimum of 48 h and homogenized with a mortar and pestle. Lichen samples were cut with stainless steel scissors into 1 cm sections and freeze-dried prior to analysis. All instruments were cleaned with 10% hydrochloric acid between samples. All strider and lichen samples (2004-2007) were weighed to approximately 10 mg and analyzed for total Hg using a direct mercury analyzer (DMA 80, Milestone Microwave Laboratory Systems, Shelton, CT, USA). The direct mercury analyzer was routinely calibrated by analyzing a certified reference material at varying weights to yield a calibration curve that covered the range of Hg in the samples. Data are reported as µg/g dry weight. Samples were run with two certified reference materials – DORM-2 (dogfish muscle, National Research Council, Ottawa, ON, certified mean value Hg = 4.64 µg/g, 95% confidence interval = 4.38 to 4.90 µg/g) and IAEA 336 (lichen, International Atomic Energy Agency, Vienna, Austria, Hg = certified mean value = 0.20 µg/g, 95% confidence interval = 0.16 to 0.24 µg/g) – for water striders and Old Man's Beard, respectively. Recoveries of DORM-2 (n = 60) and IAEA 336 (n = 17) were 4.33 ± 0.17 µg/g standard deviation (SD) (93.3 ± 3.6% SD) and 0.16 ± 0.01 µg/g SD (78.2 ± 1.6% SD), respectively. The lower value for IAEA-336 is likely due to the aliquot received, as the same batch analyzed at a second lab (n = 33) yielded similar results (mean = 0.15 ± 0.01 µg/g, recovery = 76.5 ± 3.7% SD). Sample repeats yielded average standard deviations of 0.02 µg/g both within (n = 24) and across (n = 25) analytical runs, and blanks yielded Hg that was consistently less than 10% of sample Hg. To determine if the power plant was causing increased deposition of sulphur [20] and whether S and Hg concentrations exhibited similar deposition patterns, Old Man's Beard samples from 2006 were also analyzed for percent S using a LECO CNS 2000 elemental analyzer (LECO Instruments, Mississauga, ON, Canada).

Mercury concentrations in water striders were compared to their dietary habits using the previously-reported percentage of aquatic carbon (calculated using $\delta^{13}C$) and $\delta^{15}N$ data [18]. For analysis of stable isotopes, approximately 0.2 mg of each freeze-dried, ground sample was weighed into tin cups. Samples were analyzed with a NC2500 elemental analyzer connected to a Finnigan Delta XP mass spectrometer. Isotope data are expressed using delta notation in per mil (‰) according to: $(R_{sample}/R_{standard} - 1) \cdot 1000$, where R is the raw ratio of heavy to light isotope (e.g., $^{13}C/^{12}C$) and standards are Peedee belemnite carbonate and atmospheric nitrogen for carbon and nitrogen, respectively. Accuracy and precision were monitored with commercially available standards as described in [18].

A subset of water strider samples (*A. remigis*, n = 26; *M. hesperius*, n = 6) was analyzed for methyl Hg. These samples were selected from 14 sites sampled in 2005 and 2006 and approximated the range of total Hg concentrations observed (0.05 - 0.71 µg/g). Methyl Hg extractions were done using methods outlined in [24]. Resultant solutions were analyzed by gas chromatography-mass spectrometry on a Hewlett-Packard 6890 series with HP injector series 7683 following [25]. Recovery of a certified reference material (DORM-2) averaged 98 ± 12% SD (range = 83 to 118%, n = 13).

Data were analyzed using NCSS (Kaysville, UT) and SYSTAT (ver 9, SPSS, Chicago, IL, USA) software. All Hg data for striders and *Usnea* spp. were log-transformed prior to analysis to reduce heteroscedasticity and to normalize its distribution. Based on inspection of a probability plot, percent sulphur data for *Usnea* spp. were judged to be normally distributed and hence were not transformed. To assess general patterns of strider Hg concentrations from sampling done in 2004 and 2005, analysis of variance (ANOVA) was used with site nested within recreational fishing area (2004) and site nested within region (2005). Concentrations of methyl versus total Hg were compared first between species of water striders and then between sexes using analysis of covariance (ANCOVA, intercept representing percent methyl Hg) with methyl Hg as the dependent variable and total Hg as the covariate. Equivalency of slopes was tested prior to testing intercepts. Unless otherwise mentioned, α was set at 0.05 for all statistical analyses.

For Old Man's Beard data, we examined relationships between distance (independent variable) and Hg concentrations (2006 and 2007) or percent sulphur (2006 only; dependent variables) using linear regressions. Because the same sites were sampled in 2006 and 2007 (thus violating the assumption of independence of samples for multi-year models) and samples were pooled within sites, a paired *t* test was used to determine differences in Old Man's Beard Hg concentrations between these two years. The effect of compass direction on Hg in Old Man's Beard was tested separately for 2006 and 2007 using an ANCOVA, with direction (NW, NE, SE, SW) as the categorical variable and distance from the power plant as the co-variate.

Linear regressions were used to separately test the effect of distance from the power plant on water strider male and female Hg concentrations in each of 2006 and 2007. Two sites were excluded in 2007 as outliers in Hg versus distance plots, identified by R[student] > 2. Because data were from pooled samples, paired *t* tests were used to compare Hg concentrations in striders between the latter two years. An ANCOVA was used to test the effect of direction on strider Hg concentrations separately for sexes and years. Linear regressions were used to test the effect of different water chemistry variables on strider Hg concentrations (focusing on females in 2006 and 2007 because female Hg concentrations were highly correlated with those of males). For 2006 and 2007 data, a multiple regression model was used to test for the effects of distance from the power plant and pH (the most likely driver of changes in Hg due to water quality). To examine the influence of body size (as a surrogate for growth) on Hg concentrations, paired *t* tests were used to compare Hg concentrations and body weights between sexes within species and to compare Hg concentrations between *A. remigis* and *M. hesperius* at sites where they co-existed. Sites were used to pair sexes and species in these two analyses. The influence of percent aquatic carbon in the diet on strider Hg concentrations was tested using linear regression (again focusing on females in 2006 and 2007 for reasons noted above). For those sites with no contribution of aquatic carbon to strider diet (% aquatic carbon = 0%), Hg concentrations in striders were compared to their $\delta^{15}N$ as an indicator of trophic level. For this analysis it was assumed there was no variation in baseline $\delta^{15}N$

across sites since terrestrial organic matter shows little variation (e.g., alder, $\delta^{15}N$ = -1.0 ± 0.5‰ SD, range = -2.6‰ to 1.4‰, n = 92, T.D. Jardine, unpublished data).

For the data collected at the four index sites over the growing season, results were grouped into two generations (as in Jardine et al. [18]) - the first group returned to stream surfaces after overwintering (post-winter) and the second group was the new generation that hatched in early summer (pre-winter). Adults sampled in the period after ice-out in the spring up to and including the first day when a new generation of nymphs was present (typically early July) were considered as the post-winter sample. Adults sampled for the remainder of the growing season (July – October) were made up of a new generation and considered pre-winter. This latter period also corresponded roughly to the time period when the annual spatial sampling (bullseye) was conducted. The timing of the arrival of the new generation, and hence the delineation of the two samples, varied slightly from one stream to another. Originally, the intention was to examine whether Hg concentrations varied significantly over time and between sexes at the four streams that were regularly sampled by comparing adult water strider Hg concentrations across sampling periods using general linear model analysis of variance (GLM-ANOVA). The GLM-ANOVA had three factors – site (random factor: Corbett Brook, English Brook, McKenzie Brook, and Parks Brook), sex (fixed factor: male and female), and generation (fixed factor: post- and pre-winter) separately for the two years of data (2006 & 2007) with a Bonferroni-adjusted probability of 0.025. However, because several interactions were significant ($p < 0.025$) in this model, including site *x* generation and sex *x* generation, data were further separated into four groups - two generations in each of 2006 and 2007. Within each of these groups, a GLM-ANOVA was run with two factors – sex (fixed) and site (random). Bonferroni adjusted probabilities were used with $\alpha = 0.05/4 = 0.012$.

To compare Hg concentrations in adults and nymphs, mean values for males and females were compared to those of nymphs for those times that they co-occurred (mainly summer) with two factors (stage – fixed, and site - random) in a GLM-ANOVA with $\alpha = 0.05$.

Results

Samples collected in 2004 and 2005 revealed regional patterns in water strider Hg concentrations in New Brunswick. In 2004, total Hg concentrations in water striders ranged from 0.08 to 0.52 μg/g across the 31 sites. Concentrations were typically more elevated at sites in the southwest portion of the province while lowest concentrations occurred in the northern half of the province (**Table 1**, Fig. 1). There were no significant differences among recreational fishing areas (F = 2.12, degrees of freedon (df) = 7, p = 0.064), but strong differences among sites (F = 9.17, df = 26, p < 0.001) in this year. In 2005, total Hg concentrations in striders were also significantly different among sites (F = 25.72, df = 10, p < 0.001) and had a similar range (0.06 - 0.52 μg/g) across sites as those collected in 2004. Concentrations were significantly elevated in the Grand Lake region compared to the Belledune region (F = 3.89, df = 1, p = 0.047), despite a site immediately adjacent to the Grand Lake power plant having striders with the lowest concentration recorded (0.06 μg/g) (Table 1).

