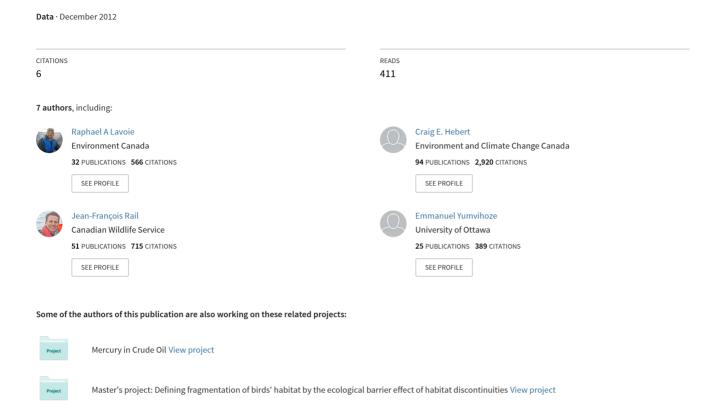
# Trophic structure and mercury distribution in a Gulf of St. Lawrence (Canada) food web using SIA



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# Trophic structure and mercury distribution in a Gulf of St. Lawrence (Canada) food web using stable isotope analysis

Raphael A. Lavoie <sup>a,\*,1</sup>, Craig E. Hebert <sup>b</sup>, Jean-François Rail <sup>c</sup>, Birgit M. Braune <sup>b</sup>, Emmanuel Yumvihoze <sup>a</sup>, Laura G. Hill <sup>a</sup>, David R.S. Lean <sup>a</sup>

- <sup>a</sup> Biology Department, University of Ottawa, 30 Marie Curie, Ottawa, ON, Canada K1N 6N5
- b Wildlife and Landscape Science Directorate, Science and Technology Branch, Environment Canada, National Wildlife Research Centre, Carleton University, Ottawa, ON, Canada K1A 0H3
- Canadian Wildlife Service Directorate, Environmental Stewardship Branch, Environment Canada, 1141 Route de l'Église, C.P. 10 100, Québec, QC, Canada G1V 4H5

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#### ABSTRACT

Even at low concentrations in the environment, mercury has the potential to biomagnify in food chains and reaches levels of concern in apex predators. The aim of this study was to relate the transfer of total mercury (THg) and methylmercury (MeHg) in a Gulf of St. Lawrence food web to the trophic structure, from primary consumers to seabirds, using stable nitrogen ( $\delta^{15}N$ ) and carbon ( $\delta^{13}C$ ) isotope analysis and physical environmental parameters. The energy reaching upper trophic level species was principally derived from pelagic primary production, with particulate organic matter (POM) at the base of the food chain. We developed a biomagnification factor (BMF) taking into account the various prey items consumed by a given predator using stable isotope mixing models. This BMF provides a more realistic estimation than when using a single prey. Lipid content, body weight, trophic level and benthic connection explained 77.4 and 80.7% of the variation in THg and MeHg concentrations, respectively in this food web. When other values were held constant, relationships with lipid and benthic connection were negative whereas relationships with trophic level and body weight were positive. Total Hg and MeHg biomagnified in this food web with biomagnification power values (slope of the relationship with  $\delta^{15}N$ ) of 0.170 and 0.235, respectively on wet weight and 0.134 and 0.201, respectively on dry weight. Values of biomagnification power were greater for pelagic and benthopelagic species compared to benthic species whereas the opposite trend was observed for levels at the base of the food chain. This suggests that Hg would be readily bioavailable to organisms at the base of the benthic food chain, but trophic transfer would be more efficient in each trophic level of pelagic and benthopelagic food chains.

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#### 1. Introduction

Mercury (Hg) is a potentially toxic metal released into the environment by natural and anthropogenic sources. The elemental form of Hg is volatile, can travel long distances in the atmosphere and can be deposited away from the point of origin (Fitzgerald et al., 1998). Mercury becomes of greater toxicological concern after methylation because methylmercury (MeHg) biomagnifies and is the most toxic form of Hg (Wolfe et al., 1998).

Food consumption is known to be an important route of exposure for MeHg uptake in animals (Hall et al., 1997). Although trophic level is a very significant factor influencing contaminant levels in aquatic organisms, the source of organic matter and therefore feeding habitat

is also believed to be important. Benthic organisms tend to have higher Hg than pelagic organisms (Cossa and Gobeil, 2000) although the opposite has been observed (Kidd et al., 2003).

Stable isotopes are used as ecological tracers to track food sources assimilated by consumers. Stable nitrogen ( $\delta^{15}$ N) and carbon ( $\delta^{13}$ C) isotopes are known to undergo predictable stepwise trophic enrichment between the diet and consumer (for review, see Jardine et al., 2006 and references therein; Post, 2002). Nitrogen isotopes can be used to estimate the trophic level of an organism since they fractionate approximately 3.4% between each trophic transfer (Post, 2002). Carbon isotopes are mainly used for information on dietary carbon sources because, although they exhibit some trophic fractionation (approximately 1‰),  $\delta^{13}$ C values are mostly defined at the primary producer level and then conserved within the food web (Post, 2002). In marine ecosystems, benthic organisms show higher  $\delta^{13}\text{C}$  values compared to pelagic organisms (France, 1995). When isotope ratios are corrected for trophic enrichment, mass balance mixing models can be used to quantitatively assess the relative contribution of different food items to consumer diets (Phillips and Gregg, 2001).

<sup>\*</sup> Corresponding author. Tel.: +1 613 562 5800x2573; fax: +1 613 562 5486. *E-mail address:* lavoie.raphael@gmail.com (R.A. Lavoie).

 $<sup>^1</sup>$  Present address: Biology Department, Queen's University, 116 Barrie, Kingston, ON, Canada K7L 3 N6. Tel.:  $+\,1\,613\,533\,6000x77503;$  fax:  $+\,1\,613\,533\,6617.$ 

The Gulf of St. Lawrence is a vast ecosystem with a high primary production and supports abundant and diverse biological communities (St. Lawrence Centre, 1996). Main anthropogenic inputs of Hg in the Gulf are from upstream waters (Cossa and Gobeil, 2000) and atmospheric deposition (Miller et al., 2005). This ecosystem has received very little attention regarding the mechanisms involved in regulating Hg distribution in food webs.

The objective of this study was to relate Hg concentrations to the trophic structure of a Gulf of St. Lawrence food web using stable isotope analysis. We determined the main factors regulating levels of THg and MeHg in this food web using i) trophic level (using  $\delta^{15}$ N), ii) level of connectivity with the benthos (using  $\delta^{13}$ C), iii) total body weight and iv) organism lipid content.

#### 2. Materials and methods

#### 2.1. Sample collection

Fish and decapod samples were collected in the Gulf of St. Lawrence within a 60 km radius of Corossol Island, Canada (50°10′N to 49°44′N and 66°59′W to 66°26′W; Fig. 1; Table 1) in August 2006 at five stations by horizontal trawling using a shrimp bottom trawl (mesh size 80/60/44 mm, codend liner 12.7 mm) for 15 min at 5 knots between 112 to 282 m depth. American sandlance (Ammodytes americanus; SAND) were caught using a nylon fyke net (mesh size of 6.25 mm) displayed at the mouth of Clet Stream in Sept-Îles Bay. Capelin (Mallotus villosus; CAPE) were sampled by hand while spawning on the beaches of the City of Sept-Îles, Littoral and benthic macroinvertebrates (amphipods, molluscs and Strongvlocentrotus droebachiensis; URCH) were collected by hand on Corossol Island beaches in 2007. Zooplankton was collected in 2007 by double oblique trawling using a Bongo net in nytex with an opening of 60 cm diameter and a mesh size of 333 µm for 24 min at 2-3 knots between 0 and 250 m depth. Zooplankton (Calanus finmarchicus; CFIN, Calanus hyperboreus; CHYP and Meganyctiphanes norvegica; MENO) was sorted by size using a stainless steel sieve with a 2 mm mesh size and then pooled by size. Adult seabirds were caught during incubation on Corossol Island between May and June 2006 (15 *Larus marinus* (GBBG) and two *Larus argentatus* (HERG) were caught in 2007) using a drop trap or a hand net and blood was collected via venipuncture of the ulnar vein. Approximately 3 mL of blood was retrieved with a 5 cc. heparinised syringe then centrifuged in the field within 12 h to separate plasma and red blood cells. All samples or tissue samples were frozen shortly after collection until they were shipped by mail on dry ice to the University of Ottawa (Ottawa, ON) where they were then kept in a freezer at  $-20\,^{\circ}\mathrm{C}$ .

