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Bioaccumulation du méthylmercure chez les invertébrés aquatiques aux latitudes tempérées et polaires : rôle des facteurs écologiques, biologiques et géochimiques

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Thèse présentée à la Faculté des études supérieures
en vue de l'obtention du grade de Philosophiae Doctor (Ph.D.)
en sciences biologiques

mars, 2009

Université de Montréal
Faculté des études supérieures

Cette thèse intitulée :

Bioaccumulation du méthylmercure chez les invertébrés aquatiques aux
latitudes tempérées et polaires : rôle des facteurs écologiques, biologiques
et géochimiques

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Une étude a été réalisée au Canada sur la bioaccumulation du méthylmercure (MeHg) chez les invertébrés de lacs et d'étangs du Québec méridionale et de l'Extrême Arctique au Nunavut. Le zooplancton et les macroinvertébrés benthiques ont été utilisés pour identifier les facteurs qui contrôlent le mouvement du MeHg dans les chaînes alimentaires pélagiques et littorales de ces deux régions distinctes : spécifiquement, ces facteurs incluent les caractéristiques physico-chimiques de l'eau et des sédiments, la morphométrie des plans d'eau et de leur bassin versant, et la taxonomie et l'alimentation des invertébrés.

Les sites échantillonnés dans l'archipel Arctique avaient des concentrations basses et relativement constantes de MeHg dans l'eau et les sédiments malgré des apports variables de mercure inorganique par les eaux de la fonte. Des processus biologiques ont mieux expliqués la teneur en MeHg dans les invertébrés que les concentrations de MeHg dans l'eau et les sédiments, la grandeur du bassin versant ou des caractéristiques physico-chimiques des sites. Ainsi, *Daphnia*, un herbivore dans la colonne d'eau, était enrichi en MeHg comparé aux autres espèces de zooplancton, et sa contribution à la biomasse zooplanctonique a mieux expliqué le niveau de mercure dans cette communauté. La densité de *Daphnia* dans les lacs arctiques a été associée avec la productivité aquatique, et un modèle conceptuel a été développé pour montrer comment le réchauffement climatique pourrait élargir la distribution de cet organisme zooplanctonique. Les voies de carbone dans les chaînes alimentaires lacustres de l'Extrême Arctique ont été examinées avec des isotopes stables de carbone et des contenus stomacaux de chironomides. Cette étude a montré que les algues benthiques

sont la source majeure d'énergie pour les chironomides et pour les ombles chevalier qui les consomment. La métamorphose a concentré le MeHg jusqu'à 3 fois plus dans les adultes de chironomides comparés aux stades immatures, et la prédation variable des larves, nymphes et adultes pourraient affecter l'accumulation du mercure dans ces poissons.

Dans les lacs tempérés du Québec, le mercure total dans les sédiments et l'eau a été influencé principalement par le transport avec le carbone organique dissous du bassin versant mais la teneur en MeHg dans les invertébrés s'est expliquée le mieux par le pH de l'eau. Le zooplancton pélagique était plus susceptible à l'accumulation du MeHg que les consommateurs primaires littoraux dans les lacs acides et les lacs humiques, et la prédation variable de ces proies pourrait affecter le transfert du mercure aux poissons.

Nous concluons que les processus biologiques et écologiques jouent un plus grand rôle dans le transfert du MeHg aux poissons que la déposition atmosphérique du mercure en Extrême Arctique. Par contre, le contrôle des processus géochimiques sur la bioaccumulation du MeHg est plus dominant dans les lacs tempérés. Dans les deux régions d'étude, la teneur en MeHg dans les invertébrés est variable entre les zones pélagiques et littorales, ce qui montre des réponses différentes aux apports de mercure entre les habitats d'un lac.

Mots clés : macroinvertébrés, zooplancton, Extrême Arctique, Québec, chironomides, *Daphnia,* littorale et pélagique, voies de carbone, isotopes stables

SUMMARY

Methylmercury (MeHg) bioaccumulation was investigated in invertebrates of lakes and ponds in the High Arctic of Nunavut and temperate Québec, Canada. Zooplankton and benthic macroinvertebrates were used to identify factors that control the movement of MeHg in pelagic and littoral food webs from these two distinct regions; specifically, physico-chemical characteristics of water and sediment, the morphometry of lakes and their watershed, and the taxonomy and diet of invertebrates.

Water bodies in the Arctic Archipelago had consistently low MeHg concentrations in water and sediment despite a range of inorganic mercury loading from snowmelt. Biological processes were key drivers of invertebrate MeHg concentration while environmental mercury levels, watershed size and habitat characteristics were secondary explanatory variables. *Daphnia*, an efficient herbivore, had elevated MeHg concentrations compared to other zooplankton species, and its biomass best explained mercury levels in this community. *Daphnia* densities in High Arctic lakes were related to aquatic productivity, and a conceptual model was developed to show how climate warming may increase the presence of these mercury-rich zooplankton. Carbon flow in High Arctic lakes was determined using carbon stable isotopes and chironomid gut contents, which indicated that chironomids, and the Arctic char that consume them, were supported primarily by benthic algae. Metamorphosis concentrated MeHg in adult chironomids up to 3 times more than in immature stages, and differential consumption of larvae, pupae and adults may affect MeHg uptake by Arctic char.

In temperate Quebec lakes, total mercury in sediment and water were mediated primarily by dissolved organic carbon transport from the drainage basin while invertebrate MeHg concentration was best explained by water pH. Pelagic zooplankton

were more susceptible to MeHg accumulation than littoral primary consumers in acidic and humic lakes, and differential consumption of these prey likely impact mercury transfer to fish.

We conclude that biological and food web processes play a greater role in MeHg transfer to fish than atmospheric mercury deposition in the High Arctic. In contrast, geochemical control of MeHg bioaccumulation is more predominant in temperate lakes. In both regions, habitat-specific variation in invertebrate MeHg concentration show that pelagic and littoral food webs can respond differently to mercury supply.

Key words: methylmercury, macroinvertebrates, zooplankton, High Arctic, Quebec, chironomids, *Daphnia*, carbon flow, habitat-specific bioaccumulation, stable isotopes

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SYNTHÈSE

LISTE DES ABBRÉVIATIONS

Français

Carbone organique dissous	COD
Méthylmercure	MeHg

Anglais

Cold vapour atomic fluorescence-spectrometry	CVAFS
Chlorophyll *a*	Chl
Dissolved organic carbon	DOC
Drainage basin area	DA
Drainage area: water body surface area	DA:SA
Drainage area: lake area	DA:LA
General linear model	GLM
Lake area	LA
Loss on ignition	LOI
Maximum depth	Z_{max}
Methylmercury	MeHg
Organic matter	OM
Principal component analysis	PCA
Total mercury	THg
Total phosphorus	TP
Volume	V
Water body surface area	SA

REMERCIEMENTS

Je suis très reconnaissant envers mon directeur, docteur Marc Amyot, de m'avoir reçu dans son laboratoire, de m'avoir guidé et, en même temps, de m'avoir donné une grande liberté dans mon travail. J'ai un grand respect pour sa clarté et ses connaissances en écologie et en biogéochimie; ses conseils ont été essentiels dans le développement des mes études et m'ont aidé à approfondir mes réflexions. Marc était très patient avec moi durant nos discussions, en particulier au début de mon doctorat quand ma capacité de m'exprimer en français étaient parfois laborieuse; je le remercie également pour cela.

Je tiens à remercier les membres du jury de ma thèse d'avoir accepté d'examiner ce travail : les docteurs Gilbert Cabana, Landis Hare et Bernadette Pinel-Alloul.

Un grand merci au chimiste analyste du labo, Dominic Bélanger, pour son enseignement, son aide, sa patience et sa disponibilité au cours de mon travail de laboratoire pendant ces quatre dernières années. Son bon sens de l'humour, sa gentillesse et son amitié ont rendu les longues heures d'analyses plus agréables.

Je voudrais également remercier Alexandre Poulain pour son encouragement, son enthousiasme et son amitié au cours de mon doctorat. La qualité de sa recherche et ses grands succès m'ont beaucoup inspiré.

J'ai eu le plaisir de connaître plusieurs personnes au laboratoire : Ariane Bouffard, qui m'a assisté avec enthousiasme durant mon premier été de terrain, Ariane Cantin, Saad Chidami, Édenise Garcia, Valérie Girard, Stéphanie Hamelin, Mylène Ratelle, Ousséni Ouedraogo et Virginie Roy. J'apprécie l'aide de plusieurs membres du département : Claudette Blanchard, Kwélé Bongue-Boma, Mélanie Bouffard, docteur Richard Carignan, docteur Antonella Cattaneo, Louise Cloutier, docteur Roxane Meranger et Ginette Méthot. Un grand merci à Louise d'avoir toujours été disponible et

enthousiaste quand je lui apportait encore un autre échantillon d'invertébrés. Elle a une passion pour son travail, et j'ai trouvé nos collaborations très agréables. Je voudrais aussi remercier Ginette pour ses identifications du zooplancton, pour sa générosité, et pour son humour qui a apporté de la vie au département.

I wish to thank my parents and brother for their continuous support over the years.

Finally, I am very grateful to my dear Roselyn, for her encouragement, love and patience during my studies. When we moved to Montreal in 2004, she made difficult sacrifices for me with respect to her career and personal life, and I am indebted to her. In parallel with my Ph.D., we embarked on another journey, that of parenthood, and I thank Amelia and Liam for grounding me in a way that only little people can.

INTRODUCTION GÉNÉRALE

Le mercure est un contaminant global qui est transporté à grande distance dans l'atmosphère et se dépose loin des sources d'émissions naturelles et anthropiques. Même en régions éloignées, la teneur en mercure est souvent élevée dans la chair de poissons (Braune et al. 1999), et ce métal lourd cause la majorité des avis de consommation du poisson en eaux douces parmi les contaminants surveillés par les gouvernements en Amérique du Nord (MOE 2007; EPA 2007). La voie principale pour le transfert du mercure aux humains est la consommation de poisson provenant des eaux douces et marines, et l'exposition excessive au méthylmercure (MeHg) est préoccupante à cause des effets négatifs sur le développement du système nerveux et son rôle potentiel dans les cardiopathies (Choi et Grandjean 2008).

Le mouvement du mercure dans l'environnement est complexe parce que ce métal existe sous plusieurs formes et subit des transformations par de nombreux processus géochimiques et microbiens. La recherche intensive au cours des dernières décennies a élucidé les processus fondamentaux du cycle du mercure (Fitzgerald et Lomborg 2004) mais plusieurs problématiques ne sont pas encore résolues. Parmi eux, le transfert du MeHg aux chaînes alimentaires aquatiques en Extrême Arctique reste peu connu, et la possibilité de contamination par la déposition intensive de mercure atmosphérique génère de l'inquiétude (AINC 2003; Macdonald et al. 2003). En régions tempérées, les facteurs qui déterminent le niveau de mercure dans les poissons sont beaucoup mieux compris mais les modèles sont biaisés par l'accent mis sur la chaîne alimentaire pélagique comparé à celle de la zone littorale (e.g., Watras et al. 1998; Pickhardt et al. 2002). La bioaccumulation du MeHg dans la chaîne alimentaire littorale reste peu comprise, et des différences avec la zone pélagique pourraient avoir des conséquences

pour la bioamplification du mercure aux poissons (Power et al. 2002; Gorski et al. 2003; Stewart et al. 2008).

L'objectif général de cette thèse est d'investiguer le transfert du mercure au sein des chaînes alimentaires lacustres en Extrême Arctique et dans la zone tempérée du Québec. J'ai utilisé les invertébrés aquatiques, spécifiquement le zooplancton pélagique et les macroinvertébrés littoraux, comme organismes indicateurs pour comparer le mouvement du mercure entre différents types de lacs et entre les habitats d'un même lac. Les invertébrés sont des bons indicateurs de la bioaccumulation du MeHg dans les chaînes alimentaires (Garcia et Carignan 1999; Tsui et Wang 2004), et ils représentent la voie principale pour son transfert aux poissons (Hall et al. 1997). J'ai appliqué une approche empirique en utilisant des données de terrain pour investiguer les facteurs clés qui contrôlent le mouvement du mercure tels que la physico-chimie de l'eau et des sédiments, la morphométrie des lacs et leurs bassins versants, la taxonomie, et la nourriture des invertébrés.

À la fin de cette introduction, je présente les objectifs spécifiques de mes études réalisées durant mon doctorat et exposées dans les 4 chapitres de cette thèse. Mais tout d'abord, je commence avec une revue brève de la littérature concernant la bioaccumulation du MeHg dans les organismes aquatiques, un survol des invertébrés lacustres, et une description de l'environnement en Extrême Arctique. La teneur en MeHg dans les organismes est contrôlée par divers processus biologiques, écologiques et géochimiques qui se réalisent à différentes échelles durant le transport du mercure à un lac, la production *in situ* du MeHg, et le transfert dans les chaînes alimentaires.

La spéciation du mercure et ses transformations dans l'environnement

Le mercure a quelques caractéristiques spéciales qui influencent ces nombreuses transformations dans l'environnement. Ce métal a une haute pression de vapeur et, par conséquent, la phase gazeuse est importante dans le cycle global (Fitzgerald et Lamborg 2004). Le mercure forme des liaisons fortes avec le soufre et ces interactions jouent un rôle clé dans ses transformations et sa spéciation (Barkay et al. 2003; Zhang et al. 2004; Schaefer et Morel 2009). En plus, les transformations biologiques sont très actives tels que les réactions oxydation-réduction du mercure inorganique et la méthylation (Fitzgerald et Lamborg 2004).

Le mercure inorganique a deux états d'oxydation, la forme élémentaire, Hg(0), et la forme ionique, Hg(II). Le mercure ionique est l'espèce la plus abondante dans les eaux douces mais c'est l'espèce organique, le MeHg, qui se bioamplifie le long de la chaîne alimentaire (Morel et al. 1998). Dans les eaux oxiques, le mercure ionique et le MeHg forment des complexes principalement avec des hydroxydes, des chlorures et des substances humiques dépendant du pH et de la concentration des chlorures mais les complexes avec les sulfides dominent en conditions anoxiques (Morel et al. 1998).

En milieux aquatiques, le mercure ionique est réduit en mercure élémentaire par des réactions photochimiques (Amyot et al. 1994) ou des transformations biologiques (Barkay et al. 1989; Poulain et al. 2004) et par la suite, il est émit vers l'atmosphère. Des réactions photochimiques également transforment le mercure élémentaire dissous en mercure ionique (Lalonde et al. 2001, 2004). Donc, l'évasion du mercure élémentaire gazeux dans la colonne d'eau varie dans le temps et l'espace selon les influences de la lumière, le carbone organique dissous (COD), la température et l'activité bactérienne sur

les réactions d'oxydation et de réduction (Siciliano et al. 2002; Fitzgerald et Lamborg 2004; Garcia et al. 2005). Le mercure ionique est transformé en MeHg principalement par la production bactérienne mais des réactions abiotiques sont possibles (Siciliano et al. 2005). La déméthylation par la lumière et les bactéries se réalise dans l'eau et dans les sédiments (Sellers et al. 1996; Pak et Bartha 1998).

Les apports de mercure aux lacs

Le mercure se trouve naturellement dans l'environnement mais, depuis la révolution industrielle, les activités anthropiques ont libéré de plus en plus de mercure vers l'atmosphère et vers les milieux aquatiques et terrestres (Fitzgerald et al. 1998). Aujourd'hui, les émissions du mercure provenant des sources anthropiques dominent le cycle global de cet élément (Mason et al. 1994; Schuster et al. 2002). Le mercure élémentaire est émis vers l'atmosphère par la combustion du charbon et des déchets, l'extraction artisanale et industrielle de l'or et la production de ciment (Fitzgerald et Lomborg 2004; UNEP 2008). Il est ensuite transporté sur de grandes distances et déposé durant des évènements de précipitation humide et sèche. L'analyse des carottes de sédiments lacustres et de tourbe indiquent que la déposition atmosphérique du mercure a augmenté durant le dernier siècle, même en régions qui sont très loin des sources (Fitzgerald et al. 1998).

Le mercure est transporté vers les lacs par l'écoulement des eaux sur le bassin versant et par la déposition atmosphérique directement sur la surface de l'eau. Le mercure inorganique déposé directement sur un lac est rapidement transformé en MeHg et transféré aux organismes aquatiques; par contre, le mercure déposé sur le bassin versant est libéré très lentement par les sols et la végétation terrestre (Harris et al. 2007). La

grandeur du bassin versant et la proportion occupée par des zones humides sont positivement reliées aux apports du mercure inorganique et également du MeHg (St. Louis et al. 1996; Fitzgerald et al. 2005; Hammershmidt et al. 2006). Les zones humides dans le bassin versant sont des endroits de haute production du MeHg à cause de l'abondance de matière organique et de sulfate (St. Louis et al. 1996). La teneur en MeHg dans les poissons et les invertébrés lacustres est souvent corrélée avec la concentration aqueuse du COD, ce qui reflète les apports de mercure provenant du bassin versant (Westcott et Kalff 1996; Garcia et Carignan 1999; Rennie et al. 2005).

La production in situ de MeHg en lacs

Le MeHg dans l'eau de lacs tempérés provient de deux sources majeures, la production *in situ* et les zones humides du bassin versant. Des bilans de masses indiquent que la production dans l'hypolimnion du lac est généralement plus importante que les apports du bassin versant par un ordre de grandeur (Sellers et al. 2001; Watras et al. 2005). La déposition atmosphérique est une source mineure de MeHg en régions tempérées (Downs et al. 1998), mais elle pourrait être plus importante en Extrême Arctique (St. Louis et al. 2005).

Les sédiments lacustres sont généralement l'endroit principal de la méthylation où la production du MeHg se réalise en conditions anoxiques dans les premiers 5 cm de profondeur (Zhang et al. 2004). Les eaux anoxiques dans l'hypolimnion et le périphyton ont été identifiées comme d'autres sites de méthylation dans un lac (Regnell et al. 1997; Watras et al. 2005; Desrosiers et al. 2006). Suite à la production dans les sédiments, le MeHg diffuse à la colonne d'eau où il est assimilé par des microorganismes, dégradé par la lumière ou les bactéries (Sellers et al. 1996; Barkay et al. 2003), ou adsorbé sur des

particules suspendues et renvoyé aux sédiments (Morel et al. 1998).

Les bactéries sulfato-réductrices sont considérées responsables pour la production du MeHg dans les écosystèmes aquatiques (Compeau et Bartha 1985) mais il est possible que les bactéries réductrices de fer soient aussi impliquées (Fleming et al. 2006). La méthylation bactérienne est une réaction enzymatique utilisant le groupe méthyle de la méthylcobalamine et le Hg (II) complexé aux sulfures inorganiques ou à d'autres ligands soufrés comme la cystéine (Barkay et al. 2003; Schaefer et Morel 2009). Le taux de méthylation en eaux douces augmente en fonction de la température de l'eau et des concentrations de Hg (II), de sulfate et de matière organique (Gilmour et al. 1992; Ramlal et al. 1993; Heyes et al. 2000). Le pH acide stimule la méthylation bactérienne probablement parce que le mercure inorganique est plus biodisponible (Kelly et al. 2003).
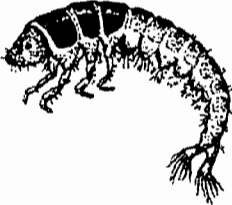
La bioaccumulation et la bioamplification du MeHg dans les chaînes alimentaires

Le MeHg est 10 à 100 000 fois plus concentré dans les algues que dans l'eau, et ce transfert représente la plus grande étape de bioaccumulation dans la chaîne alimentaire (Mason et al. 1996; Watras et al. 1998). Actuellement, ni les mécanismes pour le transport à travers la membrane cellulaire (passif ou actif), ni la spéciation du MeHg assimilée par les algues ne sont claires. Mason et al. (1996) ont conclut que le transport du MeHg à travers la membrane d'une diatomée marine était par la diffusion mais d'autres études suggèrent que le transport actif est impliqué (Moye et al. 2002; Pickhardt et Fisher 2007). Le rôle de la matière organique dissoute est également obscur, peut-être dû à la complexité de ce mélange de ligands. La formation de complexes entre le MeHg et la matière organique peut à la fois réduire ou augmenter sa biodisponibilité aux algues

(Pickhardt et Fisher 2007; Gorksi et al. 2008). Les thiols sont des ligands qui stimulent la bioconcentration du MeHg dans les algues (Lawson et Mason 1998).

La productivité d'un lac influence la concentration du MeHg dans les algues par le processus de biodilution (Pickhardt et al. 2002). La bioconcentration diminue avec une augmentation de l'abondance des algues parce que le MeHg aqueux est distribué entre plus de cellules, et par conséquent, la bioamplification au niveau du zooplancton est aussi réduite. Ce mécanisme peut expliquer pourquoi les poissons dans les lacs eutrophisés ont souvent une plus faible teneur en mercure que ceux dans les lacs oligotrophes (Chen et Folt 2005).

Selon les modèles bioénergétiques, l'accumulation du MeHg chez les consommateurs aquatiques se réalise en fonction des concentrations de mercure dans l'eau et la nourriture, le taux d'ingestion, l'assimilation, le taux d'élimination, le taux de croissance et les pertes durant les fonctions biologiques comme la métamorphose ou la reproduction (Figure 1). Le MeHg s'accumule dans les consommateurs parce que le taux d'assimilation est élevé mais le taux d'élimination est très bas (Headon et al. 1996; Lawson et Mason 1998). Les invertébrés et les poissons assimilent la plupart de leur charge en MeHg par la nourriture au lieu de la bioconcentration directement par l'eau (Hall et al. 1997; Tsui et Wang 2004). De plus, si nous supposons que les pertes par des processus biologiques sont mineures (ce qui n'est pas toujours le cas; e.g., Sarica et al. 2005), la teneur en MeHg dans les consommateurs est principalement contrôlée par la concentration dans la nourriture, le taux d'ingestion et le taux de croissance. Les invertébrés et les poissons ayant un taux de croissance plus élevé ont une plus faible teneur en mercure parce que plus de biomasse est ajouté par unité de mercure consommée (Kidd et al. 1999; Karimi et al. 2007).

$$dC_o/dt = (K_a \times C_e) + (\alpha \times C_a \times K_i) \quad -(K_d + G + K_e) \times C_o$$

Accumulation de MeHg ⟶ ... **Décontamination de MeHg** ⟶

Paramètre	Déscription	Unités
K_a	taux d'absorption de MeHg aqueux	L g^{-1} jour^{-1}
C_e	concentration de MeHg dissous dans l'eau	ng L^{-1}
α	taux d'assimilation	%
C_a	concentration de MeHg dans la nourriture	ng g^{-1}
K_i	taux d'ingestion	g g^{-1} jour^{-1}
K_d	taux d'élimination	jour^{-1}
G	taux de croissance	jour^{-1}
K_e	élimination de MeHg par la mue	jour^{-1}
C_o	concentration de MeHg dans l'organisme	ng g^{-1}

Figure 1. Modèle bioénergétique de la bioaccumulation du MeHg chez un invertébré aquatique (adapté de Roditi et al. 2000; Trudel et Rasmussen 2001). L'illustration est de University of Wisconsin-Extension (2009).

Le niveau trophique du consommateur est une des meilleures variables prédictives de leur teneur en MeHg. La concentration dans la biomasse est bioamplifiée d'environs 2 à 7 fois entre un consommateur et sa proie (Mason et Sullivan 1997; Gorski et al. 2003). En conséquence, la teneur en MeHg dans les prédateurs au sommet des chaînes alimentaires augmente avec le nombre de maillons dans la chaîne (Cabana et Rasmussen 1994; Vander Zanden et Rasmussen 1996). Le mercure a aussi tendance à se bioaccumuler en fonction de l'âge et la taille d'un poisson parce que les coûts énergétiques associés avec leur activité augmentent et les plus gros poissons consomment des plus grosses proies enrichies en mercure (Trudel et Rasmussen 2006). De même, les invertébrés avec des longs cycles de vie comme les moules d'eaux douces accumulent le mercure en fonction de l'âge et la taille de l'individu (Metcalfe-Smith et al. 1996). Par contre, cela n'est pas le cas pour d'autres macroinvertébrés avec des cycles de vie de 1–2 ans comme les odonates (Tremblay 1999).

Survol des communautés d'invertébrés lacustres

Il existe une grande diversité d'invertébrés aquatiques qui varient en termes de leur morphologie, taxonomie, mode d'alimentation et habitat. Historiquement, l'étude écologique des invertébrés a été séparée selon leur habitat : le zooplancton, qui se trouve dans la colonne d'eau et le zoobenthos, qui se trouve sur des substrats. Le macrozooplancton (individus > 200 μm) comprend 2 groupes de crustacés, les copépodes et les cladocères, mais d'autres crustacés (e.g., les mysidacés) et des larves d'insectes (e.g., *Chaoborus*) se nourrissent également dans la colonne d'eau pélagique. Les communautés de macroinvertébrés (individus > 500 μm) associés avec le benthos sont plus diversifiées et incluent les crustacés (e.g., les amphipodes, les isopodes, les

écrevisses), les mollusques (e.g., les gastéropodes, les bivalves), et un grand nombre de groupes d'insectes (e.g., les diptères, les odonates, les tricoptères, les éphémères, les hémiptères, les coléoptères).

Dans les lacs tempérés, la majorité du zoobenthos se trouve dans la zone littorale où l'habitat est plus productif et chaud comparé aux sédiments profonds (Kalff 2002). La présence des macrophytes augmente la complexité des structures dans l'habitat, ce qui soutien une plus grande diversité d'invertébrés (Heino 2008). En Extrême Arctique, les lacs n'ont pas de macrophytes et les sediments littoraux sont appauvris en matière organique, ce qui contribue probablement à la très faible diversité de macroinvertébrés. Dans ces écosystèmes, la production des consommateurs primaires est dominée par les chironomides, qui sont représentés par une dizaine d'espèces dans un lac. Une espèce de trichoptère ou de mysidacé peut être présent à faible densité (Minns 1977; Rigler 1978).

Les groupements fonctionnels d'alimentation offrent une classification des macroinvertébrés qui les sépare selon leurs rôles écologiques dans la chaîne alimentaire benthique (Merritt et Cummins 1996). Les broyeurs transforment des grosses particules de matière organique comme les feuilles en plus petites tailles pour leur consommation. Les collecteurs consomment des particules fines par la filtration de la colonne d'eau ou en les recueillant dans les sédiments. Certains herbivores comme les gastéropodes grattent les surfaces pour consommer les algues et d'autres percent les plantes ou les algues pour se nourrir des fluides dans les cellules et les tissus. Les prédateurs avalent ou percent d'autres invertébrés pour les consommer.

Les espèces de zooplancton obtiennent leur nourriture de la colonne d'eau par la filtration ou l'alimentation sélective des particules (Barnett et al. 2007). La plupart des cladocères se nourrissent par la filtration, un processus durant lequel les particules sont

recueillies avec l'aide de courants produits par les appendices. Les copépodes sont plus actifs dans leur sélection des particules et ils utilisent les pièces buccales pour saisir leurs proies (Koehl et Strickler 1981). En générale, les copépodes cyclopoïdes nagent afin d'attraper leur nourriture contrairement aux copépodes calanoïdes qui sont plus stationnaires (Barnett et al. 2007).

Parmi les invertébrés aquatiques, il y a certains groupes qui sont clairement des herbivores comme les bivalves et les gastéropodes, et d'autres qui sont des prédateurs comme les odonates et les bélostomes. Pourtant, l'alimentation omnivore est considérée très répandue, et beaucoup de macroinvertébrés et de copépodes consomment probablement un mélange de détritus, d'algues et de méiofaune (Merritt et Cummins 1996; Barnett et al. 2007). Les algues planctoniques et benthiques fournissent l'énergie aux consommateurs dans les lacs mais les apports terrestres de matière organique peuvent également être importants dans les eaux humiques (Cole et al. 2006; Solomon et al. 2008).

Bioaccumulation du MeHg dans la zone littorale

Il y a une tendance parmi les écologistes de concentrer leurs études sur les communautés dans la zone pélagique malgré l'importance des invertébrés littoraux dans les flux d'énergie aux poissons (Vadeboncoeur et al. 2002). Ce biais s'applique également à l'étude de la bioaccumulation du MeHg dans les lacs, et il existe un manque de connaissances sur le transfert du mercure dans la chaîne alimentaire de la zone littorale. Les modèles empiriques qui démontrent un lien entre la teneur en MeHg dans les invertébrés littoraux et les caractéristiques environnementales sont rares comparé au

zooplancton pélagique (Rennie et al. 2005), et les facteurs qui contrôlent la bioaccumulation chez les macroinvertébrés sont moins clairs.

Deux observations suggèrent que les zones littorales sont différentes : 1) les poissons qui se nourrissent dans la zone pélagique ont souvent une plus forte teneur en mercure que les poissons benthivores (Power et al. 2002; Kidd et al. 2003; Stewart et al. 2008), et 2) le zooplancton et les macroinvertébrés ne semblent pas répondre également lors d'une augmentation du MeHg aqueux dans l'écosystème (Paterson et al. 1998; Orihel et al. 2008). La bioaccumulation du MeHg dans la chaîne alimentaire littorale pourrait être différente à cause d'une variabilité dans l'exposition du MeHg aqueux, des différentes écologies entre les groupes d'invertébrés, ou la bioconcentration dans les ressources de base qui soutiennent la chaîne.

Le traçage des voies du carbone par isotopie

Les voies de carbone et de MeHg sont intimement liées, et les isotopes stables de carbone offrent une méthode puissante pour caractériser la chaîne alimentaire. Le rapport isotopique ($^{13}C/^{12}C$) d'un matériel est exprimé en notation delta ($\delta^{13}C$) comme la déviation en parties par mille (‰) par rapport à un étalon international. Il y a peu de fractionnement du rapport isotopique de carbone entre un consommateur et sa nourriture (0.47 ± 1.23‰; Vander Zanden et Rasmussen 2001), ce qui facilite le traçage des voies si les rapports $\delta^{13}C$ des sources de carbone sont suffisamment distinctes. Les isotopes stables de carbone sont couramment utilisés pour l'étude des chaînes alimentaires aquatiques à fin d'identifier l'alimentation dans la zone pélagique et littorale (e.g., Hecky et Hesslein 1995; Post 2002) et de déterminer le rôle des flux d'énergie autochtones et terrestres (e.g., Grey et al. 2001; Cole et al. 2006). En général, les algues

benthiques sont enrichies en $\delta^{13}C$ comparé aux algues planctoniques à cause d'une couche limite plus épaisse qui réduit la disponibilité du dioxyde de carbone et la discrimination entre les 2 isotopes stables (Hecky et Hesslein 1995). Le rapport $\delta^{13}C$ des plantes terrestres est relativement constant, oscillant autour de -28‰ (Peterson et Fry 1987).

La décomposition de la matière organique est très lente en Arctique, et il y a des grands réservoirs du vieux carbone dans les sols et la tourbe (Abbott et Stafford 1996; Schultz 2005; Ping et al. 2008). L'isotope radioactif du carbone (^{14}C) indique l'âge de la matière organique et permet d'identifier le mouvement du vieux carbone vers les lacs et dans les chaînes alimentaires. Les apports du carbone organique particulaire et dissous aux lacs arctiques sont appauvris en ^{14}C, et la couche supérieure des sédiments lacustres est souvent datée à un âge d'environ 1000 ans (Abbott et Stafford 1996). Donc, la matière organique dans les sédiments est un mélange du vieux carbone provenant du bassin versant et de la production moderne par les algues. En Alaska, la tourbe est une source importante d'énergie pour les chaînes alimentaires des eaux douces (Schell 1983; Hershey et al. 2006).

Le cycle du mercure en Extrême Arctique

Les conditions extrêmes en régions polaires influencent le mouvement du mercure dans cet environnement. Les lacs sont complètement couverts de glace pendant 8 mois, de la fin de septembre à juin, et par conséquent, ces écosystèmes sont fermés aux apports et à l'évasion du mercure pour la plupart de l'année. Les précipitations atmosphériques sont déposées principalement sous forme de neige durant l'hiver (Woo 1983), et les eaux de la fonte transportent la majorité des apports de mercure de façon intensive en juin

(Semkin et al. 2005). L'eau et les sédiments contiennent très peu de matière organique (particulaire et dissoute) et la production planctonique est très faible, ce qui empêche la rétention du mercure dans les lacs (Outridge et al. 2007). Il existe un phénomène particulier aux régions polaires où suite au lever du soleil au printemps (après plusieurs mois d'obscurité), il y a des évènements de dépositions massives de mercure atmosphérique sur la neige (Schroeder et al. 1998). Les réactions d'oxydation et de réduction à l'interface de l'atmosphère et de la neige constituent la partie du cycle de mercure la plus étudiée en Extrême Arctique (Steffen et al. 2008). Actuellement, il n'existe aucune donnée publiée sur le taux de méthylation bactérienne en eaux douces de l'Extrême Arctique mais les sols des zones humides ont le potentiel de produire le MeHg (Loseto et al. 2004b; Oiffer et Siciliano 2009). La méthylation se produit dans les sédiments de lacs arctiques en Alaska mais ces écosystèmes de plus basses latitudes sont plus productifs et sont stratifiés (Hammerschmidt et al. 2006). L'omble chevalier (*Salvelinus alpinus*) est la seule espèce de poisson dans beaucoup de lacs de l'archipel Arctique, et les facteurs qui contrôlent la bioaccumulation ne sont pas clairs malgré la surveillance de leur teneur en mercure depuis les années 1990 (Muir et al. 2005). Dans ces écosystèmes, il y a un manque de connaissances sur le transfert du mercure au sein des chaînes alimentaires aquatiques et sur la bioaccumulation du MeHg dans les maillons trophiques inférieures.

Évolution rapide de l'environnement en Extrême Arctique

Le réchauffement climatique entraîne de grands changements au niveau des écosystèmes en Arctique, dont les plus dramatiques ont été observés lors de la dernière décennie. La fonte de la banquise accélère plus rapidement que prévu, et une perte

record en 2007 suggère qu'un seuil a été franchi (NSIDC 2008). Moins de glace couvrant l'océan Arctique durant l'été augmentera la température de la région et accéléra la fonte des glaces terrestres. D'autres effets du réchauffement sont visibles, notamment l'assèchement des mares terrestres (Smol et Douglas 2007), les pertes des grandes plates-formes de glace (Mueller et al. 2008), et les glissements du pergélisol (Lamoureux 2007). De plus, la composition des communautés d'algues et d'invertébrés a changé depuis le $19^{ième}$ siècle dans les eaux douces en Arctique (Smol et al. 2005). Ces changements sont attribués à une plus longue saison sans glace en été et une augmentation de la productivité primaire (Michelutti et al. 2005; Keatley et al. 2008).