Most of the Hg in water strider tissues was in the form of methyl Hg (% methyl Hg = 87 ± 15% SD, range = 59 to 132%, n = 32, both species combined; values >100% stem from analytical error associated with methyl and total Hg determination), and there were no differences in percent methyl Hg between species (F = 0.79, df = 1, p = 0.382) or between male and female *A. remigis* (F = 0.24, df = 1, p = 0.627). A best fit equation for both sexes and both species relating methyl Hg to total Hg was: Methyl Hg = 0.865·Total Hg + 0.0025 (r^2 = 0.96).

Mercury concentrations in Old Man's Beard ranged from 0.06 μg/g to 0.52 μg/g and declined significantly with distance from the power plant in both 2006 and 2007 (p < 0.001, **Fig. 2a**). Sulphur concentrations in 2006 also declined with distance from the plant (p = 0.007, **Fig. 2b**), although the effect was not as strong as that observed for Hg (Hg versus distance r^2 = 0.41 in 2006, 0.29 in 2007; %S versus distance r^2 = 0.13, Fig. 2). There were differences in Hg concentrations between years for Old Man's Beard, with 2007 having significantly higher concentrations (t = 3.25, n = 51, p = 0.002). In 2006, there were significant differences among directions in Hg concentrations (F = 3.38, df = 3, p = 0.024), with sites to the northeast of the power plant having higher concentrations than sites to the southwest. In 2007, there were no significant differences among directions (F = 2.43, df = 3, p = 0.076).

In 2006 while the power plant was not operational, Hg concentrations in water striders showed no linear relationship with distance from the generating station for either females ($r^2 < 0.01$, n = 52, p = 0.902) or males ($r^2 < 0.01$, n = 51, p = 0.592) (**Fig. 3a**). In addition, there was no correlation between Hg concentrations in Old Man's Beard and concentrations in male ($r < 0.01$, $p > 0.05$) or female (r = -0.16, $p > 0.05$) water striders across sites for this year. In contrast to 2006, Hg concentrations in striders collected in 2007 significantly declined with distance from the plant in both females (r^2 = 0.12, p = 0.025, n = 49) and males (r^2 = 0.21, n = 46, p = 0.002) (**Fig. 3b**). Merucry concentrations significantly increased in males (t = 1.79, n = 40, p = 0.040) but not females (t = 0.97, n = 41, p = 0.169) in 2007 compared with 2006. There was no effect of direction on Hg concentrations in males or females in either 2006 or 2007 ($p > 0.05$).

Water quality variables were inconsistent predictors of Hg concentrations in water striders over the four years of study, accounting for a maximum of 64% of the variation when analyzed independently (**Table 2**). In 2004, significant relationships were observed between Hg in *A. remigis* and pH (r^2 = 0.38, $p < 0.001$), TOC (r^2 = 0.14, p = 0.030), and conductivity (r^2 = 0.22, p = 0.003). There was no relationship between Hg in striders and total Hg in water in 2004 for either strider species, but in 2005 a significant positive relationship between these two variables was observed for *A. remigis* (r^2 = 0.64, p = 0.008). Conductivity (r^2 = 0.51, p = 0.003) and TOC (r^2 = 0.41, p = 0.008) were also significant predictors of Hg in *A. remigis* in 2005 (Table 2). In 2006 and 2007, none of the water quality variables were significant predictors of Hg concentrations in *A. remigis* or *M. hesperius* (Table 2). When analyzed in a multiple regression with pH and distance as variables, trends were generally similar to those observed with distance or water quality variables alone. Stream-water pH had a weak but significant effect on female strider Hg concentrations in 2006 (r^2 = 0.10, p = 0.026) while distance had no effect (r^2 = 0.02, p = 0.310) and males showed no effect of pH ($r^2 = 0.06$, $p = 0.097$) or distance ($r^2 = 0.003$, $p = 0.682$). In 2007, female Hg concentrations were not affected by pH ($r^2 = 0.05$, $p = 0.122$) or distance ($r^2 = 0.04$, $p = 0.137$) but males showed a significant effect of distance ($r^2 = 0.10$, $p = 0.025$) and not pH ($r^2 = 0.04$, $p = 0.138$). When two outliers were included in the analysis, relationships between Hg concentrations and distance or pH were non-significant ($p > 0.05$) in the multiple regressions for males and females in both 2006 and 2007.

In both 2006 and 2007 there were between-sex differences in body size and Hg concentrations for both species of water striders. Female water striders were consistently larger than males (**Fig. 4a**). The difference in body weights between sexes was less pronounced in *A. remigis* (2006: mean % difference = 23.0 ± 10.8% SD, $t = 15.02$, n = 54, $p < 0.001$; 2007: mean % difference = 21.2 ± 14.8% SD, $t = 10.49$, $n = 47$, $p < 0.001$; Fig. 4a) than *M. hesperius* (2006: mean % difference = 61.9 ± 10.3% SD, $t = 15.79$, $n = 9$, $p < 0.001$; 2007: mean % difference = 65.4 ± 6.7% SD, $t = 19.33$, $n = 7$, $p < 0.001$; Fig. 4a). Male striders had higher Hg concentrations than females for both *A. remigis* (2006: mean % difference = 13.4 ± 31.9% SD, $t = 3.33$, $n = 50$, $p = 0.001$; 2007: mean % difference = 3.8 ± 7.6%, $t = 5.20$, $n = 47$, $p < 0.001$; **Fig. 4b**) and *M. hesperius* (2006: mean % difference = 53.7 ± 36.3% SD, $t = 5.65$, $n = 9$, $p < 0.001$; 2007: mean % difference = 58.1 ± 8.6% SD, $t = 18.41$, $n = 7$, $p < 0.001$; Fig. 4b). *Metrobates hesperius* had significantly higher Hg concentrations than *A. remigis* ($t = 2.98$, $n = 6$ sites, $p = 0.003$, data not shown) where the two species co-existed.

There was no relationship between percent aquatic carbon in the diet and Hg concentrations in *A. remigis* water striders ($p > 0.05$, **Fig. 5a**), however these analyses were limited given the large number of sites ($n = 22$ of 41, [18]) with striders having 0% aquatic carbon in the diet. For those striders that had aquatic carbon in their diets (2 - 100 %), their Hg concentrations fell within the range of those animals that relied solely on terrestrial carbon with one exception. Striders from a single site (Clark Brook, N 46.06 W 65.54) had atypically high Hg (average Hg = 2.0 µg/g) and were feeding mainly on aquatic food sources (average % aquatic carbon = 79%). For those striders with 0% aquatic carbon in the diet (i.e., entirely terrestrial feeders), $\delta^{15}N$ as a measure of trophic level explained significant variation in Hg concentrations, with high $\delta^{15}N$ (high trophic level) associated with high Hg ($r = 0.60$, $n = 25$, $p = 0.001$, **Fig. 5b**). By including distance from the power plant as a second variable in a stepwise regression, over half of the variation was accounted for ($r^2 = 0.53$), and both $\delta^{15}N$ ($p = 0.001$) and distance ($p = 0.012$) were significant.

Seasonal and inter-annual variation was high in *A. remigis* Hg concentrations at the four index sites (**Fig. 6**), but patterns in three of the four streams (exception Corbett Brook) were similar, with generally lower concentrations in the late summer/fall compared to spring. At Corbett Brook, the second generation of 2006 (adults from July to October) had Hg concentrations (0.40 - 0.60 µg/g) that remained high into the spring of 2007 after overwintering; in contrast, the second generation collected at this site in 2007 had lower concentrations (0.10 - 0.30 µg/g, Fig. 6) than those from 2006. During the pre-winter period when one-time sampling at 60 sites was conducted, the other three index sites had consistent concentrations between years. At all index sites, concentrations of Hg in males and females diverged in the spring, with male concentrations increasing relative to females (Fig. 6). Concentrations of Hg in females generally remained low (0.10 - 0.30 µg/g) throughout the growing season. Overall, there were several interactions ($p < 0.025$) in the statistical analyses between sexes, generations and sites, requiring a breakdown of the analysis. When analyzed separately by generation and year, post-winter males had significantly higher Hg than post-winter females in both 2006 ($F = 121.59$, $df = 1$, $p = 0.002$) and 2007 ($F = 48.07$, $df = 1$, $p = 0.006$). Hg concentrations among sites were not significantly different during the post-winter sample in 2006 ($F = 1.36$, $df = 3$, $p = 0.275$) but they were different in 2007 ($F = 5.26$, $df = 3$, $p = 0.004$). For pre-winter samples, Hg concentrations among sexes were not significantly different in either year (2006: $F = 3.72$, $df = 1$, $p = 0.149$; 2007: $F = 3.20$, $df = 1$, $p = 0.172$) but among sites were different during this time period in both years (2006: $F = 24.76$, $df = 3$, $p < 0.001$; 2007: $F = 4.73$, $df = 3$, $p = 0.010$). In 2006, nymphs had similar concentrations to adults ($F = 6.40$, *df* = 1, *p* = 0.086); in contrast, nymphs collected in 2007 had significantly lower Hg concentrations than those of adults (*F* = 28.51, *df* = 1, *p* = 0.013, Fig. 6).