Sampling of water was done in 2007 within 10 km of Corossol Island using a 2 L VanDorn bottle in opaque polyvinyl chloride at 0, 85 and 170 m depths. The water samples were collected in duplicate in previously hydrochloric acid-cleaned 1 L HDPE bottles. Five mL of trace metal grade hydrochloric acid was added to the sample bottles immediately in the field in order to avoid any degradation of MeHg. All bottles were sealed in two polyethylene bags and kept in a dark and cool room at 4  $^{\circ}$ C until further treatment and analysis. Particulate organic matter samples were collected in 2001 within 75 km of Corossol Island at the depth of maximum chlorophyll production (10–24 m) using a 4 L Niskin bottle. Water samples were filtered through precombusted GF/C glass-fiber filters (for methods, see Lesage et al., 2001).

#### 2.2. Sample preparation

Fish and invertebrates were thawed and weighed fresh in the laboratory using an electronic balance  $(\pm\,0.1~\rm g).$  Shrimps, molluscs, gammarids and zooplankton were pooled (2 to 300 individuals) by species and by size for sufficient tissue mass, whereas all other samples were prepared and analysed individually avoiding cross-contamination. Whole fish, shrimps, gammarids and zooplankton were homogenized whereas the soft inner tissue was homogenized for molluscs, echinoderms and crabs. Fish and invertebrate tissues were frozen with liquid nitrogen and then homogenized in stainless steel analytical mills or in a mortar and pestle. The cellular fraction of seabird blood was analysed after centrifugation. All samples were then aliquoted and

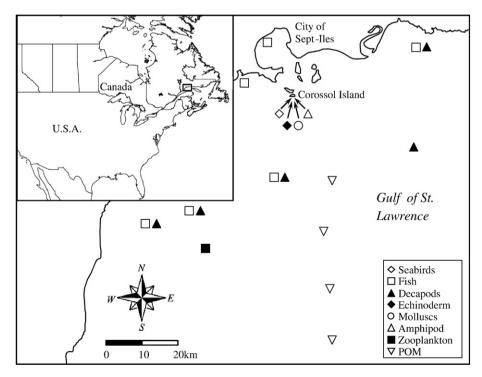


Fig. 1. Location of the sampling sites in the Gulf of St. Lawrence and on Corossol Island.

**Table 1** Mean  $(\pm SE)$   $\delta^{15}N$  and  $\delta^{13}C$  isotope values for all species collected in a Gulf of St. Lawrence food web in 2006 and 2007.

Taxa	Code	Feeding <sup>a</sup>	n	$\delta^{15}$ N (‰)	Trophic level	δ <sup>13</sup> C (‰)	Ref.b
Particulate organic matter	POM		4	$4.2 \pm 0.3$	$1.20 \pm 0.08$	$-23.2 \pm 0.6$	
Invertebrata							
Crustacea							
Zooplankton <sup>c</sup>							
Calanus finmarchicus	CFIN	PE, GR	10	$8.3 \pm 0.1$	$2.42 \pm 0.04$	$-22.7 \pm 0.1$	1
Calanus hyperboreus	CHYP	PE, GR	5	$8.0 \pm 0.1$	$2.33 \pm 0.04$	$-22.4 \pm 0.1$	1
Meganyctiphanes norvegica (Northern krill)	MENO	PE, PR/OM	6	$9.2 \pm 0.2$	$2.68 \pm 0.05$	$-21.1 \pm 0.1$	2
Amphipoda <sup>c</sup>							
Gammarellus sp. (Gammarid)	GAMA	BE, PR/SC	10	$8.1 \pm 0.1$	$2.37 \pm 0.02$	$-19.6 \pm 0.2$	3
Decapoda							
Shrimps <sup>c</sup>	SHRI	BP, PR/SC	10	$12.4 \pm 0.1$	$3.63 \pm 0.03$	$-19.6 \pm 0.2$	4
Pandalus borealis (Northern shrimp)	PABO		6	$12.4 \pm 0.1$	$3.63 \pm 0.04$	$-19.7 \pm 0.2$	
Pandalus montagui (Striped shrimp)	PMON		2	$12.6 \pm 0.6$	$3.66 \pm 0.16$	$-18.6 \pm 0.2$	
Pasiphaea multidentata (Pink glass shrimp)	PMUL		2	$12.4 \pm 0.1$	$3.61 \pm 0.01$	$-20.2 \pm 0.2$	
Chionoecetes oplio (Snow crab)	SNCR	BP, PR/SC	12	$13.2 \pm 0.2$	$3.83 \pm 0.07$	$-19.9 \pm 0.1$	5
Mollusca <sup>c</sup>							
Gastropoda							
Littorina littorea (Common periwinkle)	BIGO	BE, GR	10	$7.9 \pm 0.1$	$2.29 \pm 0.03$	$-17.3 \pm 0.1$	6
Buccinum undatum (Waved whelk)	BUCC	BE, PR/SC	10	$9.7 \pm 0.1$	$2.83 \pm 0.03$	$-17.8 \pm 0.1$	7
Tectura testudinalis (Common tortoiseshell limpet)	PATE	BE, GR	10	$6.9 \pm 0.0$	$2.00 \pm 0.01$	$-18.6 \pm 0.2$	8
Bivalvia							
Mytilus edulis (Blue mussel)	BLMU	BP, FF	21	$7.2 \pm 0.1$	$2.09 \pm 0.03$	$-19.5 \pm 0.2$	9
Echinodermata							
Strongylocentrotus droebachiensis (Green sea urchin)	URCH	BE, DF/OM	10	$5.9 \pm 0.1$	$1.69 \pm 0.01$	$-17.7 \pm 0.2$	10
Vertebrata							
Osteichtyes							
Mallotus villosus (Capelin)	CAPE	PE, PR	12	$13.2 \pm 0.1$	$3.86 \pm 0.04$	$-20.9 \pm 0.1$	11
Ammodytes americanus (American sandlance)	SAND	BP, PR	13	$11.6 \pm 0.1$	$3.38 \pm 0.03$	$-20.5 \pm 0.2$	11
Hippoglossoides platessoides (American plaice)	AMPL	BE, PR	10	$14.4 \pm 0.1$	$4.22 \pm 0.02$	$-19.2 \pm 0.2$	11
Glyptocephalus cynoglossus (Witch flounder)	WIFL	BE, PR	10	$14.5 \pm 0.2$	$4.22 \pm 0.05$	$-17.8 \pm 0.1$	11
Clupea harengus (Atlantic herring)	ATHE	PE, PR	11	$12.2 \pm 0.2$	$3.57 \pm 0.06$	$-21.3 \pm 0.1$	11
Aves							
Rissa tridactyla (Black-legged kittiwake)	BLKI	PE, PR/SC	21	$15.2\pm0.0$	$4.67 \pm 0.01$	$-18.9 \pm 0.0$	12, 13
Alca torda (Razorbill)	RAZO	BP, PR	20	$15.2\pm0.1$	$4.68 \pm 0.02$	$-19.3 \pm 0.0$	12, 14
Somateria mollissima (Common eider)	COEI	BE, PR	20	$11.1\pm0.1$	$3.47 \pm 0.03$	$-18.9 \pm 0.2$	15, 16
Larus argentatus (Herring gull)	HERG	BP, PR/SC	20	$13.0 \pm 0.3$	$4.03 \pm 0.08$	$-18.9 \pm 0.1$	12, 17
Larus marinus (Great black-backed gull)	GBBG	BP, PR/SC	20	$12.8 \pm 0.4$	$3.98 \pm 0.12$	$-19.0 \pm 0.2$	12, 18

<sup>&</sup>lt;sup>a</sup> Feeding habitat: PE=pelagic; BE=benthic; BP=benthopelagic, feeding mode: FF=filter-feeder; PR=predator; SC=scavenger; OM=omnivore; DF=detritus-feeder; GR=grazer.

fresh material was used for THg and MeHg analyses, whereas freezedried material was used for stable isotope analysis and moisture content determination. Freeze-drying was done at  $-150\,^{\circ}\text{C}$  for at least 48 h and then homogenised again into a fine powder.