Ce contexte des changements climatiques est donc important dans l'étude de la bioaccumulation du MeHg en Extrême Arctique. Des variations dans les flux de la matière organique, la productivité biologique et la température auront certainement des conséquences pour le cycle du mercure (Hammerschmidt et al. 2006). Déjà, le taux de déposition du mercure a augmenté dans les sédiments de certains lacs arctiques durant le $20^{ième}$ siècle, en partie causé par une augmentation de productivité primaire (Outridge et al. 2007). De plus, des changements dans la composition des communautés pourraient avoir des effets sur le transfert du MeHg dans les chaînes alimentaires aquatiques.

Introduction aux chapitres de la thèse

Transfert du mercure aux chaînes alimentaires dans les eaux douces de l'Extrême Arctique

Depuis la découverte des pertes massives de mercure atmosphérique vers la fin du $20^{ième}$ siècle, il y a eu des craintes de contamination par le mercure en régions polaires, et l'impact de ces apports pour les chaînes alimentaires aquatiques est considéré une

priorité de recherche (AINC 2003; Macdonald et al. 2003). Il est maintenant clair qu'une grande partie du mercure déposé sur la neige est rapidement réduite et revolatilisée à l'atmosphère (Steffen et al. 2008), néanmoins des concentrations élevées de mercure sont mesurées dans les eaux de la fonte de neige qui entrent dans les lacs au printemps (Loseto et al. 2004a; St. Louis et al. 2005).

Les buts de cette recherche dans l'archipel Arctique canadien étaient : (1) de déterminer les facteurs qui influencent la bioaccumulation du MeHg dans les invertébrés aquatiques, et (2) d'examiner l'impact de la déposition atmosphérique sur cette accumulation. J'ai testé l'hypothèse générale que la teneur en MeHg dans les invertébrés aquatiques est déterminée par les caractéristiques chimiques et morphométriques du plan d'eau et influencée par la taxonomie de ces organismes. J'ai aussi testé l'hypothèse que les sites ayant un plus grand ratio du bassin versant (superficie du bassin versant sur la superficie du lac) contiennent des invertébrés avec des concentrations élevées en MeHg parce que ces plans d'eau reçoivent plus de mercure provenant de la neige.

Les hypothèses ont été testées pour le zooplancton dans le chapitre 1 et pour les invertébrés benthiques (les chironomides) dans le chapitre 2. Le premier chapitre montre que la composition du zooplancton a une influence importante sur la teneur en MeHg dans la communauté, et donc, les déterminants de la composition sont aussi explorés. Le deuxième chapitre examine en plus de détail l'influence du bassin versant sur le mercure dans les sédiments et l'eau, et ensuite le rôle de la métamorphose dans la bioaccumulation du MeHg chez les chironomides. Le troisième chapitre porte sur l'alimentation des chironomides et l'importance des sources de carbone autochtone et terrestre. Ce thème diverge légèrement des objectifs principaux du projet en Arctique

mais cette information est toutefois pertinente pour mieux comprendre les voies d'énergie et par conséquent, du mercure dans la chaîne alimentaire.

Comparaison de la bioaccumulation du MeHg chez le zooplancton pélagique et les invertébrés littoraux de lacs tempérés du Québec

L'habitat où un poisson se nourrit dans un lac peut influencer sa teneur en mercure, et les planctivores de la zone pélagique ont souvent plus de mercure que les benthivores (Power et al. 2002; Kidd et al. 2003; Stewart et al. 2008). Ces observations suggèrent que le mouvement du mercure n'est pas le même au sein des habitats dans un lac, et une différence dans la teneur en MeHg entre les invertébrés littoraux et le zooplancton pélagique pourrait possiblement expliquer ce patron.

Les buts principaux de cette recherche sur les lacs du Québec étaient d'examiner l'influence des caractéristiques environnementales (spécifiquement le COD, le pH, et la productivité du lac) sur la bioaccumulation du MeHg chez les invertébrés aquatiques et de déterminer le rôle de l'habitat lacustre dans cette bioaccumulation. En premier lieu, j'ai testé l'hypothèse que la teneur en MeHg dans les macroinvertébrés littoraux est influencée par les mêmes facteurs environnementaux que pour le zooplancton. Ensuite, j'ai testé l'hypothèse que le zooplancton pélagique a une plus forte teneur en MeHg que les macroinvertébrés (consommateurs primaires) dans la zone littorale, ce qui est en accord avec les différences en mercure entre les poissons planctivores et benthivores souvent publiées dans la littérature. J'ai aussi investigué l'influence de la variabilité spatiale du MeHg aqueux entre l'hypolimnion, l'épilimnion et la zone littorale et le rôle du niveau trophique des invertébrés sur la bioaccumulation du MeHg. Dans le chapitre

4, je teste ces hypothèses avec des données recueillies de 8 lacs au Québec qui varient largement dans leurs caractéristiques chimiques et leur contamination en mercure.

Originalité de la thèse

La recherche présentée dans cette thèse fournit les premières conclusions publiées au sujet des influences des facteurs géochimiques, biologiques et écologiques sur la bioaccumulation du MeHg dans les chaînes alimentaires lacustres en Extrême Arctique. Les résultats portent spécifiquement sur une problématique d'actualité, celle du rôle des apports du mercure provenant du bassin versant qui ultimement ont leur origine au niveau de la déposition atmosphérique. Nous abordons également un autre sujet qui reste peu développé, les effets du réchauffement climatique sur la bioaccumulation du mercure en Extrême Arctique, et nous fournissons un modèle conceptuel qui souligne des effets potentiels à long terme sur la communauté de zooplancton. À tous les sites au Québec et en Extrême Arctique, nous avons mesuré la teneur en MeHg dans les invertébrés planctoniques et littoraux pour avoir une étude qui intègre ces deux chaînes alimentaires. Nos résultats de lacs tempérés soulignent la variabilité de la bioaccumulation à l'échelle de l'habitat; cette variabilité est peu reconnue mais peut être aussi importante que la variabilité entre lacs.

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CHAPITRE 1

Elevated methylmercury in High Arctic *Daphnia* and the role of productivity in controlling their distribution

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John Chételat and Marc Amyot

ABSTRACT

Mercury is a contaminant of concern in polar regions due to long-range atmospheric transport of this metal from southern latitudes followed by intense deposition on snow. We surveyed zooplankton in 16 lakes and ponds in the Canadian Arctic Archipelago (74–76°N) to determine their methylmercury (MeHg) concentrations and the role of environmental characteristics and taxonomic composition on accumulation processes. Zooplankton communities containing *Daphnia* (mainly *D. middendorffiana*) had on average 5 times the MeHg concentration of copepod-dominated communities. The percent biomass of *Daphnia* best explained MeHg variation in bulk zooplankton compared to water chemistry and morphometric variables. Water-column concentrations of MeHg were low at most study sites (mainly ≤ 0.07 ng L^{-1}), and *Daphnia* strongly bioaccumulated mercury through species-specific processes. Since we observed *Daphnia* in more productive water bodies (i.e., ponds, a eutrophied lake), we then tested the role of productivity in determining the distribution of this keystone herbivore using a broad-scale literature data set of 47 High Arctic lakes (65–77°N). *Daphnia* density was positively related to the amount of organic carbon in the water-column in both dissolved and particulate fractions (DOC partial $R^2_{adj} = 0.39$, $p < 0.001$; POC partial $R^2_{adj} = 0.05$, $p = 0.032$). The strong influence of DOC suggests that bacterial production is an important energy source for Arctic *Daphnia*. Our findings indicate that productivity influences the MeHg concentration of zooplankton communities through its control of species composition; specifically, low productivity limits the presence of mercury-rich *Daphnia* in many copepod-dominated lakes of the High Arctic. Aquatic productivity is expected to increase with climate warming, and we present a conceptual model that predicts how

environmental drivers could extend the distribution of *Daphnia* in lakes and alter the movement of mercury in food webs of the Canadian High Arctic.

INTRODUCTION

Mercury has been identified as a potentially serious environmental threat to the High Arctic because of intense atmospheric deposition (Ariya et al. 2004) and high concentrations observed in consumer organisms at the top of food chains including landlocked populations of Arctic char, *Salvelinus alpinus* (Muir et al. 2005). Snow and melt waters in northern Canada contain elevated levels of both inorganic mercury and the more toxic organic species, methylmercury (MeHg) (Loseto et al. 2004; St. Louis et al. 2005). Snow melt waters are the principal source of water and total mercury (THg) to small High Arctic lakes and delivery occurs during an intense 2–3 week melt period when surficial soils are still frozen (Semkin et al. 2005). Pathways of mercury transfer to food webs, once spring melt is flushed into lakes, have not been determined.

A further challenge is to identify potential alterations in the mercury cycle due to profound ecological changes that are expected to occur in the High Arctic from climate warming during the 21st century (Prowse et al. 2006). This trend is a continuation of warming over the previous 100–150 years that has already altered the composition of benthic algal and invertebrate communities in Arctic fresh waters (Smol et al. 2005). Warmer water temperatures, a longer ice-free season, and greater watershed inputs of nutrients and organic matter to lakes are expected to stimulate biological metabolism and alter the structure of aquatic communities (Prowse et al. 2006). These ecological effects may in turn alter the movement of mercury in food webs.

Consequences of atmospheric mercury deposition for aquatic food webs are currently difficult to assess due to a lack of information on biogeochemical processes that control MeHg bioaccumulation in the High Arctic, particularly for lower trophic-level organisms. Crustacean invertebrates that feed in the water column (zooplankton) are sensitive to mercury supply processes and have been used successfully in temperate lakes to identify environmental determinants of MeHg bioaccumulation in food webs (Westcott and Kalff 1996; Watras et al. 1998; Paterson et al. 1998). Mercury accumulation in zooplankton is influenced by several factors that are interconnected at different spatial or temporal scales such as taxonomic composition (Watras et al. 1998), water chemistry (Westcott and Kalff 1996; Watras et al. 1998) and watershed transport of mercury (Garcia and Carignan 1998).

Lakes of the Canadian Arctic Archipelago are extreme environments that support few species of crustacean zooplankton at low densities (Rigler et al. 1974; Patalas 1990). A short ice-free season, cold temperatures and severe nutrient stress strongly limit algal food sources for zooplankton (Markager et al. 1999). Total densities are meagre (often < 1 individual L^{-1}) and typically only one to several zooplankton species are present in upland and polar desert lakes where watersheds are barren rock with minimal plant cover and few nutrients are released to fresh waters (Rigler et al. 1974; Patalas *et al.* 1994). Greater zooplankton densities and species richness are found on islands at lower latitudes as well as in polar oases on northern islands (e.g., Ellesmere and Devon Islands)(Patalas et al. 1994). These regions have warmer waters and lush meadows in lowland areas that supply greater inputs of nutrients and organic matter to lakes (Stewart and Bernier 1984).

Copepods (Copepoda), water fleas (Cladocera, *Daphnia*) and fairy shrimp (Anostraca) are 3 dominant types of crustacean zooplankton in the High Arctic, each with different morphological and ecological characteristics. Arctic copepods have the smallest adult body size (~ 1–2 mm length), and they feed by actively capturing individual algal cells or small-sized zooplankton (Rigler et al. 1974). Arctic *Daphnia* (specifically *D. middendorffiana*) can grow to a larger size (~ 3 mm) and are highly efficient filter feeders that consume bacteria, algae and detrital particles in the water column (Bertilsson et al. 2003). Anostracans are the largest zooplankton (> 5 mm length) and filter-feed in the water column or scrape algae from bottom substrates (Daborn 1976). A negative association between the presence of copepods and *Daphnia* has sometimes been noted (Bertilsson et al. 2003); copepods tend to dominate in lakes and are often the only zooplankton species present while *Daphnia* commonly dominate in shallow ponds where copepods are sometimes unabundant (Patalas et al. 1994; Hebert and Hann 1986). Anostracans occur exclusively in fishless ponds (Bertilsson et al. 2003). Lake trout (*Salvelinus namaycush*) and Arctic char are the main predators of zooplankton in High Arctic lakes although consumption rates are low due to low prey densities (Rigler et al. 1974).

In this paper, we test the influence of water chemistry, water body morphometry and taxonomic composition on MeHg accumulation in zooplankton from 16 lakes and ponds. To our knowledge, we present the first data of MeHg concentrations in zooplankton from this region, and we identify *Daphnia* as a key vector for potential mercury transfer. Since we found *Daphnia* in more productive water bodies (i.e., ponds, a eutrophied lake), we then test the influence of productivity on the distribution of *Daphnia* using a broad-scale literature data set of 47 High Arctic lakes. Our empirical

models of present-day patterns have implications for long-term shifts in aquatic productivity and potential responses of zooplankton to climate warming. Finally, we present a conceptual model predicting how climate warming may affect zooplankton community structure and MeHg bioaccumulation in High Arctic lakes.

MATERIALS AND METHODS

Field survey for mercury accumulation in zooplankton

The sampling area encompassed Cornwallis, Somerset and Devon Islands (74–76° N) in the Canadian Arctic Archipelago (Figure 1) where air temperatures and precipitation are extremely low (long-term averages: -33°C in February, 4°C in July, annual precipitation = 150 mm, data for Resolute Bay, Environment Canada). We conducted our field work from Resolute Bay, Cornwallis Island (74°30' N, 94°55' W) and a remote camp at Truelove Lowland, Devon Island (75°40' N, 84°33' W). Truelove is a 43 km^2 polar oasis with a warmer micro-climate and lush sedge and moss meadows. In contrast, the unproductive polar desert of Cornwallis, Somerset and most of Devon Island is dominated by sedimentary bedrock with minimal plant cover.

Sixteen lakes and ponds were investigated in July and August of 2005 and 2006 (Table 1). Water bodies were sampled on only one occasion except for 3 lakes (Small, Char, Meretta) that were sampled in both years. The lakes (1 polar oasis and 10 polar desert) were relatively small in surface area (SA, most < 1.5 km^2) but all had maximum depths (Z_{max}) ≥ 8 m and all contained a population of landlocked Arctic char. Ponds (4 polar oasis and 1 polar desert) had a shallow depth (Z_{max} = 0.8–3.3 m) and were assumed to be fishless.
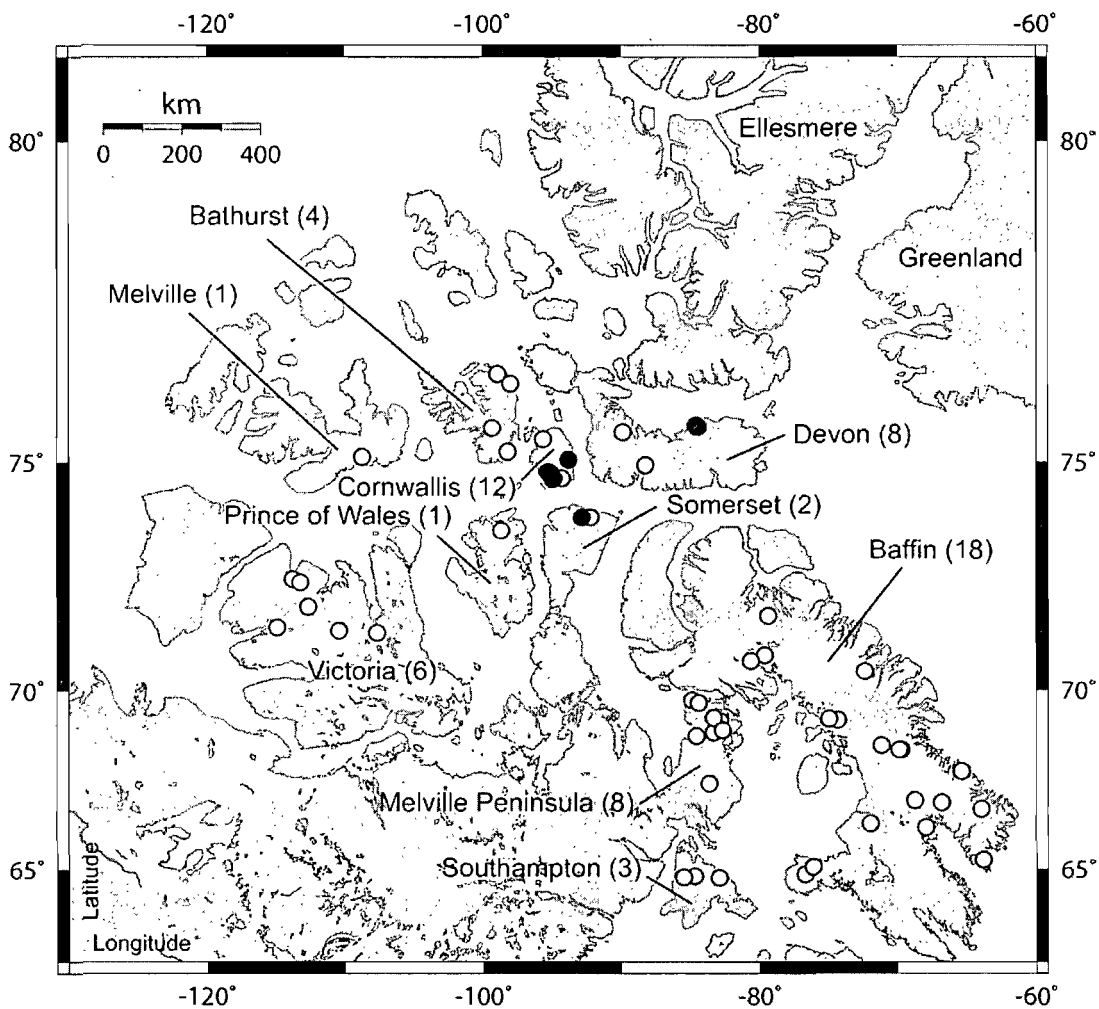
Figure 1. Map of the Canadian Arctic Archipelago with locations of sites investigated for zooplankton mercury concentrations (closed circles) and literature survey lakes examined for environmental determinants of *Daphnia* and total zooplankton densities (open circles). Circles may represent more than one water body due to the large scale, and the number of lakes on each island is in parentheses.

Table 1. Location, site description, morphometry and water chemistry of lakes and ponds investigated on 3 islands in the Arctic Archipelago for mercury concentrations in zooplankton during the summers of 2005 and 2006.

Island	Site (description)	Latitude (°N)	Longitude (°W)	Z_{max} (m)	SA (km²)	DA (km²)	pH	Temp (°C)	DOC (mg L⁻¹)	TP (µg L⁻¹)	Chl (µg L⁻¹)	THg (ng L⁻¹)	MeHg (ng L⁻¹)
												Water	
Cornwallis	Amituk (L, D)	75°02'44	93°47'15	43	0.38	26.50	8.0	2.2	< 0.6	1.3	0.2	1.12	0.03
Cornwallis	Char (L, D)	74°42'16	94°52'56	27.5	0.53	3.47	8.3	3.5	< 0.6	2.8	0.2	0.51	< 0.02
Cornwallis	Meretta (L, D)	74°41'36	94°59'38	12	0.26	8.71	8.1	2.4	1.4	3.9	0.4	0.57	0.06
Cornwallis	North (L, D)	74°46'32	95°05'42	15.5[b]	0.60	82.86	7.9	4.6	< 0.6	2.1	0.3	0.92	0.03
Cornwallis	Plateau (L, D)	74°48'36	95°12'00	14	0.70	6.33	8.2	3.1	0.8	5.0	0.3	0.50	0.05
Cornwallis	Resolute (L, D)	74°41'31	94°56'44	22	1.18	17.03	8.2	2.4	0.7	4.7	0.3	0.54	0.02
Cornwallis	Small (L, D)	74°45'37	95°03'35	11	0.14	1.50	8.1	3.4	1.4	3.6	0.4	0.52	0.05
Cornwallis	Teardrop (L, D)	74°40'48	94°59'24	8.1	0.04	0.48	8.3	3.2	< 0.6	2.6	na	0.30	0.03
Cornwallis	Tern (P, D)	74°48'00	95°05'24	3.3	0.57	11.19	8.5	3.1	1.0	2.7	0.4	0.43	0.03
Cornwallis	Twelve Mile (L, D)	74°49'12	95°20'24	9.5[b]	0.81	4.61	7.9	3.3	0.9	3.4	0.2	0.56	0.06
Devon	Immerk (L, O)	75°40'48	84°33'36	8	1.07	3.23	7.8	4.9	3.9	4.6	0.4	0.40	0.03
Devon	Phalarope (P, O)	75°39'36	84°36'36	1.8	1.95	8.04	8.2	8.4	2.9	3.9	0.4	0.45	0.07
Devon	Pond I [a] (P, O)	75°40'48	84°34'48	0.8	0.09	0.18	8.7	8.5	7.4	11.8	0.4	1.39	0.15
Devon	Pond F1 [a] (P, O)	75°40'12	84°33'36	1.2	0.05	0.12	8.5	8.0	4.7	3.8	0.4	1.30	0.03
Devon	Pond F2 [a] (P, O)	75°38'60	84°32'24	2.8	0.10	0.30	8.2	4.4	3.6	2.9	0.3	0.94	0.05
Somerset	Boomerang (L, D)	73°56'14	92°53'20	18[b]	6.63	111.25	7.8	2.2	< 0.6	1.6	0.2	0.70	0.02

Abbreviations: L = lake, P = pond, D = polar desert, O = polar oasis, Z_{max} = maximum depth, SA = surface area, DA = drainage area, Temp = temperature, DOC = dissolved organic carbon, TP = total phosphorus, Chl = chlorophyll a, na = not available
[a] unofficial name, [b] maximum observed depth

One of our field sites, Meretta Lake, Cornwallis Island (Table 1), received large quantities of untreated sewage from the Resolute Bay airport for almost 50 years from 1949 to 1998 resulting in extensive eutrophication (Douglas and Smol 2000). Lake water concentrations of total phosphorus and chlorophyll a have declined over time from highs in the early 1970's (28–70 μg L^{-1} and 3–5 μg L^{-1}, respectively) to relatively low levels since the late 1990s (< 5 μg L^{-1} and < 2 μg L^{-1}, respectively) (Kalff et al. 1972; Douglas and Smol 2000). Eutrophication of Meretta Lake resulted in long-term taxonomic shifts in the zooplankton community from dominance by a single calanoid copepod species (*Limnocalanus macrurus*; Schindler *et al*. 1974) to a mixed community of *Daphnia* species and *Cyclops scutifer* (Stewart and Macdonald 1981; Rautio and Vincent 2006; present study).

Lake SA and drainage area (DA) were measured in SIGIS v2.60 software using a combination of Landsat-7 images (ETM band 8 panchromatic, 15 m ground resolution) and digital vector maps of the Canadian National Topographic Data Base (1:250,000 scale). Z_{max} was obtained from published literature or theses for 9 sites, from depth sounding along transects with a weighted line for 4 sites, or from the Z_{max} observed during sampling for 3 sites. Lakes in the study area generally have a simple morphometry consisting of a single basin, and a strong empirical relationship exists between mean depth (Z_{mean}) and Z_{max} :

$Z_{mean} = 0.44\ Z_{max}$,

where $R^2 = 0.98$, $p < 0.001$, $n = 9$, SE of slope $\pm$ 0.03, y-intercept $p > 0.05$, and range of $Z_{max} = 1.8$–43 m. The linear regression equation included literature data on 4 lakes in the study area that were not sampled for zooplankton. The ratio of DA to water volume

(DA:V) was determined for 11 water bodies using a first order estimate of V equal to the product of Z_{mean} and SA.

Water was collected on one occasion from mid-depth in the pelagic zone of lakes with a peristaltic pump and tubing. Duplicate bottles were triple-rinsed and filled using tygon tubing for analysis of dissolved organic carbon (DOC), total phosphorus, chloride and sulphate. Water for anions and DOC was filtered (0.45 μm pore size) the same day. Trace-metal protocols were employed to collect water for total mercury (THg) and MeHg analyses. Teflon or glass amber bottles were pre-cleaned with concentrated nitric acid, rinsed 3 times with ultrapure water (Milli-Q, > 18 Mohm cm^{-1}) and placed in double ziplock bags for transport to the field. Triplicate bottles were triple-rinsed with lake water, filled at each site using acid-washed teflon tubing and preserved unfiltered with ultra-pure hydrochloric acid to 0.4% final concentration. Three 5-m integrated water samples were collected for phytoplankton chlorophyll a using a tube sampler. A vertical profile of water conductivity, pH, temperature, and dissolved oxygen was measured at 1 m intervals with a YSI 600 QS meter. The polar oasis ponds and one small lake (Teardrop) were sampled as above except that water was obtained by grab samples in the littoral zone.

Total phosphorus, DOC and anions were analyzed according to standard methods as in Garcia and Carignan (1998). Water collected for chlorophyll a was passed through filters of 0.7 μm pore-size and frozen until spectrophotometric analysis after hot ethanol extraction. Aqueous THg was determined by BrCl oxidation, $SnCl_2$ reduction, two-stage gold amalgamation and gas-phase detection with a Tekran 2600 Cold Vapour Atomic Fluorescence Spectrometer (CVAFS). Water samples for MeHg were acid-distilled to remove matrix interferences then derivatized by aqueous-phase ethylation, purged on

Tenax, and separated by gas chromatography prior to determination with a Tekran 2500 CVAFS. Procedural blanks contained 21 ± 6 pg THg and 2 ± 1 pg MeHg. Analytical detection limits, estimated as 3 times the standard deviation (SD) of 10 blanks, were 0.05 ng L^{-1} for THg and 0.02 ng L^{-1} for MeHg.

Zooplankton were collected with a large 1-m diameter net of 200 μm mesh size in the pelagic zone of each lake by vertical or horizontal hauls depending on ice and wind conditions. Ponds were sampled with horizontal tows in an inflatable boat except for 1 pond where the net was dragged while wading due to its shallow depth. Large volumes of water were filtered to collect ample biomass for mercury analysis (typically > 150 m^3). Two or 3 replicate samples, transferred into clean polypropylene containers, were collected from different locations in each water body to account for spatial variation except for Boomerang Lake were only 1 sample could be obtained due to logistic constraints. Zooplankton biomass for mercury analyses was frozen, and approximately 30–50 mL was also preserved with 5% formaldehyde or 70% ethanol in separate jars for taxonomic analysis. In the laboratory, zooplankton were freeze-dried and ground to a powder with an acid-washed glass mortar and pestle.

Most zooplankton samples were analyzed in bulk (i.e., all taxa pooled together; $n = 45$) but fairy shrimp (anostracans) and *Daphnia middendorffiana* were isolated from several sites for determination of taxon-specific MeHg concentration ($n = 16$). Fairy shrimp occurred in the water column and on sediment and were removed from benthic grabs in 4 ponds at Truelove Lowland. At least 20 fairy shrimp were collected per sample (1–3 samples per pond), washed in a petri-dish with ultrapure Milli-Q water using acid-cleaned tweezers, frozen in plastic scintillation vials and later freeze dried. Large-bodied individuals (length ~ 3 mm) of *D. middendorffiana* were removed with

acid-washed tweezers from bulk freeze-dried material collected in Meretta Lake and 2 ponds at Truelove Lowland. From 50–80 individuals of *D. middendorffiana* were pooled per sample and 3 samples per site were analyzed.

THg concentration of zooplankton (ng g^{-1} dry weight) was determined with a Direct Mercury Analyzer (DMA-80) in which typically 15–50 mg of dried and ground sample was combusted at 750°C and the mercury vapour was retained on a gold trap for analysis by cold vapour atomic absorption spectrometry. Procedural blanks contained ≤ 80 pg THg. Certified reference material (TORT-2, National Research Council of Canada) was analyzed every 10 samples and recoveries averaged 290 ± 4 ng g^{-1} (n = 16), corresponding to 107 ± 2% of the certified value.

The MeHg concentration of zooplankton (ng g^{-1} dry weight) was derivatized by aqueous-phase ethylation using NaBEt$_4$ and measured by CVAFS based on the method of Bloom (1989). Prior to analysis, typically 10–50 mg of dried and ground sample was digested in 5 mL of 4M HNO$_3$ at 55°C for 16 hours. Procedural blanks contained 1 ± 1 pg MeHg. Certified reference material (TORT-2) was analyzed every 10 samples, and recoveries averaged 148 ± 15 ng g^{-1} (n = 24), corresponding to 97 ± 10% of the certified value.

Taxonomic composition of the zooplankton was examined to determine the dominant species present in bulk samples. At least 200 individuals were identified by a zooplankton taxonomist (Ginette Méthot, Département de sciences biologiques, Université de Montréal, Montréal, Canada) to species or genus in one sample collected from each water body, except Meretta Lake where duplicate samples were counted in 2005 and 2006. The volume of water filtered with the zooplankton net was not

measured, and the relative contribution of each taxon to sample biomass (% biomass) was estimated using microscope enumeration data with the equation:

Biomass (%) = $(W_iA_i / \Sigma W_iA_i)$ X 100,

where W_i is the average dry weight of species i in μg and A_i is the number of individuals of species i enumerated in the sample. The length of 25 individuals of each taxon or immature copepod stage ($n < 25$ for rare taxa) was measured in each sample to the nearest 0.02 mm with the ocular micrometer of a dissecting microscope. Dry weight biomass (μg) was then estimated using length-weight regressions from the literature: Arctic *Daphnia* (Yurista 1999; Van Geest et al. 2007a), *Cyclops scutifer* (Bottrell et al. 1976), *Limnocalanus macrurus* (Rigler et al. 1974; Conway 1977) and fairy shrimp (Daborn 1974).

Literature survey lakes

Zooplankton densities and a suite of environmental characteristics were available for 47 High Arctic lakes measured in aquatic resource surveys administered by the Government of Canada (Stewart and Macdonald 1981; Stewart and Bernier 1982, 1984, 1988a, 1988b). The data set encompassed a broader geographic area (65–77°N latitude) than the mercury field survey including 9 islands of the Arctic Archipelago and the Melville Peninsula (Figure 1). In July or August of the years 1980 to 1985, one-time measurements of 2–4 replicates were taken in each lake for surface-water temperature, conductivity, particulate concentrations of phosphorus, nitrogen and carbon in the water column, DOC, chloride, sulphate, phytoplankton chlorophyll *a*, depth of zooplankton haul, and zooplankton density. Zooplankton were obtained from vertical tows with a Wisconsin net of 73 μm mesh size and all samples were identified by one taxonomist

(K. Patalas, Freshwater Institute, Winnipeg, Canada). Gill-net surveys were conducted in these lakes making available data on the presence of fish species, mainly Arctic char and lake trout. Methods for sample collection, identification of zooplankton, and chemical analyses were consistent between years. Dissolved phosphorus and pH data were not included due to quality issues. Five lakes were excluded due to extreme water chemistry values caused by high suspended solids (secchi depth ≤ 0.1 m) or brackish water.

Data analysis

Multiple linear regression analysis was conducted to determine the contribution of explanatory variables to among-site variation in zooplankton MeHg concentration. Forward selection multiple regression was run separately for each of the 3 explanatory matrices (taxonomic, water chemistry, morphometric), and a full regression model was then computed with all significant explanatory variables ($p < 0.05$) obtained in the previous step. The following variables were included for water chemistry (pH, conductivity, water temperature, and concentrations of total phosphorus, DOC, sulphate, chloride, THg and MeHg), water body morphometry (Z_{max}, SA, DA, DA:SA, DA:V) and taxonomy (% biomass data of zooplankton taxa $> 5\%$ in at least 1 sample: *C. scutifer*, *Daphnia* spp., anostrocans, unidentified immature cyclopoids). Percent biomass of *L. macrurus* was excluded from the analysis due to a strong negative correlation with % biomass of *Daphnia* (Pearson $r = -0.74$, $p = 0.001$, $n = 16$). Chlorophyll data were excluded because of a missing value for one lake although concentrations were consistently low (Table 1). Values below detection were reported as half the detection limit, and data were averaged over both years for 3 lakes sampled in 2005 and 2006.

Principal Component Analysis (PCA) was conducted on the literature lake survey data set (n = 47) to identify the main gradients of environmental variation among sampling sites. The data set consisted of 9 environmental variables (water temperature, haul depth, conductivity, particulate phosphorus, nitrogen and carbon concentrations, particulate carbon to phosphorus ratio [C:P, molar], DOC and phytoplankton chlorophyll a) and 2 spatial variables (latitude, longitude). Sulphate and chloride were excluded due to missing values. Total zooplankton and *Daphnia* densities were projected on the PCA biplot as passive variables to identify possible associations with environmental and spatial gradients and they did not influence the ordination axes. PCA was performed on transformed, centered and standardized variables.

Regression analysis was also used to identify variables explaining among-site variation in *Daphnia* and total zooplankton densities. The forward selection procedure was run separately on 3 different explanatory matrices with environmental, biotic or spatial variables. The environmental and spatial matrices were those described above for PCA. The biotic matrix consisted of 3 variables (total zooplankton density and binary coding for the presence-absence of lake trout and Arctic char).

Computations for PCA were performed with R statistical package (http://cran.r-project.org) using the *vegan* library. All other statistical tests were performed in SPSS 14.0. To normalize and/or linearize data, variables were log, log x + 0.01 (for *Daphnia* density), square-root or arcsine transformed. Means were compared with Student's t-tests and are presented ± 1 SD, unless otherwise stated.

RESULTS

Zooplankton mercury survey

Zooplankton mercury concentrations varied an order of magnitude among lakes and ponds ranging from 30–297 ng THg g^{-1} and 10–269 ng MeHg g^{-1} (Table 2). The proportion of THg in the form of MeHg averaged 58% in zooplankton although there was a large range among sites (23–88% MeHg). The MeHg concentration of zooplankton in Meretta Lake was surprisingly high (269 ± 128 ng g^{-1}) compared to natural lakes (29 ± 13 ng g^{-1}, $n = 10$) and was more similar to levels observed in polar oasis ponds (145 ± 25 ng g^{-1}, $n = 4$).

The zooplankton consisted of few species, and mercury concentrations differed among the dominant taxa. Communities in 4 polar oasis ponds and Meretta Lake contained *Daphnia* (mainly *D. middendorffiana*) and either *C. scutifer* or anostracans while the 10 lakes and polar desert pond were dominated by a single copepod species, either *C. scutifer* or *L. macrurus* (≥ 90% biomass) (Table 2). The large-bodied *D. middendorffiana* isolated from 2 ponds and Meretta Lake had, on average, twice the MeHg concentration of anostracans and 8 times the MeHg of copepod species (Figure 2). Similarly, bulk zooplankton samples with > 20% *Daphnia* biomass contained 5 times the MeHg (184 ± 58 ng g^{-1}, $n = 4$) of copepod-dominated communities (36 ± 23 ng g^{-1}, $n = 11$) (t-test, $p < 0.001$). The proportion of THg in the form of MeHg was also higher in bulk samples with *Daphnia*, averaging 78 ± 9% ($n = 4$) compared to 50 ± 17% in copepods ($n = 11$) (t-test, $p = 0.009$).