Discussion

The present study examined the physical, chemical and biological factors affecting Hg concentrations in water striders collected across the province of New Brunswick, Canada. Variation in water strider Hg concentrations was related to distance from the coal fired generating station, sex, body size, and trophic level, highlighting the importance of both abiotic and biotic factors in determining Hg concentrations in this organism. Water striders revealed regional patterns of Hg concentrations in New Brunswick that may be related to atmospheric Hg deposition and landscape characteristics, with striders from the northern part of the province having lowest Hg concentrations and those from the southern part having highest concentrations. These organisms feed mainly on terrestrial carbon (>50%; [18]); this likely explains the weaker relationship between water chemistry parameters and their Hg concentrations, and suggests that striders may be more useful as indicators of Hg availability in the terrestrial rather than aquatic environment.

Spatial studies with sentinel species are useful for identifying areas of high and low contaminant concentrations [4]. In the present study, Hg concentrations in striders collected in 2004 were highest in the southwest region (Fig. 1 and Table 1) and generally decreased in a southwest to northeast direction; this pattern is consistent with studies on other organisms in the region [8]. In the earlier study, yellow perch (*Perca flavescens*) and loons (*Gavia immer*) from lakes in the Lepreau Region (southwest NB) showed elevated Hg concentrations. In the present study, Hg analyses of water striders and Old Man's Beard in 2006 and 2007 also showed elevated concentrations (>0.40 µg/g) in the Grand Lake region in south-central NB (Fig 2, 3). Areas characterized by higher concentrations of Hg in either water striders or *Usnea* spp. may potentially contain fish with high Hg concentrations, and therefore could be targeted as locations for more detailed food web sampling.

Concentrations of Hg in both sentinel species varied considerably among sites that were at similar distances from the coal fired generating station and this may be due to spatial variability in the atmospheric deposition of this pollutant. Prior monitoring and modeling efforts for the Grand Lake power plant revealed that S deposition was affected by: prevailing wind direction, which is generally directed towards the northeast; topography, with greater S deposition occurring on the ridges than valleys located along the northeast direction; plume height, as overall S deposition rates can be expected to decrease with increasing plume height; and variations in atmospheric stability, with highest S deposition patterns occurring during unstable and neutral conditions [20]. Deposition of Hg in this area could also be affected by these processes and explain some of the among-site differences for both striders and *Usnea* spp. at comparable distances from the generating station; however examination of these processes was beyond the limits of the present study.

We found increased concentrations of Hg in striders collected near the coal-fired power plant (~10-50 km away) in 2007 when compared to 2006, possibly due to the unanticipated shutdown that occurred during the first year of sampling. Given their strong linkages to terrestrial carbon [18], the main source of Hg for water striders would be from Hg in terrestrial insects, which could respond relatively quickly to changes in deposition rates via transfer from terrestrial vegetation [26]. Links have been shown to exist between Hg deposition from precipitation and Hg concentrations in biota [27], suggesting that on relatively large spatial and temporal scales, Hg deposition may predict areas with high Hg risk [27]. Determining the relationship between Hg deposition and Hg in water striders will require sampling across a much broader range of Hg deposition, such as that observed across North America [27], than that represented in this study.

In 2006 when striders and lichen were sampled during a shutdown of the generating station, only lichen showed decreasing Hg concentrations with increasing distance from the plant (Fig 2). In contrast, in 2007 when the plant was operational, both lichen and striders showed higher Hg concentrations at sites closer to the power plant. Differences in lifespan of these sentinel species and responsiveness to changes in atmospheric deposition may explain the among-year variability.

Consistently high Hg concentrations in *Usnea* spp. nearest the source may simply reflect a longer lifespan and Hg accumulation from previous years or decades when the power plant was operating at a greater capacity, burning coal with a higher concentration of Hg, or not yet using emission control technology. Striders, meanwhile, have a one-year lifespan and exhibit rapid turnover of their body tissues [18]; hence they are more likely to reflect recent exposure to Hg.

While Hg concentrations in striders and lichens were higher closer to the coal-fired generating station at Grand Lake (Figs. 2, 3), maximum concentrations of Hg occurred at different distances for these two sentinels. The major zone of influence indicated by lichens (~0-10 km from the power plant) is comparable to that found for a chlor-alkali plant in New Brunswick [22] and for ground level measurements of gaseous Hg around a chlor-alkali plant in Sweden [28]; in contrast, strider Hg concentrations peaked at distances 10 to 50 km from the generating station and were poorly correlated with Hg concentrations in *Usnea* spp. This suggests some differences in Hg exposure for the two sentinels, even though atmospheric deposition is expected to exert some control over Hg concentrations in both *Usnea* spp. (via direct uptake) and striders (indirectly via vegetation and riparian insects given the importance of terrestrial carbon in their diets, [18]). Although biogeochemical cycling of Hg is not well understood and the spatial differences between these two sentinel species cannot be explained at present, the variability in Hg concentrations may be due to the fact that lichen take up inorganic Hg directly either through gaseous or particulate-bound forms whereas Hg in striders (the majority of which is methyl Hg) would be affected by various chemical and biological processes after it is deposited onto the terrestrial or aquatic landscape and taken up into its prey. It is also possible that their concentrations reflect the deposition of different forms of Hg; lichen concentrations may be more reflective of particulate-bound Hg deposited closer to the generating station whereas strider concentrations may reflect higher deposition of gaseous forms of Hg^{2+} at distances further removed from the power plant [11]. In the Grand Lake Region, it is possible that deposition of Hg bound on particulates occurs closer to the power plant than the deposition of gaseous Hg^{2+}. Old Man's Beard situated to the northeast of the power plant had higher concentrations than those to the southwest in 2006, consistent with the prevailing wind direction for the area and previously measured patterns of SO2 deposition [20]. This suggests that dry deposition was an important source of Hg to lichens because most precipitation (i.e., storm events) originates from the opposite direction, the northeast.

Results from this study concurred with others that have found lower than expected Hg concentrations in aquatic consumers at sites immediately adjacent to emission sources [29,30]. Another possible explanation for the spatial differences between strider and lichen Hg concentrations described above may be due to decreased bioavailability of Hg to striders living closer to the power plant. This decreased bioavailability may be due to an inhibition of methylation of Hg or to the concurrent deposition of selenium [30]. For example, lakes near Sudbury, Ontario metal smelters with high Se concentrations in water have biota with lower total and methyl Hg concentrations than lakes far away from the smelters with low Se concentrations [30]. Selenium can interfere with Hg binding sites in proteins and thus limit Hg assimilation, as well as participating in the demethylation of methyl Hg [31]. While previous studies have not found unusually high Se concentrations in New Brunswick wildlife (e.g., [32]), these surveys were not conducted in the Grand Lake region. It is known, however, that Se co-accumulates with S in sulfide-carrying coal beds such as those of the Grand Lake area [33]. The local burning of this coal with a high S content of 6.6% [19] would therefore add Se as a logical associate to the local S and Hg emission and deposition patterns, but whether this deposition is sufficient to affect Hg uptake by striders remains to be resolved.

Water chemistry, particularly acidity and organic matter content, is typically a determinant of Hg concentrations in aquatic organisms [10]. Recent work on blackflies, which reside low on the food chain as primary consumers, showed strong relationships between Hg concentrations and pH and dissolved organic carbon [14], likely because low pH and high dissolved organic carbon may increase the availability of Hg to lower-trophic-level organisms [13]. In the present study striders had Hg concentrations that were not consistently correlated with pH and TOC of the streams across sampling years; however, among-site variability in water chemistry is likely inconsequential for species such as water striders that derive the majority of their biomass from the terrestrial environment [18] and are thus disconnected from processes occurring in the aquatic environment.

While relationships between Hg concentrations in water striders and stream water chemistry were inconsistent, there were consistent and significant differences within sites between sexes and species. Within sites, females of both species had larger body sizes and lower Hg concentrations than males. Males and females hatch and grow to adulthood at the same time, meaning differences in size are most likely due to differences in growth and differences in Hg between sexes suggest growth dilution of Hg by females [16]. Furthermore, *M. hesperius* attain smaller maximum body sizes than *A. remigis* (Fig. 4a, Fig. 5a) yet have higher Hg concentrations, suggesting a link between growth and Hg concentrations across species. Mercury concentrations in fishes can be affected by differences in feeding rates, food conversion efficiency and growth [15]. Since *A. remigis* populations in NB have a single generation each year (T.D. Jardine, unpublished data) and *A. remigis* mean adult body sizes differed between sites by 72% in males and 66% in females, among-site differences in body size likely reflect differences in growth and food availability. These growth differences among sites could therefore confound assessment of spatial patterns in Hg concentrations and contribute to some of the variability observed here.