#### 2.3. Total mercury analysis (THg)

Total Hg concentrations in animal tissue samples were measured by cold vapour atomic absorbance spectrometry (CVAAS) using a Mercury SP-3D analyser (Nippon Instruments, Osaka, Japan) following United States Environment Protection Agency (USEPA) method 7473 (U.S. EPA, 1998). Each sample was run in duplicate and coefficients of variation were below 15%. Blanks and check standards were run in duplicate every five to seven samples. Two standard reference materials (DORM-2 and TORT-2) from the Canadian National Research Council were analysed in duplicate every 15 samples with recoveries of  $97.2 \pm 1.0\%$  (mean  $\pm$  SE); n = 53 and  $97.5 \pm 2.2\%$ ; n = 6, respectively. Concentrations of THg in samples were expressed in nanogram per gram dry weight (ng/g dw, except otherwise stated) but analyses were carried out on fresh (wet) tissue. Moisture content for each sample was measured by weighing the fresh homogenate on an analytical balance ( $\pm 0.1 \text{ mg}$ ) before and after being freeze-dried at -150 °C for 48 h. The instrument detection limit for THg analysis was 0.1 ng/g ww.

Total Hg analysis in water was done on unfiltered samples by oxidation, purge and trap, desorption by cold vapour atomic fluorescence spectrometry (CVAFS) using a Series 2600 Mercury Analysis System (Tekran, Knoxville, US) following USEPA method 1631 (U.S. EPA, 2002). Blanks (field and laboratory) and standards from a stock of mercury reference solution were tested every three samples. Two samples were spiked to calculate the recovery of the method. Each sample was run in duplicate and coefficients of variation were below 15%. The recovery of the spiked samples was  $102.7 \pm 0.65\%$  (mean  $\pm$  SE; n=2) and the recovery of the standards was  $97.3 \pm 2.06\%$  (mean  $\pm$  SE; n=7). The protocol was followed in a class 100 mercury-free clean room. Total Hg concentrations of the samples were expressed in nanogram per litre (ng/L). The method detection limit was 0.05 ng/L.

#### 2.4. Methylmercury analysis (MeHg)

Methylmercury analysis was done by capillary gas chromatography (GC) coupled with atomic fluorescence spectrometry (AFS; P S Analytical, Orpington, UK) using a GC system model HP 6890 (Agilent [Hewlett Packard], Little Falls, US). Protocols were modified from Cai et al. (1997) and Cai et al. (1996) in animal tissue and water samples, respectively. Each sample was run in duplicate and coefficients of variation were below 20%.

b References for feeding habitat and feeding mode of organisms: 1, Conover (1988); 2, Lass et al. (2001); 3, Cruz-Rivera and Hay (2000); 4, Savenkoff et al. (2006); 5, Lovrich and Sainte-Marie (1997); 6, Olsson et al. (2007); 7, Himmelman and Hamel (1993); 8, Steneck (1982); 9, Hawkins et al. (1996); 10, Himmelman and Steele (1971); 11, Scott and Scott (1988); 12, Lavoie et al. (forthcoming); 13, Baird (1994); 14, Hipfner and Chapdelaine (2002); 15, Guillemette et al. (1992); 16, Goudie et al. (2000); 17, Pierotti and Good (1994); 18, Good (1998)

<sup>&</sup>lt;sup>c</sup> Several individuals of the same species were pooled (2-300) and the associated sample size (n) represents the number of pools.

Animal tissue samples were digested using potassium hydroxide. Methylene chloride ( $CH_2Cl_2$ ), sodium thiosulfate ( $Na_2S_2O_3$ ) and a mixture of nitric acid ( $HNO_3$ ), potassium bromide (KBr) and copper (II) sulfate ( $CuSO_4$ ) were added to the samples. Methylene chloride was then transferred in a glass insert through a layer of anhydrous sodium sulfate ( $Na_2SO_4$ ). Each sample was run in duplicate. One blank and three standard reference materials (DORM-2, TORT-2 or DOLT-3) from the Canadian National Research Council were tested every five to seven samples with recoveries of  $100.6\pm1.6\%$  ( $mean\pm SE$ ); n=17,  $96.1\pm1.4\%$ ; n=27 and  $105.4\pm2.0\%$ ; n=4, respectively. Concentrations of MeHg in samples were expressed in nanogram per gram dry weight (ng/g dw, except otherwise stated; see 2.3. Total mercury analysis (THg)). The absolute detection limit was 0.2 ng/g for animal tissue samples.

To measure MeHg in water samples, sulfhydryl-cotton fiber was packed in screening columns for pre-concentration of the organomercurials, then acidic KBr:CuSO<sub>4</sub> mixture was used for elution. The extraction was done using CH<sub>2</sub>Cl<sub>2</sub> and samples were passed through a layer of anhydrous Na<sub>2</sub>SO<sub>4</sub>. Calibration standards were prepared in duplicate and CH<sub>2</sub>Cl<sub>2</sub> was added. A matrix spike sample was prepared in duplicate using solutions of methylmercuric chloride (CH<sub>3</sub>HgCl). Samples, blanks (field and laboratory), matrices and standards were subjected to GC-AFS and were run in duplicate. The recovery of the spiked samples was  $102.3 \pm 0.72\%$  (mean  $\pm$  SE; n = 2). Methylmercury concentrations of the samples were expressed in nanogram per litre (ng/L). The absolute detection limit was and 0.01 ng/L for water samples.

#### 2.5. Stable isotope analysis

The concentration and the isotopic composition of organic carbon and nitrogen in animal tissue samples were determined by flash combustion at 1800 °C on an Elemental Analyser (Carlo Erba, Milan, Italy) coupled with a ConFlo III interface (ThermoFinnigan, Bremen, Germany) to a Delta Plus Advantage isotope ratio mass spectrometer (IRMS; ThermoFinnigan, Bremen, Germany). Data were normalized using internal standards previously calibrated with international standards IAEA-CH-6, IAEA-NBS22, IAEA-N1, IAEA-N2, USGS-40 and USGS-41. Analytical precision is  $\pm 0.2\%$ . Stable isotope values of particulate organic matter (POM) were provided by V. Lesage (Fisheries and Oceans Canada, pers. comm.). The isotopic composition of POM samples was determined on an isochrom continuous-flow IRMS connected to an Elemental Analyser (Carlo Erba, Milan, Italy; for methods, see Lesage et al., 2001).

## 2.6. Statistical analysis and calculations

Mercury concentrations on dry weight were reported to correct for interspecific differences in moisture content, except for biomagnification power statistics where wet and/or dry weight were reported to allow comparisons with other studies. Trophic level (TL) was determined relative to *Tectura testudinalis* (PATE) as baseline (TL<sub>T. testudinalis</sub>) which we assumed to occupy TL 2. This organism is a semi-sedentary primary consumer species that has a relatively long lifespan. Trophic levels (except for seabirds) were assessed using a modification of Hobson and Welch (1992) equation:

$$TL_{consumer} = 2 + \left(\delta^{15}N_{consumer} - \delta^{15}N_{T.~testudinalis}\right)/3.4 \tag{1}$$

where TL<sub>consumer</sub> and  $\delta^{15}$ N<sub>consumer</sub> are TL and  $\delta^{15}$ N of the organism of interest, respectively,  $\delta^{15}$ N<sub>T. testudinalis</sub> is the  $\delta^{15}$ N of *T. testudinalis* (6.9  $\pm$  0.1‰; mean  $\pm$  SE; n = 10), and 3.4 is the isotopic trophic enrichment factor for most organisms (Post, 2002). We used a trophic enrichment factor of 2.6‰ for seabirds (Bearhop et al., 2002):

$$TL_{bird} = 3 + \left(\delta^{15}N_{bird} - \delta^{15}N_{\textit{T. testudinalis}} - 2.6\right)/3.4 \tag{2}$$