Table 2. Percent biomass of dominant species and mercury concentrations in zooplankton communities in 16 High Arctic lakes and ponds. Mercury values are means (± 1 SD) of 2–5 bulk samples. Taxa from 5 sites that were isolated for species-specific mercury analysis are identified in bold (data presented in Figure 2).

Site (description)	Taxonomic composition (percent biomass)	THg (ng g^{-1})	MeHg (ng g^{-1})
Amituk (L, D)	Lim.mac (100)	83 ± 4	42 ± 1
Char (L, D)	Lim.mac (100)	53 ± 2	28 ± 2
Meretta (L, D)	**Dap.mid** (52), Cyc.scu (31), Dap.sp (16)	297 ± 119	269 ± 128
North (L, D)	Lim.mac (98)	66 ± 1	25 ± 0.4
Plateau (L, D)	Lim.mac (100)	74 ± 1	22 ± 2
Resolute (L, D)	Lim.mac (100)	45 ± 2	29 ± 1
Small (L, D)	Lim.mac (100)	77 ± 31	41 ± 16
Teardrop (L, D)	Lim.mac (100)	75 ± 8	48 ± 5
Tern (P, D)	Cyc.scu (99)	113 ± 8	92 ± 10
Twelve Mile (L, D)	Lim.mac (100)	45 ± 0.4	10 ± 2
Immerk (L, O)	Lim.mac (100)	30 ± 4	11 ± 2
Phalarope (P, O)	**Dap.mid** (76), Cyc.scu (24), **Anos.** (0)[a]	229 ± 20	170 ± 10
Pond I (P, O)	**Anos.** (77), Dap.mid (22)	190 ± 42	156 ± 35
Pond F1 (P, O)	**Anos.** (94), Dap.mid (6)	154 ± 0.1	113 ± 4
Pond F2 (P, O)	**Dap.mid** (48), **Anos.** (46), Imm.cyc (5)	212 ± 9	140 ± 10
Boomerang (L, D)	Cyc.scut (90), Lim.mac (7), Dap.sp (2)	104 ± na	50 ± na

Abbreviations: L = lake, P = pond, D = polar desert, O = polar oasis, Lim.mac = *Limnocalanus macrurus*, Cyc.scu = *Cyclops scutifer*, Dap.mid = *Daphnia middendorffiana*, Dap.sp = *Daphnia* species, Anos. = anostracans, Imm.cyc = immature cyclopoids, na = not available

[a] Anostracans were not found in bulk zooplankton samples in Phalarope Lake but were isolated from benthic samples.
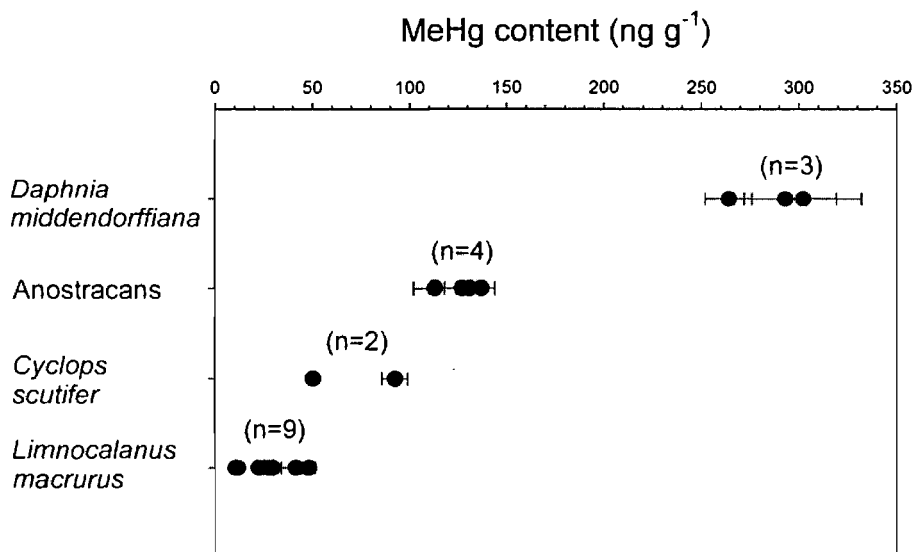
Figure 2. Taxonomic variation of MeHg concentrations in zooplankton. Data points are

site means (± 1 standard error), and the number of water bodies examined for each taxon

is indicated. MeHg concentrations in *L. macrurus* and *C. scutifer* were determined on

bulk samples where either taxon was 90% of total biomass. Concentrations for *D.*

middendorffiana and anostracans were determined on sorted individuals (see Table 2 for

sites where taxa were sorted).

Lakes and ponds surveyed for zooplankton mercury concentrations had alkaline waters that were generally cold and dilute in total phosphorus, DOC, chlorophyll *a*, THg and MeHg (Table 1). The 4 polar oasis ponds on Devon Island, which contained *D. middendorffiana*, had above-average environmental conditions associated with greater productivity; specifically higher water temperatures (4.5–8.5°C), total phosphorus (2.9–11.8 µg L^{-1}) and DOC (3.6–7.4 µg L^{-1}). Aqueous MeHg was also slightly more concentrated in Pond I (0.15 ng L^{-1}). Sites differed widely in their water depth, water body SA and DA (Table 1).

Percent biomass of *Daphnia* was the best predictor of zooplankton MeHg concentration in lakes and ponds (n = 16) among water chemistry, morphometric and taxonomic variables (Figure 3). Forward selection multiple regression, run separately for each of the 3 explanatory data sets, identified one significant water chemistry variable (pH: R^2_{adj} = 0.26, p = 0.024), two significant morphometric variables (DA:V and DA:SA: R^2_{adj} = 0.42, p = 0.011) and one significant taxonomic variable (% *Daphnia* biomass: R^2_{adj} = 0.80, p < 0.001). DA:SA was removed from the morphometric model and not considered further because it was marginally collinear with DA:V (Pearson r = 0.48, p = 0.062) and had a lower partial R^2_{adj}. In a full model containing all forward-selected variables from the 3 explanatory data sets, the presence of *Daphnia* explained the greatest portion of the variance in MeHg concentration (partial R^2_{adj} = 0.80, p < 0.001) followed by DA:V (partial R^2_{adj} = 0.06, p = 0.036) and water pH (partial R^2_{adj} = 0.03, p = 0.056).

Explanatory models of Daphnia and total zooplankton densities

In the literature survey of 47 High Arctic lakes, *Daphnia* and total zooplankton densities ranged from 0–6.2 ind. L^{-1} and 0.03–47.1 ind. L^{-1}, respectively. *D. longiremis* was the most common *Daphnia* species found (47% of lakes) followed by *D. middendorffiana* (11%) and *D. longispina* (4%). On average, lakes that contained *Daphnia* had shallower depths, higher densities of total zooplankton, higher particulate C:P, and higher DOC (Table 3). *Daphnia* were more common in lakes at lower latitudes in the Archipelago, and geographic associations with environmental variables were evident (Table 3, Figure 4). Nutrient-poor, low conductivity waters were common in the eastern Arctic, especially on Baffin Island, where the study lakes were typically over granite bedrock. Lakes farther west (Melville Peninsula and Victoria and Southhampton islands) had higher conductivity waters, higher DOC and slightly higher nutrient concentrations due to sedimentary rock basins and more vegetated shorelines (Stewart and Bernier 1984). Most lakes contained Arctic char (89%) except some western sites on Victoria Island while lake trout only occurred in some lower latitude lakes (30%) and was not found to the east on Baffin Island.
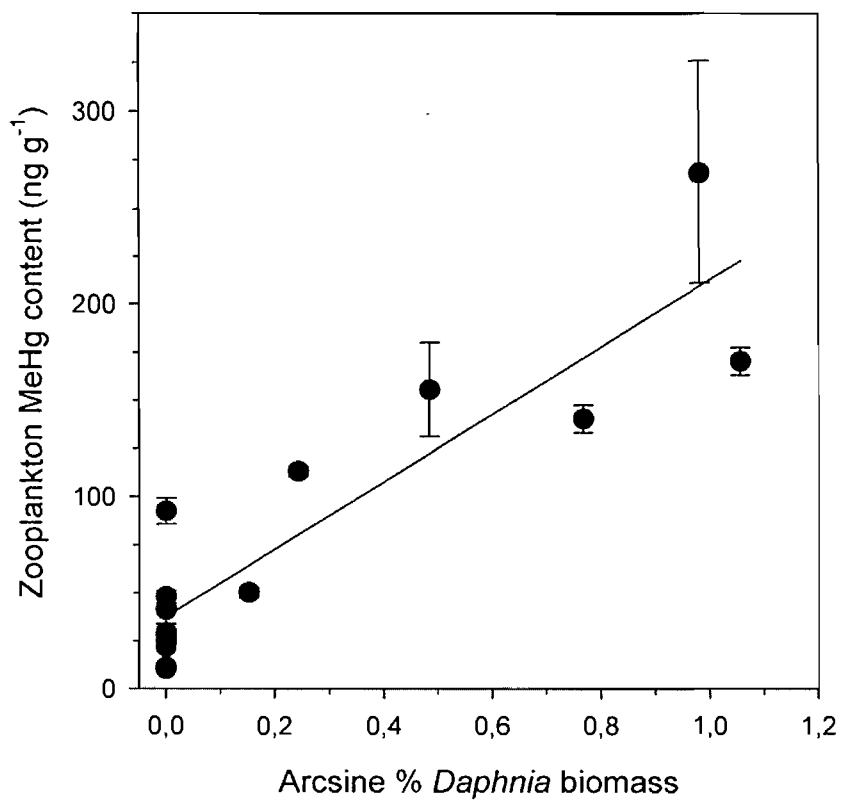
Figure 3. Relationship between the average MeHg concentration in zooplankton (± 1 standard error) and % biomass of *Daphnia* in bulk samples from 16 lakes and ponds (MeHg$_{zoop}$ = 175.230 x + 37.663, R^2_{adj} = 0.80, p < 0.001).

Table 3. Means and ranges of water quality variables, morphometric characteristics and geographic coordinates of 47 High Arctic lakes from the literature survey. Means and ranges are presented separately for lakes with and without *Daphnia* present, and differences were tested with Student's t-tests (ns = not significant, $p > 0.05$).

Characteristic	Lakes with *Daphnia* ($n = 22$)		Lakes without *Daphnia* ($n = 25$)		t-test p
	Mean	Range	Mean	Range	
Water temperature (°C)	7.1	5.0–10.0	6.2	0.5–12.0	ns
Conductivity (μS cm^{-1})	84	4–200	129	5–833	ns
Particulate phosphorus (μg L^{-1})	2.7	1.0–7.0	2.9	1.0–6.0	ns
Particulate nitrogen (μg L^{-1})	43	8–206	29	1–60	ns
Particulate carbon (μg L^{-1})	332	75–947	280	23–740	ns
Particulate C:P (molar)	391	98–903	267	59–671	0.011
Chlorophyll a (μg L^{-1})	0.5	0.2–1.2	0.4	0.1–0.8	ns
DOC (mg L^{-1})	2.6	0.5–5.5	1.5	0.2–4.5	0.004
Cl$^-$ (mg L^{-1})	1.9	0.4–6.9[a]	14.3	0.3–223	ns
SO$_4^{-2}$-S (mg L^{-1})	0.6	0.1–2.9[a]	1.1	0.1–11.1	ns
Zooplankton haul depth (m)	7	1–22	12	3–45	0.013
Zooplankton density (ind. L^{-1})	17.8	0.03–47.1	7.1	0.04–37.6	0.001
SA (km^2)	23.0	2.1–107.6[b]	504.7	0.5–5063[c]	ns
Latitude (decimal °N)	68.87	64.73–74.95	71.61	65.30–76.58	0.007
Longitude (decimal °W)	86.42	66.82–114.95	85.38	63.80–113.83	ns

[a] $n = 21$, [b] $n = 15$, [c] $n = 11$
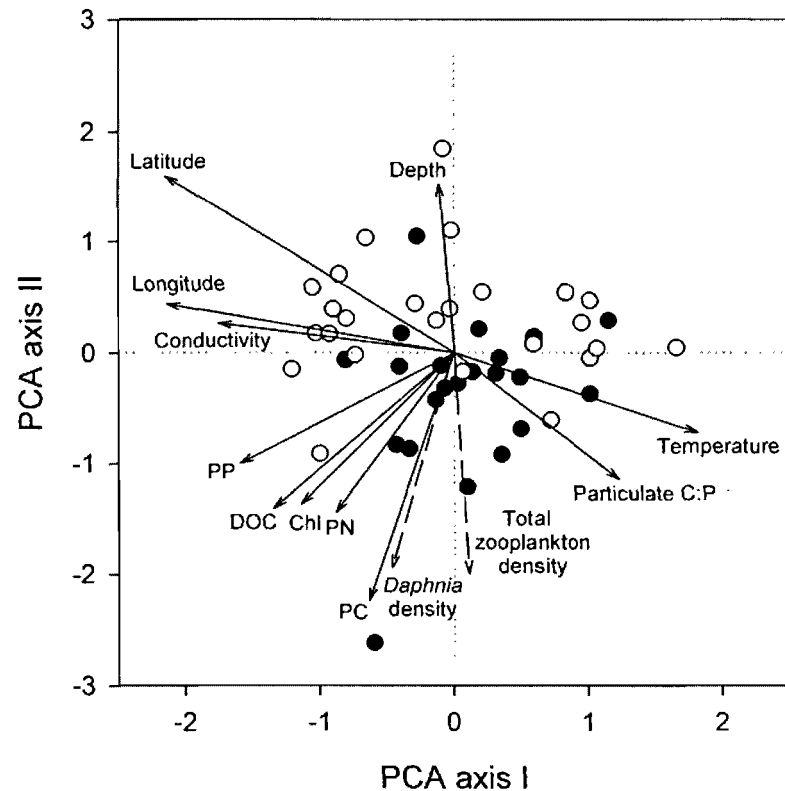
Figure 4. PCA correlation biplot of gradients in environmental and spatial variables of 47 High Arctic lakes examined for determinants of *Daphnia* and total zooplankton densities. Axis I (λ = 2.92) and axis II (λ = 2.32) accounted for 27% and 21% of the total variation among sites, respectively. *Daphnia* and total zooplankton densities were projected as passive variables on the biplot (dashed-line arrows). Sites were categorized according to the presence of *Daphnia* (closed circles) or its absence (open circles). Chl is chlorophyll *a* and PN, PP, and PC are particulate concentrations of nitrogen, phosphorus and carbon.

Daphnia and total zooplankton densities were influenced by productivity-related variables (Table 4). Forward selection identified water-column concentrations of DOC (partial $R^2_{adj} = 0.39$, $p < 0.001$) and particulate carbon (partial $R^2_{adj} = 0.05$, $p = 0.032$) as the main explanatory variables for *Daphnia* density (Figure 5). *Daphnia* density was also significantly correlated with particulate nitrogen and chlorophyll *a* ($R^2_{adj} = 0.10$–0.11, $p \leq 0.017$; Figure 4) but these variables were not forward-selected into the model. Total zooplankton density was most strongly correlated with particulate carbon concentration (partial $R^2_{adj} = 0.26$, $p < 0.001$) followed by water temperature (partial $R^2_{adj} = 0.20$, $p < 0.001$) and DOC (partial $R^2_{adj} = 0.11$, $p = 0.001$). A test of biotic variables identified a strong positive covariation between *Daphnia* density and total zooplankton density (partial $R^2_{adj} = 0.39$, $p < 0.001$), a positive association with the presence of lake trout (partial $R^2_{adj} = 0.08$, $p = 0.033$), and a negative association with the presence of Arctic char (partial $R^2_{adj} = 0.04$, $p = 0.042$). *Daphnia* density and total zooplankton density were negatively correlated with latitude and positively correlated with longitude which explained approximately half of the variation compared to models with environmental predictors.

Table 4. Linear regression models explaining variation in *Daphnia* density (log DD; log x + 0.01 transformed) and total zooplankton density (sqrt ZD) among 47 High Arctic lakes. Models were determined by forward-selecting explanatory variables separately from environmental, biotic and spatial matrices.

Explanatory Matrix	Model	Model R^2_{adj}	F	p
Environmental	log DD = 0.343 DOC + 0.051 sqrt particulate carbon − 3.008	0.44	18.98	< 0.001
	sqrt ZD = 0.196 sqrt particulate carbon + 0.331 temperature + 0.478 DOC − 3.547	0.57	20.88	< 0.001
Biotic	log DD = 0.202 sqrt ZD + 0.475 lake trout − 0.631 arctic char − 1.610	0.51	16.85	< 0.001
Spatial	log DD = − 0.144 latitude + 0.029 longitude + 6.185	0.20	6.89	0.002
	sqrt ZD = − 0.370 latitude + 0.051 longitude + 24.589	0.27	9.61	< 0.001
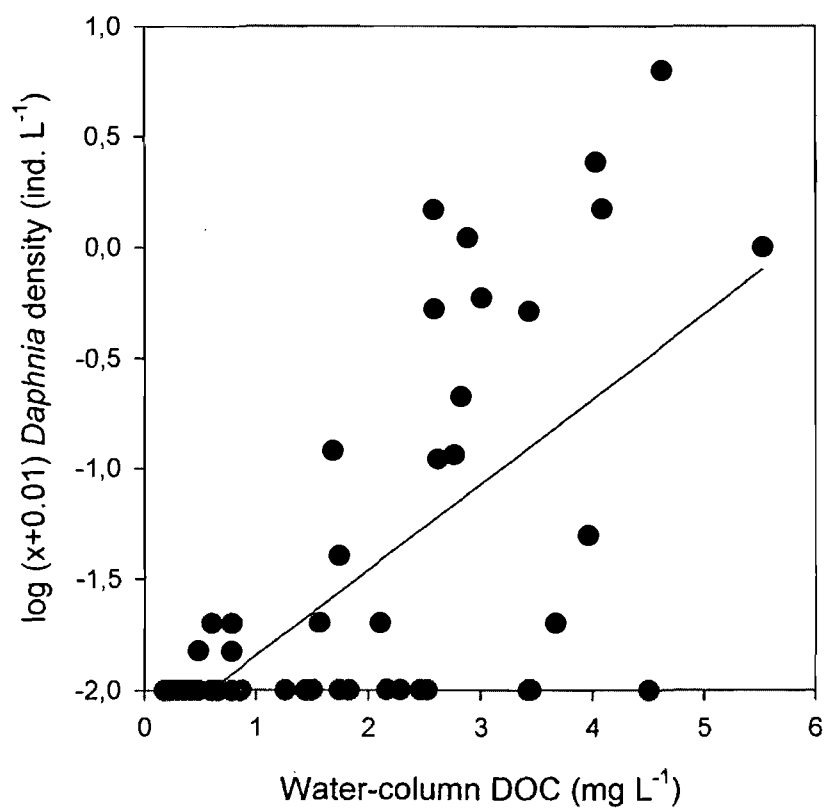
Figure 5. Relationship between *Daphnia* density (log x + 0.01 transformed) and the water-column concentration of DOC in 47 High Arctic lakes (log *Daphnia* density = 0.387 x – 2.233, R^2_{adj} = 0.39, p < 0.001).

DISCUSSION

Species-specific MeHg bioaccumulation

Daphnia were far more concentrated with mercury than copepods or anostracans, and species-specific processes were primarily controlling this high MeHg accumulation. These taxonomic differences were not due to variation in mercury supply among sites because MeHg concentrations in water were low and relatively uniform. Further, *D. middendorffiana* isolated from Pond F2 and Phalarope Lake had roughly double the MeHg of anostracans isolated from those same water bodies. In temperate lakes, *Daphnia* also have higher mercury concentrations compared to copepods (Watras et al. 1998; Pickhardt et al. 2005).

Diet is the main source of MeHg to zooplankton (Tsui and Wang 2004), and therefore, elevated MeHg in *Daphnia* may be due to differences in feeding. *Daphnia* are very effective grazers and have higher feeding rates than copepods and anostracans in High Arctic fresh waters (Bertilsson et al. 2003). Greater food consumption per unit body weight would result in greater uptake of MeHg. Alternatively, species-specific differences in bioaccumulation may result from the consumption of different diet items with variable MeHg content. Arctic *Daphnia* can feed extensively on small-sized cells (0.2–1 µm) and obtain a significant amount of their energy from bacteria whereas copepods preferentially feed on larger prey due to different food acquisition strategies (Bertilsson et al. 2003; Karlsson et al. 2003; Van Geest et al. 2007b). Bacteria could be an important pathway for mercury transfer because these micro-organisms consume dissolved organic substances in the water column that strongly bind MeHg. In addition,

D. middendorffiana sometimes feed at the sediment surface where MeHg concentrations may be higher (Wilhelm et al. 1998; Rautio and Vincent 2006).

Species-specific differences in MeHg accumulation highlight the importance of biological factors in the movement of mercury through High Arctic food webs. This finding is in contrast to much research effort that has focused on abiotic mercury supply processes to fresh waters. At present, many gaps exist in our knowledge of the mercury cycle for this region although it is clear that atmospheric deposition rates to snow are high (Ariya et al. 2004) and spring melt waters are the main transport vector of THg to High Arctic lakes (Semkin et al. 2005; Loseto et al. 2004). Two lines of evidence from our investigation suggest these loads are not having a large effect on mercury transfer to pelagic food webs. MeHg concentrations were consistently low (< 50 ng g^{-1}) in zooplankton of natural lakes, and little variation in zooplankton MeHg was correlated to DA:V along a wide gradient in drainage basin size and water volume. Flushing of melt water through the lake outflow in spring results in $> 50\%$ loss of THg inputs from the drainage basin (Semkin et al. 2005) which may explain the small influence of drainage basin size observed in this study. Lakes are still ice-covered when most snow melts, and this cold, low-density runoff passes directly under the ice to the outflow with little mixing into the underlying water column (Semkin et al. 2005). Further, the potential for bacterial methylation in lake sediment is low due to oxic conditions and low concentrations of organic matter and inorganic mercury (Hammerschmidt et al. 2006). Future research should assess watershed mercury loads and *in situ* methylation in these systems to confirm these results.

Role of productivity in the distribution of Daphnia

We found that ecosystem productivity plays an important role in the distribution of *Daphnia* in lakes of the Canadian High Arctic. We observed greater *Daphnia* densities in lakes that supported more zooplankton and had higher water-column concentrations of DOC and particulate carbon, suggesting *Daphnia* respond to greater food availability. The association between *Daphnia* density and water-column DOC likely reflects the importance of bacteria as a food source since bacterial production is stimulated by dissolved organic substrates (Hessen *et al.* 2004). Sites from the zooplankton mercury survey also indicated a positive relationship between % *Daphnia* biomass and DOC ($R^2_{adj} = 0.22$, $p = 0.039$, $n = 16$). Water-column DOC was probably terrestrial in origin but the particulate carbon was a mix of allochthonous organic matter and phytoplankton, as suggested by positive correlations to both DOC (Pearson $r = 0.29$, $p = 0.053$, $n = 47$) and chlorophyll *a* (Pearson $r = 0.37$, $p = 0.011$, $n = 47$). DOC contains nutrients and can stimulate both bacterial and phytoplankton production (Hessen *et al.* 2004).

Experimental studies and field surveys conducted on Arctic fresh waters corroborate our finding that food supply is a primary determinant of *Daphnia* distribution. The growth of Arctic *Daphnia* is probably carbon-limited (Van Geest et al. 2007a) and bacterial consumption is important (Bertillson et al. 2003; Karlsson et al. 2003; Van Geest et al. 2007b) due to extremely low photosynthetic rates by phytoplankton (Markager et al. 1999). Experimental phosphorus and nitrogen additions in an Alaskan lake increased phytoplankton production and the density of the resident *D. longiremis,* demonstrating its growth was food-limited (O'Brien et al. 2005). *In situ* experiments with *D. middendorffiana* in Alaska also showed that greater resource availability

strongly enhanced its growth, survivorship and reproduction (Yurista and O'Brien 2001). Field surveys in Alaska, the Canadian Arctic Archipelago and Svalbard found that *Daphnia* dominance was positively related to water-column total phosphorus (Sweetman and Smol 2006), bacterial production (Bertilsson et al. 2003), particulate carbon concentration, and food quality measured by the C:P ratio (Van Geest et al. 2007b).

Total zooplankton density, represented primarily by copepods, responded differently to environmental factors than *Daphnia* in the literature lake survey. Water temperature positively influenced total zooplankton density but not that of *Daphnia* (p = 0.351, n = 47). Resource availability may have more control on *Daphnia* density than water temperature even though warmer waters increase the length of the ice-free season and zooplankton growth rates (Shuter and Ing 1997). Particulate carbon explained more variation in total zooplankton density (copepods) than DOC but DOC explained more variation in *Daphnia* density. This pattern coincides with feeding differences, specifically the importance of bacteria for *Daphnia* and larger phytoplankton for copepods.

Some of the unexplained variation in the *Daphnia* density model may be due to planktivorous feeding by fish. O'Brien et al. (2004) noted that individuals of *D. middendorffiana* occurred in only half of the Alaskan lakes with fish but 90% of lakes without fish. Further, they found that *D. middendorffiana* individuals were smaller in lakes containing fish perhaps due to predation pressure. Recolonization processes following glaciation may have also affected the present distribution of *Daphnia* in the Arctic Archipelago since zooplankton species richness is greater in water bodies closer to the Beringia glacial refuge in the western Arctic (Hebert and Hann 1986).

Projected changes in zooplankton community structure with climate warming

The present-day influence of productivity on *Daphnia* density suggests that climate warming may result in the expansion of their distribution. Currently, zooplankton communities of High Arctic lakes are species-poor and typically dominated by one to several species of copepods with cladocerans often absent (Patalas et al. 1994). We present here a conceptual model of how a long-term shift could occur towards a more diverse zooplankton, and specifically how *Daphnia* may appear in many lakes, as aquatic productivity increases with climate warming (Figure 6). Warmer waters up to 10–18°C by the year 2100 (Sharma et al. 2007) will extend the ice-free growing season and stimulate production rates of microbial plankton and *Daphnia* (Shuter and Ing 1997; Karlsson et al. 2005). Greater food and nutrient requirements due to higher metabolic rates should be met. Melting permafrost soils and greater terrestrial plant cover will increase watershed inputs of nutrients and organic matter to fresh waters (Prowse *et al.* 2006), stimulate algal and bacterial production (Karlsson et al. 2005), and enhance *Daphnia* growth (Shortreed and Stockner 1986; Hessen *et al.* 2004; Karlsson et al. 2005). In addition, the onset of thermal stratification will improve the light environment for phytoplankton production by reducing the depth of the mixing zone (Korhola *et al.* 2002). *Daphnia* expansion to new lakes could occur through local colonization processes (e.g., surface water connections with ponds and dispersal by birds or wind) because *Daphnia*, in particular *D. middendorffiana*, are ubiquitous in ponds across the Arctic Archipelago (Hebert and Hann 1986). Shifts in zooplankton composition may be more pronounced in shallow lakes because climate change will have a greater and earlier impact on those systems. Site-specific factors such as food quality, fish predation and

the amount of nutrient and DOC loadings will also affect shifts in zooplankton communities.

Long-term monitoring data and paleolimnological evidence indicate that *Daphnia* are already responding to climate warming in sub-Arctic lakes of northern Finland (Korhola et al. 2002), Alaska (Schindler et al. 2005), and Siberia (Hampton et al. 2008). *Daphnia* have increased in abundance in these lakes over the last 40–60 years associated with shifts in the phytoplankton community, earlier ice thaw in spring, or warmer water temperatures. In Lake Alegaknik of Alaska, the growth of sockeye salmon was stimulated, in part, by the increase in cladoceran densities (Schindler et al. 2005).

The anthropogenically-impacted Meretta Lake is an example from the High Arctic where *Daphnia* successfully colonized a lake following an increase in productivity. Before sewage inputs started, the copepod *L. macrurus* was the only known crustacean zooplankter in Meretta similar to other ultraoligotrophic lakes in the area (Schindler *et al.* 1974). In 2005 and 2006, we found the large-bodied *D. middendorffiana* was the dominant zooplankter followed by the copepod *C. scutifer*, and 1 or 2 smaller unidentified *Daphnia* species (Table 2). There is insufficient long-term information to clearly identify the mechanisms stimulating *Daphnia* growth in Meretta Lake although an increase in food supply from nutrient enrichment was probably a key driver. Impacts on the Arctic char population may also have been a contributing factor. Nevertheless, Meretta Lake demonstrates that *Daphnia* will colonize new lakes when environmental conditions become more favourable for growth.

Warmer air temperature

Longer ice-free
growing season

+ Plant
productivity

+ Inputs of DOC &
nutrients

Warmer water

Melting permafrost

Thermal stratification
begins, improving light
environment for algae

+ Bacterial and
algal production

+ Daphnia
production

+ Pelagic flow of
energy and MeHg
to fish
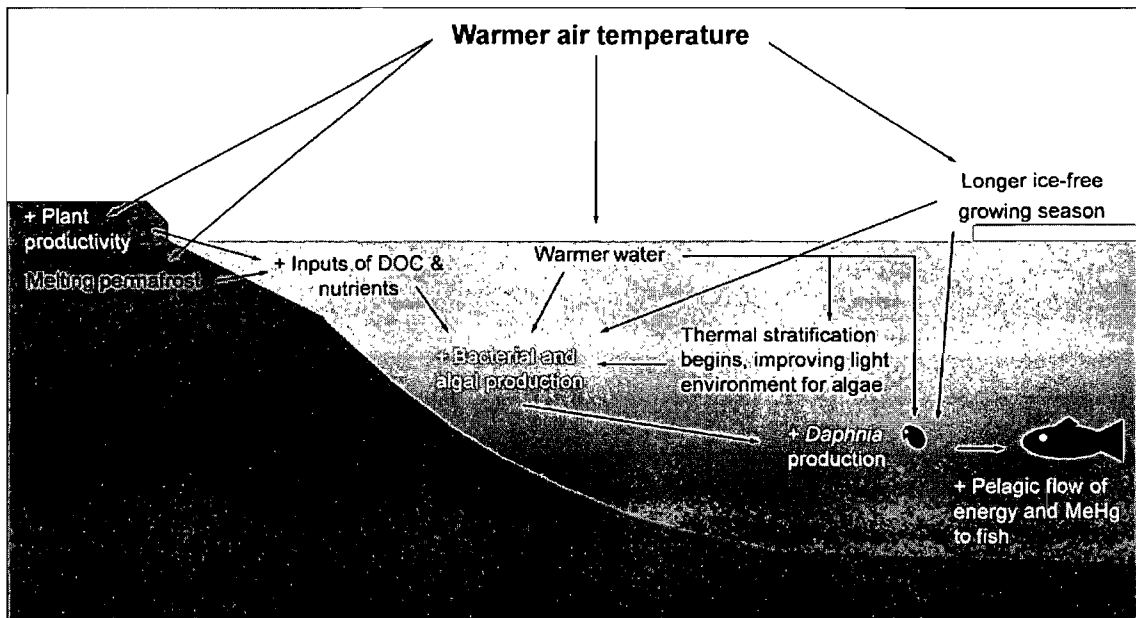
Figure 6. Conceptual diagram showing how environmental drivers associated with climate warming (black text) and ecological responses (white text) are predicted to stimulate *Daphnia* growth in High Arctic lakes.

Potential implications of climate warming for MeHg transfer

We predict that MeHg accumulation will increase in pelagic food webs if *Daphnia*, particularly *D. middendorffiana*, were to expand their geographic distribution. Presently, energy flows primarily through benthic rather than planktonic pathways in High Arctic lakes because landlocked populations of Arctic char feed almost entirely on chironomids due to low zooplankton densities (Hobson and Welch 1995). Climate change over the next century may cause a shift in energy flow from benthic to pelagic food webs as aquatic productivity increases. *Daphnia* could provide a new prey for juvenile fish that is energetically preferable to copepods and also become an important pathway for mercury transfer because it has higher mercury content than copepods. In the case of Meretta Lake, the colonizing *D. middendorffiana* also had a higher MeHg content (293 ± 45 ng g^{-1}) than emerging chironomids (135 ± 36 ng g^{-1}, n = 6, chapitre 2). The Arctic mercury cycle will change in yet unknown ways with climate warming; however, the species-specific characteristics of *Daphnia* are such that it will continue to strongly bioaccumulate MeHg as it does presently in both Arctic and temperate ecosystems (Watras et al. 1998; Pickhardt et al. 2005; this study).

In temperate lakes, greater aquatic productivity reduces mercury transfer in pelagic food webs through bloom dilution and enhanced growth rates of zooplankton (Pickhardt et al. 2005; Karimi et al. 2007). Bloom dilution by phytoplankton occurs when the pool of bioavailable aqueous mercury is divided among more algal cells. Higher zooplankton growth rates reduce MeHg accumulation because more biomass is produced per unit of food (and mercury) consumed. These processes occur in more productive systems (i.e., mesotrophic to eutrophic lakes) and are not likely applicable to High Arctic lakes which

are so resource-poor. A slight increase in algal or bacterial production in ultraoligotrophic lakes may have a dramatic effect on zooplankton communities but be insufficient to reduce mercury transfer through biomass dilution.

Conclusion

Our findings highlight the importance of ecological interactions between productivity and species composition for mercury accumulation in communities of High Arctic zooplankton. The presence of *Daphnia* is a key determinant of mercury concentration, and *Daphnia* density is related to productivity, as indicated mainly by DOC. Since DOC stimulates bacterial production (Karlsson et al. 2005), bacteria may play a critical role as a pathway for both energy and mercury transfer in High Arctic fresh waters. Future research on links between watershed DOC, microbial metabolism, and zooplankton community structure is a promising avenue to test predictions of zooplankton responses to climate warming. Geographic expansion of *Daphnia* during the 21st century could significantly alter mercury accumulation in lake food webs of the Canadian High Arctic.