The sex difference in growth and Hg for *A. remigis* is not due to source of food or trophic level as indicated by stable isotope studies of this species [18], but could be due to differences in feeding rate, activity level or loss of Hg during egg deposition. There are major differences between sexes in the spring in activity levels, where males aggressively seek out female partners for copulation (A. Sih, University of California, Davis, CA, USA, personal communication). Increased activity relative to food consumption can increase Hg concentrations [15], but body size and Hg differences between sexes are also evident during the fall. While it is also possible that females may lose part of their Hg burden via egg production, nymph Hg concentrations were similar to breeding females at all four sites suggesting no net loss of Hg through this pathway. During the late summer (pre-winter) when the majority of sampling was conducted, differences between males and females were not apparent and Hg concentrations were generally more stable at the index sites. However, inter-annual variation may be high at certain sites, e.g., Corbett Brook where Hg concentrations in late summer 2006 were approximately 0.45 μg/g and in late summer 2007 were approximately 0.15 μg/g. These large, unexplained changes in Hg concentrations indicate the short-term relevance of strider contamination levels relative to longer-lived species such as fish and possibly *Usnea* spp.

Stable isotope ratios suggested no link between carbon sources and Hg concentrations in striders. The majority of strider populations exclusively use terrestrial energy (22 of 41 sites had 0% aquatic carbon, [18]), and only in rare instances do striders derive the majority of their biomass from aquatic prey (7 of 41 sites had >50% aquatic carbon, [18]). There was no relationship between percent aquatic carbon in the strider diet and Hg concentrations (Fig 6a). The lack of a direct link between carbon source and Hg concentrations in striders contrasts to previous work in lakes, where animals connected to the pelagic zone have higher Hg concentrations than those that use littoral energy [17]. In the present study it was expected that animals foraging in streams on aquatic biofilm, which is a mixture of algae, fungi and bacteria, may be exposed to higher amounts of Hg due to methylation by sulfur-reducing bacteria [34]. However, this methylation of Hg requires anoxic conditions [34] that were rarely encountered in the well-oxygenated streams of this study (minimum dissolved oxygen concentration for sites sampled in 2004 = 6.4 mg/L, T.D. Jardine, unpublished data). Striders that use terrestrial carbon can get that energy either from consumption of terrestrial insects or of aquatic insects that process terrestrial particulate organic matter. These latter two sources are likely low in Hg due to limited methylation in the terrestrial environment [35,36]. Enhanced methylation has been shown, however, to occur as a result of the flooding of terrestrial vegetation [37], and the highest concentrations observed in the present study were at a site (Clark Brook) where strider Hg concentrations increased from 0.4 and 0.3 μg/g in 2006 to 2.1 and 1.8 μg/g in 2007 in females and males, respectively, possibly due to flooding of the area upstream of the site by beavers in the latter year (T.D. Jardine, personal observation). At this site, striders were feeding on aquatic prey (aquatic C = 79%), suggesting a link between methyl Hg release from flooded vegetation and subsequent uptake by algae. Flooding could therefore exert greater control over Hg concentrations in stream biota than all other factors examined here.

For those striders that were entirely connected to the terrestrial food source pathway, trophic level explained significant variation in Hg concentrations across sites (Fig. 6b), likely reflecting biomagnification stemming from the consumption of larger insects that are positioned higher in the food chain [38] or cannibalism. Water striders had a high proportion of their total Hg as methyl Hg, not surprising given their status as obligate predators and the enhanced biomagnification of methyl relative to inorganic mercury at higher trophic levels [13]. Earlier studies have shown that percent methyl Hg is related to position in the food chain for benthic invertebrates (e.g., 35-50% methyl Hg in grazers-detritivores and 70-95% methyl Hg in predators, [39]). Because methyl Hg is the more toxic form of Hg and subsequently of greater interest in fish, wildlife, and human health studies [1], a high proportion of total Hg as methyl Hg in a sentinel species is considered a positive attribute.

The combination of environmental sentinels in this study was useful for determining where follow-up work on Hg cycling may be warranted, as the two sentinels provided different types of information on Hg availability to ecosystems. While *Usnea* spp. provided a clear picture of Hg deposition near the power plant, water striders appeared more likely to reflect the complexities associated with Hg cycling within terrestrial and aquatic food webs. Spatial assessments of Hg contamination using water striders as a sentinel will therefore require an appreciation of their ecological characteristics (such as potential growth rates and trophic level) as well as variation in their Hg concentrations over the course of the growing season. In terms of absolute abundance, sampling striders in the fall provides the highest likelihood of capturing individuals in sufficient numbers to analyze for total Hg and methyl Hg, and to perform other analyses including stable isotopes or other contaminants. Due to their smaller body size, rapid growth rates, low Hg concentrations and limited availability, nymphs should only be sampled in studies concerned with ontogenetic or seasonal changes in Hg concentrations. Male striders present problems given their greater seasonal variability in Hg concentrations, particularly in the spring. This leaves females as the best candidate for sampling given their more stable Hg concentrations over time and their larger body size.

Overall, striders appear to have limited utility as a sentinel for aquatic Hg contamination simply because the majority of their biomass is derived from the terrestrial environment and they have no secondary route of exposure to this contaminant (i.e., waterborne Hg, [40]). However, a strong connection to the terrestrial environment may lend them to a role in linking measured Hg concentrations with predicted atmospheric Hg deposition, allowing a better understanding of spatial and temporal trends in Hg contamination, as well as serving as indicators of Hg concentrations in other organisms that consume terrestrial insects such as brook trout [7]. Also, their apparent ability to undergo rapid change in Hg concentrations (based on seasonal data) may make them useful as short-term indicators of Hg availability, although this would have to be tested through controlled experimentation. Understanding the poor correlation between Hg in striders and Hg in *Usnea* spp. will also require further examination to better model the relationship between Hg emissions, deposition, and resultant concentrations in aquatic biota.

Acknowledgement--The authors thank T. Arciszewski, P. Emerson, A. Fraser, S. Fraser, L. Giardi, K. Lippert, A. Townsend, J. Penny, T. McMullen, C. Blanar, C. Poole, R. Keeler, P. Brett, T. Barrett, R. Engelbertink, M. Sullivan, C. Ritchie, S. McWilliam, N. Swain, M. Sabean, M. Nasr, D. Perkman, L. Sweeney, D. Banh, J. O'Keefe, C. Paton, M. Savoie, A. McGeachy, O. Nwobu, E. Yumvihoze, L. Baker, B. Wyn, E. Campbell, and E. Belyea for field and lab assistance. Funding was provided by the O'Brien Humanitarian Trust, the NB Wildlife Trust Fund, the NB Environmental Trust Fund, the Grand Lake Meadows Fund, and the Natural Sciences and Engineering Research Council Discovery, Canada Graduate Scholarship and Canada Research Chair programs. Comments from H. Swanson, N. Burgess, and K. Munkittrick improved the quality of this manuscript.

References

1. Boening DW. 2000. Ecological effects, transport, and fate of mercury: A general review. *Chemosphere* 40:1335-1351.

2. Cunningham PA, Smith SL, Tippett JP, Greene A. 1994. A national fish consumption advisory database – A step towards consistency. *Fisheries* 19:14-23.

3. Hylander LD, Goodsite ME. 2006. Environmental costs of mercury pollution. *Sci Total Environ* 368:352-370.

4. Beeby A. 2001. What do sentinels stand for? *Environ Pollut* 112:285-298.

5. Andersen NM. 1990. Phylogeny and taxonomy of water striders, genus *Aquarius* Schellenberg (Insecta, Hemiptera, Gerridae), with a new species from Australia. *Steenstrupia* 16:37-81.

6. Fairbairn DJ. 1986. Does alary polymorphism imply dispersal polymorphism in the waterstrider, *Gerris remigis*? *Ecol Entomol* 11:355-368.

7. Jardine TD, Al TA, MacQuarrie KTB, Ritchie CD, Arp PA, Maprani A, Cunjak RA. 2005. Water striders (family Gerridae): Mercury sentinels in small freshwater ecosystems. *Environ Pollut* 134:165-171.

8. Evers DC, Han Y-J, Driscoll CT, Kamman NC, Goodale MW, Fallon Lambert K, Holsen TM, Chen CY, Clair TA, Butler T. 2007. Biological mercury hotspots in the Northeastern United States and Southeastern Canada. *BioScience* 57:1-15.

9. Hrabik TR, Watras CJ. 2002. Recent declines in mercury concentration in a freshwater fishery: Isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. *Sci Total Environ* 297:229-237.

10. Watras CJ, Back RC, Halvorsen S, Hudson RJM, Morrison KA, Wente SP. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci Total Environ* 219:183-208.

11. Schroeder WH, Munthe J. 1998. Atmospheric mercury - An overview. *Atmos Environ* 32:809-822.

12. Garty J. 2001. Biomonitoring atmospheric heavy metals with lichens: theory and application. *Crit Rev Plant Sci* 20:309-371.

13. Mason RP, Reinfelder JR, Morel FMM. 1996. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Environ Sci Technol* 30:1835-1845.