Biomagnification power of Hg was assessed using the slope (b) of the simple linear regression including all organisms:

$$Log_{10}[Hg] = b\left(\delta^{15}N\right) + a \tag{3}$$

where a is the intercept. That equation is analogous to the equation developed by Broman et al. (1992) which used untransformed data. Food web magnification factors (FWMFs) were calculated using Eq. 3 with TL instead of  $\delta^{15}$ N with b being used as follow (Fisk et al., 2001):

$$FWMF = 10^b (4)$$

This measurement represents the biomagnification potential over the entire food web taking into account the different trophic enrichment factors and correcting for the baseline. Biomagnification factor (BMF) was calculated for simple predator–prey interactions (Riget et al., 2007):

$$BMF = [Hg]_{predator} / [Hg]_{prev}$$
 (5)

where [Hg] is the Hg concentration of a predator and its main prey. The term BMF is a magnification factor between prey and predator and is comparable to FWMF, which is a magnification factor averaged over the entire food web. The Eq. 5 is valid with the assumption that a predator consumes a single prey type. We used stable isotope mixing models (IsoError: Phillips and Gregg, 2001; IsoSource: Phillips and Gregg, 2003; IsoConc: Phillips and Koch, 2002) to quantify the proportion of sources (PS) that were likely to be found in the diet of the predators and modified Eq. 5 for PS correction:

$$BMF_{PSC} = [Hg]_{predator} / \left( \sum_{i=1}^{n} ([Hg]_{prey i} \times f_{prey i}) \right)$$
 (6)

where  $[Hg]_{prey\,i}$  is the Hg level and  $f_{prey\,i}$  is the proportion of each prey item in the diet of the predator. Proportions of sources are provided in Table 2. An increment of 1% and a tolerance of  $\pm 0.1\%$  were applied when using IsoSource (Phillips and Gregg, 2003). Phillips and Gregg (2003) suggest reporting a range of feasible solutions for each source, but the mean was used for the calculation of BMF<sub>PSC</sub>. Prey items for a given predator were chosen based on literature (Table 2). When too many sources were possible, we combined sources with similar isotopic signatures or sources within a given trophic guild (Phillips et al., 2005) and we were able to group sources in five categories. We used IsoConc and IsoError when two and three sources were judged possible, respectively. When using IsoError, the isotope with the greatest difference among the isotopic signatures of the sources was used (i.e.,  $\delta^{15}$ N) to minimise the proportional standard error. For the other models,  $\delta^{15}$ N and  $\delta^{13}$ C were used.

Backward stepwise multiple linear regressions (MLR) were performed on THg and MeHg including TL (using  $\delta^{15}$ N), connectivity with the benthos (using  $\delta^{13}$ C), lipid content (using *C:N* ratio; see below) and total weight as independent variables. Lipid content values were transformed using the arcsine of their square root (Zar, 1999), whereas logarithmic transformations (to the base 10) were applied to THg, MeHg and weight values. Sequential MLR was used as a remediation procedure for multicollinearity between explanatory variables (Graham, 2003). This was done by removing variability shared with other variables using residual transformations and by running MLR on transformed variables (Graham, 2003). Variables were standardized by averaging to zero and setting the standard deviation to 1. Lipid content was calculated using the ratio of the concentration of organic carbon over the concentration of organic nitrogen (C:N) contained in the tissue analysed for stable isotope analysis. This calculation is based on a study using a wide range of

Table 2
Difference in trophic level between simple predator–prey interactions ( $\Delta$ TL), biomagnification factors of simple (BMF) and complex predator–prey interactions (corrected for proportions of sources; BMF<sub>PSC</sub>) and FWMFs for THg and MeHg (ng/g dw). Proportions of sources are also shown. BMFs in bold are higher than FWMFs.

Predator Prey	Prey	ΔTL	THg		MeHg		Proportions of	Ref.a
			BMF	BMF <sub>PSC</sub>	BMF	BMF <sub>PSC</sub>	sources	
UCC	GAMA	0.46	2.67	3.38	4.64	11.1	not used	1
	BLMU	0.74	2.15		5.70		0.380	
	URCH	1.14	5.21		26.7		0.620	
HRI	MENO	0.95	3.35	3.81	16.1	19.4	0.688	2
	CHYP	1.30	3.40		32.2		0.313 <sup>b</sup>	
	CFIN	1.21	14.4		38.0			
	GAMA	1.26	4.10		6.06		not used	
NCR	Zooplankton <sup>c</sup>	1.35	3.95	2.08	17.7	2.10	0.368°	3
	GAMA	1.46	3.58		4.27		0.369	
	SHRI	0.20	0.87		0.70		0.264	
APE	MENO	1.18	0.67	0.83	3.67	5.06	0.492	4
	CHYP	1.53	0.68		7.35		0.508 <sup>b</sup>	
	CFIN	1.44	2.86		8.66			
AND	MENO	0.70	1.79	2.62	12.1	9.54	not used	4
	СНҮР	1.05	1.82		24.1		0.635 <sup>b</sup>	-
	CFIN	0.96	7.69		28.4		0.030	
	GAMA	1.01	2.19		4.53		0.365	
MPL	SAND	0.84	1.50	1.58	1.07	1.27	0.498 <sup>d</sup>	4
2	CAPE	0.36	4.04	1.50	3.49		0.100	•
	BUCC	1.39	1.24		1.04		0.502	
VIFL	SAND	0.84	1.71	1.79	1.28	1.52	0.492 <sup>d</sup>	4
, II L	CAPE	0.36	4.60	1.75	4.20	1.52	0.132	•
	BUCC	1.39	1.41		1.25		0.508	
THE	MENO	0.89	3.11	4.36	18.4	30.3	0.270	4
	CHYP	1.24	3.16		36.8	30.3	0.730 <sup>b</sup>	•
	CFIN	1.15	13.4		43.4		0.750	
LKI	SAND	1.29	13.0	15.8	13.7	19.6	0.509	5
LICI	CAPE	0.81	34.8	13.0	45.0	15.0	0.331	3
	SHRI	1.04	6.93		10.3		0.160	
AZO	SAND	1.30	25.7	42.5	34.9	62.1	0.370	5
nzo	CAPE	0.82	69.0	72.3	114	02.1	0.630	3
OEI	BLMU	1.38	16.7	13.0	62.5	33.9	0.727 <sup>e</sup>	6
OLI	URCH	1.78	40.5	13.0	293	33.3	0.727	O
	SNCR	-0.36	5.80		11.9		0.273	
IERG	FISH	0.41	17.0	11.8	20.2	21.5	0.201 <sup>d</sup>	5
LKG	DECA	0.30	6.67	11.0	11.6	21.5	0.268 <sup>f</sup>	3
	MENO	1.35	20.9		159		0.244	
	BLMU	1.94	20.6		73.2		0.163	
	BUCC	1.20	9.59		12.8		0.103	
BBG	FISH	0.36	34.7	24.2	48.2	51.4	0.123 0.201 <sup>d</sup>	5
מממ	DECA	0.25	13.6	4.4	27.6	J1. <del>4</del>	0.268 <sup>f</sup>	J
SAZNATE	DUCC	1.15					0.123	
WMF	MENO BLMU BUCC	1.30 1.89 1.15	42.7 42.1 19.6 3.81		379 175 30.7 6.46		0.244 0.163 0.123	

<sup>a</sup>References for the diet of predators: 1, Himmelman and Hamel (1993); 2, Savenkoff et al. (2006); 3, Lovrich and Sainte-Marie (1997); 4, Scott and Scott (1988); 5, Lavoie et al. (forthcoming); 6, Guillemette et al. (1992). Proportions include: <sup>b</sup>Calanus hyperboreus (CHYP) and C. finmarchicus (CFIN); <sup>c</sup>Meganyctiphanes norvegica (MENO), CHYP and CFIN; <sup>d</sup>Mallotus villosus (CAPE) and Ammodytes americanus (SAND); <sup>e</sup>Mytilus edulis (BLMU) and Strongylocentrotus droebachiensis (URCH); <sup>f</sup>Pandalus borealis, P. montagui and Pasiphaea multidentata (SHRI) and Chionoecetes oplio (SNCR).

taxonomic groups and TLs in a marine food web (McConnaughey and McRoy, 1979):

Lipid content = 
$$93/(1 + [0.246 \times C : N - 0.775]^{-1})$$
 (7)

To test if the connectivity with the benthos (increase in  $\delta^{13}$ C values) was a good predictor of Hg biomagnification, an Analysis of Covariance (ANCOVA; Type III sums of squares) was done on THg and MeHg concentrations of organisms for each feeding habitat (benthic, pelagic, and benthopelagic) with  $\delta^{15}$ N or trophic level as covariates. Organisms were grouped into categories based on their feeding habitat using information from published literature (see Table 1). Simple linear regressions of Hg against  $\delta^{15}$ N or trophic level for each feeding habitat were used after ANCOVA since all terms of the latter model were significant.