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CHAPITRE 2

Metamorphosis in chironomids, more than mercury supply, controls the transfer of methylmercury to fish in High Arctic lakes

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ABSTRACT

Lake-dwelling Arctic char (*Salvelinus alpinus*) are monitored internationally as a sentinel species for effects of atmospheric mercury deposition on Arctic fresh waters. We investigated the control of mercury supply and biological processes on the methylmercury (MeHg) concentration of their main food, aquatic chironomids, in 22 lakes and ponds in the Canadian High Arctic. Total mercury (THg) concentrations in sediment (corrected for organic matter content) increased with the drainage basin to lake area ratio, suggesting a gradient in mercury loading among study sites. MeHg concentrations in sediment and water were low and relatively uniform along this THg supply gradient, suggesting MeHg production in High Arctic lakes is weakly coupled to inorganic mercury supply. Metamorphosis was a key biological process that concentrated MeHg in adult chironomids 1.7–2.9 times more than in immature stages. Drainage basin ratios, environmental mercury levels and habitat characteristics were also significant factors but they explained less variation in chironomid MeHg concentration than their degree of maturity. Chironomid larvae, pupae and adults are distinct mercury sources for fish, and we provide evidence from nitrogen stable isotopes and published feeding studies that suggest differential consumption of these stages may affect MeHg uptake by Arctic char. We conclude that biological and food web processes have a greater impact on MeHg transfer to fish than atmospheric mercury deposition in High Arctic lakes.

INTRODUCTION

Arctic char (*Salvelinus alpinus*), with its circumpolar distribution, is used internationally as a sentinel species to detect spatial and temporal trends in the global

transport of mercury to Arctic fresh waters (AMAP 2005). This metal is a contaminant of concern in polar regions because atmospheric mercury is deposited intensively on snow following polar sunrise (Steffen et al. 2008), snow and melt waters often contain elevated concentrations of mercury (Loseto et al. 2004; St. Louis et al. 2005), and high burdens have been reported in top predatory animals because of biomagnification (Braune et al. 1999). The Arctic is also undergoing rapid environmental change from climate warming which is anticipated to impact the mercury cycle (Hammerschmidt et al. 2006). Populations of landlocked char have been sampled in high latitude lakes of Canada (~ 75°N) since the 1990s, and mercury levels in muscle tissue range an order of magnitude from 0.15–1.5 μg g^{-1} wet weight (Muir et al. 2005). While cannibal feeding by larger char is one factor that enhances mercury bioaccumulation (Muir et al. 2005), the absence of information on mercury in lower trophic levels may hinder the interpretation of spatial and temporal trends in food web biomagnification of this metal.

Chironomids (Diptera: Chironomidae) play a key role in the transfer of mercury to landlocked Arctic char in high latitude lakes (> 70°N) of Canada because they are a primary food source in many lakes. Few species can survive under the extreme environmental conditions imposed on these ecosystems, and lake food webs are simple, consisting of Arctic char, chironomids, and chironomid food sources in sediment (algae, bacteria, detrital organic matter) (Hobson and Welch 1995). Chironomid production is far greater than that of zooplankton or other macroinvertebrates in these lakes (Welch 1976), making it the main source of food and as a consequence, the main vector of methylmercury (MeHg) to landlocked char. These ecosystems differ from lower latitude Arctic lakes where zooplankton can be an important diet item for Arctic char (Johnson 1980).

Chironomids are holometabolous insects and pass through 4 stages in their life cycle: eggs, larvae, pupae and adults. Fertilized eggs are deposited on the water surface, sink to sediment and hatch within a month (Welch 1976). Larvae grow slowly in sediment, passing through 4 successive instars and typically require 2 to 3 years to reach maturity in the High Arctic (Oliver 1968; Welch 1976). In spring or summer of the final year in their life cycle, late fourth instar larvae develop wing pads, molt to pupae (2 week inactive phase when adult structures are formed), and then swim to the water surface where adults cast their pupal skin (exuvium) and emerge to mate.

In this study, we investigated the control of mercury supply and biological processes that affect MeHg concentrations of chironomids in lakes and ponds of the Canadian High Arctic. We estimated mercury supply by measuring environmental concentrations and by comparing water bodies with different drainage basin ratios (drainage basin area: water body surface area). Snow melt is the main source of total mercury (THg) to High Arctic lakes (Semkin et al. 2005), and we hypothesized that sites with larger drainage basin ratios receive greater loadings of aqueous mercury originating from snow. Subsequent *in situ* methylation of inorganic Hg and MeHg uptake into the food web should result in higher concentrations in chironomids. Sediment production of MeHg in Alaskan lakes is positively related to drainage basin ratios because of the importance of this inorganic mercury load for methylation rates (Hammerschmidt et al. 2006). We sampled water bodies in barren polar deserts as well as a polar oasis with lush meadows to account for potential influences of drainage basin type since the amount of organic matter transported from drainage basins could affect the mercury cycle. Biological processes, namely growth and metamorphosis, were examined by comparing mercury accumulation in the different stages of chironomid development.

We demonstrate that metamorphosis plays a dominant role in controlling MeHg concentrations in chironomids and that mercury supply is of secondary importance due to low and relatively uniform environmental levels across sites. Different development stages of chironomids represent distinct sources of MeHg, and we provide evidence from nitrogen isotope ratios and published diet studies of Arctic char that different feeding on these stages likely affects MeHg uptake by fish. These findings have fundamental implications for the roles of atmospheric deposition and food web dynamics in the mercury cycle of High Arctic lakes.

MATERIALS AND METHODS

Field sampling

Water bodies were investigated on 3 islands of the Canadian Arctic Archipelago (Cornwallis, Devon, Somerset, 74–76°N latitude) in July and August of 2005 and 2006 (Figure 1). This High Arctic region has a severe climate with cold temperatures (February mean = -33°C, July mean = 4°C), low annual precipitation (~ 150 mm) and a very short ice-free season of approximately 6–8 weeks. Seventeen lakes and 5 ponds were sampled mostly located near Resolute Bay, Cornwallis Island (74°30' N, 94°55' W) or a remote field camp at Truelove Lowland, Devon Island (75°40' N, 84°33' W). Truelove Lowland is a 43 km^2 polar oasis with a warmer microclimate than Resolute (Bliss 1977), and drainage basins are covered with lush meadows of sedge and moss. In contrast, other study sites have polar desert drainage basins of barren sedimentary rock with typically < 5% plant cover (Bliss 1977). The study lakes had maximum depths≥ 7 m and all are known to contain populations of landlocked Arctic char except one (Titti Lake). Ponds had maximum depths < 3.5 m and were assumed to be fishless.
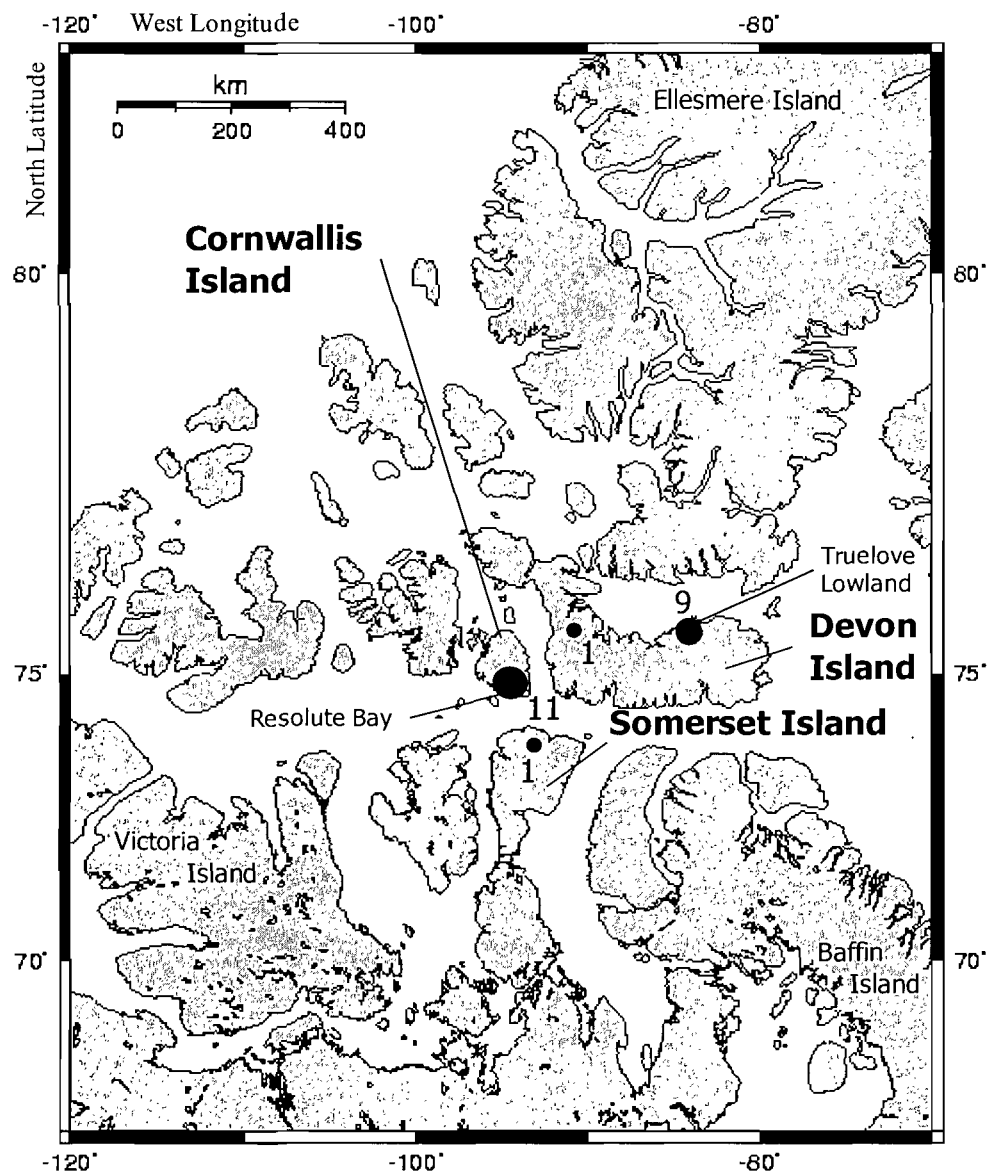
Figure 1. Locations of study areas on 3 islands in the Canadian Arctic Archipelago. The number of water bodies sampled is presented for each area.

Each site was sampled on one occasion except 4 lakes sampled in both 2005 and 2006 (see Supplemental Table S1 for site descriptions). Chironomids in High Arctic lakes are abundant at shallow depths (~ 2–4 m) (Welch 1973; Welch 1976; Minns 1977) allowing them to emerge before the ice has completely melted. Mating occurs mainly on substrates (ice, water surface, shoreline rocks) rather than by swarming due to nearly continuous winds (Welch 1976). From July to early, August, adults and pupae were collected from 3 near-shore stations in each water body by removing individuals from ice or water surfaces (occasionally shoreline rocks) using tweezers or a fine-mesh net. Larvae were also collected at 3 stations per lake with a 500 μm D-frame net by kick-sweeping sediment in water 0.5–1.25 m deep. In addition, larvae were occasionally collected from profundal sediment with an Ekman grab (n = 5) or caught in off-shore waters with a zooplankton net (n = 4). Benthic primary producers (macroscopic *Nostoc* spheres, filamentous algae) were collected from 1–4 stations in 7 water bodies (n = 15).

Chironomids were washed in ultra-pure water, separated by development stage (adult, pupa, larva), placed in plastic scintillation vials and frozen. Samples collected from the 3 stations per lake were treated as separate replicates. Adult samples typically contained > 100 individuals but pupae and larvae samples contained less individuals (~ 10, range = 1–> 20). Fewer than 3 replicates were obtained for larvae and pupae at some sites. Some individuals were preserved in concentrated ethanol for taxonomic identification. The maturity of larvae varied from 3rd or early 4^{rth} instars that needed an additional year of growth (Welch 1976) to 4^{rth} instars ready to emerge that summer or next spring (Oliver 1968). Chironomid subfamilies were pooled together, with the exception of larvae from

the predatory subfamily Tanypodinae, which were separated from non-predatory taxa when present at some polar oasis sites.

Water was obtained as surface grabs from a near-shore station (~ 1 m depth) in each water body and also mid-depth at a pelagic station in 75% of the lakes (due to logistic constraints). For total mercury (THg) and MeHg analyses, triplicate acid-cleaned bottles of amber glass or teflon were rinsed with lake water prior to collection and preserved with HCl. Deep-water mercury samples were collected with acid-washed teflon tubing and a peristaltic pump. Inflow waters of 1 polar oasis and 2 polar desert lakes were sampled on 1–4 occasions for mercury by surface grabs. Ancillary water chemistry samples for anions (chloride, sulfate), dissolved organic carbon (DOC, 0.45 μm filtration), and total phosphorus were collected in duplicate along with mercury samples. Conductivity, pH, dissolved oxygen and water temperature were measured *in situ* with a YSI probe. Site water quality is summarized in Supplemental Table S2.

Sediment was collected by Ekman grab from three near-shore stations (~ 1–2 m depth) in 18 of the 22 water bodies where larvae were sampled. Each sample of sediment was taken from the top 5 cm layer, avoiding sediment directly in contact with the Ekman, and frozen in plastic scintillation vials. In 2006 only, profundal sediment was collected in lakes ($n = 7$) at 1–2 stations ≥ 6.5 m deep using the same method.

Maximum water depth (Z_{max}) was obtained either from the literature ($n = 14$ sites), from depth sounding along transects with a weighted line ($n = 4$), or from the Z_{max} observed during sampling ($n = 4$). Surface area (SA) and drainage basin area (DA) of water bodies were measured in SIGIS v2.60 software using Landsat-7 images and digital maps of the Canadian National Topographic Data Base.

Laboratory analyses

MeHg was extracted from lyophilized and homogenized samples of chironomid (n = 206), algae (n = 15) or sediment (n = 50) by digestion in 4M HNO_3 at 55°C for 16 hours. Some samples that contained small amounts of material (1–10 mg) were weighed intact on a microbalance (0.06 mg accuracy) and then homogenized directly in the digestion vial with an acid-cleaned glass rod. Water samples for MeHg analysis were pre-distilled with additions of KCl and H_2SO_4 to remove matrix interferences. Comparison of distillation and acid extraction methods for sediment MeHg analysis yielded similar results except for lower recovery by acid digestion on a few samples with high organic content. MeHg was extracted from those samples (n = 12) by aqueous distillation as for water samples but with the additional reagent $CuSO_4$. MeHg extract was derivatized by aqueous ethylation using $NaBEt_4$, trapped with Tenax and measured with a Tekran 2500 cold vapour atomic fluorescence spectrometer (CVAFS). MeHg burden (pg ind^{-1}) was measured for a subset of chironomid samples (n = 88) using mean body weights determined separately for each digestion (sample mass divided by the number of individuals).

THg concentration in sediment (n = 62) and adult chironomids (n = 74) was measured with a Direct Mercury Analyzer (DMA-80) in which sample was combusted at 750°C and the mercury vapour was retained on a gold trap for analysis by cold vapour atomic absorption spectrometry. Aqueous THg was determined on 50 mL samples by BrCl oxidation, $SnCl_2$ reduction, two-stage gold amalgamation and gas-phase detection with a Tekran 2600 CVAFS. Water DOC was measured in a Pt-catalyzed Shimadzu TOC-5000

analyzer. Organic matter (OM) content of sediment was determined by loss on ignition (LOI) in an oven at 550°C for 2 hours.

Recoveries of certified reference materials for mercury were $97 \pm 11\%$ of MeHg ($n = 133$) and $106 \pm 3\%$ of THg ($n = 19$) in TORT-2 lobster hepatopancreas (National Research Council of Canada), $91 \pm 17\%$ of MeHg ($n = 23$) in IAEA-405 estuarine sediment (International Atomic Energy Agency), and $99 \pm 6\%$ of THg ($n = 16$) in SO-2 soil (CANMET Mineral and Energy Technology). Analytical detection limits, estimated as 3 times the standard deviation (SD) of 10 blanks, were 0.04 ng MeHg g^{-1} for 250 mg of sediment and 0.05 ng THg L^{-1} and 0.02 ng MeHg L^{-1} for 50 mL aliquots of water.

Stable isotope ratios of nitrogen and carbon were measured in chironomids (larvae $n = 46$, pupae $n = 19$, adult $n = 76$) at the G.G. Hatch Stable Isotope Laboratory at the University of Ottawa (Ottawa, Canada) on a DeltaPlus XP Isotope Ratio Mass Spectrometer. Stable isotope ratios were expressed in delta notation (δ) as the parts per thousand (‰) deviation from standards of atmospheric N_2 gas for $\delta^{15}N$ and Vienna PeeDee Belemnite for $\delta^{13}C$. Analytical precision was $\leq 0.2‰$.

Data analysis

A general linear model (GLM) was used to test the effects of development stage (larvae, pupae, adults), mercury supply (DA:SA ratio, MeHg concentration in sediment and water), and habitat charactersistics (DOC, water temperature) on the MeHg concentration in chironomids. Four water bodies without sediment data were excluded from the model ($n = 183$). Main effects were tested using Type III sum-of-squares (SS), and effect sizes for factors in the model were evaluated with the partial ETA squared coefficient (effect SS divided by the effect SS plus error SS). Variables were log or

arcsine transformed, if required, to meet assumptions of statistical tests and half the detection limit was used for values below detection. Means are presented ± 1 SD unless otherwise specified.

RESULTS AND DISCUSSION

Organic carbon and drainage basin influences on mercury supply

Concentrations of sediment mercury were very low at our High Arctic sites (Table 1). THg and MeHg in near-shore sediment averaged 5.8 ± 2.8 ng g^{-1} and 0.13 ± 0.17 ng g^{-1}, respectively, which is less than half of levels found in sediment of lower latitude lakes (Hammerschmidt et al. 2006; Watras et al. 1998). Mercury concentrations in profundal sediment were higher but still comparatively low (Table 1). Water-column concentrations of mercury averaged 0.62 ± 0.33 ng THg L^{-1} and 0.04 ± 0.03 ng MeHg L^{-1}, with slightly higher MeHg observed in 1 pond (Pond I, 0.15 ng L^{-1}). Our aqueous MeHg concentrations were consistent with other studies of lakes on Cornwallis (0.05 ± 0.01 ng L^{-1}; Loseto et al. 2004) and Ellesmere islands (0.04 ± 0.03 ng L^{-1}; St. Louis et al. 2005).

Organic carbon was sparse in sediment (5 ± 8 %LOI) and water (1.7 ± 1.9 mg DOC L^{-1}) and had a strong influence on the environmental distribution of mercury. THg and MeHg concentrations in sediment were positively related to OM content (linear regression R^2_{adj} = 0.55–0.65, $F \geq$ 74.4, $p <$ 0.001, n = 62, Supplemental Figure S1). Y-intercepts for the linear regression models had low values, suggesting that most THg and MeHg was bound to OM rather than inorganic particles (intercepts: 2.4 ng THg g^{-1}, 0.02 ng MeHg g^{-1}). Similarly, MeHg concentration in the water column was slightly higher in more DOC-rich waters (linear regression R^2_{adj} = 0.21, F = 6.5, p = 0.019, n = 22).

Table 1. Dry weight contents of OM, THg and MeHg in bulk sediment from near-shore and profundal zones of study sites.

Characteristic	Near-shore sediment (n = 18 lakes and ponds)		Profundal sediment (n = 7 lakes)	
	Mean	Range	Mean	Range
OM (% LOI)	3.7	1.3–12.2	17.1	2.0–31.5
THg (ng g^{-1})	5.8	2.7–12.2	26.9	12.1–50.7
THg (ng g OM^{-1})	206	93–529	257	91–710
MeHg (ng g^{-1})	0.13	< 0.04–0.64	0.52	0.13–1.09
MeHg (ng g OM^{-1})	3.3	0.9–17.7	3.6	2.1–6.3
% MeHg	2.1	0.5–8.7	1.9	0.9–3.3

Drainage basin ratio significantly affected the THg concentration of sediment (Figure 2). THg in both near-shore and deep-water sediment was higher at sites with larger drainage ratios, after correcting for the amount of OM present. This finding suggests that water bodies with larger drainage ratios received greater THg loads, most likely from surface runoff during spring freshet which is the principal source of THg to High Arctic fresh waters (Semkin et al. 2005). In contrast, MeHg in near-shore sediment (OM-corrected) was not related to inorganic mercury supply estimated either by sediment THg or drainage basin ratio (p = 0.30, n = 18). In profundal sediment, OM-corrected MeHg and THg contents were marginally related (linear regression R^2_{adj} = 0.34, F = 4.0, p = 0.10, n = 7) but drainage basin ratio had no effect on the former (p = 0.44, n = 7).
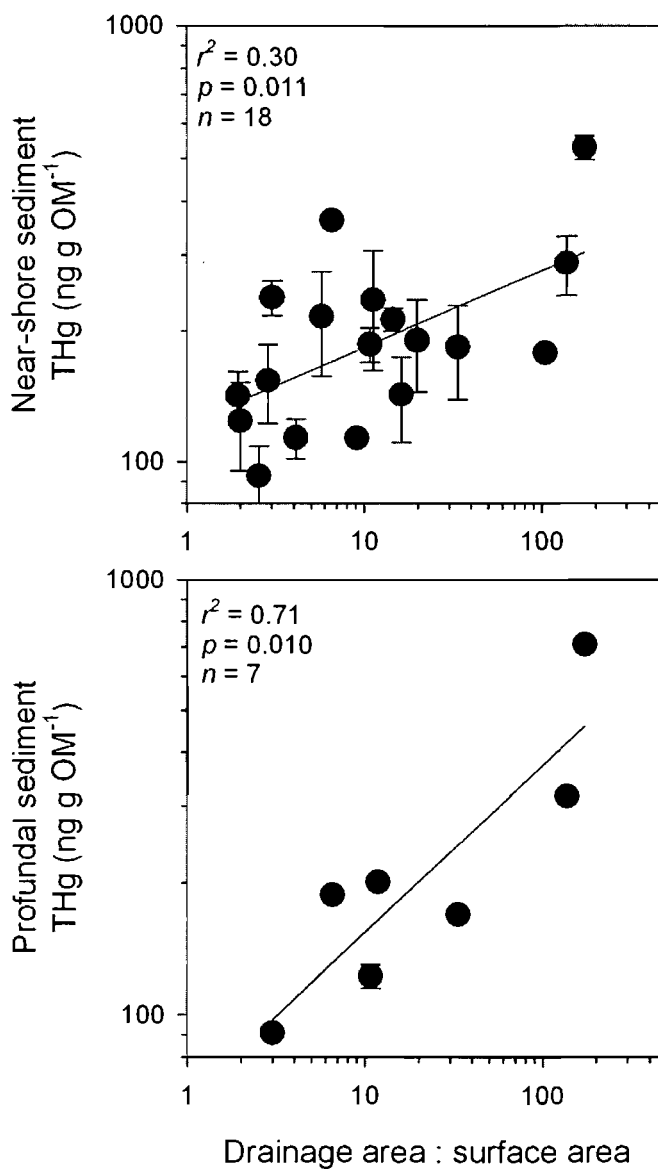
Figure 2. Relationship between drainage basin ratio and the dry weight concentration of

sediment THg (corrected for OM content) in near-shore and profundal zones. Means ± 1

standard error are presented for near-shore sediment (*n* = 3 replicates) while profundal

sediment data are mostly single samples.

We found consistently low levels of MeHg in water and sediment at sites along a gradient in THg supply suggesting *in situ* MeHg production was weakly coupled to inorganic mercury loading. Information is currently lacking on mercury methylation rates in High Arctic lakes, and we suggest that the capacity of the sediment bacterial community to generate MeHg may be strongly limited by poor environmental conditions for methylation rather than the availability of inorganic mercury. Specifically, methylation rates may be limited by small pools of organic substrate in sediment, cold temperatures, alkaline water (pH ~ 8), and a well-mixed, oxygenated water column (Benoit et al. 2003; Kelly et al. 2003; Hammerschmidt et al. 2006).

Summer-time terrestrial inputs of aqueous MeHg may also be low as suggested by our limited sampling of inflows to a few lakes. Terrestrial DOC was high in seepage from meadows at the polar oasis (3.3–10.3 mg DOC L^{-1}, $n = 3$) and resulted in higher water-column DOC in the 8 water bodies there (3.7 ± 1.9 mg L^{-1}) compared to polar desert sites (0.6 ± 0.4 mg L^{-1}, $n = 14$). However, surface seepage from the oasis had similar MeHg concentrations (0.02–0.07 ng L^{-1}, $n = 3$) to low-DOC inflows from 2 polar desert drainage basins (0.02–0.07 ng L^{-1}, $n = 8$). Likewise, average water-column MeHg concentrations did not differ between water bodies at polar oasis and desert sites (*t*-test, *t* = 1.6, $p = 0.13$, $n = 22$).

Bioaccumulation of MeHg in chironomids

The MeHg concentration in chironomids is primarily determined by the concentration of MeHg in their diet, the amount of food consumed (resulting in MeHg uptake), and changes in biomass during development (Roditi et al. 2000). Potential diet sources, specifically algae and sediment OM, were investigated for their influence on MeHg

concentrations in chironomid larvae. There was not a significant association between MeHg concentrations in algae and larvae (linear regression R^2_{adj} = 0.38, F = 4.7, p = 0.084, n = 7 water bodies), and no relationship was found between MeHg concentrations in near-shore sediment (OM-corrected) and the larvae collected there (p = 0.31, n = 18). Low inter-lake variation in MeHg concentrations of chironomid food sources (sediment = 3.3 ± 3.8 ng g OM^{-1}, benthic algae = 2.5 ± 2.7 ng g^{-1}) may explain the lack of a strong dietary influence.

In contrast, concentrations of MeHg in chironomids strongly increased during growth and metamorphosis (Figure 3, Table 2). Adults were 1.7 times more concentrated with MeHg than pupae and 2.9 times more concentrated than immature larvae when samples were averaged over all sites. MeHg was the predominant form of mercury in adult chironomids, averaging 82 ± 15% of THg concentrations (n = 74). We inferred changes in MeHg concentration during chironomid development by comparing different individuals in each stage rather than following the same individuals through time. This approach may have introduced additional variation to the analysis due to differences in taxonomy between stages or degree of maturity in the larvae. Nevertheless, adults were consistently elevated in MeHg relative to larvae in all 17 lakes and 5 ponds (Figure 4). Relative MeHg concentrations in pupae were more variable. Inter-annual variation in the MeHg concentration of larvae and adults from 4 lakes was low for 2 consecutive sampling years (Supplemental Figure S2).

Adult chironomids had higher concentrations of MeHg than pupae due to a reduction in body weight during emergence and mating with no associated loss in MeHg burden (one-way ANOVA, F = 16.7, p < 0.001, n = 88, Figure 3). About 10% of pupal dry weight is lost when the pupal exuvium is shed (Welch 1973), and this skin was found to

be mercury-poor (1.0 ± 0.5 pg MeHg, n = 12). Since adults do not feed, an additional ~

20–50% of body dry weight can be lost when energy reserves are consumed during

mating (Hamburger et al. 1996). Larvae had the lowest MeHg concentrations because

they had the lowest burdens and were still growing (Figure 3). This process is not unique

to the High Arctic since other bioaccumulating compounds (e.g., organochlorines,

cadmium) concentrate during metamorphosis in chironomids of lower latitudes (Currie

et al. 1997; Bartrons et al. 2007).

Table 2. General linear model explaining MeHg concentrations of chironomids in

relation to their development stage, mercury supply and habitat characteristics

(model R^2 = 0.56, n = 183).

Response variable	Factor	Effect	Effect size[a]	F	p
log MeHg$_{concentration}$	Development stage	+	0.44	68.0	< 0.001
	Water temperature	–	0.07	13.2	< 0.001
	log MeHg$_{sediment}$[b]	+	0.04	8.2	0.005
	log MeHg$_{water}$	+	0.04	6.5	0.012
	log DA:SA	+	0.03	4.9	0.029
	log DOC	–	0.02	4.3	0.040

[a] Partial Eta squared coefficient

[b] Corrected for OM content
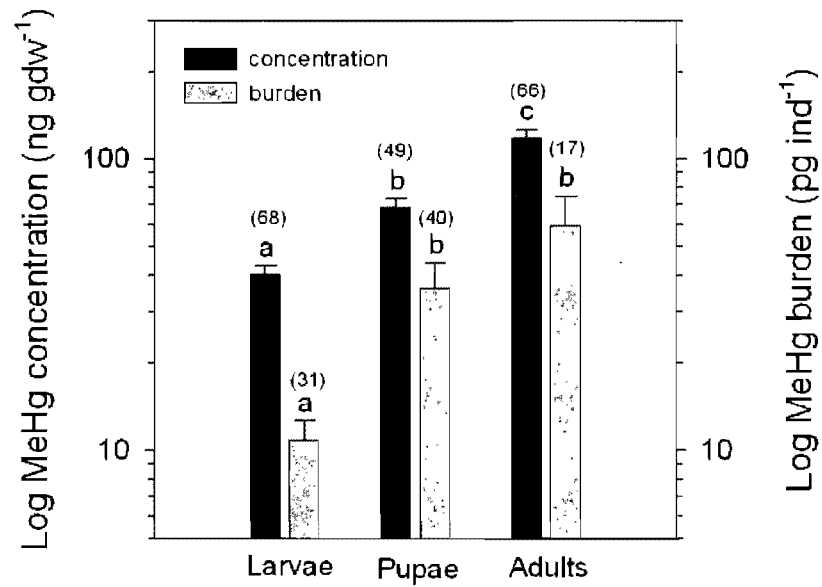
Figure 3. Comparison of MeHg concentrations or burdens between chironomid stages.

Means ± 1 standard error with different letters are statistically different (Bonferroni $p <$

0.05) and were tested with the GLM for concentrations (Table 2) and a one-way

ANOVA for burdens (see text). Sample sizes are in parentheses.

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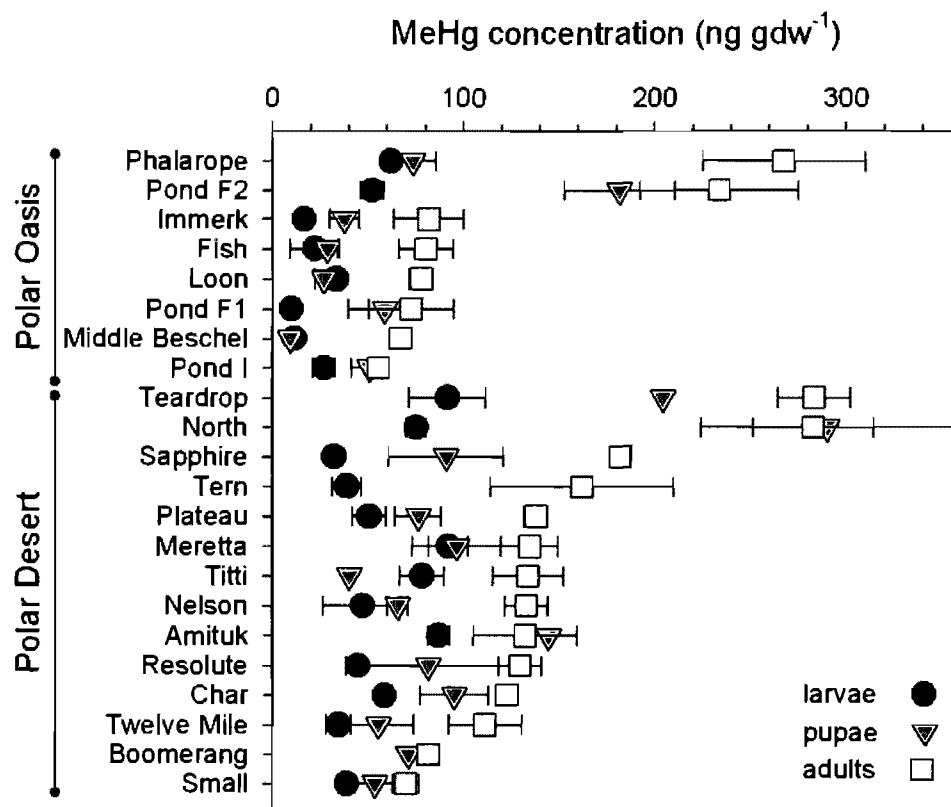
Figure 4. MeHg concentrations of chironomid larvae, pupae and adults at each of the study sites categorized according to drainage basin type. Means are ± 1 standard error.

A GLM identified the relative importance of biological processes, mercury supply, and habitat characteristics for MeHg bioaccumulation in chironomids (Table 2). Development stage explained the most variation in chironomid MeHg concentration, and significant but secondary effects were found for water temperature, MeHg concentrations in sediment and water, DA:SA, and DOC (Table 2). The model indicated that MeHg concentrations in chironomids were influenced more by their biological development than by among-site variation in mercury supply and habitat characteristics. The specific developmental effects were an increase in MeHg concentration during growth from immature larvae to pupae and a further increase in MeHg concentration from pupae to adults due to loss of body mass without an associated loss in MeHg (Figure 3).

Chironomids had lower MeHg concentrations at sites with warmer temperatures and higher DOC which were mainly found at the polar oasis (Table 2, Supplemental Figure S3). DOC may have had an inhibitory effect on MeHg bioaccumulation by reducing mercury bioavailability in the water column (Kelly et al. 2003). Taxonomic differences could explain the observed pattern in MeHg accumulation along a temperature gradient. The MeHg concentration of adult chironomids was positively related to the percent abundance of individuals from the subfamily Diamesinae in samples from 2006 (linear regression $R^2_{adj} = 0.22$, $F = 5.3$, $p = 0.038$, $n = 16$). Diamesinae prefer cold water (Barley et al. 2006), and their percent abundance at our study sites was negatively related to water temperature (linear regression $R^2_{adj} = 0.22$, $F = 5.3$, $p = 0.037$, $n = 16$). Adult chironomids from North Lake (which had the highest MeHg concentration; Figure 4) were sorted into the 2 main subfamilies present (Orthocladinae and Diamesinae), and Diamesinae were on average 2.7 times more concentrated with MeHg than

Orthocladinae. However, sites where Diamesinae adults were abundant did not always have high MeHg concentrations (e.g., Char and Meretta lakes) and it is unclear why this taxonomic group sometimes accumulated more mercury.