14. Harding KM, Gowland JA, Dillon PJ. 2006. Mercury concentration in black flies *Simulium* spp. (Diptera, Simuliidae) from soft-water streams in Ontario, Canada. *Environ Pollut* 143: 529-535.

15. Trudel M, Rasmussen JB. 2006. Bioenergetics and mercury dynamics in fish:A modeling perspective. *Can J Fish Aquat Sci* 63:1890-1902.

16. Karimi R, Chen CY, Pickhardt PC, Fisher NS, Folt CL. 2007. Stoichiometric controls of mercury dilution by growth. *Proc Nat Acad Sci USA* 104:7477-7482.

17. Kidd KA, Bootsma HA, Hesslein RH, Lockhart WL, Hecky RE. 2003. Mercury concentrations in the food web of Lake Malawi, East Africa. *J Gt Lakes Res* 29 (Suppl 2):258-266.

18. Jardine TD, Kidd KA, Polhemus JT, Cunjak RA. 2008. An elemental and stable isotope assessment of water strider feeding ecology and lipid dynamics: Synthesis of lab and field studies. *Freshw Biol* 53: 2192-2205.

19. Zhao J, Brereton C, Grace JR, Jim Lim C, Legros R. 1997. Gas concentration profiles and NO_x formation in circulating fluidized bed combustion. *Fuel* 76: 853-860.

20. Meng F-R, Bourque CPA, Belczewski RF, Whitney NJ, Arp PA. 1995. Foliage responses of spruce trees to long-term low-grade sulfur dioxide deposition. *Environ Pollut* 90:143-152.

21. Robinson-Lewis, L. 2000. Modifying the National Pollutant Release Inventory. Minister of Public Works and Government Services Canada, Ottawa, ON.

22. Sensen M, Richardson DHS. 2002. Mercury levels in lichens from different host trees around a chlor-alkali plant in New Brunswick, Canada. *Sci Total Environ* 293:31-45.

23. Fairbairn DJ, Vermette R, Kapoor NN, Zahiri N. 2003. Functional morphology of sexually selected genitalia in the water strider *Aquarius remigis*. *Can J Zool* 81:400-413.

24. Al-Reasi HA, Ababneh FA, Lean DR. 2007. Evaluating mercury biomagnifications in fish from a tropical marine environment using stable isotopes ($\delta^{13}C$ and $\delta^{15}N$). *Environ Toxicol Chem* 26:1572-1581.

25. Cai Y, Tang G, Jaffe R, Jones R. 1997. Evaluation of some isolation methods for organomercury determination in soil and fish samples by capillary gas chromatography-atomic fluorescence spectrometry. *Int J Environ Anal Chem* 68:331-345.

26. Hintelmann H, Harris R, Heyes A, Hurley JP, Kelly CA, Krabbenhoft DP, Lindberg S, Rudd JWM, Scott KJ, St.Louis VL. 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. *Environ Sci Technol* 36:5034-5040.

27. Hammerschmidt CR, Fitzgerald WF. 2005. Methylmercury in mosquitoes related to atmospheric mercury deposition and contamination. *Environ Sci Technol* 39:3034-3039.

28. Wangberg I, Barregard L, Sallsten G, Haeger-Eugensson M, Munthe J, Sommar J. 2005. Emissions, dispersion and human exposure of mercury from a Swedish chlor-alkali plant. *Atmos Environ* 39:7451-7458.

29. Anderson WL, Smith KE. 1977. Dynamics of mercury at coal-fired power plant and adjacent cooling lake. *Environ Sci Technol* 11:75-80.

30. Belzile N, Chen Y-W, Gunn JM, Tong J, Alarie Y, Delonchamp T, Lang C-Y. 2005. The effect of selenium on mercury assimilation by freshwater organisms. *Can J Fish Aquat Sci* 63:1-10.

31. Cuvin-Aralar MLA, Furness RW. 1991. Mercury and selenium interaction: a review. *Ecotoxicol Environ Saf* 21:348-364.

32. Burgess NM, Evers DC, Kaplan JD. 2005. Mercury and other contaminants in common loons breeding in Atlantic Canada. *Ecotoxicology* 14:241-252.

33. Yudovich Ya E, Ketris MP. 2006. Selenium in coal: a review. *Int J Coal Geol* 67:112-126.

34. Gilmour CC, Henry EA, Mitchell R. 1992. Sulfate stimulation of mercury methylation in fresh-water sediments. *Environ Sci Technol* 26:2281-2287.

35. Grigal DF. 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. *Environ Rev* 10:1-39.

36. Rudd JWM. 1995. Sources of methyl mercury to freshwater ecosystems: A review. *Water Air Soil Pollut* 80:697-713.

37. Hall BD, Rosenberg DM, Wiens AP. 1998. Methyl mercury in aquatic insects from an experimental reservoir. *Can J Fish Aquat Sci* 55:2036-2047.

38. Cabana G, Rasmussen JB. 1994. Modelling food-chain structure and contaminant bioaccumulation using stable nitrogen isotopes. *Nature* 372:255-257.

39. Tremblay A, Ludwig B, Meili M, Cloutier L, Pichet P. 1996. Total mercury and methylmercury contents of insects from boreal lakes: Ecological, spatial and temporal patterns. *Water Qual Res J Can* 31:851-873.

40. Hall BD, Bodaly RA, Fudge RJP, Rudd JWM, Rosenberg DM. 1997. Food as the dominant pathway of methylmercury uptake by fish. *Water Air Soil Pollut* 100:13-24.

Table 1. Total Hg (µg/g dry wt) in water striders collected in eight recreational fishing areas (as designated by the provincial authority in New Brunswick, Canada, see Fig. 1) in 2004 and two regions with point sources of Hg (Belledune and Grand Lake) in 2005 (*n* = No. of sites sampled). Different capital letters indicate significantly different means (tested separately for the two years of study).

Location	*n*	Total Hg (Standard Error)	Range
Recreational Fishing Area (2004)			
Southwest (SW)	6	0.26 (0.05)A	0.15 to 0.69
Lower St. John (LSJ)	4	0.22 (0.06)A	0.12 to 0.42
Inner Bay of Fundy (IBF)	5	0.20 (0.03)A	0.12 to 0.26
Upper St. John (USJ)	4	0.15 (0.04)A	0.08 to 0.27
Miramichi (MIR)	6	0.14 (0.01)A	0.10 to 0.17
Southeast (SE)	4	0.14 (0.02)A	0.09 to 0.19
Restigouche (REST)	4	0.13 (0.02)A	0.08 to 0.15
Chaleur (CHA)	3	0.13 (0.03)A	0.09 to 0.19
Region (2005)			
Grand Lake	6	0.35 (0.06)A	0.06 to 0.46
Belledune	7	0.15 (0.02)B	0.09 to 0.25

Table 2. Best-fit equations relating log-transformed water strider mercury concentrations and log-transformed water quality characteristics in New Brunswick, Canada streams. All equations are in

the form y = mx + b, n is the number of streams sampled, and TOC is total organic carbon. P-values in italics are significant at $\alpha = 0.05$.

Year	Species	n	Variable	Slope	Intercept	r^2	p
2004	*Aquarius remigis*	36	TOC	0.16	-0.90	0.14	*0.030*
			pH	-2.12	0.88	0.38	*<0.001*
			Water Hg			0.02	0.390
			Conductivity	-0.29	-0.27	0.22	*0.003*
	Metrobates hesperius	9	TOC	0.46	-0.96	0.24	0.171
			pH			<0.01	0.954
			Water Hg			0.33	0.109
			Conductivity			<0.01	0.933
2005	*A.remigis*	15	TOC	0.48	-1.01	0.41	*0.008*
			pH			0.09	0.300
			Water Hg	0.49	-0.85	0.64	*0.008*
			Conductivity	-0.52	0.33	0.51	*0.003*
2006	*A.remigis*	51	TOC			0.05	0.313
			pH			0.06	0.144
			Conductivity			0.02	0.328
	M.hesperius	9	TOC			0.29	0.145
			pH			0.12	0.514
			Conductivity			0.02	0.763
2007	*A.remigis*	49	TOC			0.04	0.208
			pH			0.01	0.561
			Conductivity			0.06	0.090

Figure Legends

Figure 1. Location of streams sampled in 2004 (open circles) and 2005 (open circles) (**A**) and in 2006 and 2007 (**B**) in New Brunswick, Canada. Point sources of Hg are marked with stars in the Belledune region and the Grand Lake region, and the Grand Lake power plant sits at the center of the bullseye in the years 2006 and 2007. Acronyms in (A) are recreational fishing areas designated by the Department of Natural Resources and include: SW (Southwest), LSJ (Lower St. John), IBF (Inner Bay of Fundy), USJ (Upper St. John), MIR (Miramichi), SE (Southeast), REST (Restigouche), and CHA (Chaleur).

Figure 2. Mean total mercury concentrations (µg/g dry wt) (**A**) and mean percent sulphur (dry wt) (**B**) in Old Man's Beard (*Usnea* sp.) relative to distance from a coal-fired power plant in New Brunswick, Canada in 2006 (open circles, solid best-fit line) and 2007 (solid diamonds, hatched best-fit line).