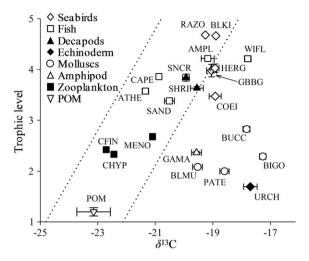
The homogeneity of the variances and the normality of the residuals were tested to ensure that assumptions were not violated.

Tukey's HSD test was used for multiple comparison analysis. Statistical analyses were performed using S-Plus (version 8.0) and a significance threshold ( $\alpha$ ) of 0.05 was used.

#### 3. Results

## 3.1. Trophic structure

Trophic levels ranged from  $1.20\pm0.08$  for POM to  $4.68\pm0.02$  for Alca torda (RAZO) and  $\delta^{13}$ C values ranged from  $-17.3\pm0.1$  for Littorina littorea (BIGO) to  $-23.2\pm0.6\%$  for POM (Fig. 2; Table 1). A positive correlation was found between TL and  $\delta^{13}$ C ( $r^2=0.67$ ; p<0.001; n=174) for organisms that obtained energy from pelagic sources (between dashed lines, L. marinus (GBBG) and L. argentatus (HERG) included; Fig. 2). A correlation for the whole food web resulted in a poor fit of the data ( $r^2=0.03$ ; n=276), but was significant (p=0.01). Organisms were generally enriched in  $^{13}$ C as their connection with the benthos increased (Fig. 3; Table 1). Analysis

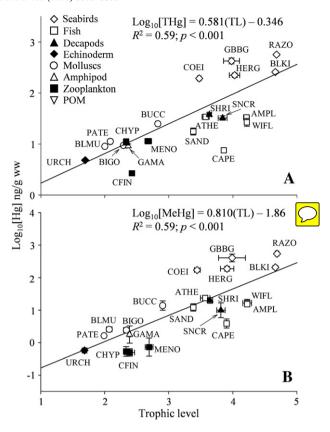


**Fig. 2.** Relationship between trophic level and  $\delta^{13}$ C (‰; mean  $\pm$  SE) values for all species collected in a Gulf of St. Lawrence food web. Dashed lines represent the boundaries (min–max  $\delta^{13}$ C values) of a theoretical food web derived from POM with an increase of 1‰ of  $\delta^{13}$ C per trophic level. POM values were kindly contributed by V. Lesage (Fisheries and Oceans Canada, pers. comm.).

of variance (ANOVA) indicated that this trend was valid for fish and invertebrates for both interspecific comparisons (fish:  $F_{4,51} = 83.9$ ; p < 0.001; invertebrates:  $F_{10,103} = 93.6$ ; p < 0.001) and among habitat comparisons (fish:  $F_{2,53} = 84.1$ ; p < 0.001; invertebrates:  $F_{2,111} = 175$ ; p < 0.001). Seabirds did not show any significant interspecific ( $F_{4,96} = 1.24$ ; p = 0.298) or among habitat ( $F_{2,98} = 1.51$ ; p = 0.23) differences in  $\delta^{13}$ C values.

# 3.2. Mercury in organisms

Total Hg concentrations ranged between  $12.6\pm0.6$  and  $1789\pm98$  ng/g dw and MeHg ranged between  $2.55\pm0.55$  and  $1777\pm137$  ng/g dw (Fig. 4; Table 3). Percentage of MeHg ranged from  $46.9\pm7.1$  to  $64.8\pm2.6\%$  (mean  $\pm$  SE) for whole fish; from  $6.4\pm2.0\%$  to  $56.9\pm11.6\%$  for invertebrates; and from  $97.5\pm0.8$  to  $99.8\pm0.1\%$  for seabirds (Table 3).



**Fig. 4.** Mean  $(\pm SE)$  concentrations (ng/g ww) for (A) THg and (B) MeHg in relation to trophic level.

# 3.3. Trophic level and mercury

Simple linear regressions revealed that total Hg (on a wet weight basis) biomagnified in this food web ( $F_{1,270} = 272$ ; p < 0.001;  $R^2 = 0.50$ ) with a biomagnification power of 0.170 ( $Log_{10}[THg] = 0.170(\delta^{15}N) - 0.293$ ). Although MeHg showed a significant relationship with  $\delta^{15}N$  ( $Log_{10}[MeHg] = 0.235(\delta^{15}N) - 1.53$ ;  $F_{1,137} = 145$ ; p < 0.001;  $R^2 = 0.51$ ), the slope was not significantly steeper than for

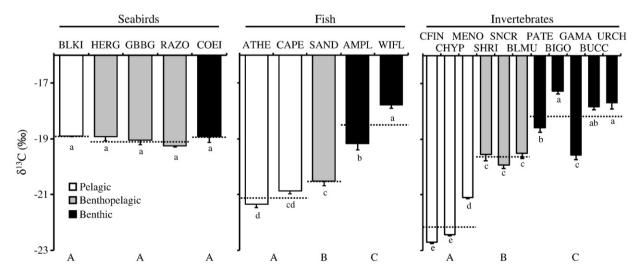


Fig. 3. Stable carbon isotope values (‰) for all species collected. Organisms were classified by habitat: pelagic (white), benthic (black) or benthopelagic (gray). Dashed lines represent the average for the habitats and do not vary significantly when sharing common capital letters. Individuals sharing common lower case letters do not vary significantly within a taxonomic group.

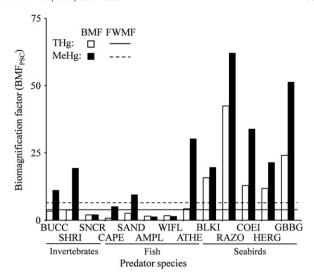
**Table 3**Mean  $(\pm SE)$  THg, MeHg  $(ng/g \, dw)$ , percentage of MeHg (%) and water content values (%) for all species collected. Latin and common names are provided in Table 1.