Effect of metamorphosis on chironomid $\delta^{15}N$ ratios

We observed differences in the $\delta^{15}N$ ratios of chironomid stages associated with extensive restructuring of nitrogen-rich protein tissues during metamorphosis. The $\delta^{15}N$ ratios of larvae ranged from 1.2–6.8‰ among lakes indicating differences in the baseline signature (Supplemental Figure S4). On average (mean ± 1 SE), pupae were enriched in $\delta^{15}N$ by 2.1 ± 0.4‰ relative to larvae and emergent adults were enriched by an additional 1.0 ± 0.3‰ in $\delta^{15}N$ relative to pupae (t-tests, $t \geq 3.6$, $p \leq 0.018$, $n = 12$–14 sites). Enrichment of $\delta^{15}N$ during metamorphosis occurs in a variety of insect groups without a change in diet (Doi et al. 2007; Tibbets et al. 2008). Differences in $\delta^{13}C$ between larvae and pupae were not significantly different from zero (t-tests, $p > 0.05$), confirming that nitrogen isotope patterns in this study were likely not due to diet effects. Nitrogen isotope enrichment occurs because $\delta^{15}N$-depleted protein is preferentially catabolized and subsequently eliminated in larval excrement or meconium of emerging adults (Tibbets et al. 2008). Loss of $\delta^{15}N$-depleted exuvium could also result in enrichment during emergence (Doi et al. 2007).

These $\delta^{15}N$ patterns have important implications for food web studies in High Arctic lakes. The difference in $\delta^{15}N$ between larvae and adults of ~ 3‰ is close to the 3.4‰ $\delta^{15}N$ enrichment that occurs between a consumer and its diet (Vander Zanden and Rasmussen 2001). As a result, a char that mostly consumes larvae would be depleted in

δ^{15}N by 2–3‰ compared to one that consumes pupae and adults even though the two individuals have the same trophic level. Nitrogen isotope ratios have been used in feeding studies of Arctic char to identify fish with cannibalistic or chironomid diets (Guiger et al. 2002; Muir et al. 2005) and to infer trophic level for comparison of mercury between fish (Muir et al. 2005). A δ^{15}N range of ~ 5‰ is often observed between individual adult Arctic char within a lake (Hobson and Welch 1995; Guiger et al. 2002; Muir et al. 2005) when in theory, a maximum difference of 3.4‰ should occur between fish that only eat invertebrates and those that only eat fish. This broad range in reported δ^{15}N of Arctic char suggests that differential consumption of chironomid stages may commonly occur and affect the δ^{15}N of these fish. Caution is required when using nitrogen isotope ratios to interpret trophic position and dietary sources of MeHg.

Chironomid stages as distinct sources of MeHg

We estimated MeHg uptake by char feeding on different chironomid stages. Average concentrations of each stage were corrected for their nutritional quality using caloric content (larvae: 5 kcal g dw^{-1}, pupae and adults: 5.5 kcal g dw^{-1}; Welch 1973, 1976) and assuming an assimilation effeciency of 80% (Trudel and Rasmussen 2001). We estimated a transfer to Arctic char of 6.5 ng MeHg per kcal^{-1} of larvae consumed, 9.9 ng MeHg per kcal^{-1} of pupae and 17.2 ng MeHg per kcal^{-1} of adult chironomid. As an example scenario, MeHg uptake from a diet of 25% larvae, 50% pupae and 25% adults would be 1.7 times higher than a diet of 100% larvae.

Arctic char may feed on a particular chironomid stage depending on the size of the fish or the time of year. For example, in lakes on Ellesmere Island in the Arctic Archipelago, larger char fed selectively on pupae at the lake surface during the period of

emergence while smaller char (< 20 cm) inhabited very shallow areas, feeding mostly on chironomid larvae (Parker and Johnson 1991). Similarly, adult chironomids were an important diet item for Arctic char > 17 cm in a Greenland lake (~ 15–30% of gut contents) but were little consumed by fish less than that size (Riget et al. 1986). Chironomid pupae and adults are only present during emergence from June to August, and larvae are a more prominent diet item at other times of the year (Johnson 1980; Riget et al. 1986; Hobson and Welch 1995). Differential consumption of chironomid stages depending on fish size and season likely affects the amount of MeHg bioaccumulated in Arctic char.

Implications for the role of atmospheric mercury deposition

This study provides strong evidence that drainage basin inputs of THg, which are primarily from atmospheric deposition (Semkin et al. 2005), have less impact on mercury biomagnification than biological and food web processes in High Arctic fresh waters. Unique ecological conditions in this extreme environment may dampen the movement of mercury from the atmosphere to aquatic food webs. In spring, snowpack can receive high loads of inorganic mercury during atmospheric depletion events although a significant fraction is reduced and returned to the atmosphere within several days (Steffen et al. 2008). Preliminary findings in Arctic Alaska indicate that increased atmospheric deposition due to spring-time mercury depletion events has little impact on MeHg accumulation in Arctic food webs (Hammerschmidt and Fitzgerald 2008). Elevated levels of inorganic mercury are found in High Arctic snow melt (Loseto et al. 2004; St. Louis et al. 2005) but more than 50% of THg loads from melt water flow under ice and exit the outflow of lakes without mixing into the water column due to differences

in density (Semkin et al. 2005). Low organic carbon in water and sediment reduce mercury retention in lakes (Outridge et al. 2007). *In situ* MeHg production is probably limited more by extreme environmental conditions than inorganic mercury loading (as discussed earlier), and losses by photodegredation may be high due very clear water (Hammerschmidt and Fitzgerald 2006). Future research should determine mercury methylation rates in High Arctic lakes.

The Canadian Arctic Archipelago is undergoing rapid environmental change as a result of climate warming, and the cycling of mercury is expected to increase because of greater watershed loadings to lakes, scavenging by algae and detritial OM, and enhanced MeHg production in sediment (Hammerscmidt et al. 2006; Outridge et al. 2007). A warmer Arctic will also have consequences for food webs by stimulating growth rates and altering the species composition of aquatic communities. Interactions between mercury supply and food web processes will ultimately determine future biomagnification of MeHg to Arctic char.

ACKNOWLEDGEMENTS

SUPPLEMENTARY INFORMATION

Table S1. Location and size of lakes and ponds investigated on 3 islands in the Canadian High Arctic during the summers of 2005 and 2006.

Island	Site (description)	Year	Latitude (°N)	Longitude (°W)	Z_{max} (m)	SA (km²)	DA (km²)	DA:SA
Cornwallis	Amituk (L, D)	2005	75°02'44"	93°47'15"	43	0.38	26.50	70.0
Cornwallis	Char (L, D)	2005-06	74°42'16"	94°52'56"	27.5	0.53	3.47	6.5
Cornwallis	Meretta (L, D)	2005-06	74°41'36"	94°59'38"	12	0.26	8.71	33.5
Cornwallis	Nelson (L, D)	2006	74°41'24"	94°19'12"	11	0.61	104.87	172.6
Cornwallis	North (L, D)	2005-06	74°46'32"	95°05'42"	15.5[c]	0.60	82.86	137.5
Cornwallis	Plateau (L, D)	2005	74°48'36"	95°12'00"	14	0.70	6.33	9.0
Cornwallis	Resolute (L, D)	2005	74°41'31"	94°56'44"	22	1.18	17.03	14.5
Cornwallis	Small (L, D)	2005-06	74°45'37"	95°03'35"	11	0.14	1.50	10.8
Cornwallis	Teardrop (L, D)	2006	74°40'48"	94°59'24"	8.1	0.04	0.48	11.9
Cornwallis	Tern (P, D)	2006	74°48'00"	95°05'24"	3.3	0.57	11.19	19.8
Cornwallis	Twelve Mile (L, D)	2005	74°49'12"	95°20'24"	9.5[b]	0.81	4.61	5.7
Devon	Fish (L, O)	2006	75°39'36"	84°33'00"	7	1.21	2.34	1.9
Devon	Immerk (L, O)	2006	75°40'48"	84°33'36"	8	1.07	3.23	3.0
Devon	Loon (L, O)	2006	75°41'24"	84°28'12"	8.5	0.20	21.33	104.5
Devon	Middle Beschel (L, O)	2006	75°39'00"	84°28'12"	10	0.34	5.44	16.2
Devon	Phalarope (P,O)	2006	75°39'36"	84°36'36"	1.8	1.95	8.04	4.1
Devon	Pond I[a] (P, O)	2006	75°40'48"	84°34'48"	0.8	0.09	0.18	2.0
Devon	Pond F1[a] (P, O)	2006	75°40'12"	84°33'36"	1.2	0.05	0.12	2.5
Devon	Pond F2[a] (P, O)	2006	75°38'60"	84°32'24"	2.8	0.10	0.30	2.9
Devon	Sapphire (L, D)	2005	75°21'00"	89°29'00"	9[b]	0.11	1.19	11.2
Devon	Titti (L, D)	2006	75°40'48"	84°22'48"	7.5	0.10	0.58	5.8
Somerset	Boomerang (L, D)	2005	73°56'14"	92°53'20"	18[b]	6.63	111.25	16.8

L = lake, P = pond, D = polar desert, O = polar oasis, Z_{max} = maximum depth, SA = surface area, DA = drainage area

[a] Unofficial name

[b] Maximum observed depth during sampling

Table S2. Means and ranges of water chemistry characteristics of the study lakes and ponds ($n = 22$).

Characteristic	Mean	Range
Water temperature (°C)	5	2–9
Conductivity ($\mu S\ cm^{-1}$)	159	96–252
pH	8.2	7.8–8.6
Total phosphorus ($\mu g\ L^{-1}$)	3.4	1.2–11.8
DOC ($\mu g\ L^{-1}$)	1.7	< 0.6–7.4
SO_4^{2-}-S ($mg\ L^{-1}$)	0.88	0.02–4.79
Cl^- ($mg\ L^{-1}$)	5.9	1.0–20.0
THg ($ng\ L^{-1}$)	0.62	0.07–1.39
MeHg ($ng\ L^{-1}$)	0.04	< 0.02–0.15
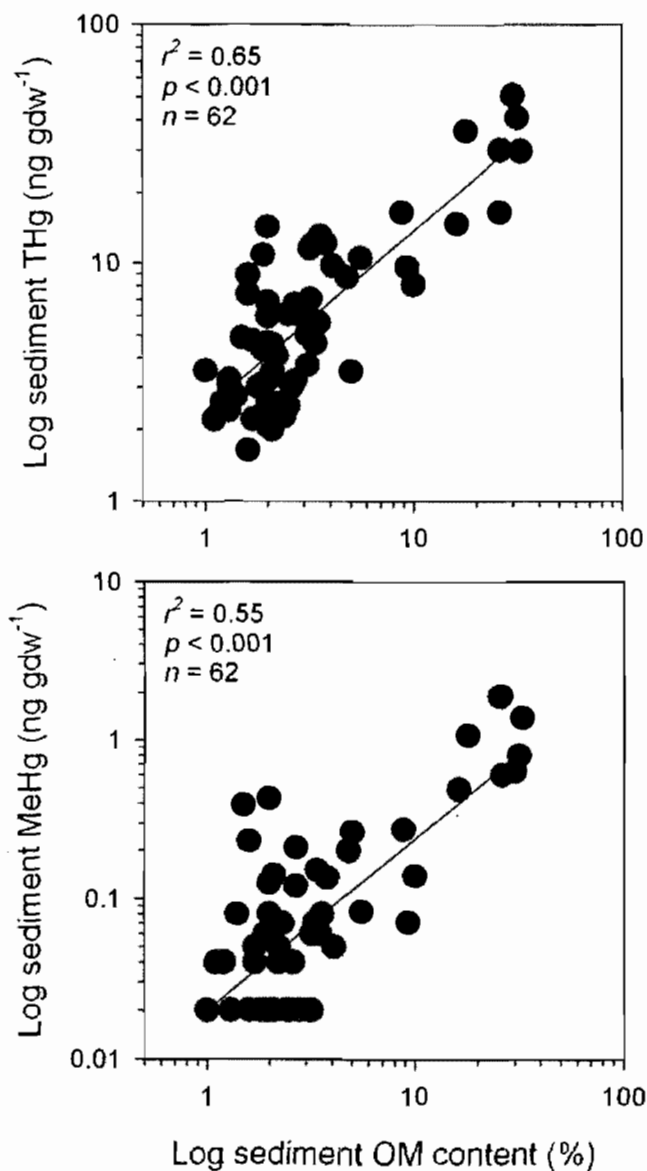
Figure S1. Influence of organic matter content (% LOI) on sediment concentrations of THg and MeHg. Note that the line of identical sediment MeHg concentrations in the bottom panel is samples below the detection limit of 0.04 ng g^{-1}.
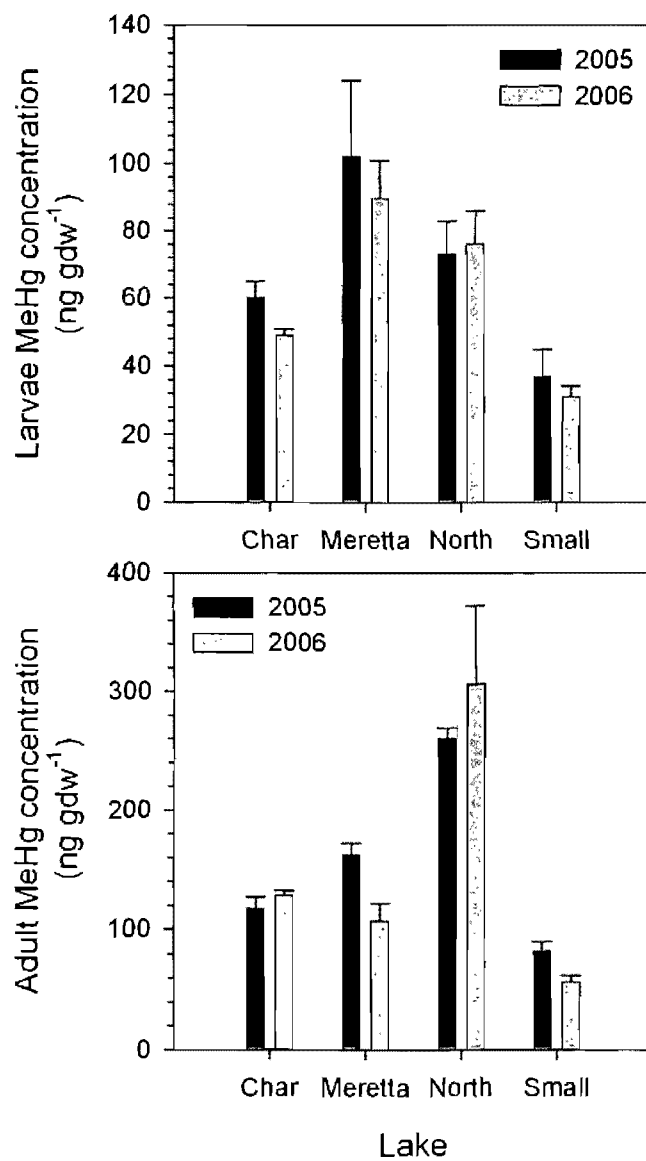
Figure S2. Inter-annual variation of MeHg concentrations in chironomid larvae and adults sampled in 4 lakes in 2005 and 2006. Means are ± 1 standard errror.
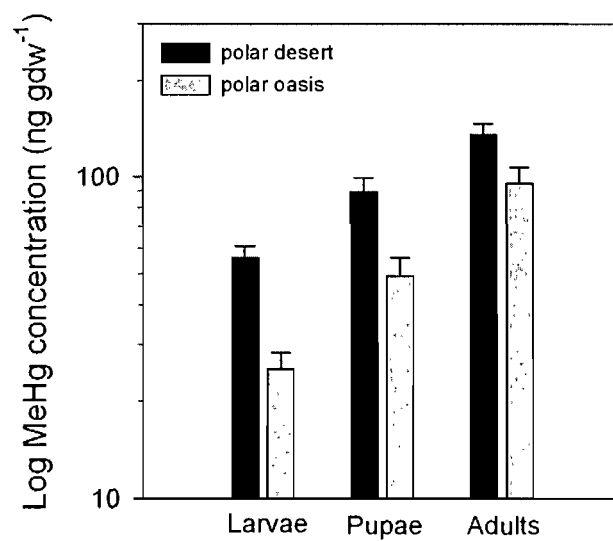
Figure S3. Variation of MeHg concentrations in chironomid stages between polar oasis and polar desert water bodies (two-way ANOVA, effect of basin type F = 44.1, p < 0.001, n = 206).
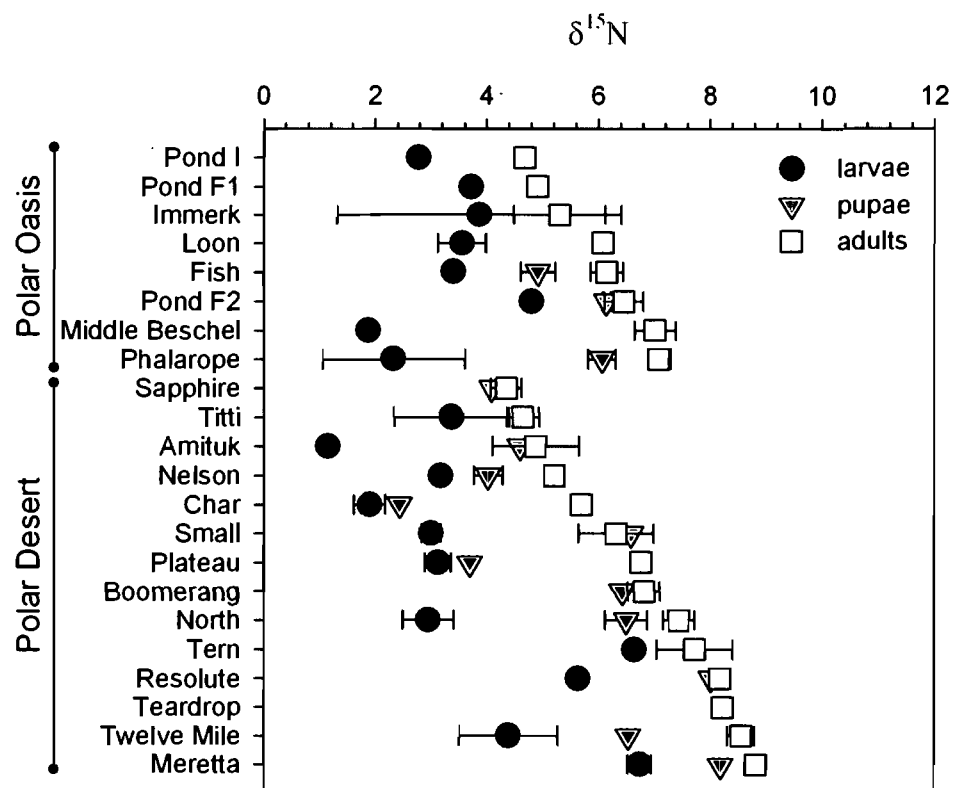
Figure S4. δ^{15}N ratios of chironomid larvae, pupae and adults at each of the study sites categorized according to drainage basin type. Means are ± 1 standard error of 2–7 samples although some values for larvae and pupae are single samples.

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CHAPITRE 3

Benthic algae support food webs of High Arctic lakes in watersheds of varying productivity

John Chételat, Louise Cloutier, and Marc Amyot

ABSTRACT

Lakes in the Canadian High Arctic have very low biological production due to extreme climatic conditions and low watershed loadings of nutrients and organic matter (OM). We investigated the role of autochthonous and terrestrial carbon in supporting these aquatic food webs by determining the diet of the dominant primary consumer, aquatic chironomids. In 2005 and 2006, chironomids were collected from 17 lakes, 5 ponds and 4 inflow streams on 3 islands of the Arctic Archipelago (~ 74–76°N). Sampling sites were located in barren polar desert watersheds and in a polar oasis with lush sedge-moss meadows. Stomach content analysis of close to 600 larvae indicated that chironomids ingested a mix of diatoms and detrital OM with little variation among most genera. Carbon stable isotope ($\delta^{13}C$) ratios of adult chironomids in 17 lakes (mean ± 1 SD = -24.9 ± 2.8‰) were closest to those of benthic algae (-23.7 ± 3.6‰) and more enriched than terrestrial OM (-28.3 ± 2.1‰) and pelagic carbon (-33.1 ± 2.0‰). The dominant role of algal carbon in their diet was also reflected by a strong covariation between the $\delta^{13}C$ of chironomids and benthic algae among water bodies (R^2_{adj} = 0.88, p = 0.012, n = 5). Radiocarbon measurements on chironomids from 2 lakes showed that old carbon originating from terrestrial peat did not support their production. Chironomid diet did not differ between watershed types despite greater terrestrial OM loading at the polar oasis. Our findings indicate that chironomids, and the Arctic char that consume them, are supported primarily by benthic algae in lakes of the Canadian Arctic Archipelago, in contrast to Arctic lakes at lower latitudes where peat, methanotropic bacteria, and phytoplankton can be relevant energy sources for consumers.

INTRODUCTION

Energy pathways are fundamental characteristics of ecosystems because of their influence on the flow of materials (e.g., nutrients, contaminants) and the structure of food webs. In freshwater ecosystems, the importance of both autochthonous and terrestrial energy sources has been demonstrated, though their relative influence varies considerably depending on the availability of the resources and linkages with the watershed (Marczak et al. 2007). Terrestrial OM is expected to be a primary basal resource for aquatic food webs where allochthonous inputs are high relative to autotrophic production (e.g., humic lakes and headwater streams) and less relevant in eutrophic or clearwater systems (Carpenter et al. 2005; Marczak et al. 2007; Pace et al. 2007).

Lakes in the Canadian Arctic Archipelago are among the most unproductive fish-bearing ecosystems in the world. Cold temperatures, short open-water seasons, and low nutrient inputs limit algal production to meager levels, most of which occurs on lake-bottom substrates rather than in the water column (Welch and Kalff 1974; Markager et al. 1999). Fish growth is very slow (< 0.05 g C m^{-2} year^{-1}; Rigler 1978), and it takes from 10–17 years for an individual to reach 20 cm in length (Minns 1977). Terrestrial plant growth is equally meager, particularly in polar deserts, and watershed exports of OM are very low (Semkin et al. 2005). For example, the load of terrestrial carbon to Char Lake, Cornwallis Island (75° N), was estimated at 2.5 g C m^{-2} year, representing only 12% of annual primary production (Rigler 1978). For this reason, it has been assumed that food webs of ultraoligotrophic clearwater lakes in the High Arctic are supported by autochthonous primary production (e.g., Hobson and Welch 1995).

Productive pockets of the High Arctic, termed polar oases, have higher watershed inputs of OM originating from lush tundra meadows. Terrestrial carbon is potentially a more relevant energy subsidy to aquatic food webs at these sites as is the case in lower-latitude Arctic lakes of Alaska and Sweden (Schell 1983; Karlsson et al. 2003). An examination of lakes that differ in watershed productivity may provide a preliminary view of how climate change can impact carbon flow in High Arctic fresh waters.

Non-biting midges (Diptera, Chironomidae) are the primary trophic link between basal resources and fish in High Arctic lakes (Minns 1977; Hobson and Welch 1995). These ecosystems have an impoverished diversity of aquatic species, and the food web consists essentially of Arctic char (*Salvelinus alpinus*), chironomids and basal resources with only a few other invertebrates occurring at low densities (e.g., opossum shrimp, caddis flies, copepod zooplankton) (Rigler 1978). Chironomid larvae are deposit feeders that ingest a mix of bacteria, algae and detritus (Berg 1995), although predatory chironomids (Tanypodinae) are also found in some ponds and lakes. Sediment detritus is a complex mixture of OM originating from autochthonous production (e.g., phytoplankton, benthic algae) and terrestrial inputs (e.g., plant fragments, soil OM, peat). Similarly, bacteria consumed by chironomids may obtain their energy from dissolved or particulate OM of autochthonous or terrestrial origin. The relative importance of putative resources has not been determined for chironomids in High Arctic fresh waters.

The stable isotope ratio of carbon ($^{13}C/^{12}C$) is a powerful tracer of basal resources in aquatic food webs. Only minor fractionation of carbon isotope ratios occurs between a consumer and its diet (Vander Zanden and Rasmussen 2001), and carbon sources can be identified if the isotopic signature of each source is distinct. Algae from shallow benthic

zones typically differ in their $^{13}C/^{12}C$ ratio from pelagic phytoplankton because of differences in boundary layer thickness (Hecky and Hesslein 1995). The lighter ^{12}C isotope is preferentially fixed by algae when carbon dioxide is abundant but isotopic discrimination decreases when CO_2 becomes less available such as in benthic algal mats. Two common applications of carbon stable isotopes to food web studies are estimations of carbon contributions from benthic and pelagic zones (e.g., Hecky and Hesslein 1995) or from autochthonous and terrestrial OM (e.g., Karlsson et al. 2003).

In this study, we examined the diet of chironomids (the dominant primary consumer) in freshwater ecosystems of the Canadian Arctic Archipelago. Our main objective was to determine the extent to which chironomids are supported by autochthonous or terrestrial carbon. We sampled sites in polar oasis and desert ecosystems with contrasting levels of terrestrial plant cover, and we expected that terrestrial OM would be a greater component of chironomid diet at the polar oasis where shoreline areas were productive meadows. Although our primary focus was on carbon flow in lakes, we also sampled several ponds and inflow streams which provided additional information on chironomid feeding and spatial variation in carbon stable isotope ratios. We used multiple lines of evidence from gut contents, carbon stable isotopes and radiocarbon to identify the primary pathway of carbon supply to chironomids and Arctic char that consume them.

MATERIALS AND METHODS

Field sampling

The study area encompassed Cornwallis, Devon and Somerset Islands (~ 74–76° N) in the Canadian Arctic Archipelago. The landscape is predominately polar desert characterized by exposed sedimentary rock and < 5% plant cover (Bliss 1977; Annexe

1). Annual precipitation is low (150 mm), and the summers are short and cold (approximately 90 days per year have a maximum temperature > 0°C). Polar oases with lush sedge and moss meadows are rare in the study area and only occur in a few lowland areas on Devon Island where water is better retained and the microclimate is warmer (Bliss 1977; Annexe 1). Most of our polar desert study sites were close to the community of Resolute Bay on Cornwallis Island (74°30' N, 94°55' W) while polar oasis sites were sampled at the 43 km² Truelove Lowland on Devon Island (75°40' N, 84°33' W; Bliss 1977).

We investigated 17 lakes, 5 ponds and 4 inflow streams in the summers of 2005 and 2006 (Table 1). The lakes and ponds had cold water temperatures (2–9°C), alkaline pH (7.8–8.6) and moderate conductivities (96–252 μS cm^{-1}). Inflows had a wider range of water temperatures due to their smaller size (1–14°C). All lakes except Titti were known to contain a population of landlocked Arctic char. Shallow water bodies with a maximum depth (Z_{max}) < 3.5 m were defined as ponds and assumed to be fishless. Lakes and ponds were sampled on one occasion except 4 lakes (Char, Meretta, North, Small) that were sampled in both years. Inflows were sampled once for chironomids but 4 times over a 4 week period for water quality. Meretta Lake and its 2 inflows were impacted by untreated sewage discharge from a military-airport complex at Resolute Bay from 1949–1998 although the lake's water quality has recently returned close to background levels for the area (Douglas and Smol 2000).

Table 1. Location and characteristics of study sites on 3 islands in the Canadian Arctic Archipelago.

Island	Site (description)	Lat	Long	Z_{max}	SA	DA	TP	DOC	Chl	Adult chiro $\delta^{13}C$§
Lakes										
Cornwallis	Amituk (D)	75°02'44"	93°47'15"	43	0.38	26.5	1.2	< 0.6	0.2	-24.2 ± 3.6
Cornwallis	Char (D)	74°42'16"	94°52'56"	27.5	0.53	3.5	2.6	< 0.6	0.2	-26.1 ± 0.8
Cornwallis	Meretta (D)	74°41'36"	94°59'38"	12	0.26	8.7	4.1	1.2	0.4	-21.5 ± 0.6
Cornwallis	Nelson (D)	74°41'24"	94°19'12"	11	0.61	104.9	1.8	< 0.6	0.1	-24.2 ± 0.4
Cornwallis	North (D)	74°46'32"	95°05'42"	15.5‡	0.60	82.9	2.4	< 0.6	0.4	-25.6 ± 1.2
Cornwallis	Plateau (D)	74°48'36"	95°12'00"	14	0.70	6.3	3.9	0.8	0.3	-20.2 ± 0.5
Cornwallis	Resolute (D)	74°41'31"	94°56'44"	22	1.18	17.0	4.4	0.7	0.3	-23.1 ± 0.2
Cornwallis	Small (D)	74°45'37"	95°03'35"	11	0.14	1.5	3.6	1.6	0.4	-23.3 ± 1.2
Cornwallis	Teardrop (D)	74°40'48"	94°59'24"	8	0.04	0.5	2.6	< 0.6	nd	-24.7 ± 0.2
Cornwallis	Twelve Mile (D)	74°49'12"	95°20'24"	9.5‡	0.81	4.6	3.0	0.8	0.2	-22.6 ± 1.1
Devon	Fish (O)	75°39'36"	84°33'00"	7	1.21	2.3	4.5	2.8	nd	-26.1 ± 0.4
Devon	Immerk (O)	75°40'48"	84°33'36"	8	1.07	3.2	4.6	4.4	0.4	-26.1 ± 0.5
Devon	Loon (O)	75°41'24"	84°28'12"	8.5	0.20	21.3	1.8	1.2	nd	-28.1 ± 0.5
Devon	Mid. Beschel (O)	75°39'00"	84°28'12"	10	0.34	5.4	4.3	2.7	nd	-30.9 ± 0.8
Devon	Sapphire (D)	75°21'00"	89°29'00"	9‡	0.11	1.2	1.5	< 0.6	0.2	-27.7 ± 0.4
Devon	Titti (D)	75°40'48"	84°22'48"	7.5	0.10	0.6	1.8	0.6	nd	-29.5 ± 0.8
Somerset	Boomerang (D)	73°56'14"	92°53'20"	18‡	6.63	111.3	1.8	< 0.6	0.2	-22.4 ± 0.2
Ponds										
Cornwallis	Tern (D)	74°48'00"	95°05'24"	3.3	0.57	11.2	2.8	0.9	0.4	-27.9 ± 1.5
Devon	Phalarope (O)	75°39'36"	84°36'36"	1.8	1.95	8.0	3.9	2.9	0.4	-23.3 ± 0.4
Devon	Pond F1 † (O)	75°40'12"	84°33'36"	1.2	0.05	0.1	3.8	4.7	0.4	-21.2 ± 0.7
Devon	Pond F2 † (O)	75°38'60"	84°32'24"	2.8	0.10	0.3	2.9	3.6	0.3	-26.5 ± 0.4
Devon	Pond I † (O)	75°40'48"	84°34'48"	0.8	0.09	0.2	11.8	7.4	0.4	-25.1 ± 0.2
Inflows										
Cornwallis	Char Inflow (D)	74°42'36"	94°53'24"	nd	nd	nd	8.4	0.7	nd	nd
Cornwallis	Meretta Inf.1 (D)	74°42'00"	94°58'48"	nd	nd	nd	8.8	3.0	nd	nd
Cornwallis	Meretta Inf.2 (D)	74°42'00"	94°59'24"	nd	nd	nd	3.2	2.3	nd	nd
Cornwallis	North Inflow (D)	74°46'12"	95°05'24"	nd	nd	nd	3.5	0.8	nd	nd

D = polar desert, O = polar oasis, Lat = latitude (°N), Long = longitude (°W), Z_{max} = maximum depth (m), SA = surface area (km^2), DA = drainage area (km^2), TP = total phosphorus ($\mu g\ L^{-1}$), DOC = dissolved organic carbon ($mg\ L^{-1}$), Chl = chlorophyll _a_ ($\mu g\ L^{-1}$), chiro = chironomid, nd = not determined, Inf. = inflow, Mid. = Middle; † Unofficial name, ‡ Maximum observed depth during sampling, § Mean $\delta^{13}C$ ± 1 SD (‰)

Chironomids undergo complete metamorphosis with 4 growth stages (embryo, larva, pupa, adult), and we collected larvae and adults from 3 stations in each water body. In the High Arctic, chironomids are abundant at shallow depths (~ 2–4 m) allowing them to emerge before the ice has completely melted (Welch 1976; Minns 1977). Mating occurs mainly on substrates (ice, water surface, shoreline rocks) rather than by swarming due to nearly continuous winds. Adults (n = 76) were obtained from near-shore ice or water surfaces (occasionally shoreline rocks) using tweezers or a fine-mesh net. Larvae samples (n = 46) were collected with a 500 µm D-frame net by kick-sweeping sediment in water 0.5–1.25 m deep. Chironomids sampled from different stations in a lake were treated as separate replicates. Profundal larvae were obtained by Ekman grab from 2 lakes (Small and Immerk) and by off-shore zooplankton tows in Meretta Lake. Two inflows entering Meretta lake and 1 inflow entering Char and North lakes were sampled for larvae (n = 4) on one occasion by kick-sweeping sediment at one station. On the day of collection, chironomids were washed in ultrapure water, separated by development stage (adult, larva), placed in plastic scintillation vials and frozen. All chironomid taxa were pooled together except predatory Tanypodinae (present at a few polar oasis sites) were separated from non-predatory larvae. A portion of larvae were preserved in concentrated ethanol for gut content analysis and taxonomic identification.

Additional biological material was collected and frozen to determine stable carbon isotope ratios of potential dietary sources for chironomids. Zooplankton provided an estimate of the signature of pelagic seston and were collected in duplicate or triplicate with a large 1-m diameter net of 200 µm mesh size in the pelagic zone of 11 lakes (n = 36) by vertical or horizontal hauls depending on ice and wind conditions. Macroscopic benthic algae (i.e., filaments and *Nostoc* spheres, n = 30 samples) were collected in near-

shore areas from 5 lakes (Char, Immerk, Middle Beschel, Small, Titti) and 1 pond (Phalarope). Profundal samples of *Nostoc* were obtained with an Ekman grab in Small and Immerk lakes. We estimated the carbon isotope ratio of terrestrial OM using literature data for High Arctic terrestrial C_3 plants (leaves and stems, $n = 7$; Blake 1991) and for unfrozen High Arctic peat soil ($n = 14$; Givelet et al. 2004), supplemented by 2 plant leaf samples we collected at Truelove Lowland.

Total phosphorus and DOC (0.45 µm filtration) were measured in water taken in duplicate bottles as surface grabs from 1 near-shore station (~ 1 m depth) in each water body and 1 mid-depth pelagic station in 75% of the lakes. Deep-water samples were collected with tygon tubing and a peristaltic pump. Three 5-m integrated water samples were collected for phytoplankton chlorophyll *a* using a tube sampler in 12 lakes where as grab samples were taken from ponds. Conductivity, pH, dissolved oxygen and water temperature were measured with a YSI 600 QS meter (YSI Incorporated, Yellow Springs, OH, USA).