Figure 3. Mercury concentrations in female (solid diamonds, solid best-fit line) and male (open circles, hatched best-fit line) water striders (*Aquarius remigis*) in New Brunswick, Canada in 2006 (**A**) and 2007 (**B**) relative to distance from a coal-fired power plant (Fig. 1).

Figure 4. Correlation between male and female wet weights (**A**) and mercury concentrations (**B**) for *Aquarius remigis* in New Brunswick Canada streams in 2006 (open diamonds, solid best-fit line) and 2007 (solid diamonds, hatched best-fit line). Inset: Correlation between male and female wet weights (**A**) and mercury concentrations (**B**) for *Metrobates hesperius* in 2006 (x, solid best-fit line) and 2007 (+, hatched best-fit line).

Figure 5. Mercury concentrations in *Aquarius remigis* in New Brunswick Canada streams in relation to (**A**) the percentage of aquatic carbon in the diet, and (**B**) $\delta^{15}N$ as an indicator of trophic level for those streams with water striders having 0% aquatic carbon in the diet.

Figure 6. Total mercury concentrations (µg/g dry wt) in *Aquarius remigis* females (solid diamonds), males (open circles) and nymphs (open triangles) from four New Brunswick, Canada streams during the growing season in 2006 and 2007.

Figure 6.

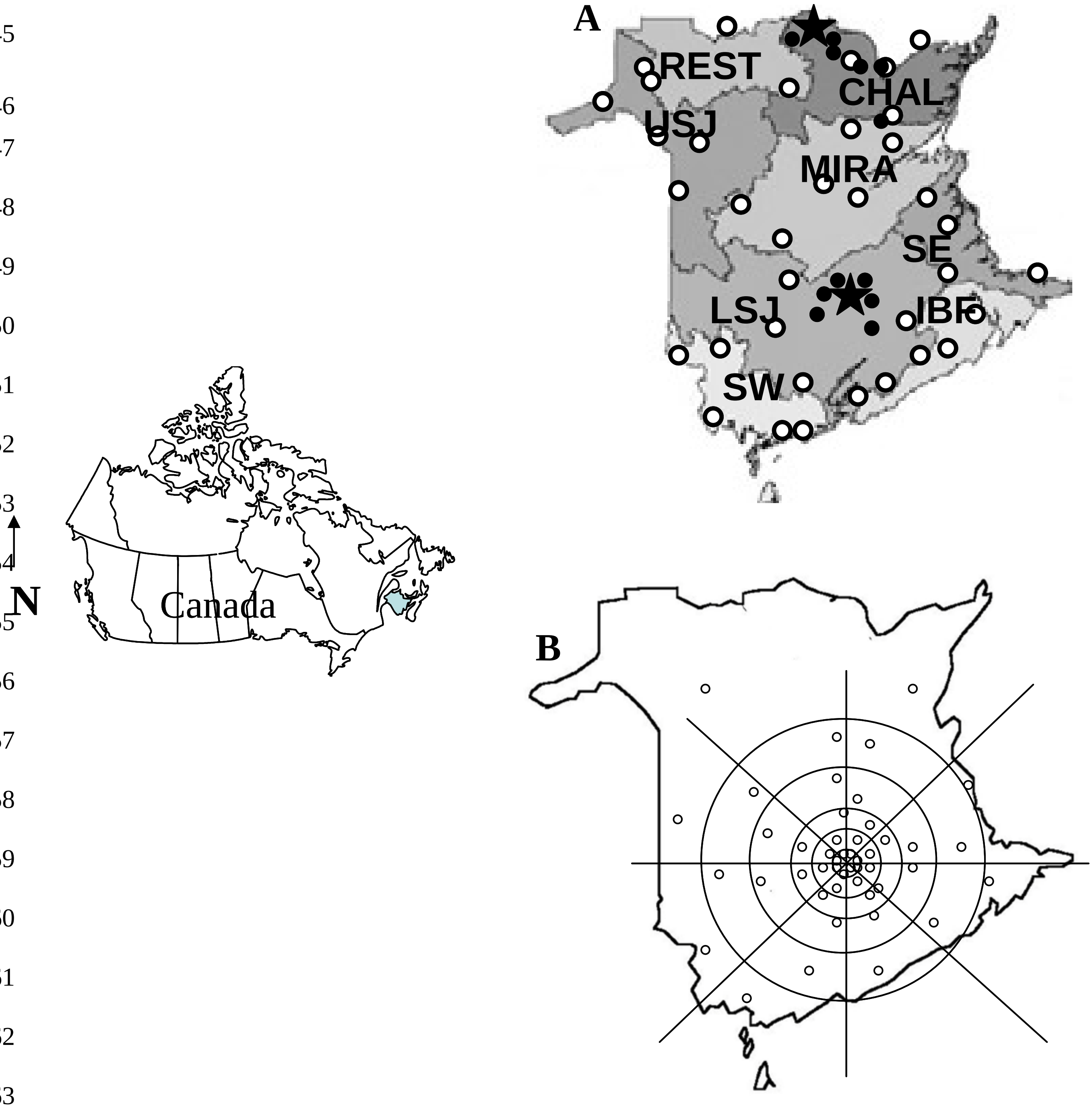


Figure 7.

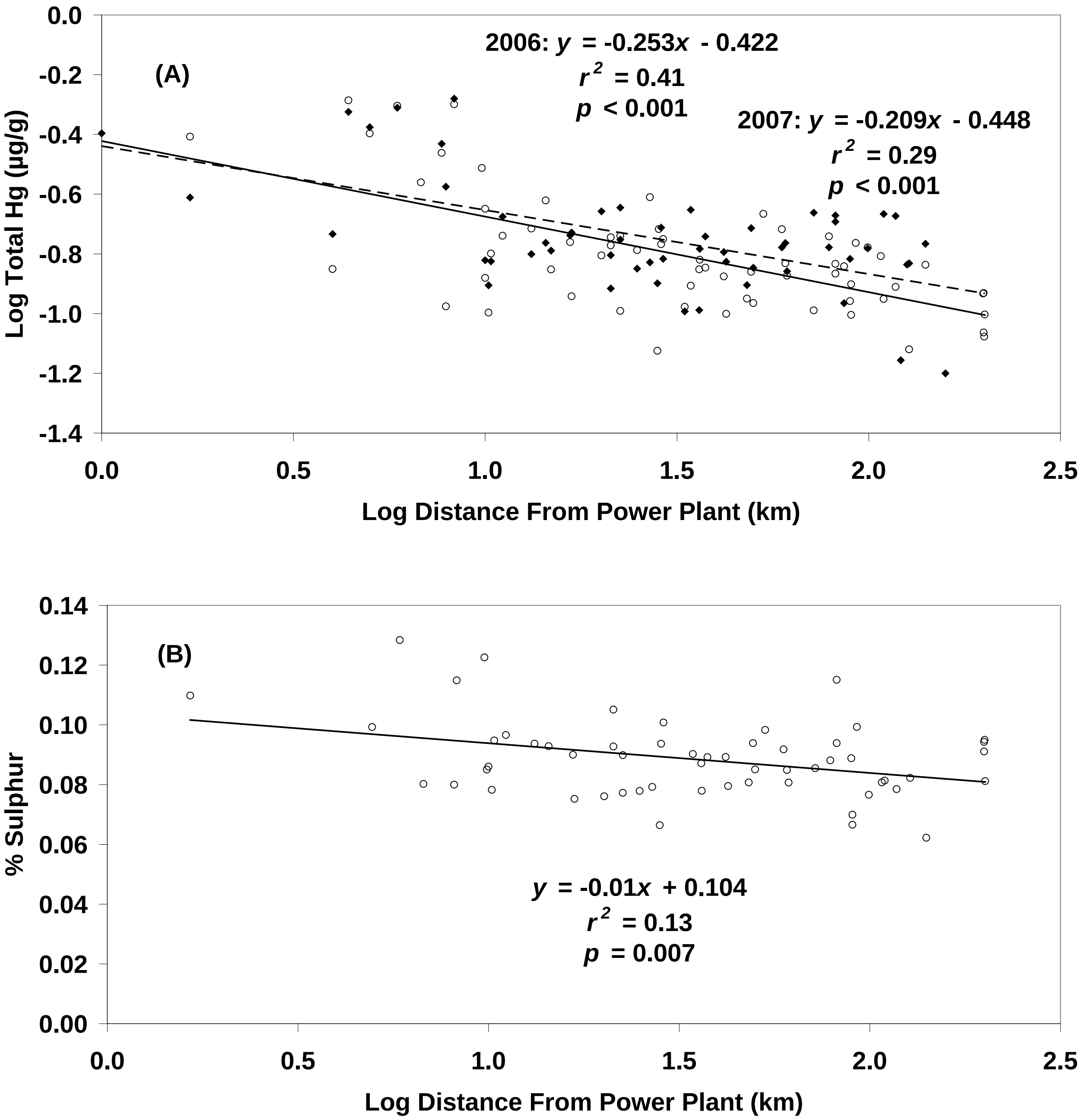

(A)
2006: y = -0.253x - 0.422
r2 = 0.41
p < 0.001
2007: y = -0.209x - 0.448
r2 = 0.29
p < 0.001
Log Total Hg (µg/g)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0.0
0.5
1.0
1.5
2.0
2.5
Log Distance From Power Plant (km)
(B)
y = -0.01x + 0.104
r2 = 0.13
p = 0.007
% Sulphur
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.0
0.5
1.0
1.5
2.0
2.5
Log Distance From Power Plant (km)

Figure 8.