Taxa	nª	n <sup>b</sup>	THg (ng/g dw)	MeHg (ng/g dw)	MeHg (%)	H <sub>2</sub> O (%)
Invertebrata						
Crustacea						
Zooplankton	ıc					
CFIN	10	5	$12.6 \pm 0.6$	$2.55 \pm 0.55$	$21.4 \pm 5.5$	$78.2 \pm 0.8$
CHYP	5	5	$64.7 \pm 7.5$	$3.89 \pm 1.08$	$6.4\pm2.0$	$82.5 \pm 0.9$
MENO	6	5	$60.2 \pm 4.5$	$6.49 \pm 2.62$	$10.0 \pm 3.6$	$80.6\pm1.2$
Amphipoda <sup>c</sup>						
GAMA	10	7	$39.2 \pm 3.1$	$14.7 \pm 4.5$	$33.0 \pm 10.3$	$75.9 \pm 0.8$
Decapoda						
SHRI <sup>c</sup>	10	5	$138 \pm 11$	$75.2 \pm 12.9$	$51.0 \pm 7.8$	$71.8 \pm 0.5$
PABO	6	5	$139 \pm 15$	$75.2 \pm 12.9$	$51.0 \pm 7.8$	$71.3 \pm 0.7$
PMON	2	0	$167 \pm 15$	not analysed	not analysed	$72.4 \pm 0.4$
PMUL	2	0	$108 \pm 23$	not analysed	not analysed	$72.5 \pm 1.2$
SNCR	12	5	$231 \pm 19$	$103 \pm 38$	$45.2 \pm 14.7$	$84.6 \pm 1.4$
Mollusca <sup>c</sup>						
Gastropoda						
BIGO	10	5	$50.5 \pm 1.8$	$12.8 \pm 1.3$	$25.4 \pm 2.1$	$81.3 \pm 0.5$
BUCC	10	5	$127 \pm 8$	$84.7 \pm 19.1$	$56.9 \pm 11.6$	$80.0\pm0.5$
PATE	10	5	$50.8 \pm 1.3$	$9.32 \pm 0.42$	$19.1 \pm 1.1$	$82.2 \pm 0.3$
Bivalvia						
BLMU	21	13	$104 \pm 6$	$24.3 \pm 2.5$	$24.8 \pm 2.9$	$88.7 \pm 0.5$
Echinoderm	ata					
URCH	10	5	$42.0 \pm 3.6$	$5.31 \pm 1.04$	$12.5 \pm 2.0$	$88.0 \pm 0.6$
Vertebrata						
Osteichtyes						
CAPE	12	8	$28.1 \pm 2.2$	$17.5 \pm 3.0$	$57.8 \pm 7.6$	$72.1 \pm 0.4$
SAND	13	8	$71.2 \pm 16.2$	$54.7 \pm 20.1$	$64.8 \pm 2.6$	$69.5 \pm 1.3$
AMPL	10	8	$146 \pm 38$	$77.4 \pm 18.8$	$56.1 \pm 5.5$	$77.0 \pm 0.8$
WIFL	10	7	$179 \pm 22$	$100 \pm 27$	$46.9 \pm 7.1$	$78.5 \pm 0.8$
ATHE	11	8	$104 \pm 11$	$69.2 \pm 6.1$	$63.7 \pm 4.5$	$65.0 \pm 1.0$
Aves						
BLKI	21	7	$805 \pm 52$	$688 \pm 81$	$95.0 \pm 1.2$	$66.5 \pm 0.5$
RAZO	20	7	$1789 \pm 98$	$1777\pm137$	$99.8 \pm 0.1$	$69.9 \pm 0.8$
COEI	20	7	$640 \pm 36$	$565 \pm 53$	$97.5 \pm 0.8$	$68.9 \pm 0.6$
HERG	20	7	$724 \pm 69$	$624\pm135$	$99.4 \pm 0.2$	$66.5 \pm 0.4$
GBBG	20	7	$1540 \pm 212$	$1611 \pm 427$	$99.8 \pm 0.1$	$67.4 \pm 0.6$

- <sup>a</sup> Sample size (n) used for THg.
- <sup>b</sup> Sample size used for MeHg analysis.
- $^{\rm c}$  Several individuals of the same species were pooled (2–300) and the associated sample size (n) represents the number of pools.

THg  $(F_{1,137}=2.53;\ p=0.114)$ . On a dry weight basis, the equations become:  $\log_{10}[{\rm THg}]=0.134(\delta^{15}{\rm N})+0.739$  for THg  $(F_{1,270}=187;\ p<0.001;\ R^2=0.41)$  and  $\log_{10}[{\rm MeHg}]=0.201(\delta^{15}{\rm N})-0.507$  for MeHg  $(F_{1,137}=114;\ p<0.001;\ R^2=0.45)$  with a significant difference between the slopes of THg and MeHg  $(F_{1,137}=10.4;\ p=0.002)$ . Relationships between Hg (on a wet weight basis) concentrations and TL were significant for both THg  $(F_{1,270}=388;\ p<0.001;\ R^2=0.59)$  and MeHg  $(F_{1,137}=196;\ p<0.001;\ R^2=0.59;\ Fig.\ 4)$ . Contrary to the relationship with  $\delta^{15}{\rm N}$  on a wet weight basis, the slope for MeHg was significantly steeper than for THg  $(F_{1,137}=5.24;\ p=0.024)$ . Slopes were not as steep on a dry weight basis ( $\log_{10}[{\rm THg}]=0.463({\rm TL})+0.682;\ F_{1,270}=260;\ p<0.001;\ R^2=0.49$  for THg and  $\log_{10}[{\rm MeHg}]=0.695({\rm TL})-0.569$  for MeHg;  $F_{1,137}=152;\ p<0.001;\ R^2=0.53)$ , but a significant difference between the slopes of THg and MeHg remained  $(F_{1,137}=15.9;\ p<0.001)$ .

Food web magnification factors were 3.81 for THg and 6.46 for MeHg (ww; Fig. 5; Table 2). For invertebrates and fish, biomagnification factors of THg corrected for proportion of source (BMF<sub>PSC</sub>) were lower than the FWMF whereas for seabirds, BMF<sub>PSC</sub> were higher than the FWMF. Some invertebrates and fish showed higher BMF<sub>PSC</sub> of MeHg than the FWMF while seabirds were still higher that the FWMF (Fig. 5). Uncorrected BMFs were highly variable for a given predator and were showing discrepancies with BMF<sub>PSC</sub> (Table 2).



**Fig. 5.** Biomagnification factors corrected for proportions of sources of THg (white bars) and MeHg (black bars). Food web magnification factors for the entire food web are shown for THg (full line) and MeHg (dashed line).

#### 3.4. Mercury and connectivity with benthos

Total Hg concentrations in water increased with depth in a curvilinear fashion (second order polynomial regression:  $F_{2,3} = 50.5$ ; p = 0.005;  $R^2 = 0.97$ ), whereas MeHg did not show any trend with values consistently low throughout the water column (simple linear regression:  $F_{1,4} = 1.41$ ; p = 0.30;  $R^2 = 0.26$ ; Table 4). This resulted in a decrease of MeHg percentage in a linear trend (simple linear regression:  $F_{1,4} = 9.12$ ; p = 0.039;  $R^2 = 0.70$ ) reaching  $6.4 \pm 0.2\%$  at 170 m depth compared to  $27.6 \pm 5.2\%$  for the surface water.

An ANCOVA between Hg and feeding habitats using  $\delta^{15}N$  or trophic level as covariates revealed that the effect of habitat, trophic position parameter ( $\delta^{15}N$  or trophic level) and the interaction between habitat and trophic position parameter were all significant for both THg (p < 0.05; n = 272) and MeHg (p < 0.05; n = 139). Individual simple linear regressions (SLRs) were therefore used for each feeding habitat (Table 5). All SLR models were highly significant and the amount of variance accounted for by the models was greatest for pelagic organisms followed by benthopelagic followed by benthic organisms. Furthermore, model slopes increased from benthic to benthopelagic to pelagic organisms. Model slopes for pelagic and benthopelagic organisms were not significantly different from each other (p>0.05), but were greater than that for benthic organisms (p<0.05). The value of the intercepts showed the opposite trend: pelagic < benthopelagic < benthic. Values of biomagnification power of MeHg were greater than for THg for each feeding habitat taken individually.

# 3.5. Trophic position and physical characteristics to predict mercury concentration

A sequential MLR using total weight (wet), lipid content, trophic level and benthic connection ( $\delta^{13}$ C) revealed that organism lipid content was the most significant predictor in the THg model (p<0.001; t= -24.5; n= 272;  $R^2$ = 0.627) followed by total weight (p<0.001; t= 10.1;  $R^2$ = 0.117), trophic level (p<0.001; t= 3.48;  $R^2$ = 0.027) and benthic connection (p= 0.039; t= -2.08;  $R^2$ = 0.004; Table 6). When other variables were held constant, relationships were positive for weight (b'= 0.449) and trophic level (b'= 0.167), whereas they were negative for lipid content (b'= -0.682) and benthic connection (b'= -0.080). The general model explained 77.4% of the variability in THg concentration in this food web (F<sub>(0.05)4,267</sub>= 229; p<0.001). The model was different for MeHg showing lipid content as

**Table 4**Mean ( $\pm$  SE) THg and MeHg concentrations (ng/L) and percentage of MeHg (%) in water samples in relation to depth (0, 85 and 170 m). The significance of the overall models and the slopes (b) are given for every measurement. Slopes in bold are significantly different than zero.