Z_{max} was obtained either from the literature ($n = 14$ sites), from depth sounding along transects with a weighted line ($n = 4$), or from the Z_{max} observed during sampling ($n = 4$). Surface area (SA) and drainage basin area (DA) of water bodies were measured in SIGIS v2.60 software using Landsat-7 images and digital maps of the Canadian National Topographic Data Base.

Laboratory analyses

Stable isotope ratios of carbon were measured at the G.G. Hatch Stable Isotope Laboratory at the University of Ottawa (Ottawa, Canada) on a DeltaPlus XP Isotope Ratio Mass Spectrometer interfaced by a Conflo II to a Vario EL III elemental analyzer.

Prior to isotope analysis, chironomid, zooplankton and plant samples were freeze-dried and homogenized into a powder with an acid-cleaned glass rod or mortar and pestle. *Nostoc* spheres were analyzed whole due to their small size and hardness. Homogenized samples of adult chironomids usually contained more than 100 individuals but those of larvae contained fewer individuals (generally around 10). Stable isotope ratios were expressed in delta notation ($\delta^{13}C$) as the parts per thousand (‰) deviation from the Vienna PeeDee Belemnite standard and the analytical precision was ≤ 0.2‰.

Activity of the radioactive ^{14}C isotope was measured on 1 sample of benthic macroalgae and 1 adult chironomid sample from 2 lakes to determine if chironomids were consuming old terrestrial carbon from peat. The analyses were conducted by accelerator mass spectrometry at the Center for Applied Isotope Studies at the University of Georgia (Athens, GA, USA). ^{14}C activities were expressed as percent modern carbon relative to the Oxalic Acid I standard and were corrected for isotope fractionation to a $\delta^{13}C$ ratio of -25‰.

Larvae from a portion of the study sites (9 lakes, 5 ponds, 4 inflow streams) were mounted permanently on slides for gut content analysis after clearing with Hoyer's solution on a heating block for ~ 24 hours. Bleaching allowed easier examination of gut contents although as a consequence much organic material was digested. The following items could be distinguished in the guts: 1) inorganic sediment mixed with detritus, 2) diatom frustules, 3) cell walls of algal filaments, and 4) invertebrate exoskeletons. From 5–65 larvae from each site were examined giving a total sample size of 578. Larvae with empty guts were not included in the data set. Head capsule width was measured with an eye-piece micrometer to the nearest 10 μm. Larvae were identified to genus using Oliver

and Roussel (1983), Wiederholm (1983), and Merritt et al. (2008). The following characteristics were visually estimated for each larva: % of gut length with contents (fullness), amounts of gut contents (sediment/detritus, diatoms), proportion of individuals with algal filaments, proportion of individuals with invertebrate remains, and types of animal remains. The abundance of sediment/detritus and diatoms was rated using a 0–6 scale where 0 = none, 1 = trace (e.g., only a few diatoms), 2 = low, 3 = low-moderate, 4 = moderate, 5 = moderate-high and 6 = high. All gut contents were examined by a chironomid taxonomist (Louise Cloutier, Département de sciences biologiques, Université de Montréal, Montréal, Canada) who had no prior knowledge of water body characteristics or stable isotope results. In addition, all larvae were examined twice on two separate days to ensure consistency in the visual ratings.

Data analysis

Both adult and larval chironomids were collected at most sites and in general, their $\delta^{13}C$ ratios were similar (Spearman *rho* = 0.70, *p* = 0.001, *n* = 19) although larval samples tended to be more variable, partly because they were composites of fewer individuals (as described above). Therefore, we used adults rather than larvae to estimate the average $\delta^{13}C$ ratio of chironomids from a water body. We used larvae to investigate within-lake spatial variation in the $\delta^{13}C$ ratio of chironomids because they were collected from discrete depths and locations, in contrast with adults that were obtained from water and ice surfaces and may have emerged from a broader area.

Laboratory feeding studies show that the $\delta^{13}C$ of chironomid larvae reflects the isotopic ratio of their diet with minimal fractionation (0–0.3‰) when fed algae or sediment (Goedkoop et al. 2006; Doi et al. 2006). Therefore, no correction was applied

for $\delta^{13}C$ fractionation between chironomids and their diet.

Ordinary least-square regressions were performed to test linear associations between chironomid $\delta^{13}C$ ratios and potential explanatory variables. This regression method provides a biased slope coefficient when both variables have large error, and therefore, a model II major axis regression was computed using a program from Legendre (2001) to estimate the linear slope coefficient for key relationships. Frequency distributions of $\delta^{13}C$ ratios of adult chironomids and potential carbon sources were fit with Gaussian curves and tested for significance using non-linear regression in SigmaPlot 10 (Systat Software, Inc., San José, CA, USA). Means are presented ± 1 standard deviation with the exception of regression slopes where standard errors are provided.

RESULTS

Stomach contents of chironomid larvae

Diatoms and sediment detritus were the most common diet items found in guts of larvae from lakes, ponds and inflow streams (Table 2). Sediment inorganic and detrital particles were ingested by larvae at all the study sites and were generally moderate in abundance in guts. Semi-quantitative estimates of diatom abundance in guts were more variable ranging from complete absence in larvae at the Char and North inflows to moderate/high abundance (rating of 4–5) in larvae at ponds F1, F2 and I as well as at Resolute and Plateau lakes. Invertebrate remains were generally absent from larval guts except at ponds F1 and I where abundant carnivorous chironomids from the subfamily Tanypodinae consumed other chironomids, anostracans, ostracods and cladocerans. Remnants of algal filaments were found in a small portion of individuals at most sites

(~ 15–30%) although they were more common in larvae from Small Lake and especially

in a eutrophied inflow of Meretta Lake. These observations indicate that most

chironomid larvae primarily obtained their energy from diatoms and potentially also

from detrital OM of autochthonous or terrestrial origin.

Table 2. Gut contents and $\delta^{13}C$ ratios of chironomid larvae from High Arctic sites.

Sites	# of larvae	Median % fullness[†]	Median rating[‡] Sed/Det	Diatoms	% with filaments[§]	% carnivory[§]	Larvae $\delta^{13}C$ (‰ ± 1 SD)
Lakes							
Char	57	30	4	3	19	0	-26.8 ± 1.7
Loon	18	60	4	2	0	0	-26.5 ± 1.5
Meretta	42	23	2	2	17	5	-22.6 ± 3.3
Middle Beschel	31	30	4	2	26	3	-28.8 ± 0.8
North	39	50	4	2	15	0	-26.4 ± 2.4
Plateau	12	83	4	5	33	0	-25.7 ± 1.9
Resolute	7	20	2	4	29	0	-25.6 ± 0.2
Small	42	55	4	3	64	0	-25.3 ± 1.6
Titti	53	20	4	3	25	2	-27.1 ± 1.2
Ponds							
Phalarope	49	20	2	2	27	2	-23.7 ± 0.02
Pond F1	49	35	2(4)	2(4)	14(32)	59	-17.5 ± 1.8
Pond F2	65	40	3	4	14	2	-25.5 ± 1.0
Pond I	20	50	4(4)	4(4)	20(27)	30	-23.3
Tern	9	30	4	2	33	0	-28.8
Inflows							
Char Inflow	38	25	6	0	0	0	-30.7
Meretta Inflow 1	29	30	4	2	85	0	-26.8
Meretta Inflow 2	13	40	4	4	46	0	-25.4
North Inflow	5	25	3	0	20	0	-29.8

Sed/Det = inorganic sediment and detritus, gut contents in parentheses for ponds F1 and I are for non-carnivorous larvae only

† Percent of gut length with contents

‡ Amount rated on a 0–6 scale where 0 = none and 6 = high abundance

§ Percent of larvae with filamentous algae or invertebrates in gut

Carbon isotope evidence for chironomid diet sources

$\delta^{13}C$ ratios were, on average, distinct between potential carbon sources with benthic algae having more enriched ratios than pelagic carbon (estimated using zooplankton) and terrestrial OM (Figure 1). The average $\delta^{13}C$ ratio of adult chironomids from 17 lakes ($-24.9 \pm 2.8‰$) was closest to that of benthic algae ($-23.7 \pm 3.6‰$) although a $> 10‰$ range was observed for both groups. $\delta^{13}C$ ratios of adult chironomids also overlapped to a lesser extent with those of terrestrial OM ($-28.3 \pm 2.1‰$) but not pelagic carbon ($-33.1 \pm 2.0‰$).

We examined whether differences in diet or the isotopic signature of benthic algal or planktonic carbon could explain the wide range in chironomid $\delta^{13}C$ ratios among water bodies. A strong correlation between the $\delta^{13}C$ of adult chironomids and benthic algae indicates that this autochthonous carbon was a primary energy source even in lakes where chironomid $\delta^{13}C$ was depleted (Figure 2). The slope of the relationship was nearly 1 (0.99 ± 0.28, model II, major axis regression) which is consistent with a similar contribution of benthic algal carbon to chironomid diet across the range in $\delta^{13}C$ ratios. The $\delta^{13}C$ ratios of zooplankton were not significantly related to those of adult chironomids in 11 lake and 5 ponds, suggesting that planktonic carbon was not a dominant source of energy in their diet ($R^2_{adj} = 0.01$, $p = 0.307$, $n = 16$). Larval chironomids consumed diatoms in all the lakes and ponds, and for those systems, no relationship was found between the median rating of diatom abundance in guts and larval $\delta^{13}C$ ratios ($R^2_{adj} \leq 0.07$, $p \geq 0.335$, $n = 5-9$, Table 2). However, larvae in the stream inflows that consumed more diatoms tended to have a more enriched $\delta^{13}C$ ($R^2_{adj} = 0.91$, $p = 0.032$, $n = 4$). The correlation was strongly influenced by 2 inflow sites

where the median larvae had only detritus in their guts and had depleted $\delta^{13}C$ ratios comparable to terrestrial OM. Thus, with the possible exception of inflows, the baseline isotopic signature of algae, rather than diet, appeared to be the primary driver of variation in chironomid $\delta^{13}C$ among lakes and ponds.

Nevertheless, 2 observations suggested that chironomids could be utilizing terrestrial carbon as a secondary source of energy. We found high variability of up to 7‰ in the $\delta^{13}C$ ratios of chironomid larvae in several lakes, and larvae obtained near shorelines and stream inflows sometimes had depleted ratios close to that of terrestrial carbon (Supplemental Figure S1). In addition, adult chironomids were depleted in $\delta^{13}C$ relative to benthic macroalgae by 3.3 ± 1.1‰ in the 5 water bodies where site-specific data were available. This difference suggested that chironomids were perhaps not supported 100% by algae. Watershed inputs of terrestrial OM in the High Arctic consist largely of old carbon, and peat can represent a considerable portion of OM in lake sediment (Abbot and Stafford 1996, Wolfe and King 1999). We expected that chironomids would have lower activity of the radioactive isotope ^{14}C if they were consuming terrestrial OM, and we tested it by analyzing a macroalgal and adult chironomid sample from 1 polar desert lake (Small) and 1 polar oasis lake (Immerk). The ^{14}C activity was greater than 100% modern for all samples and the values were the same for both algae and chironomids in each lake, which clearly indicates that old carbon was not a prevalent energy source (Table 3).
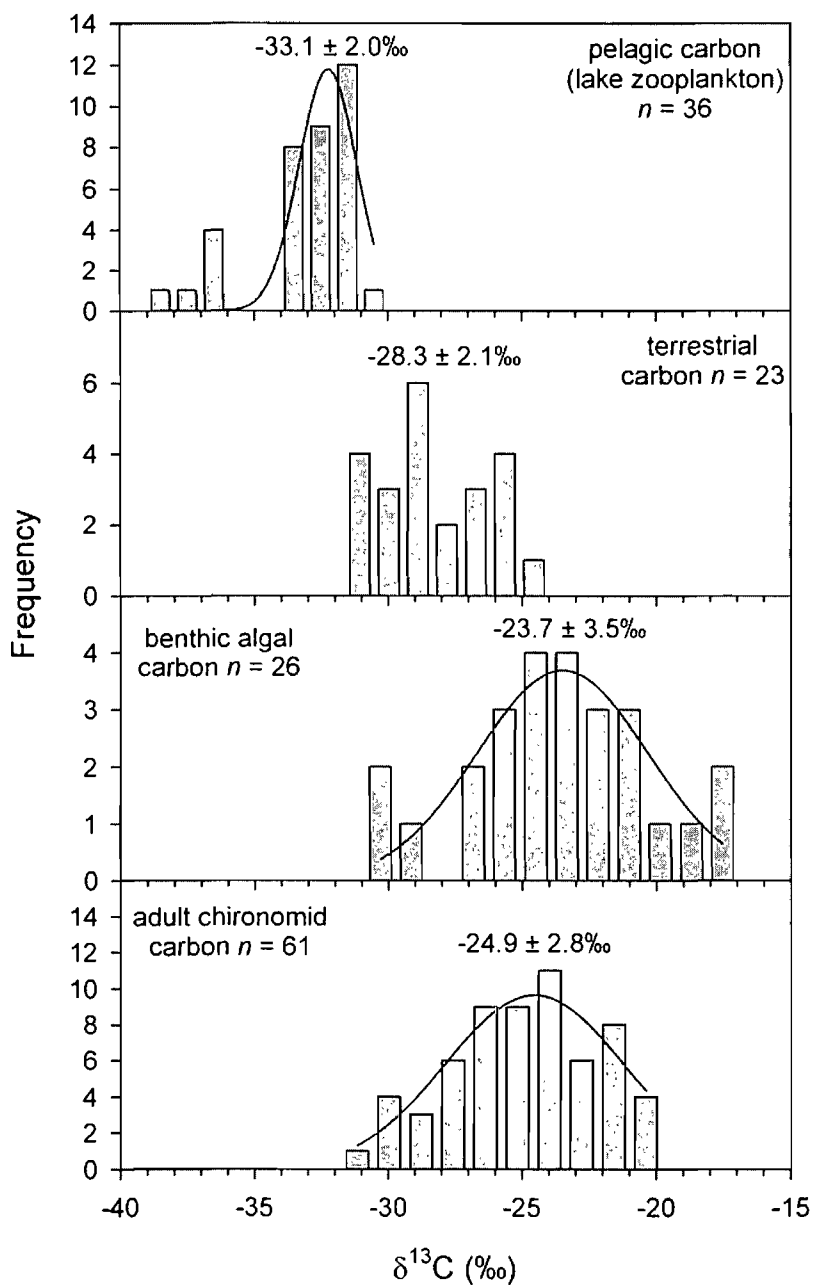
Figure 1. Frequency distribution of $\delta^{13}C$ ratios of adult chironomids and potential diet sources in High Arctic lakes. Gaussian curves fit to each distribution were significant (non-linear regression, $F_{2,6-9} \geq 5.6$, $p \leq 0.027$) except for terrestrial OM ($p = 0.502$, no curve presented). Mean $\delta^{13}C$ ratios are $\pm$ 1 SD.
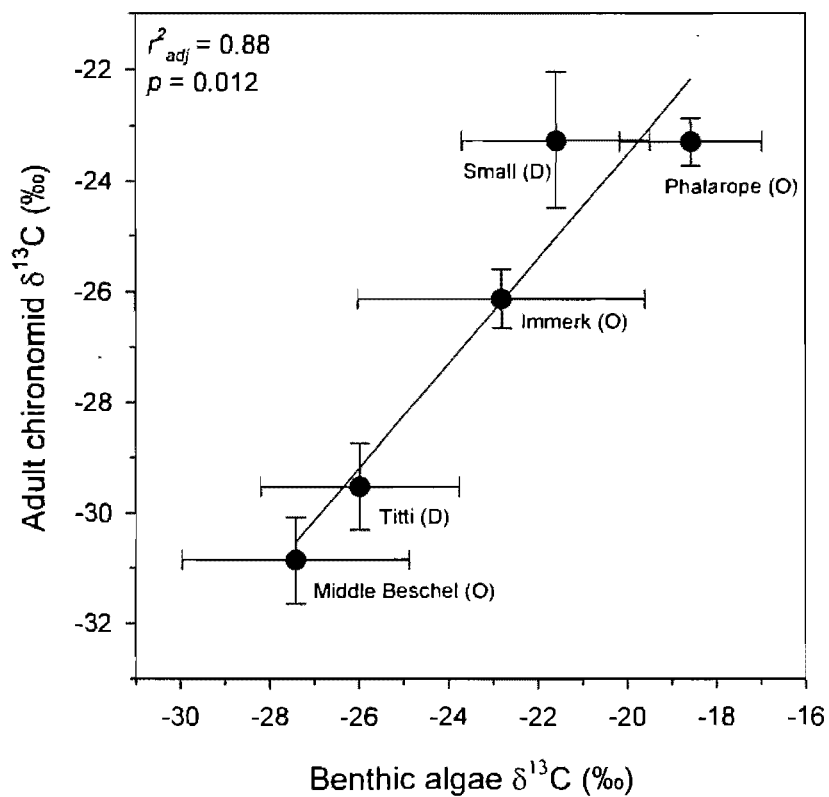
Figure 2. Relationship between the $\delta^{13}C$ ratios of adult chironomids and benthic algae from 5 water bodies in polar oasis (O) and polar desert (D) watersheds. Values are means $\pm$ 1 SD of 3–6 samples for chironomids and 3–11 samples for algae.

Table 3. ^{14}C activity measured on an algal and an adult chironomid sample from 2 lakes.

Lake	Watershed type	Biota	δ^{13}C (‰)	Percent modern C
Small	Polar desert	Benthic algae	-20.2	103.37
		Chironomid	-24.5	102.03
Immerk	Polar oasis	Benthic algae	-26.0	108.38
		Chironomid	-26.1	108.44

Table 4. Variation of *Nostoc* and chironomid larvae δ^{13}C ratios with depth in 3 lakes.

Lake	Depth (m)	Nostoc δ^{13}C (‰)	Chironomid larvae δ^{13}C (‰)
Small	1	-23.3 ± 1.2	-24.8 ± 1.6
	2	-18.1 ± 0.8	-27.1
	4	-22.6 ± 0.3	nd
	7	-22.6 ± 2.1	-26.1
	9	-22.1 ± 1.1	nd
Immerk	1	-21.4 ± 3.4	-28.7
	5	-24.0 ± 0.7	-29.6
Meretta	1	nd	-23.0 ± 3.6
	> 4	nd	-21.1

nd = not determined

Values are single determinations or means ± 1 SD of 2–5 samples. Larvae of > 4 m depth in Meretta Lake were obtained from zooplankton hauls in the water column of the pelagic zone. Maximum depths are 11, 8 and 12 m for Small, Immerk and Meretta lakes, respectively.

Although pelagic carbon was highly depleted in $\delta^{13}C$ relative to chironomids, it is also possible that autochthonous OM settling from the water column was a minor energy source. In that case, one would expect the $\delta^{13}C$ ratios of chironomids to be more depleted at greater depths where this OM source accumulates due to sedimentation and sediment-focusing. In 3 lakes where we obtained larvae from several water depths, we found only minor differences of 1–2‰ between the average $\delta^{13}C$ values of larvae collected from shallow near-shore stations and those of deeper waters (Table 4). Highly depleted $\delta^{13}C$ ratios (< -30‰) were not observed in profundal zones. Likewise, no systematic enrichment or depletion in $\delta^{13}C$ occurred in *Nostoc* algae collected at different depths in 2 lakes.

Watershed influences on chironomid diet

At the polar oasis, a greater influence of terrestrial OM loading was reflected in higher water-column concentrations of DOC (3.7 ± 1.8 mg L^{-1}, $n = 8$ lakes and ponds) compared to water bodies at polar desert sites (0.6 ± 0.4 mg L^{-1}, $n = 14$ lakes and ponds). Water-column concentrations of total phosphorus were, on average, only slightly higher at the polar oasis (4.7 ± 3.0 µg L^{-1} versus 2.7 ± 1.0 µg L^{-1} in polar deserts), and chlorophyll *a* was generally similar between the 2 watershed types (< 0.5 µg L^{-1}, Table 1).

We found no evidence to indicate that chironomid diet was different between polar oasis and desert sites. Adult chironomids in polar oasis lakes were slightly depleted in $\delta^{13}C$ (-27.8 ± 2.3‰, $n = 4$) compared to those in oasis ponds (-24.0 ± 2.3‰, $n = 4$) or polar desert lakes (-24.5 ± 2.6‰, $n = 13$); however, these differences were due to more depleted algal $\delta^{13}C$ ratios (Figure 2). The abundance of diatoms in larval guts was

similar at polar oasis ponds and lakes (median rating = 3, 25th – 75th percentiles = 2–4, n

= 231) and polar desert water bodies (median rating = 2, 25th – 75th percentiles = 2–4, n

= 261), suggesting that diatom consumption was prevalent in both watershed types.

Finally, the ^{14}C activity of chironomids from 2 lakes indicated that consumption of

terrestrial OM was not related to watershed type (Table 3). Contrary to our expectation,

terrestrial OM consumption was not stimulated by the presence of lush sedge-moss

meadows at the polar oasis, and autochthonous carbon was the primary energy source

for chironomids in both watershed types.

Diet variation among chironomid genera

The gut contents of common chironomid genera indicated a similar breadth in diet

(Supplemental Table S1). A total of 14 genera from 4 subfamilies (Diamesinae,

Chironominae, Orthocladiinae, Tanypodinae) were found in at least 2 study sites. All

genera were collector-gatherers except the predatory Procladius, most genera (9) were

free-living sprawlers, and 5 were known burrowers or tube builders (Davies 1975;

Merritt et al. 2008). All genera ingested a mix of sediment, detritus and diatoms with

only one exception. Syndiamesa from the subfamily Diamesinae was primarily a

detritivore, and diatoms were rarely found in their guts. Genera from the subfamily

Chironominae tended to ingest more algae (i.e., median diatom rating of 4–5) as did a

few Orthocladiinae (e.g., Corynoneura, Eukiefferiella, Paracladius). Most chironomid

taxa fed on filamentous algae to some degree except for Procladius, Syndiamesa and

Hydrobaneus who very rarely had filaments in their guts. Procladius exhibited

widespread carnivory (81% of individuals) and 5 other genera also consumed

invertebrates on occasion (1–38%). These gut content observations suggest that common chironomid taxa in High Arctic fresh waters were predominately generalist feeders.

DISCUSSION

Energy flow in lake food webs of the High Arctic

Our study highlights the dominant role of benthic algal production for food webs of ultraoligotrophic lakes in polar oasis and polar desert watersheds of the Canadian Arctic Archipelago. Benthic algae, specifically diatoms, were the primary carbon source for chironomids, although we cannot unequivocally rule out minor contributions of detritus originating from pelagic or terrestrial sources. Low utilization of the latter energy sources is consistent with carbon fluxes for High Arctic lakes; specifically low terrestrial OM loadings from watersheds (Semkin et al. 2005) and very low rates of phytoplankton photosynthesis (Markager et al. 1999). In Char Lake, which was one of our polar desert study sites, 80% of annual primary production occurs in the benthos while only 20% comes from phytoplankton (Welch and Kalff 1974), and terrestrial carbon loadings were estimated at only 12% of total primary production (Rigler 1978).

We did not examine landlocked Arctic char, the top consumer in our study lakes, but basal resource consumption by chironomids reflects the carbon flow to fish because they are the main diet item (Hobson and Welch 1995). This tight trophic link between Arctic char and chironomids is reflected in a strong correlation between our $\delta^{13}C$ ratios of chironomids from 6 polar desert lakes and literature values for Arctic char from those same sites (Figure 3, char $\delta^{13}C$ data from Muir et al. 2005). The slope of the relationship was nearly 1 (1.1 ± 0.26, model II, major axis regression) which is consistent with a

similar contribution of chironomid carbon to char diet across the range in $\delta^{13}C$ ratios. The carbon stable isotope evidence is supported by stomach content observations for Arctic char in polar desert (Johnson 1980) and polar oasis lakes (Minns 1977; Guiger et al. 2002).
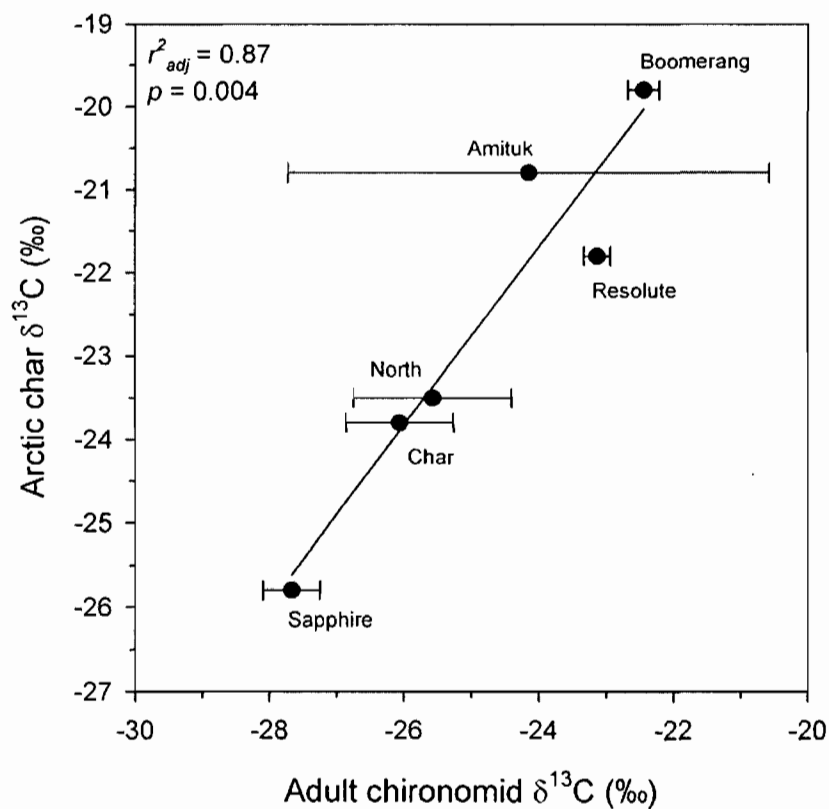
Figure 3. Relationship between the $\delta^{13}C$ ratios of adult chironomids and Arctic char from 6 of the polar desert lakes. Carbon stable isotope ratios for chironomids were measured in this study (mean ± 1 SD of 2–6 samples) while values for Arctic char (mean of 8–55 fish per lake) were obtained from Muir et al. (2005).

Carbon flow in High Arctic food webs is different in 2 significant ways from other Arctic lakes at lower latitudes. First, terrestrial carbon is not an important energy source in contrast to lakes in Alaska (Schell 1983) and northern Quebec (Bunn et al. 1989). Second, little autochthonous carbon from the pelagic zone is transferred to Arctic char either through chironomid production or through consumption of zooplankton in contrast to fish in lakes in the Northwest Territories (Hecky and Hesslein 1995; Kidd et al. 1998) and northern Quebec (Power et al. 2002).

We suggest that several features of our study sites can account for differences in carbon flow compared to Arctic lakes in less extreme polar environments. Dilute water-column concentrations of nutrients (total phosphorus < 5 µg L^{-1}), colder water temperatures ($< 8°C$) and a very short open-water season of $\sim$ 6-8 weeks (half the season of lakes near the Arctic Circle) severely limit phytoplankton production in the High Arctic (Markager et al. 1999). This meager production results in low densities of crustacean zooplankton (often < 1 individual L^{-1}; Stewart and Macdonald 1981) that are insufficient for substantial energy flow to Arctic char. Further, sedimentation rates of pelagic carbon are probably too low to subsidize chironomid diet. Under ultraoligotrophic conditions, benthic algal production is greater than that of phytoplankton due to a greater supply of nutrients to benthic films, either from pore water in soft sediment or from the recycling of nutrients within the films (Riber and Wetzel 1987; Hansson 1992; Vadeboncoeur et al. 2003).

In Arctic Alaska, DOC of terrestrial origin and old carbon from peat are significant basal resources supporting aquatic food webs (Schell 1983; Hershey et al. 2006). Although watershed export rates of terrestrial OM are most likely greater at lower latitudes, many High Arctic lakes have considerable stores of old carbon in sediment

(Abbot and Stafford 1996) including one our study sites, Immerk Lake (Wolfe and King 1999). In addition, lakes at polar oases have more substantial water-column concentrations of DOC. Given that algal production rates are so low in High Arctic fresh waters, it is somewhat surprising that terrestrial carbon does not subsidize chironomid production.

Low bacterial activity and a lack of sustained anoxia in profundal waters may explain the decoupling of terrestrial subsidies to chironomid diet. The microbial community associated with detritus is thought to be of greater nutritional value for chironomids than the detritus itself (Berg 1995). Though little information on heterotrophic processes exists for High Arctic fresh waters, bacterial activities are probably very low (Morgan and Kalff 1972) but would be stimulated by inputs of nutrients and DOC (Hessen et al. 2004; Wilhelm et al. 2004). Cold temperatures may reduce the efficiency of bacterial metabolism of terrestrial carbon (Jansson et al. 2008). In stratified hypoxic lakes of Alaska, methanotropic bacteria are an important energy source for profundal chironomids as indicated by their depleted $\delta^{13}C$ signatures $< -35‰$ (Hershey et al. 2006). We found no evidence that methanotrophic bacteria were consumed by chironomids at our study sites because larvae collected from deeper waters in 3 lakes had $\delta^{13}C$ ratios $> -30‰$, which is not surprising given the lack of anoxia in the water column.

Potential biases in carbon source partitioning

We assumed that the $\delta^{13}C$ of macroalgae was representative of the $\delta^{13}C$ for diatoms, which were the main algal group consumed by chironomids. We adopted this approach because of methodological difficulties in separating microscopic diatoms from detritus.

The assumption appears justified by a positive correlation between the $\delta^{13}C$ ratios of chironomids and macroalgae (Figure 2). Nevertheless, $\delta^{13}C$ ratios of diatoms and macroalgae could differ because of micro-habitat variation in boundary layer thickness (Hecky and Hesslein 1995) or variation in the concentration and $\delta^{13}C$ of CO_2 at the sediment surface compared to overlying water. These processes could explain our observations of considerable within-lake variation of larval $\delta^{13}C$ ratios in some lakes (up to 7‰, Supplemental Figure S1). Microhabitat characteristics of sediment can lead to large differences in the $\delta^{13}C$ of individual chironomids that burrow or build tubes (Grey et al. 2004).

We did not address the role of aquatic moss as a basal resource because it was not found at most of our study sites (Minns 1977; J. Chételat, personal observations). However, aquatic moss grows in 2 of the polar desert study lakes, North and Char, where this biomass could potentially support chironomid production either through direct grazing or consumption of detritus from senescent plants. Aquatic moss has a similar $\delta^{13}C$ ratio to benthic algae and terrestrial OM (-21‰ to -31‰) (Blake 1991; Hobson and Welch 1995), making its consumption difficult to identify using carbon stable isotopes alone. We did not observe moss fragments in larval guts from Char or North lakes.

Potential impacts of climate warming in the High Arctic

There are large stores of carbon in High Arctic soils (Ping et al. 2008) that will be released to lakes as permafrost melts with climate warming, and the associated increase in nutrient loading is anticipated to stimulate algal primary production (Prowse et al. 2006). Our results suggest that heterotrophic pathways are currently not important in the

transfer of energy to High Arctic chironomids and fish that consume them. However, greater loadings of terrestrial carbon in conjunction with other physico-chemical changes to lakes (e.g., warmer waters, thermal stratification, higher nutrient concentrations) could alter basal resources and the flow of carbon through aquatic food webs. Future research should examine the potential impact of climate warming on carbon flow in high latitude lakes. Information on heterotrophic processes is particularly lacking such as bacterial production rates, the main sources of carbon consumed, and limiting factors for OM degradation. Warmer temperatures could potentially stimulate heterotrophic pathways in High Arctic lakes and increase the complexity of energy flow to include terrestrial subsidies to aquatic food webs, similar to lower latitudes such as in Arctic Alaska.

Conclusion

High Arctic lakes are at the extreme end of the productivity spectrum among freshwater ecosystems, and despite the low supply of autochthonous carbon for primary consumers, we found that terrestrial carbon was not an important energy subsidy. Chironomids were supported primarily by benthic algae in lakes of the Canadian Arctic Archipelago, in contrast to lower-latitude Arctic lakes where peat, methanotropic bacteria, and phytoplankton can be relevant energy sources to primary consumers (Schell 1983; Hecky and Hesslein 1995; Hershey et al. 2006). Further, we did not find differences in chironomid diet between watershed types despite greater terrestrial OM loading at the polar oasis. Our study underscores that carbon pathways in aquatic food webs vary among Arctic regions in North America.

ACKNOWLEDGEMENTS

SUPPLEMENTAL INFORMATION
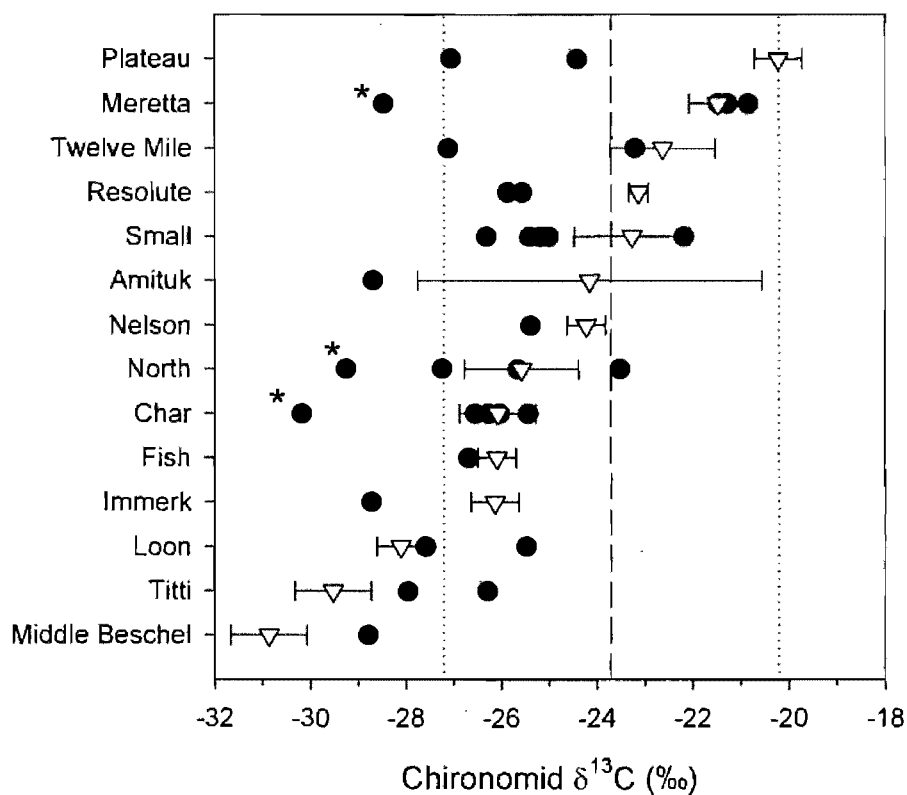
Figure S1. $\delta^{13}C$ ratios of chironomid larvae collected from near-shore areas (circles, single samples) compared to lake-mean ratios of adult chironomids (triangles, ± 1 SD). Data points with an asterix are stations close to a stream inflow. The mean $\delta^{13}C$ ratio (± 1 SD) of benthic algae is presented as a reference line.