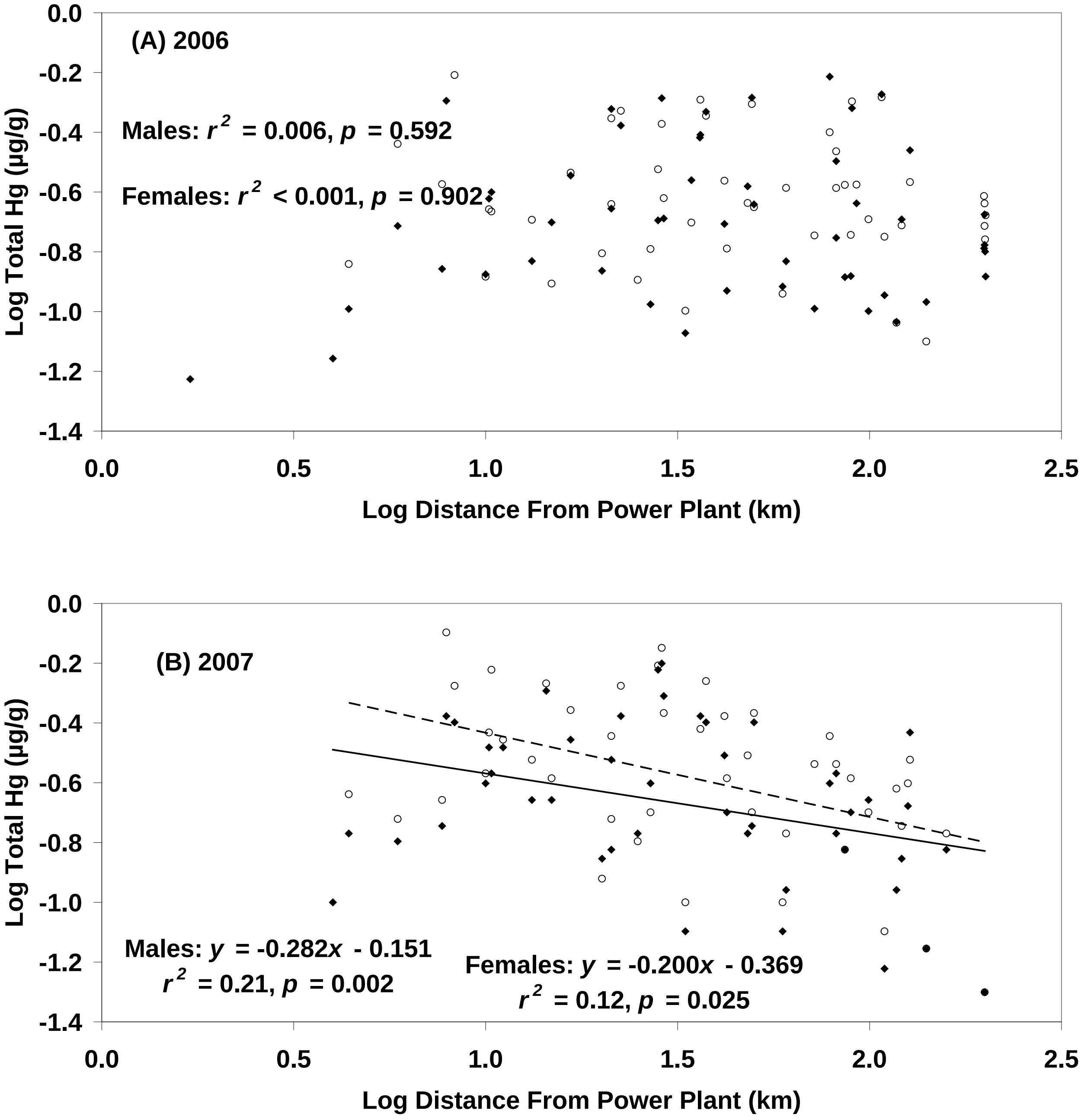

(A) 2006
Males: r^2 = 0.006, p = 0.592
Females: r^2 < 0.001, p = 0.902
Log Total Hg (µg/g)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0.0
0.5
1.0
1.5
2.0
2.5
Log Distance From Power Plant (km)
(B) 2007
Males: y = -0.282x - 0.151
r^2 = 0.21, p = 0.002
Females: y = -0.200x - 0.369
r^2 = 0.12, p = 0.025
Log Total Hg (µg/g)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0.0
0.5
1.0
1.5
2.0
2.5
Log Distance From Power Plant (km)

Figure 9.

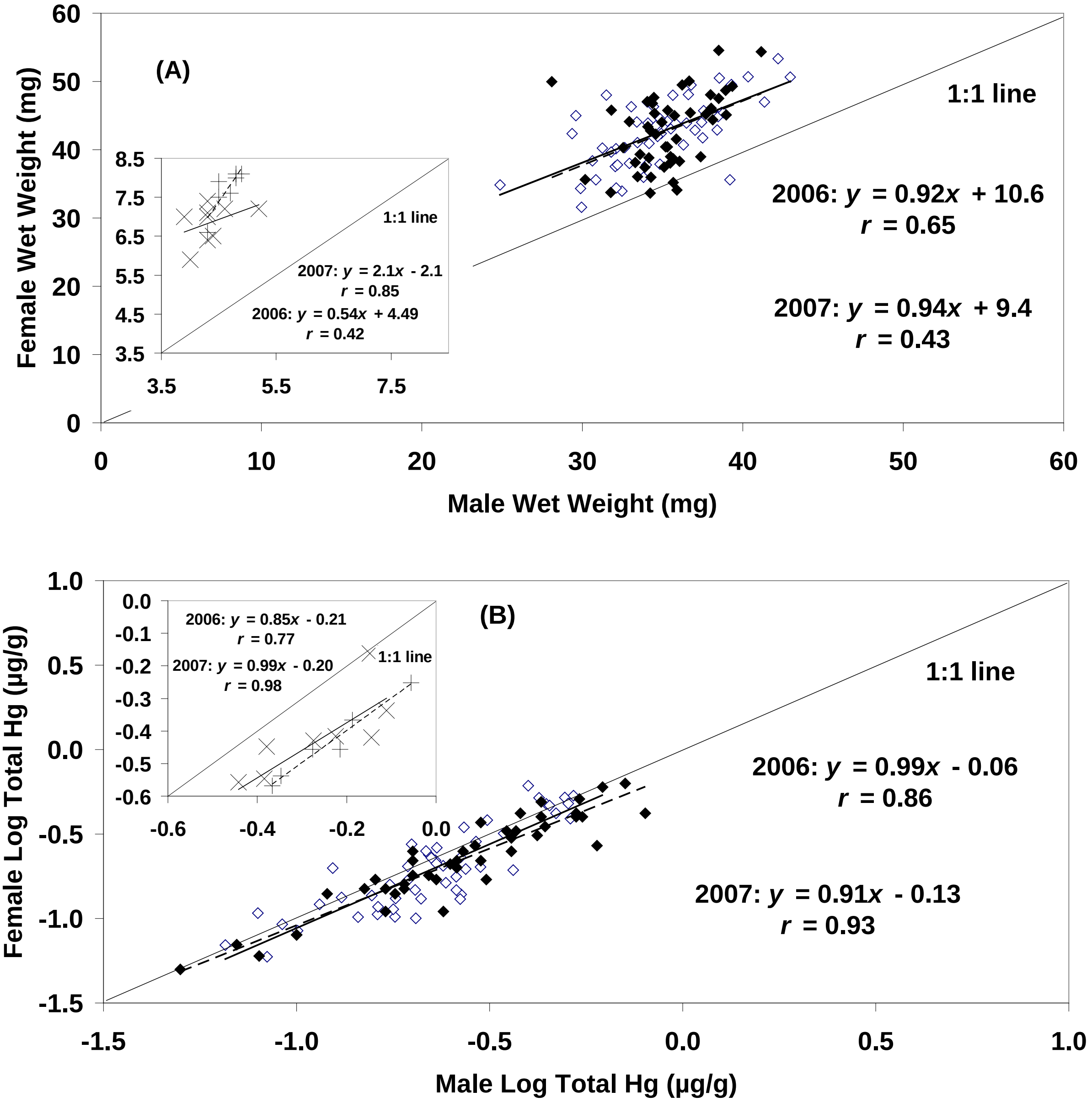

(A)
Female Wet Weight (mg)
Male Wet Weight (mg)
0
10
20
30
40
50
60
1:1 line
2006: y = 0.92x + 10.6
r = 0.65
2007: y = 0.94x + 9.4
r = 0.43
8.5
7.5
6.5
5.5
4.5
3.5
3.5
5.5
7.5
1:1 line
2007: y = 2.1x - 2.1
r = 0.85
2006: y = 0.54x + 4.49
r = 0.42
(B)
Female Log Total Hg (µg/g)
Male Log Total Hg (µg/g)
1.0
0.5
0.0
-0.5
-1.0
-1.5
1:1 line
2006: y = 0.99x - 0.06
r = 0.86
2007: y = 0.91x - 0.13
r = 0.93
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.6
-0.4
-0.2
0.0
2006: y = 0.85x - 0.21
r = 0.77
2007: y = 0.99x - 0.20
r = 0.98
1:1 line

Figure 10.