Depth (m)			p	$R^2$	b	$b^2$
Surface $(n=2)$	85 (n=2)	170 (n=2)				
$0.458 \pm 0.126$ $0.117 \pm 0.001$	$0.531 \pm 0.052$ $0.124 \pm 0.005$	$1.67 \pm 0.022$ $0.107 \pm 0.002$	0.005 <sup>a</sup> 0.301	0.97 0.26	<b>-0.004</b> -0.001	< 0.001
	Surface $(n=2)$ $0.458 \pm 0.126$ $0.117 \pm 0.001$	Surface $(n=2)$ 85 $(n=2)$ $0.458 \pm 0.126$ $0.531 \pm 0.052$ $0.117 \pm 0.001$ $0.124 \pm 0.005$	Surface $(n=2)$ 85 $(n=2)$ 170 $(n=2)$ $0.458 \pm 0.126$ $0.531 \pm 0.052$ $1.67 \pm 0.022$ $0.117 \pm 0.001$ $0.124 \pm 0.005$ $0.107 \pm 0.002$	Surface $(n=2)$ 85 $(n=2)$ 170 $(n=2)$ 0.458 $\pm$ 0.126 0.531 $\pm$ 0.052 1.67 $\pm$ 0.022 0.005 <sup>a</sup>	Surface $(n=2)$ 85 $(n=2)$ 170 $(n=2)$ $0.458 \pm 0.126$ $0.531 \pm 0.052$ $1.67 \pm 0.022$ $0.005^a$ $0.97$ $0.117 \pm 0.001$ $0.124 \pm 0.005$ $0.107 \pm 0.002$ $0.301$ $0.26$	Surface $(n=2)$ 85 $(n=2)$ 170 $(n=2)$ 0.458 $\pm$ 0.126 0.531 $\pm$ 0.052 1.67 $\pm$ 0.022 0.005 <sup>a</sup> 0.97 <b>-0.004</b> 0.117 $\pm$ 0.001 0.124 $\pm$ 0.005 0.107 $\pm$ 0.002 0.301 0.26 -0.001

<sup>&</sup>lt;sup>a</sup> Significance of the quadratic polynomial model. <sup>b</sup> Values were arcsine-transformed for statistical analyses.

the most significant predictor in the model (p<0.001; t=-8.69; n=139;  $R^2$ =0.736) followed by tropic level (p=0.003; t=3.02;  $R^2$ =0.047), benthic connection (p=0.014; t=-2.49;  $R^2$ =0.016) and weight, which was the least significant predictor in the model (p=0.018; t=2.39;  $R^2$ =0.008). Similar to THg, relationships were positive for weight (b'=0.194) and trophic level (b'=0.191) and negative for lipid content (b'=-0.374) and benthic connection (b'=-0.116). The general model explained 80.7% of the variation of MeHg in this food web (F(0.05)4,134=140; p<0.001).

### 4. Discussion

#### 4.1. Trophic structure

Trophic structure of the Gulf of St. Lawrence food web was similar to that observed in the North Water Polynya of northern Baffin Bay where a positive correlation was obtained between  $\delta^{15} \rm N$  and  $\delta^{13} \rm C$  for pelagic organisms but no pattern was apparent for benthic organisms (Hobson et al., 2002). Our isotopic values were similar to those found by Lesage et al. (2001) in the St. Lawrence Gulf and Estuary. This implies that overall interactions of key species are rather stable suggesting that food web structure is similar over space and time. Organisms and POM should be sampled during a complete annual cycle in future studies to avoid possible temporal fluctuations in Hg and stable isotope values. Nevertheless, similarities between the results of our study and those of Lesage et al. (2001) suggest low interannual variability.

The source of energy for our Gulf of St. Lawrence food web was greatly derived from pelagic sources (65% of species) since pelagic predatory species such as BLKI and RAZO were enriched in <sup>13</sup>C and <sup>15</sup>N relative to POM, zooplankton and pelagic fish. However, other upper TL species such as WIFL and COEI seemed to feed on benthic species, whereas HERG and GBBG obtained their energy from a mixture of both pelagic and benthic food webs. In general, benthic fish and

**Table 5** Results of simple linear regression models of THg and MeHg (ng/g ww) of organisms against  $\delta^{15}$ N or trophic level for each habitat. Slopes sharing the same letter are not significantly different. Logarithmic transformations (to the base 10) were applied to THg and MeHg values.

Terms	n	b	а	$F_{(0.05)1,n-2}$	р	$R^2$
THg * $\delta^{15}$ N						
Pelagic	65	0.218 <sup>A</sup>	-1.20	115	< 0.001	0.65
Benthopelagic	116	0.194 <sup>A</sup>	-0.40	163	< 0.001	0.59
Benthic	91	0.111 B	0.28	48.5	< 0.001	0.35
MeHg * δ <sup>15</sup> N						
Pelagic	38	0.320 <sup>A</sup>	-2.94	91.1	< 0.001	0.72
Benthopelagic	52	0.263 <sup>A</sup>	-1.50	89.1	< 0.001	0.64
Benthic	49	0.163 <sup>B</sup>	-0.80	32.4	< 0.001	0.41
THg * trophic level						
Pelagic	65	0.697 <sup>A</sup>	-1.08	147	< 0.001	0.70
Benthopelagic	116	0.649 A	-0.43	243	< 0.001	0.68
Benthic	91	0.416 B	0.15	72.9	< 0.001	0.45
MeHg * trophic lev	/el					
Pelagic	38	1.029 <sup>A</sup>	-2.76	107	< 0.001	0.75
Benthopelagic	52	0.872 <sup>A</sup>	-1.49	131	< 0.001	0.72
Benthic	49	0.595 <sup>B</sup>	-0.93	43.1	< 0.001	0.48

invertebrates had higher  $\delta^{13}$ C values compared to organisms that inhabited either pelagic or benthopelagic environments. Seabirds with such different feeding ecology were expected to vary in their  $\delta^{13}$ C values, but surprisingly, there were no significant differences. This could be interpreted by a common carbon source for these seabirds. Alternatively, this could be explained by the omnivory of some seabird species resulting in the integration of many different carbon sources (Hobson, 1993; Thompson et al., 1999).

The low  $\delta^{13}$ C values in POM indicate that a proportion of allochthonous sources of primary production came from freshwater systems (Jardine et al., 2006) such as the St. Lawrence River and/or other freshwater tributaries. POM would therefore be imported from freshwater ecosystems as well as produced *in situ*. Low  $\delta^{13}$ C values for POM in our investigation could partly explain the lower  $\delta^{13}$ C values found in pelagic organisms compared to benthic organisms (Hobson et al., 2002).

#### 4.2. Mercury distribution

Percentage of MeHg over THg for whole fish in this study was much lower than reported for the muscle portion of fish with an estimate of over 95% (Bloom, 1992; Grieb et al., 1990). This divergence is due to the difference in the percentage of MeHg in different organs such as liver and kidney which are known to have a lower proportion of MeHg than muscle tissue (Kim et al., 1996) and this reduces the overall proportion of MeHg in whole fish.

Relationships with  $\delta^{15}$ N indicated that THg and MeHg (on a wet weight basis) biomagnified at similar rates in this food web, whereas relationships on a dry weight basis or relationships with TL revealed that MeHg biomagnified at a higher rate than THg. The former result was surprising considering that MeHg is known to be the mercury

**Table 6** Results of final backward multiple linear regression models of THg and MeHg (ng/g dw) with lipid content, total weight, trophic level and benthic connection ( $\delta^{13}$ C) as predictors. Lipid content values were transformed into the arcsine of their square root and logarithmic transformations (to the base 10) were applied to THg, MeHg and weight values.