Table S1. Feeding habits and gut contents of common chironomid genera found in High Arctic lakes, ponds and inflow streams.

Genus	Feeding habit	Mean capsule width (μm)	# of sites	# of larvae	Median % fullness[†]	Median rating[‡] Sed/Det	Diatoms	% with filaments[§]	% carnivory[§]
Subfamily Diamesinae									
Pseudodiamesa	sprawler	520	3	8	30	2	3	25	38
Syndiamesa	sprawler	300	2	45	25	6	0	4	0
Subfamily Chironominae									
Dicrotendipes	burrower	450	2	7	50	4	4	43	14
Micropsectra	sprawler	290	7	143	20	4	2	20	0
Paratanytarsus	sprawler	330	3	8	45	3	5	50	0
Stictochironomus	burrower	380	6	23	50	4	4	48	9
Subfamily Orthocladiinae									
Corynoneura	sprawler	180	5	20	30	4	4	15	0
Cricotopus-Orthocladius	burrower/tube builder/sprawler	350	10	148	50	4	3	33	1
Eukiefferiella	sprawler	330	7	9	30	4	4	33	0
Hydrobaenus	sprawler	340	3	26	50	4	2	4	0
Orthocladius (Pogonocladius)	sprawler/burrower	470	3	16	28	3	2	44	0
Paracladius	sprawler	360	2	15	50	4	4	27	0
Psectrocladius	sprawler/burrower	420	6	33	40	4	2	52	3
Subfamily Tanypodinae									
Procladius	sprawler	700	3	36	30	2	2	3	81

Sed/Det = inorganic sediment and detritus. Feeding habits are from Merritt et al. (2008).

[†] Percent of gut length with contents, [‡] Amount rated on a 0–6 scale where 0 = none and 6 = high abundance, [§] Percent of larvae with filamentous algae or invertebrates in gut

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CHAPITRE 4

Habitat-specific bioaccumulation of methylmercury in invertebrates of Quebec lakes

John Chételat and Marc Amyot

ABSTRACT

We examined habitat-specific bioaccumulation of methylmercury (MeHg) in aquatic food webs by comparing concentrations in pelagic zooplankton to those in littoral macroinvertebrates from 8 small lakes in southern Quebec, Canada. Total mercury concentrations in water and sediment were related to water color and dissolved organic carbon, reflecting watershed transport processes to the study lakes, whereas MeHg concentrations in water and invertebrates were more related to water pH. Pelagic zooplankton and littoral macroinvertebrates both increased in MeHg concentration along our sampled gradient in mercury supply, however, zooplankton were more susceptible to MeHg bioaccumulation than littoral macroinvertebrates in mercury-enriched lakes. The difference in MeHg concentration between pelagic and littoral primary consumers increased from approximately 0 ng g^{-1} up to 160 ng g^{-1} in relation to 2 factors, higher aqueous MeHg in the hypolimnion and lower water pH. Differences in MeHg between these potential prey groups are likely sufficient to impact mercury accumulation in fish, which is consistent with studies from the literature that show pelagic-feeding fish often have higher mercury levels than littoral fish. Our findings suggest that the importance of habitat-specific feeding for mercury transfer to fish will be more pronounced in acidic, brown-water lakes than in alkaline lakes with clear or eutrophic waters. Habitat-specific bioaccumulation is probably driven by several factors including more efficient transfer of aqueous MeHg into the pelagic food web as well as differences in ecological and life history characteristics between zooplankton and macroinvertebrates.

INTRODUCTION

The habitat where a fish feeds in a lake can affect the amount of methylmercury (MeHg) that accumulates in its body. Specifically, pelagic-feeding fish tend to have higher burdens of MeHg than fish that feed in the littoral zone (Power et al. 2002; Gorski et al. 2003; Ethier et al. 2008). Differences in MeHg levels among fish species reflect this influence where, for example, whitefish (*Coregonus clupeaformis*) and white sucker (*Catostomus commersoni*) that commonly feed on benthic invertebrates tend to have lower MeHg burdens than zooplanktivores such as cisco (*Coregonus artedi*) (Strange et al. 1991; Tremblay 1999). Among-lake variation in the MeHg burden of predatory species such as northern pike (*Esox lucius*) is also related to their consumption of either planktivores or benthivores (Gorski et al. 2003).

Most evidence for the influence of habitat-specific feeding on mercury bioaccumulation is based on correlations between fish mercury levels and their carbon stable isotope ratios (e.g., Power et al. 2002), and it is unclear what factors are driving these patterns. Two main mechanisms could explain habitat-specific bioaccumulation in fish: differences in fish growth rates or MeHg accumulation in diet items. MeHg may bioaccumulate more in zooplankton in the pelagic zone than littoral invertebrates as a result of variation in exposure to MeHg or food web structure. Alternatively, consumption of benthic invertebrates may result in faster growth compared to fish that feed on zooplankton because of lower energetic costs associated with capturing larger prey (Saint-Jacques et al. 2000). Faster growth rates would in turn decrease MeHg accumulation in littoral feeders because of growth dilution (Swanson et al. 2006). To our

knowledge, neither explanation of habitat-specific bioaccumulation has been explicitly tested.

Lake biomagnification studies have largely focused on simplified food chain models in the pelagic zone (i.e., phytoplankton $\rightarrow$ zooplankton $\rightarrow$ planktiverous fish $\rightarrow$ pisciverous fish) even though littoral benthic invertebrates are a key component of fish diet (Vadeboncoeur et al. 2002). Littoral food webs are more complex, and benthic macroinvertebrate diversity is far greater than in the zooplankton, which could explain the relatively small number of field studies on MeHg bioaccumulation in littoral invertebrates (but see Tremblay 1999; Allen et al. 2005; Cremona et al. 2008) as well as the lack of empirical models for zoobenthos (Rennie et al. 2005). A lake is often assumed to be homogenous with respect to bioaccumulation in primary consumers yet field experiments indicate that zooplankton and benthic invertebrates may not respond identically to increases in mercury loading. Experimental flooding of a small lake to form a reservoir resulted in a > 10 fold increase in MeHg concentration of zooplankton and < 1–4 fold increase in benthic invertebrates (Hall et al. 1998; Paterson et al. 1998). Similarly, spiking of isotope-labelled inorganic mercury to mesocosms in a lake revealed that zooplankton responded more rapidly than benthic invertebrates to inter-annual changes in aqueous MeHg (Orihel et al. 2008).

MeHg bioaccumulation in aquatic invertebrates is controlled by environmental factors that affect the supply of MeHg to food webs, namely inorganic mercury loading (Harris et al. 2007), pH (Watras et al. 1998), and dissolved organic carbon (DOC) (Rennie et al. 2005). Acidic waters increase the bioavailability of inorganic mercury (Kelly et al. 2003) and stimulate bacterial methylation (Gilmour and Henry 1991;

Miskimmin et al. 1992). DOC forms strong complexes with mercury and is an important vector for watershed transport to lakes from terrestrial and wetland sources (St. Louis et al. 1996; Garcia and Carignan 1999). DOC may also reduce the photodegradation of MeHg by inhibiting light penetration through the water column (Sellers et al 1996).

Lake productivity can also influence MeHg bioaccumulation in aquatic invertebrates through growth dilution processes. As phytoplankton production increases, the concentration of mercury per algal cell decreases resulting in less transfer to zooplankton (Pickhardt et al. 2002). A similar reduction in mercury concentration occurs in periphyton that have higher growth rates (Hill and Larsen 2005). Zooplankton with higher growth rates also have lower MeHg concentrations because more biomass is produced per unit of food (and MeHg) consumed (Karimi et al. 2007).

The principal objective of this study was to examine habitat-specific bioaccumulation of MeHg by comparing concentrations in littoral macroinvertebrates to those in pelagic zooplankton collected from 8 lakes in southern Quebec, Canada. These small-sized water bodies were chosen to range widely in environmental conditions that affect MeHg bioaccumulation (water pH, DOC, productivity), and they covered a large gradient in mercury supply. First, we examined whether MeHg bioaccumulation in littoral macroinvertebrates is influenced by the same environmental variables as for pelagic zooplankton. Then we tested the hypothesis that pelagic zooplankton have higher MeHg concentrations than littoral primary consumers in a given lake, a pattern that would be consistent with observed habitat-specific accumulation in fish. We also examined the spatial variability of aqueous mercury concentrations in a lake and its influence on MeHg bioaccumulation in invertebrates. Our findings indicate that pelagic zooplankton and littoral primary consumers can differ widely in MeHg concentrations

even though their trophic level is similar, and this variation may be due to more efficient mercury transfer to the pelagic food web as well as the ecological and life history characteristics of these 2 invertebrate groups.

MATERIALS AND METHODS

Field sampling

Eight small lakes were selected in regions of southern Québec, Canada to encompass a wide range in productivity, water colour and pH (Tables 1, 2). Five of the lakes are located on Precambrian Shield bedrock in either the Laurentians north of Montreal (Marois, Morency, Pin Rouge) or in the Mastigouche Reserve west of Trois Rivières (Blanc, Pyrole). These sites have relatively undisturbed drainage basins of mixed conifer and deciduous forest although there is cottage development around lakes in the Laurentians. The other 3 lakes (Parker, St. George, Waterloo) are located on sedimentary bedrock of the St. Lawrence lowlands in the Estrie region east of Montreal. Waterloo and St. George are shallow non-stratifying lakes that have been eutrophied by agricultural activities in their drainage basins, and Parker receives large amounts of humic substances from upstream wetlands.

Each study lake was sampled twice in 2005 during June and September for littoral macroinvertebrates, pelagic zooplankton, and water chemistry. Zooplankton and macroinvertebrates were collected in each lake at 3 pelagic and 3 littoral stations, respectively. Water was sampled mid-depth in the epilimnion and the hypolimnion at one pelagic station and at 0.5 m depth from the surface at one littoral station. In Waterloo and St. George lakes where no thermal stratification occurred, pelagic water was taken at depths of 0.5 m from the surface and 0.5 m from the bottom in the lake

center. *In situ* measurements of water temperature, pH, conductivity, and dissolved oxygen were made with a YSI 600 QS meter at the same pelagic and littoral stations sampled for water chemistry.

Crustacean zooplankton were collected with a 1 m diameter net of 200 μm mesh size by vertical hauls starting from the lake bottom. Waterloo and St. George lakes were sampled by horizontal tows at 1–2 m from the water surface due to their shallow depth. Zooplankton biomass from each pelagic station was transferred into a separate clean polypropylene container and frozen until mercury analysis. Approximately 30–50 mL of zooplankton sample was also preserved with 5% formaldehyde in separate jars for taxonomic analysis.

Table 1. Location and physical characteristics of the 8 study lakes in Québec, Canada.

Lake	Region	Latitude °N	Longitude °W	Stratified	LA km^2	DA km^2	Z_{max} m	$Z_{hypoxia}$ m
Blanc	Mastigouche	46°35'	73°33'	yes	0.25	3.3	11	10
Pyrole	Mastigouche	46°34'	73°22'	yes	0.09	1.0	10	5
Marois	Laurentians	45°51'	74°08'	yes	0.99	6.0	23	17
Morency	Laurentians	45°56'	74°02'	yes	0.26	2.3	20	12
Parker	Estrie	45°20'	72°19'	yes	0.23	27.8	9	5
Pin Rouge	Laurentians	45°58'	74°02'	yes	0.15	6.6	14	4
St. George	Estrie	45°39'	71°53'	no	0.51	7.8	4	n.o.
Waterloo	Estrie	45°20'	72°31'	no	1.47	32.5	5	n.o.

LA = lake area, DA = drainage area, Z_{max} = maximum depth, $Z_{hypoxia}$ = depth at which dissolved oxygen < 1 mg L^{-1} in September, n.o. = hypoxia not observed.

Table 2. Chemical characteristics of water and sediment in the 8 study lakes. Water chemistry values are grand means of measurements from the epilimnion, hypolimnion and littoral zone taken in June and September of 2005 (n = 6 for *in situ* measurements, n = 12–18 for analytical results). Sediment mercury concentrations are means of triplicate measurements on littoral sediment collected in September 2005. Note that Morency Lake was sampled more frequently than other study lakes (12 dates between 2005–2007), and grand means of all data are presented (n = 48 for *in situ* measurements, n = 64–126 for water analyses except colour n = 6 and sediment n = 7).

Lake	pH	Cond. $\mu S\ cm^{-1}$	Cl^{-1} $mg\ L^{-1}$	SO_4^{-2}-S $mg\ L^{-1}$	DOC $mg\ L^{-1}$	Color $mg\ Pt\ L^{-1}$	TP $\mu g\ L^{-1}$	Chl a $\mu g\ L^{-1}$	Water$_{MeHg}$ $ng\ L^{-1}$	Water$_{THg}$ $ng\ L^{-1}$	Sed$_{THg}$ $ng\ g^{-1}$	Sed$_{MeHg}$ $ng\ g^{-1}$
Blanc	5.2	13	0.1	1.0	6.0	46	7.4	0.9	0.17	2.31	275	1.51
Pyrole	5.7	17	0.2	1.1	7.1	64	10.4	1.6	0.57	3.25	263	1.13
Marois	7.5	182	29.0	5.3	3.3	10	6.2	1.0	0.06	0.44	83	1.23
Morency	7.4	121	17.1	2.6	3.5	13	8.3	2.0	0.04	0.66	84	0.88
Parker	6.9	71	2.3	1.0	10.5	129	16.2	5.0	0.22	3.35	197	0.61
Pin Rouge	6.9	52	4.2	1.5	6.8	76	10.3	2.4	0.11	1.96	67	1.33
St. George	8.1	113	8.5	2.1	7.6	34	33.5	13.2	0.06	1.37	14	0.14
Waterloo	7.5	148	16.3	1.6	8.0	56	38.7	22.9	0.09	1.63	121	0.46
Min	5.2	13	0.1	1.0	3.3	10	6.2	0.9	0.04	0.44	83	0.14
Max	8.1	182	29.0	5.6	10.5	129	38.7	22.9	0.57	3.35	275	1.51
Max:Min	1.6	14	290	5.6	3.2	12.9	6.2	25.4	14.3	7.6	3.3	10.8

Cond. = conductivity, DOC = dissolved organic carbon, TP = total phosphorus, Chl a = chlorophyll a, Sed = sediment, Min = minimum, Max = maximum.

Macroinvertebrates were collected near shore by sweeping surficial sediment and macrophytes in water < 1.25 m deep using a D-frame net of 500 μm mesh size. Net contents were sorted on site in plastic bins using tweezers, and macroinvertebrates were placed in lake water for transport back to the laboratory. On the same day, individuals were separated into the following broad taxonomic groups: (1) Insecta: alderfly larvae (Megaloptera, Sialidae), belostoma (Hemiptera, Belostomatidae), caddisfly larvae (Trichoptera), chironomid larvae (Diptera, Chironomidae), damselfly larvae (Odonata, Zygoptera), dragonfly larvae (Odonata, Anisoptera), mayfly larvae (Ephemeroptera), and ranatra (Hemiptera, Nepidae); (2) Mollusca: bivalves (Bivalvia, Unionoida), snails (Gastropoda); and (3) Crustacea: isopods (Isopoda), amphipods (Amphipoda). Invertebrates were rinsed in ultrapure water with acid-cleaned tweezers, and frozen in plastic scintillation vials until mercury analysis. Gut contents were not depurated, and tests conducted on several taxa (amphipods, isopods, mayfly, caddisfly and damselfly larvae) indicated that depuration for approximately 24 hrs in containers with a fine-mesh false bottom (to avoid coprophagy) did not alter invertebrate MeHg content (Annexe 2). Taxa from each littoral station were stored separately and treated as replicate samples. All invertebrate groups were not necessarily obtained at all littoral stations or all lakes, and a sample generally consisted of ~ 10 individuals for most primary consumer taxa and ~ 4 individuals for larger predatory macroinvertebrates.

Water was collected in triplicate for THg and MeHg analyses with a peristaltic pump and acid-washed Teflon tubing. Teflon vials for total mercury (THg) and glass amber bottles for MeHg were pre-washed with acid in the laboratory, double-bagged for transportation, and triple-rinsed with lake water prior to collection. THg and MeHg samples were preserved with BrCl or ultrapure HCl, respectively. Duplicate plastic

bottles were also filled for ancillary chemical analyses (0.45 μm filtered: DOC, color, sulfate, chloride; unfiltered: total phosphorus) with water collected at the same depths as mercury samples using a Van Dorn bottle or tygon tubing. Three water samples integrated over the depth of the epilimnion were collected with a tube sampler for phytoplankton chlorophyll *a*.

In September only, sediment was collected for mercury and organic matter content with an Eckman dredge from the 3 littoral stations where macroinvertebrates were sampled. Each sample of sediment was taken from the top 5 cm layer, avoiding sediment directly in contact with the Eckman, and frozen in plastic scintillation vials.

Additional sampling was conducted in Morency Lake in 2006 and 2007 to examine temporal variation in the MeHg concentrations of pelagic zooplankton and littoral macroinvertebrates. Monthly visits were made between April and October in 2006, and 3 visits were made in 2007 (May, July, October). The same methods from the 2005 lake survey were continued in Morency Lake with the following exceptions: only 1 pelagic station and 2 littoral stations were sampled for zooplankton and macroinvertebrates, respectively; water chemistry samples were collected from 2 littoral stations instead of only 1; ancillary water characteristics were not measured on some dates (colour in 2006 & 2007; total phosphorus, chloride, sulfate, phytoplankton chlorophyll *a* in 2007); additional sediment was collected from the 2 littoral stations in April and October of 2006; and, benthic algae were sampled in 2006 by collecting macroscopic filamentous mats (monthly from May to October).

Laboratory analyses

Zooplankton (n = 60), macroinvertebrates (n = 331), algae (n = 8) and sediment (n = 28) were freeze-dried for 48 hours and then homogenized with an acid-washed glass rod or mortar and pestle. MeHg was extracted from invertebrates, algae, and sediment by digestion in 4M HNO_3 at 55°C for 16 hours. Water samples for MeHg analysis (n = 264) were predistilled with additions of KCl and H_2SO_4 to remove matrix interferences. MeHg extract was derivatized by aqueous ethylation using $NaBEt_4$, trapped with Tenax and measured with a Tekran 2500 cold vapor atomic fluorescence spectrometer (CVAFS).

Aqueous THg (n = 264) was determined on 50 mL samples by BrCl oxidation, $SnCl_2$ reduction, two-stage gold amalgamation and gas-phase detection with a Tekran 2600 CVAFS. THg concentration in sediment (n = 28) was measured with a Direct Mercury Analyzer (DMA-80) in which sample was combusted at 750°C and the mercury vapour was retained on a gold trap for analysis by cold vapour atomic absorption spectrometry. Organic matter content of sediment was determined by loss on ignition in an oven at 550°C for 2 hours.

Water collected for chlorophyll *a* was passed through filters of 0.7 mm pore size and frozen until spectrophotometric analysis after hot ethanol extraction. DOC was measured in water with a Pt-catalyzed Shimadzu TOC-5000 analyzer. Chloride and sulfate were analyzed by ion chromatography. Total phosphorus in water was determined with a spectrophotometer following persulfate digestion and reaction with molybdenum blue. Water color was measured by light absorption at 440 nm wavelength and converted to platinum units (mg Pt L^{-1}) using the equation of Cuthbert and del Giorgio (1992).

Recoveries of certified reference materials for mercury were 98 ± 11% of MeHg

(mean ± 1 SD, $n = 122$) in TORT-2 lobster hepatopancreas (National Research Council

of Canada), 101 ± 6% of MeHg ($n = 4$) in IAEA-405 estuarine sediment (International

Atomic Energy Agency), and 98 ± 3% of THg ($n = 9$) in SO-2 soil (CANMET Mineral

and Energy Technology). Analytical detection limits, estimated as 3 times the standard

deviation (SD) of 10 blanks, were 0.04 ng MeHg g^{-1} for 250 mg of sediment and 0.05 ng

THg L^{-1} and 0.02 ng MeHg L^{-1} for 50 mL aliquots of water.

Taxonomic composition of the zooplankton was examined to identify the dominant

species present in bulk samples. At least 200 individuals were identified to genus or

species in 2 samples per lake, 1 collected in June and 1 in September 2005. The volume

of water filtered with the zooplankton net was not measured, and the prevalence of

individual taxa within the community was estimated by percent abundance using the

enumeration data. In addition, each sample was examined in its entirety for the presence

of large but rare predatory taxa such as *Chaoborus*; however, abundances were not

determined for those taxa.

Data analysis

MeHg concentrations of zooplankton and macroinvertebrates were pooled over

stations and sampling dates to obtain a lake mean for each invertebrate group. The

average MeHg concentrations of littoral primary and secondary consumers in each lake

were estimated by pooling macroinvertebrate groups according to literature observations

of trophic level (Merritt and Cummins 1996). We considered macroinvertebrates with

the following feeding modes to be primary consumers: shredders (caddisfly and

chironomid larvae), collector-gatherers (amphipods, isopods and larvae of caddisflies,

mayflies and chironomids), collector-filterers (bivalves), and scrapers (gastropods, caddisfly and mayfly larvae). Pelagic zooplankton were also considered primary consumers because communities were composed primarily of omnivorous and filter-feeding taxa, and predatory zooplankton were not abundant in the samples (see results). Predatory engulfers (damselfly, dragonfly and alderfly larvae) and predatory piercers (Belostoma, Ranatra) were considered secondary consumers. Bivalves were excluded from calculations of lake-mean MeHg in littoral primary consumers because this group had unusually high concentrations relative to all other invertebrate groups with the same assumed trophic level (see results and Supplemental Figure S1).

Principal component analysis (PCA) was conducted to present the main gradients of environmental variation among the study lakes. MeHg concentrations of pelagic zooplankton and littoral primary and secondary consumers were projected on the PCA biplot as passive variables to identify possible associations with environmental gradients and they did not influence the ordination axes. PCA was performed with R statistical package (http://cran.r-project.org) on transformed, centered and standardized variables. PCA was also conducted on Hellinger-transformed species abundance data to identify lakes with similar zooplankton taxonomic composition (Legendre and Gallagher 2001). A zooplankton taxon was included in the data set if it had an abundance > 1% in at least 1 lake.

Two-way repeated measures ANOVAs were run to test for effects of habitat (fixed factor: epilimnion, hypolimnion, littoral zone) and sampling date (random factor: June, September) on aqueous THg and MeHg concentrations. Probability values of multiple comparisons were Holms-corrected to adjust the experiment-wise error rate (Legendre and Legendre 1998). Variables were log or square-root transformed to meet the

assumptions of statistical tests. Aqueous MeHg concentrations for some zones in Marois Lake (6 bottles in June, 3 in September) and Morency (9 bottles in June 2005, 2 bottles in August 2006) were not included in the data set due to contamination or loss of sample.

Forward-selection multiple regression analysis was used to identify environmental variables that best explained the MeHg concentrations of each invertebrate group (pelagic zooplankton, littoral primary and secondary consumers). The explanatory variables were maximum lake depth, drainage area: lake area, water pH, sediment concentrations of THg and MeHg, and water concentrations of chlorophyll a, total phosphorus, MeHg, THg, DOC and colour. Littoral or epilimnetic measurements of water characteristics were used for littoral macroinvertebrates and zooplankton, respectively. Water conductivity, chloride and sulfate were excluded from the regression analysis due to strong collinearity with pH. One-way ANOVAs were run to test within-lake differences in MeHg concentration between the invertebrate groups, and probability values of multiple comparisons were Holms-corrected.

RESULTS

Water and sediment Hg

Aqueous concentrations of THg ranged almost an order of magnitude among the 8 study lakes and were primarily associated with water colour (Table 2, Figure 1). Lakes with larger drainage basin ratios (drainage area: lake area) had darker waters (R^2_{adj} = 0.64, p = 0.010, n = 8) and higher DOC concentrations (R^2_{adj} = 0.48, p = 0.034, n = 8), reflecting greater terrestrial inputs of humic substances. Lake-mean concentrations of aqueous THg were strongly correlated with water colour suggesting that much of this

mercury was also transported from the drainage basin (R^2_{adj} = 0.88, p < 0.001, n = 8). THg concentrations were generally similar in the epilimnion, hypolimnion, and littoral zone of a lake and were correlated with water colour in all of the zones (Figure 2). In 3 of the lakes (Blanc, Pyrole, Pin Rouge), THg was more concentrated in hypolimnetic waters than in the other 2 zones, while in Waterloo Lake, aqueous THg was highest in the littoral zone (data not shown; repeated measures ANOVAs, effect of habitat: $F_{2,6}$ ≥ 9.8, p ≤ 0.013). In all of those cases, darker water colour could explain the higher THg concentrations. Parker Lake was an exception having hypolimnetic waters with more colour but significantly lower THg than in the epilimnion or littoral zone (effect of habitat on THg: $F_{2,6}$ = 22.8, p = 0.002).

Lake-mean concentrations of aqueous MeHg ranged more than order of magnitude among the study lakes (Table 2) and were related most to water pH (R^2_{adj} = -0.49, p = 0.032, n = 8) but were also marginally correlated with water colour (R^2_{adj} = 0.41, p = 0.053)(Figure 1). Significant production of hypolimnetic MeHg likely occurred in 4 of the lakes (Blanc, Pyrole, Parker, Pin Rouge), inferred by higher aqueous concentrations found in the hypolimnion compared to the epilimnion and the littoral zone (Figure 3). In Pyrole and Blanc, average concentrations were higher (repeated measures ANOVAs, effect of habitat: $F_{2,6}$ ≥ 11.8, p ≤ 0.013), whereas in Parker and Pin Rouge, only late summer MeHg levels were higher relative to the epilimnion and littoral zone (inset of Figure 3). In September, prior to fall turn-over, most of the hypolimnion was hypoxic in 3 of those 4 lakes (dissolved oxygen < 1 mg L^{-1}, Table 1), making it possible for water-column methylation (Watras et al. 2005). In Waterloo Lake, aqueous MeHg in the littoral zone was higher than in pelagic waters (effect of habitat, $F_{2,6}$ = 129.8, p < 0.001). The littoral station of the lake was in a large wetland with high macrophyte cover.
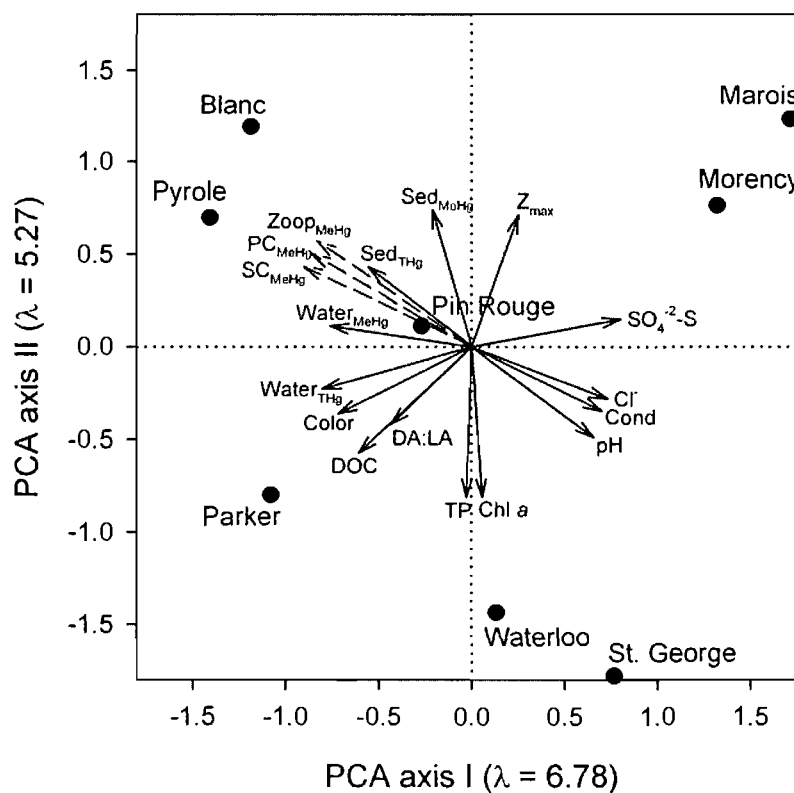
Figure 1. Principal component analysis correlation biplot of environmental characteristics and invertebrate MeHg concentrations in the 8 study lakes. The MeHg concentrations of pelagic zooplankton ($Zoop_{McHg}$), littoral primary consumers (PC_{McHg}) and secondary consumers (SC_{McHg}) were projected passively on the biplot and did not influence the ordination. Sed = sediment, Z_{max} = maximum depth, Cond = conductivity, Chl a = chlorophyll a, TP = total phosphorus, DOC = dissolved organic carbon, DA:LA = drainage area: lake area
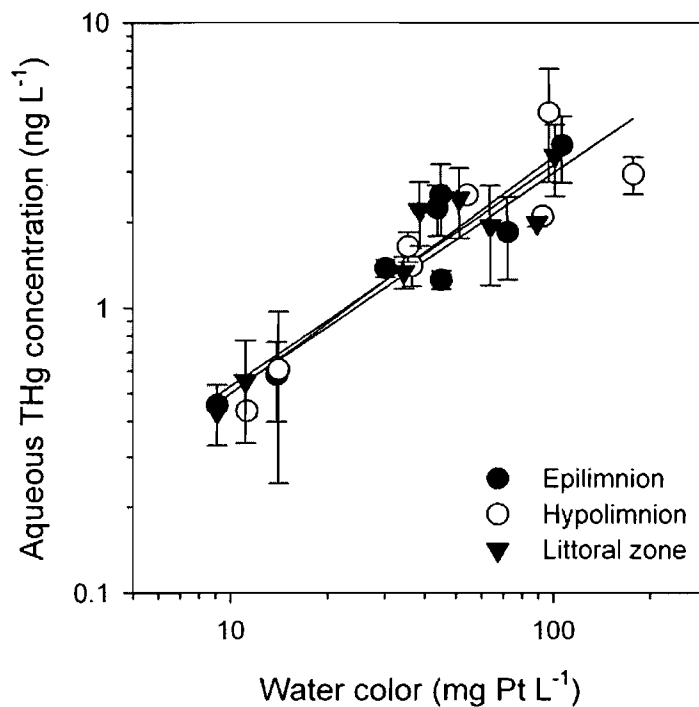
Figure 2. Relationship between log-transformed aqueous THg concentrations and water colour in the epilimnion (R^2_{adj} = 0.86, p = 0.001, n = 8), hypolimnion (R^2_{adj} = 0.82, p = 0.001, n = 8), and littoral zone (R^2_{adj} = 0.88, p < 0.001, n = 8). Data points are lake means ± 1 SE.
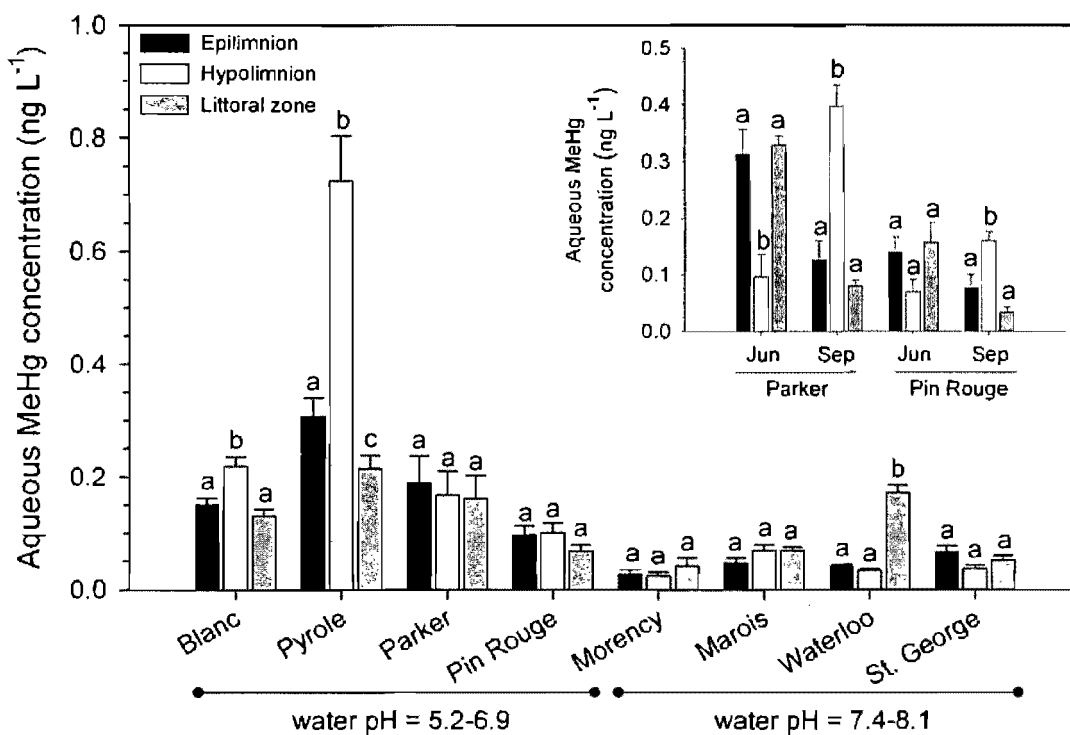
Figure 3. Aqueous concentrations of MeHg in the epilimnion, hypolimnion, and littoral zone of the study lakes measured in June and September of 2005 (mean ± 1 SE, $n = 6$, except for Marois Lake $n = 3$). Concentrations with different letters were significant according to Holms-corrected multiple comparisons ($p < 0.05$). The inset figure presents MeHg concentrations separately for June and September in Parker and Pin Rouge because of large seasonal variation (within-month pairwise comparisons only). Waterloo and St. George lakes did not stratify, so concentrations identified as epilimnion and hypolimnion are values measured 0.5 m from the surface and bottom, respectively. Mercury concentrations presented for Morency Lake are for June and September of 2006 because no MeHg data were available for June 2005.