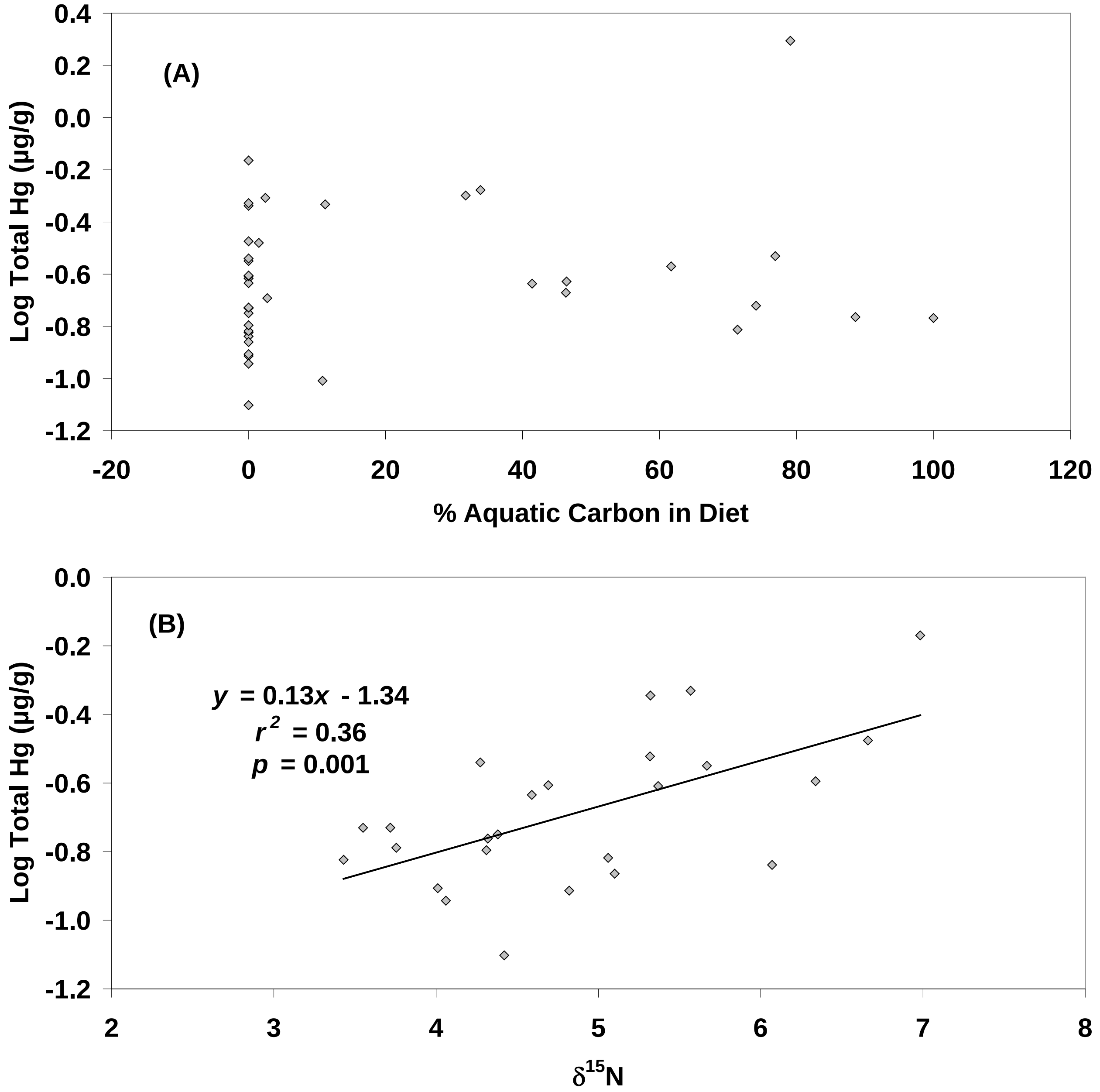
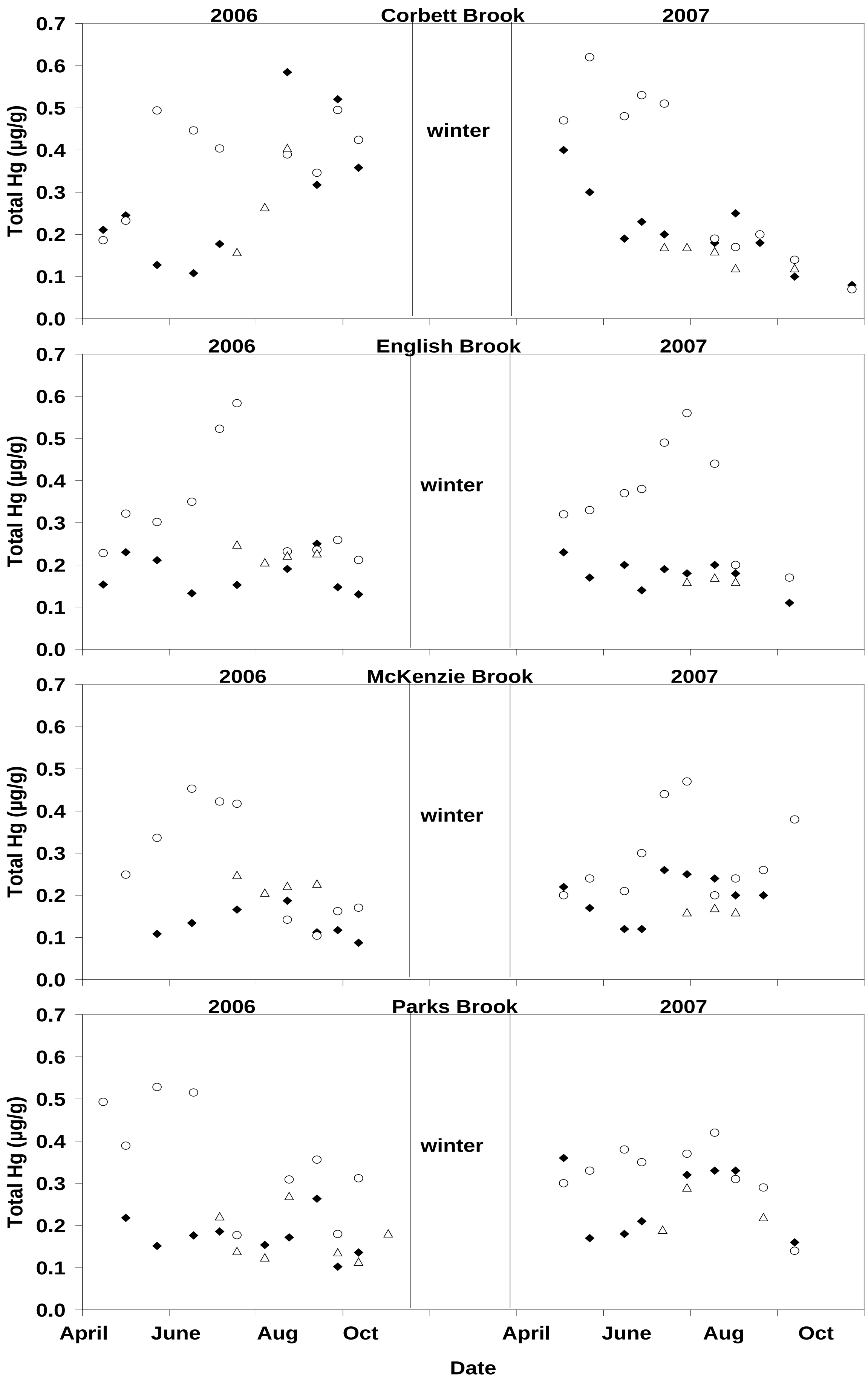

(A)
Log Total Hg (µg/g)
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-20
0
20
40
60
80
100
120
% Aquatic Carbon in Diet
(B)
y = 0.13x - 1.34
r 2 = 0.36
p = 0.001
Log Total Hg (µg/g)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
2
3
4
5
6
7
8
δ15N

Figure 6.


2006
Corbett Brook
2007
winter
2006
English Brook
2007
winter
2006
McKenzie Brook
2007
winter
2006
Parks Brook
2007
winter
Total Hg (µg/g)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
April
June
Aug
Oct
April
June
Aug
Oct
Date