Terms	b' a	SE	t	$F_{(0.05)k,n}^{\ \ b}$	p	$R^2$
THg						
Intercept	< 0.001	0.029	< 0.001		1.000	
Lipid content	-0.682	0.028	-24.5		< 0.001	0.627
Weight	0.449	0.044	10.1		< 0.001	0.117
Trophic level	0.167	0.048	3.48		< 0.001	0.027
Benthic connection	-0.080	0.039	-2.08		0.039	0.004
$(\delta^{13}C)$						
Total				229	< 0.001	0.774
MeHg						
Intercept	0.140	0.042	3.35		0.001	
Lipid content	-0.374	0.043	-8.69		< 0.001	0.736
Trophic level	0.191	0.063	3.02		0.003	0.047
Benthic connection	-0.116	0.047	-2.49		0.014	0.016
$(\delta^{13}C)$						
Weight	0.194	0.081	2.39		0.018	0.008
Total				140	< 0.001	0.807

<sup>&</sup>lt;sup>a</sup> Standardized partial coefficients (b').

<sup>&</sup>lt;sup>b</sup> Degrees of freedom = 4, 267 for THg levels and 4, 134 for MeHg levels.

species that biomagnifies (Watras et al., 1998). The higher affinity of MeHg for thiol groups (Wolfe et al., 1998) is expected to generate a higher biomagnification potential for MeHg than for THg. Biomagnification power of THg and MeHg (slopes of relationships with  $\delta^{15}$ N) on wet and dry weight in our study were within the range (0.07 (Al-Reasi et al., 2007) to 0.32 (Jarman et al., 1996)) of other studies around the world. The high variance suggests that Hg trophodynamic differs with location, although more data are needed on those food webs (e.g., physicochemistry of water) and on other food webs around the world.

Higher and lower than predicted Hg concentrations (THg and MeHg) based on  $\delta^{15}$ N values were found for several species. This was also reflected in BMF<sub>PSC</sub> where seabirds were higher, and most fish and invertebrates were lower than FWMF. This discrepancy could be due to inter-taxa differences in energy requirements. Seabirds were the only homeotherms included in this study. Homeotherms have greater energetic requirements to sustain their metabolism; therefore, compared to poïkilotherms they consume more prey per unit body mass and will incur greater exposure to contaminants (Fisk et al., 2001). Furthermore, the turnover rate of Hg is slower (half-life of 44–65 days; Monteiro and Furness, 2001) than the turnover rate of  $\delta^{15}$ N (half-life of 14 days; Bearhop et al., 2002) in blood of seabirds. Higher MeHg exposure in birds through consumption of higher TL prey two months before blood sampling would be reflected in MeHg concentrations but not in  $\delta^{15}$ N values.

FWMF and BMF<sub>PSC</sub> were greater for MeHg than for THg and the values were comparable with highly bioaccumulative lipophilic persistent organic pollutants (POPs; Fisk et al., 2001). BMF<sub>PSC</sub> and uncorrected BMF in our study showed different results. The high variability of uncorrected BMF for a given predator and the discrepancy with BMF<sub>PSC</sub> indicates that uncorrected BMF could lead to erroneous estimates when using a single prey species. Biomagnification assessment using complex (BMF<sub>PSC</sub>) rather than simple (uncorrected BMF) predator–prey interactions seems preferable since the former calculation integrates a weighted average of potential prey items likely to constitute a realistic diet of the predators and therefore a realistic exposure to Hg.

Values of biomagnification power were greater for pelagic and benthopelagic species compared to benthic species. The generally higher concentrations of Hg at the base of the food chain (intercept) in benthic-feeding organisms compared to pelagic-feeding organisms may have resulted from greater access to the MeHg pool in the sediment layer (Cossa and Gobeil, 2000). The methylation process mediated by sulfate-reducing bacteria in the anoxic zone of sediments (Compeau and Bartha, 1985) could influence MeHg uptake for organisms living and/or feeding in the benthos. However, it seems that this pool of mercury in the benthos was not transferred efficiently through the food chain as biomagnification power was greater in pelagic and benthopelagic species compared to benthic species. Similar trends have been observed where pelagic fish were found to have generally higher Hg concentrations than benthic fish (Kidd et al., 2003) and this may be due to higher inputs of contaminants in the pelagic food web or to lower growth rate of pelagic organisms (Kidd et al., 2001). Alternatively, it has been suggested that higher levels were reached in pelagic species because MeHg ingested from particulate organic matter was more bioavailable than from direct ingestion of sediments (Chen et al., 2009). This is supported by the high percentage of MeHg found in water samples from the surface and intermediate depths in this study. Our study suggests that Hg is more bioavailable to benthic species at the base of the food chain, but trophic transfer efficiency is higher in pelagic and benthopelagic species.

When considering seabirds separately, Hg levels could not be adequately explained by trophic position as some higher trophic levels species showed low Hg concentrations (e.g., BLKI), whereas some lower trophic level species showed high Hg concentrations (e.g., GBBG). Moreover, very similar  $\delta^{13}$ C values were found across all

seabird species and habitat difference could not be used to explain variations in Hg levels. This lack of relationship could be explained by migratory patterns as species that spend more time in higher latitudes may exhibit higher Hg concentrations due to Hg deposition in these latitudes (Braune et al., 2005). This is shown by migratory species such as HERG and BLKI (Baird, 1994; Pierotti and Good, 1994) which migrate south and exhibit the lowest Hg concentrations observed in this study, whereas more resident species such as GBBG and RAZO (Good, 1998; Hipfner and Chapdelaine, 2002) showed the highest Hg concentrations. A similar effect of migration on Hg levels was observed in the eggs of these seabird species (Lavoie et al., 2010).

Total Hg and MeHg concentrations increased with body size and decreased with lipid content when all other variables were held constant with lipid content being the most significant predictor for both models. Organisms occupying higher TLs are generally larger in size and this determines the range of prey sizes they can consume and consequently their Hg exposure (Desta et al., 2008). MeHg binds to water-soluble thiol groups of amino acids such as cysteine and methionine contained in proteins (Wolfe et al., 1998). An increase in lipid content is therefore reflected in a limited amount of binding sites available in tissues for MeHg to bind (Nakao et al., 2007). Higher proportions of lipids in tissues would also have a dilution effect on Hg already contained in tissues therefore decreasing the overall Hg concentration. Organisms containing a higher proportion of lipids in their tissues are therefore expected to have lower Hg concentrations.

When all other variables were held constant, THg and MeHg concentrations decreased with connectivity with benthos. This supports that mercury is generally less bioavailable for organisms relying on benthic food sources.

#### 5. Conclusions

Simultaneous measurements of contaminants and ecological tracers have provided new insights into the trophic structure and distribution of Hg in a Gulf of St. Lawrence food web showing a major effect of TL and physical characteristics. Biomagnification of Hg in this study was in the range of other food webs around the world, but variations in biomagnification between these food webs suggest that trophodynamics is site-specific. More studies need to be done to explain variations between food webs. We showed that it was possible to calculate biomagnification factors (BMF) taking into account proportions of the various prey items consumed by a given predator, therefore providing a more realistic estimation than when using a single prey. Evidence suggests that connection to benthos was important in explaining variability in Hg concentrations. Mercury levels showed an overall decrease with  $\delta^{13}C$  when other variables (lipid, weight and trophic level) were held constant. Moreover, pelagic and benthopelagic organisms showed greater biomagnification power than benthic organisms, whereas Hg levels at the base of the food chain were higher for benthic species compared to pelagic and benthopelagic species. This may be the result of greater bioavailability of Hg in low trophic level organisms feeding in deep waters of this system, whereas Hg was transferred more efficiently in pelagic and benthopelagic food chains, resulting in greater biomagnification values. Negative relationships between Hg and lipid content suggest that lipids restrict binding sites (mostly proteins) for MeHg and have a dilution effect on Hg already contained in tissues. This study provided new information on the trophic structure and distribution of Hg in the Gulf of St. Lawrence. However, additional ecological tracers (e.g., fatty acids) as well as dietary analyses are needed in future studies to evaluate dynamics of contaminants in aquatic ecosystems. Also, more species need to be considered to provide an accurate assessment of trophic transfer of contaminants in this food web.

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