THg and MeHg concentrations in littoral sediment were spatially variable both within and among lakes due primarily to differences in organic matter content (THg: R^2_{adj} = 0.83, p < 0.001, n = 28; MeHg: R^2_{adj} = 0.74, p < 0.001, n = 28). Water pH was also a significant explanatory variable of among-lake variation in sediment THg (R^2_{adj} = -0.59, p = 0.016, n = 8) and marginally related to sediment MeHg (R^2_{adj} = -0.35, p = 0.071, n = 8) (Figure 1). However, the organic matter content of littoral sediment decreased in relation to water pH (R^2_{adj} = -0.67, p = 0.008, n = 8), and therefore, the association between sediment mercury and water pH may be due to covariation. After normalizing for organic matter content, THg in sediment was correlated to water DOC (R^2_{adj} = 0.48, p = 0.034, n = 8) but no association was found for sediment MeHg (p > 0.66, n = 8).

Environmental influences on invertebrate MeHg accumulation

The MeHg concentrations of pelagic zooplankton and littoral primary and secondary consumers ranged widely among lakes from 17–388 ng g^{-1} and were most strongly associated with water pH (Figure 1, 4). Forward-selection multiple regression identified water pH as the only explanatory variable for each of the 3 invertebrate groups. Other variables not selected by the regression analysis but still significantly correlated (p < 0.05) to invertebrate MeHg concentrations were water colour and concentrations of THg and MeHg in water and sediment. Interestingly, the MeHg concentrations of macroinvertebrates and zooplankton were more strongly related to aqueous MeHg in the hypolimnion than in the epilimnion or littoral zone regardless of their habitat (Table 3). Water-column concentrations of DOC and surrogates of lake productivity (total phosphorus, chlorophyll a) were not significant explanatory variables (p > 0.05).

Table 3. Pearson correlations (r) between the MeHg concentrations of invertebrates (ng g^{-1}) and aqueous MeHg concentrations (ng L^{-1}) measured in the epilimnion, hypolimnion, and littoral zone. All variables were log-transformed. $*$ $p < 0.05$, $**$ $p < 0.01$, $***$ $p < 0.001$

	Aqueous MeHg		
Invertebrate group	**Epilimnion**	**Hypolimnion**	**Littoral zone**
Pelagic zooplankton ($n = 8$)	0.75*	0.84**	0.45
Littoral primary consumer ($n = 34$)	0.48**	0.55***	0.45**
Littoral secondary consumer ($n = 23$)	0.63**	0.66***	0.49*

Figure 4. Linear regression models relating water pH to the MeHg concentrations (ng g-1) in pelagic zooplankton (logMeHg = 4.59 - 0.39 pH), littoral primary consumers (logMeHg = 3.69 - 0.28 pH), and littoral secondary consumers (logMeHg = 4.03 - 0.29 pH). Average pH in the epilimnion and littoral zone were used for zooplankton and littoral macroinvertebrates, respectively. Data points for littoral invertebrates are means (± 1 SE) of individual taxa.

Log littoral secondary consumer MeHg (ng g^{-1})

Log littoral primary consumer MeHg (ng g^{-1})

Log zooplankton MeHg (ng g^{-1})

Water pH

$R^2_{adj} = 0.68$
$p < 0.001$
$n = 23$

$R^2_{adj} = 0.65$
$p < 0.001$
$n = 34$

$R^2_{adj} = 0.88$
$p < 0.001$
$n = 8$
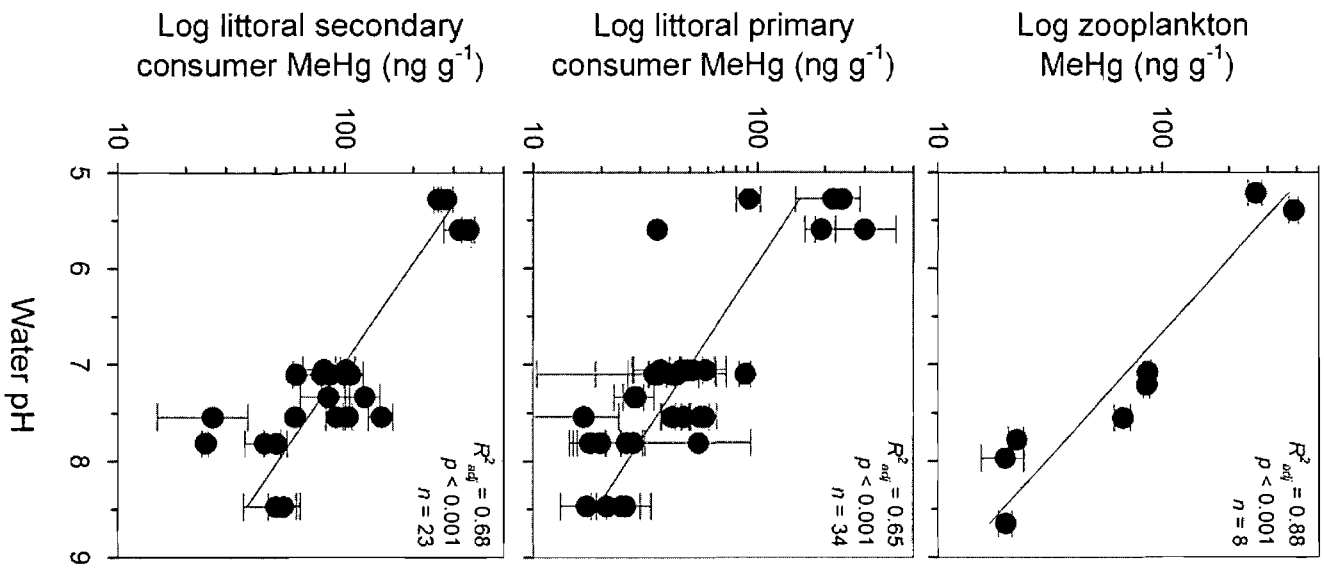
Temporal variation of MeHg in water, algae, and invertebrates in Morency Lake

MeHg concentrations in water, algae, and invertebrates were measured monthly in Morency Lake from April to October of 2006 to investigate temporal patterns. Concentrations of aqueous MeHg and filamentous algae in the littoral zone were highest in spring and declined over the summer (Figure 5A). In contrast, MeHg concentrations of amphipods, isopods, mayfly larvae and caddisfly larvae were relatively stable over the 7 month period (Figure 5B). Dragonfly larvae appeared to increase slightly in MeHg over the season although high variability was observed in September and October (Figure 5C). Therefore, no temporal coupling was found between the MeHg concentrations of macroinvertebrates and concentrations in water or algae in the littoral zone. In contrast, MeHg in pelagic zooplankton followed MeHg concentrations in epilimnetic waters with the highest values in spring and lower values from June to October (Figure 5D).

Comparison of MeHg concentrations between invertebrate groups

Littoral invertebrate taxa generally had MeHg concentrations that were consistent with their assumed trophic level (i.e., primary or secondary consumer). Within the littoral zone of each lake, the average MeHg concentration of secondary consumers was always significantly higher than that of primary consumers (one-way ANOVAs, Holms-corrected $p \leq 0.011$, mean ratio $\pm$ 1 SD = 2.1 $\pm$ 0.7) except in Pyrole Lake due to elevated MeHg in 2 caddisfly larvae samples (Holms-corrected $p = 0.055$, Supplementary Figure S1). Likewise, most macroinvertebrate taxa of the same assumed trophic level had similar MeHg concentrations (Supplementary Figure S1). There were a few exceptions, however, specifically bivalves, alderflies, caddisflies, and chironomids.

Filter-feeding bivalves from 3 lakes (mostly fingernail clams, Sphaeriidae) had very high MeHg concentrations (range = 35–256 ng g^{-1}) while the predatory alderfly larvae tended to have less MeHg than other secondary consumers. Caddisfly larvae in Blanc and Pyrole lakes had concentrations of MeHg that ranged roughly an order of magnitude between sampling stations or dates. We categorized caddisfly larvae as primary consumers but some species are known to be predatory which may explain the large variation in those lakes. Littoral chironomids in Morency Lake had an average MeHg concentration less than half that of most other primary consumers.

The MeHg concentration of pelagic zooplankton was compared to that of littoral macroinvertebrates to determine if mercury bioaccumulation differed between the two habitats (Figure 6). In 5 lakes (Blanc, Morency, Parker, Pin Rouge, Pyrole), pelagic zooplankton had significantly higher concentrations of MeHg than littoral primary consumers (one-way ANOVAs, Holms-corrected $p < 0.05$). In contrast, pelagic zooplankton from 2 other lakes (Marois, St. George) had MeHg concentrations that were not significantly different from primary consumers (one-way ANOVAs, Holms-corrected $p > 0.05$). Zooplankton had significantly lower MeHg concentrations than littoral secondary consumers in 4 lakes (Marois, Morency, St. George, Waterloo; Holms-corrected $p < 0.05$) but there was no significant difference in the more contaminated lakes (Blanc, Parker, Pin Rouge, Pyrole). Waterloo was the only lake where the MeHg concentration of zooplankton was significantly lower than littoral primary consumers (one-way ANOVA, Holms-corrected $p < 0.05$). Waterloo was a special case because 2 littoral stations were in a large wetland while the third station was not, and the MeHg concentration of primary consumers was higher at the wetland stations. When the stations were separated, the MeHg concentration in zooplankton was not significantly

different from primary consumers at the non-wetland station (one-way ANOVA, Holms-corrected $p > 0.05$) but signficantly lower compared to the wetland stations (Holms-corrected $p < 0.05$). Only 1 predatory macroinvertebrate sample was obtained at the non-wetland station which prevented a comparison of wetland effects on secondary consumers.

Habitat-specific bioaccumulation in relation to aqueous MeHg and pH

Differences in MeHg concentration between pelagic zooplankton and littoral primary consumers were greater in lakes with higher aqueous MeHg. When the 6 lakes that stratified were compared, the difference in MeHg concentration between zooplankton and littoral primary consumers increased from approximately 0 ng g^{-1} up to 160 ng g^{-1} in lakes with higher hypolimnetic MeHg ($R^2_{adj} = 0.70$, $p = 0.024$, Figure 7). Water pH was also a significant explanatory variable for all 8 study lakes ($R^2_{adj} = 0.75$, $p = 0.004$, Figure 7), reflecting associations between pH, aqueous MeHg production, and invertebrate MeHg concentration. In Waterloo Lake, higher aqueous MeHg concentrations in the littoral zone relative to pelagic waters were consistent with higher MeHg concentrations of wetland macroinvertebrates relative to zooplankton.

Figure 5. Temporal variation of MeHg concentrations in water, benthic algae and invertebrates in Morency Lake from April to October 2006. Macroinvertebrates (damselflies, dragonflies, amphipods, isopods, mayflies) were collected at 2 stations in the littoral zone and zooplankton at 1 station in the pelagic zone. Means ± 1 SE are replicates of 2–6 samples for water and 2 samples for invertebrates, although some invertebrate and most algae and zooplankton values are single samples. The reference line for water MeHg concentration is the analytical detection limit.

Figure legends within plots:

A — Littoral water, Epilimnetic water, Benthic algae

B — Amphipods, Mayflies, Isopods

C — Dragonflies, Damselflies

D — Pelagic zooplankton

Date in 2006
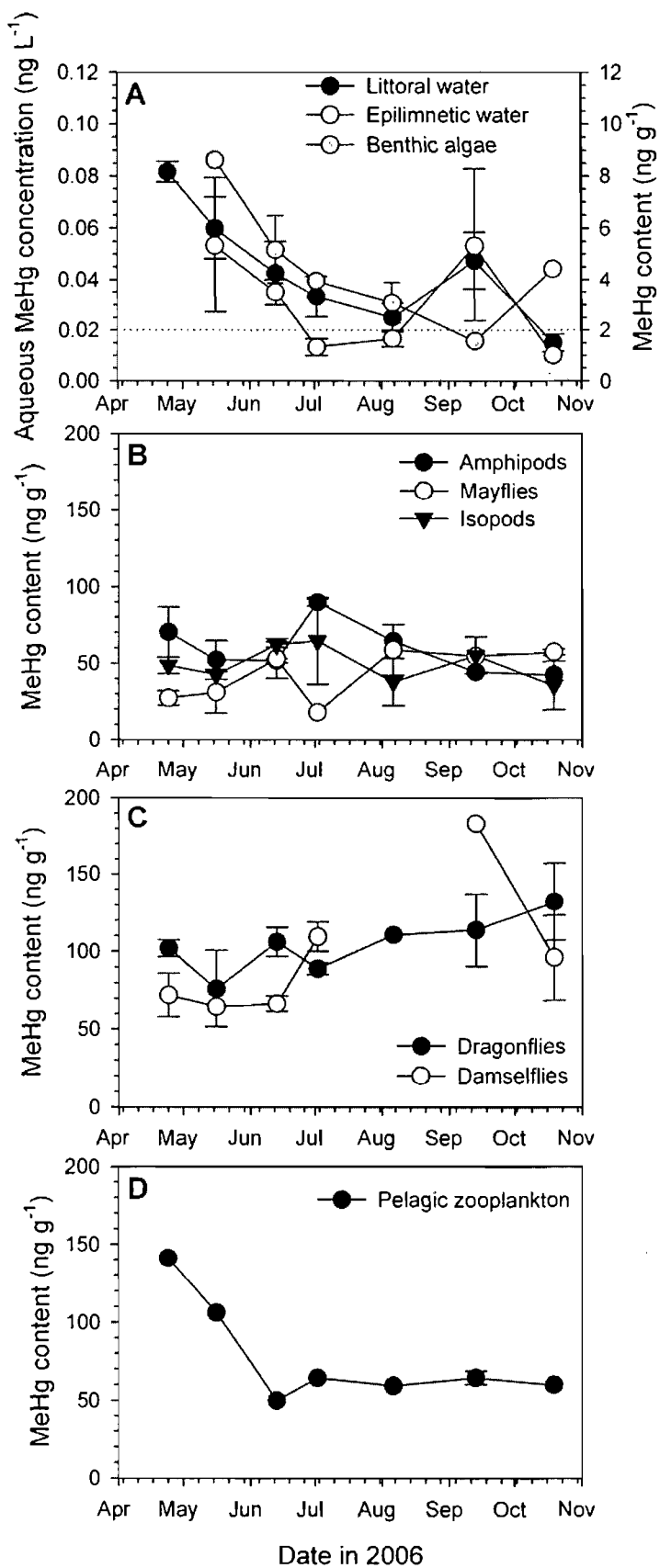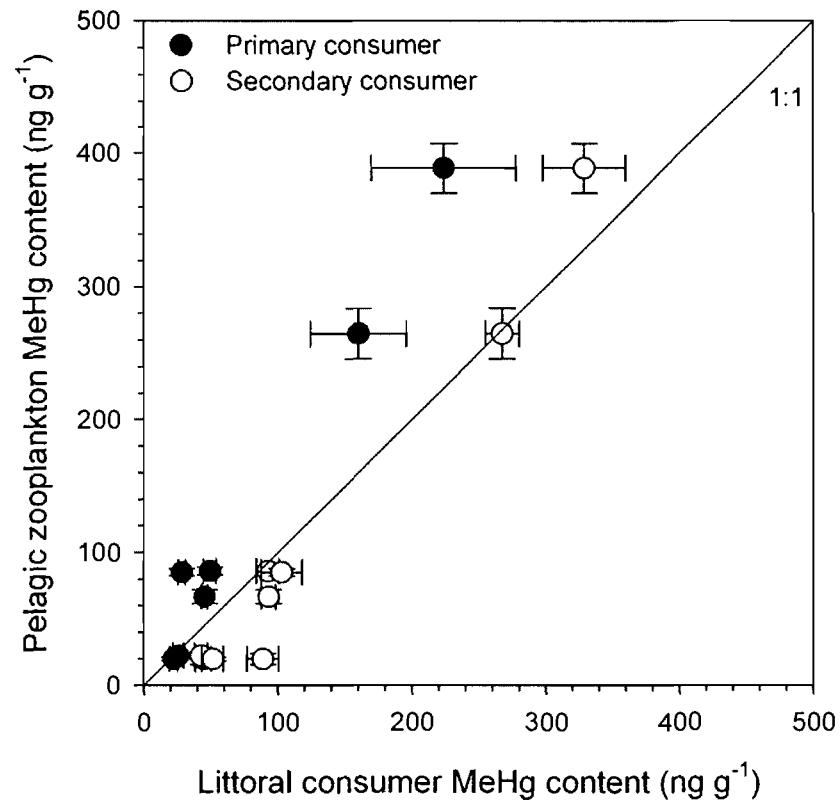
Figure 6. Comparisons of average MeHg concentrations (± 1 SE) in pelagic zooplankton to primary and secondary consumer macroinvertebrates from the littoral zone.
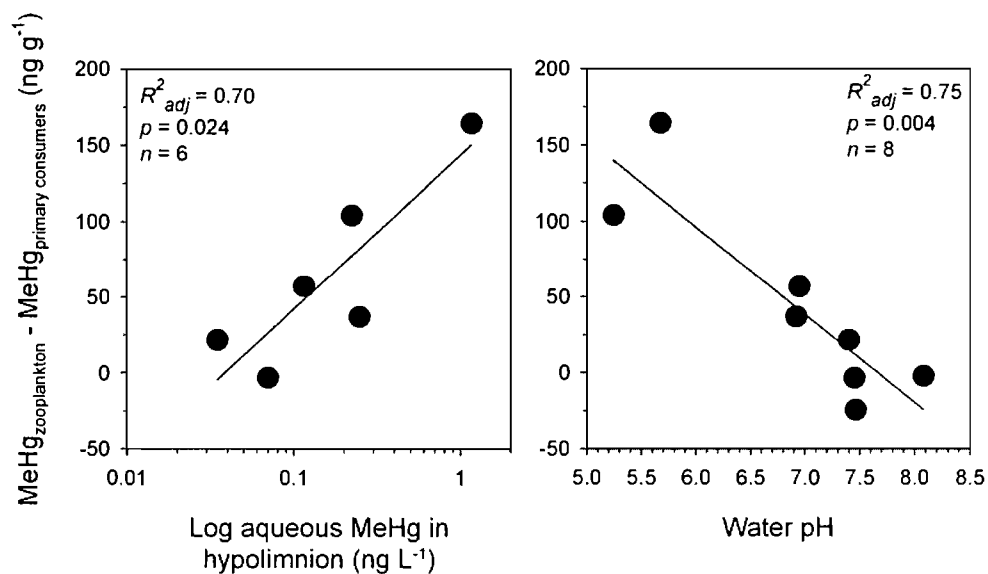
Figure 7. The difference in MeHg concentration between pelagic zooplankton and littoral primary consumers in relation to aqueous MeHg concentration in the hypolimnion and water pH. Note that Waterloo and St. George lakes were not included in the left panel because they are shallow lakes that did not thermally stratify.

Role of zooplankton composition

We found no evidence to suggest that mercury-rich zooplankton in some lakes was due to a higher trophic position of the community. Although we did not directly measure the trophic level of zooplankton, taxonomic identification of the communities indicated that highly predatory species were very low in abundance (< 2.5%, *Epischura lacustris*, *Polyphemus pediculus*) or were absent from most mercury-enriched lakes (*Leptodora kindtii*, *Hydracarina*). *Chaoborus* was found in 4 lakes (Blanc, Pyrole, Parker, Pin Rouge), but this predatory dipteran larva is unusual in having a lower MeHg content than crustacean zooplankton (Paterson et al. 1998, Watras et al. 1998). This trend was confirmed in Pyrole Lake in June 2005 where isolated *Chaoborus* had a MeHg concentration of 233 ng g^{-1}(n = 1) compared to 353 ± 13 ng g^{-1} (n = 3) in bulk zooplankton.

MeHg concentrations in zooplankton were not strongly associated with the taxonomic composition of the community. MeHg concentrations were not correlated to the percent abundance of calanoid copepods (R^2_{adj} = 0.08, p = 0.256, n = 8), cyclopoid copepods (R^2_{adj} = 0, p = 0.449, n = 8) or cladocerans (R^2_{adj} = 0.09, p = 0.238, n = 8) in the community. The main zooplankton species in the lakes are presented in a PCA in which the first axis separated the lakes with zooplankton dominated by calanoid copepods from those where cyclopoids and cladocerans were more important (Figure 8). The second PCA axis separated out lakes where the cladoceran *Daphnia* spp. or the calanoid *Leptodiaptomus minutus* were abundant. Zooplankton communities with higher MeHg concentrations (Blanc, Pyrole, Parker, Pin Rouge) had a varied taxonomic composition, and in general, the taxa present could not explain the bulk mercury levels.

However, the cladoceran *Holopedium gibberum* was important in Blanc and Pyrole lakes and may have contributed to the high bulk MeHg concentrations (Figure 8) given that it can have elevated MeHg relative to other taxa (Watras et al. 1998).

DISCUSSION

Role of water colour and pH

Hg concentrations in water and littoral sediment were strongly related to water color or DOC while invertebrate MeHg concentrations were best explained by pH. These observations are consistent with a survey of Wisconsin lakes by Watras et al. (1998), where humic substances played a key role in the complexation of inorganic mercury and its transport to lakes while pH influenced MeHg supply to food webs. Our study lakes with lower pH had higher concentrations of aqueous MeHg, probably due to greater bacterial methylation rates (Miskimmin et al. 1992). Invertebrates from both the pelagic and littoral zones increased in MeHg concentration along a gradient in water pH, and therefore, environmental factors affecting MeHg production impact bioaccumulation in both food webs (Rennie et al. 2005; Harris et al. 2007). However, significant differences were observed in MeHg concentration between pelagic zooplankton and littoral macroinvertebrates, suggesting that habitat-specific processes affect food web responses to greater mercury supply.
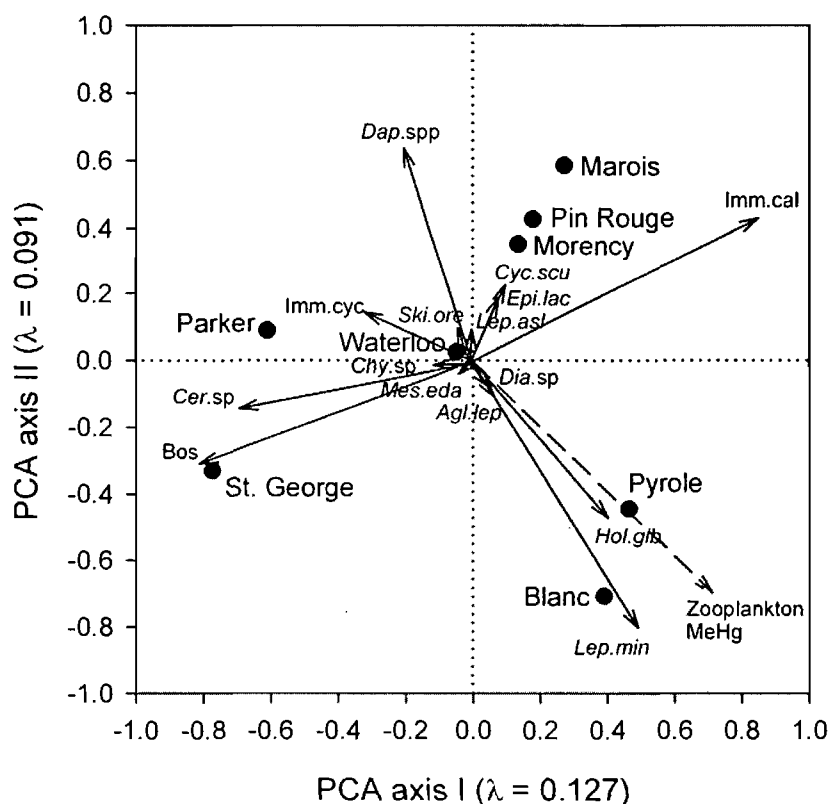
Figure 8. Principal component analysis distance biplot of zooplankton communities in the 8 study lakes. Lakes closer together have a more similar zooplankton composition. Note that rare taxa (< 1% abundance) were not included in the analysis. Zooplankton MeHg concentration was projected passively on the biplot. *Agl.lep* = *Aglaodiaptomus leptopus*, Bos = *Bosminidae*, *Cer*.sp = *Ceriodaphnia* species, *Chy*.sp = *Chydorus* species, *Cyc.scu* = *Cyclops scutifer*, *Dap*.spp = *Daphnia* species, *Dia*.sp = *Diaphanosoma* species, *Epi.lac* = *Epischura lacustris*, *Hol.gib* = *Holopedium gibberum*, *Lep.min* = *Leptodiaptomus minutus*, *Lep.asl* = *Leptodiaptomus aslandi*, Imm.cal = Immature calanoids, Imm.cyc = Immature cyclopoids, *Mes.eda* = *Mesocyclops edax*, Ski.ore = *Skiptodiaptomus oregonensis*

Littoral-pelagic differences in invertebrate MeHg concentration

We found that, in lakes with greater MeHg supply, pelagic zooplankton (which were predominately primary consumers) had more MeHg than littoral primary consumers, from 40 ng g^{-1} to as much as 160 ng g^{-1} more. The magnitude of these differences is, in the more extreme cases (e.g., Blanc and Pyrole lakes), similar to among-lake variation in invertebrate MeHg concentration and is probably sufficient to strongly impact mercury transfer to fish consuming these prey. Littoral primary consumers are typically more important in the diet of fish than predatory macroinvertebrates (Vander Zanden et al. 1997; Cremona et al. 2008), and therefore, differences between zooplankton and primary consumers are likely the most relevant for mercury transfer to fish. Habitat-specific variation in invertebrate MeHg can explain, at least in part, elevated mercury levels in pelagic fish relative to littoral feeders (e.g., Ethier et al. 2008; Stewart et al. 2008). However, we cannot discount the possibility that growth rates of fish feeding on benthic or littoral prey are also a contributing factor to habitat-specific patterns in fish mercury levels (Swanson et al. 2006). Further, the reverse can also occur, where fish feeding in a littoral wetland will have higher mercury levels than fish that feed in the open water (Chumchal et al. 2008). We observed this scenario for invertebrates in Waterloo Lake where primary consumers from an extensive wetland had more MeHg than pelagic zooplankton.

Pelagic zooplankton were more susceptible to MeHg bioaccumulation than littoral macroinvertebrates in mercury-enriched lakes, and several mechanisms could potentially lead to more efficient transfer of mercury in the pelagic food web. Zooplankton are primarily supported by bacteria and algae in the water column whereas littoral zones are

more complex habitats with additional benthic resources that are readily consumed by macroinvertebrates, including particulate organic matter of terrestrial origin and autochthonous detritus from phytoplankton, periphyton and macrophytes (Solomon et al. 2008). Consumption of detrital organic matter could dampen the transfer of MeHg to primary consumers because this energy source does not accumulate newly produced MeHg from the water, in contrast to living bacteria or algae. Detrital consumption could also explain the relatively stable MeHg levels of macroinvertebrates observed in Morency Lake. For phytoplankton, smaller microbial cells can be enriched in MeHg compared to larger algae in the plankton and perhaps also the benthos (Pickhardt and Fisher 2007). Likewise, thinner boundary layers around planktonic cells could potentially result in greater bioconcentration of MeHg relative to benthic mats where thick boundary layers reduce diffusion. However, benthic mats may also be sites of methylation (Desrosiers et al. 2006). Another possibility is that zooplankton may be exposed to higher MeHg concentrations than littoral macroinvertebrates due to vertical migrations into the hypolimnion although a whole-lake experiment using mercury isotope tracers indicated that most hypolimnetic MeHg is transfered to zooplankton after fall turn-over (Harris et al. 2007). Further, zooplankton in a shallow non-stratified reservoir had higher MeHg concentrations than littoral macroinvertebrates, which suggests that exposure in the hypolimnion is not necessary for habitat-specific bioaccumulation (Paterson et al. 1998).

Life cycle length may also influence MeHg bioaccumulation in aquatic invertebrates. Crustacean zooplankton, particularly cladocerans, tend to have short life cycles of < 10–100 days (Gillooly 2000) compared to macroinvertebrates that often require at least 1 year to reach maturity (Merritt and Cummins 1996). As a result, zooplankton may

respond more rapidly to pulses of MeHg supply whereas the mercury concentration of macroinvertebrates reflects long-term exposure (Orihel et al. 2008). Temporal patterns in Morency Lake indicated that littoral macroinvertebrates did not follow short-term changes of MeHg in littoral water and benthic algae. In contrast, zooplankton in the same lake showed an association between aqueous supply and their MeHg concentration. However, the temporal trend in zooplankton MeHg may also have been influenced by shifts in community composition from dominance by over-wintering adult copepods in spring to juvenile copepods and cladocerans afterwards.

Role of productivity

Lake productivity, estimated by total phosphorus and phytoplankton chlorophyll a, did not explain invertebrate MeHg concentrations in our study lakes although there was probably insufficient statistical power to detect an effect with the small number of lakes. Biomass dilution is an important process in eutrophic lakes that reduces MeHg concentrations in aquatic food webs (Pickhardt et al. 2002; Karimi et al. 2007). We suggest that habitat-specific bioaccumulation may not be relevant in eutrophic lakes because the MeHg concentrations of aquatic invertebrates are generally low and therefore any differences between pelagic and littoral invertebrates would also likely be small. In our 2 eutrophic study lakes (St. George and non-wetland sites in Waterloo), zooplankton and macroinvertebrate primary consumers had very low MeHg < 25 ng g^{-1}.

Potential bias in invertebrate comparisons

MeHg concentrations in littoral and pelagic invertebrates were measured using different methods for each group; levels in zooplankton were determined on bulk

samples while those in macroinvertebrates were determined on individual taxa. This approach was used because of differences in organism size and the nature of sampling methods required for littoral or pelagic habitats. As a consequence, zooplankton samples contained grazers, omnivores and predators while littoral macroinvertebrates were separated according to their trophic category. The main potential bias resulting from this approach is that taxon-specific MeHg concentrations were not measured for the zooplankton, and bulk samples represented a mix of taxa with potentially different trophic positions. However, variation in trophic position cannot account for the observed habitat-specific patterns. Zooplankton communities were dominated by grazer and omnivore taxa, and therefore the MeHg measured in bulk samples primarily reflected the concentrations of planktonic primary consumers. Littoral macroinvertebrates in the same trophic category generally had similar MeHg concentrations despite a broad range in life histories and food acquisition strategies (Supplementary Figure S1), and therefore, our separation of littoral taxa into primary and secondary consumers (based on feeding habits reported in the literature) adequately explained average trophic effects. Minor differences in trophic position (i.e., < 1 level) due to omnivory were not accounted for, and more precise estimates of trophic position using stable isotopes (particularly for caddisflies and alderflies) could potentially improve the bioaccumulation models. Nevertheless, 65–88% of the variation in invertebrate MeHg concentrations was explained by water pH alone, and habitat-specific differences in MeHg bioaccumulation were largely explained by environmental factors (70–75%), specifically aqueous MeHg in the hypolimnion and water pH.

Conclusion

Mercury accumulates in aquatic organisms as a result of supply processes that control MeHg production and bioavailability as well as food web processes that regulate trophic transfer to consumers. These processes interact at different spatial scales, and among-lake or whole-lake variation of MeHg bioaccumulation has generally received the greatest attention. Our study indicates that mercury supply and food web processes can also differ within a lake, resulting in habitat-specific bioaccumulation of MeHg. Pelagic and littoral zones are both important habitats for fish feeding, and their invertebrate prey can differ considerably in MeHg concentration, by as much as 160 ng g^{-1}. This variation is likely driven, in part, by MeHg uptake at the base of food webs, and will therefore be greatest in systems where high MeHg production occurs such as in acidic, humic lakes but not in alkaline clearwater or eutrophic lakes where MeHg bioaccumulation is often lower.

SUPPLEMENTAL INFORMATION

Figure S1. MeHg concentrations in pelagic zooplankton and littoral macroinvertebrate taxa in the 8 study lakes. Sample sizes are indicated in parentheses. The MeHg concentrations in alderflies, dragonflies, damselflies, mayflies, caddisflies, chironomids are for their larval stage.

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SYNTHÈSE

SYNTHÈSE

Le destin du mercure dans les lacs de l'Extrême Arctique : rôles des processus géochimiques, biologiques et écologiques

Le mercure inorganique est transporté vers les eaux douces principalement par la fonte de la neige en Extrême Arctique (Semkin et al. 2005), et les apports augmentent avec le ratio de la superficie du bassin versant sur la superficie du lac. Dans cette étude, les sites d'échantillonnage ont couvert un gradient d'apports de mercure total, ce qui a été confirmé par l'association entre le ratio du basin versant et la concentration de mercure total dans les sédiments (après une correction pour la teneur en matière organique). Les concentrations de MeHg dans l'eau et les sédiments ont été basses et relativement semblables entre les sites malgré un gradient dans les apports de mercure. Ces observations suggèrent que la production bactérienne du MeHg dans l'Extrême Arctique est faiblement liée aux apports de mercure inorganique, probablement à cause des conditions environnementales tels que le manque de matière organique, la basse température, et les eaux à pH alcalin et bien oxygénées. Des caractéristiques physico-chimiques des sites, en particulier les concentrations de MeHg dans l'eau et les sédiments, la grandeur du bassin versant, le pH, la température et le carbone organique dissous, expliquent une portion faible mais significative de la teneur en MeHg dans les chironomides ou le zooplancton.

Nous avons trouvé que la teneur en MeHg dans les invertébrés aquatiques s'explique le mieux par des processus biologiques. Les daphnies avaient une teneur élevée en MeHg comparé aux autres espèces de zooplancton, et leur biomasse a expliqué la plupart de la variabilité dans le niveau de MeHg de la communauté. Pour les

chironomides, la métamorphose a concentré le MeHg jusqu'à 3 fois plus dans les adultes comparés aux larves. L'omble chevalier dans ces lacs consomme principalement les chironomides, et la prédation variable des différents stages (les larves, les nymphes et les adultes) pourraient affecter l'accumulation du mercure dans ces poissons. Ces résultats indiquent que les processus biologiques et écologiques jouent un rôle central dans la bioaccumulation du MeHg et les facteurs géochimiques sont secondaires dans cet environnement extrême.

Alimentation des invertébrés aquatiques en Extrême Arctique et les implications pour le transfert du mercure

Nos observations sur les chironomides et les daphnies et celles de la littérature sur les anostracés et les copépodes arctiques indiquent que les groupes dominants d'invertébrés aquatiques se nourrissent de différentes sources d'énergies. Les chironomides obtiennent leur carbone principalement des algues benthiques, et les daphnies broutent les bactéries, les algues planctoniques, et les particules de détritus dans la colonne d'eau, mais aussi peut-être les algues benthiques (Bertilsson et al. 2003; Rautio et Vincent 2006). Le carbone terrestre n'a pas été une source d'énergie importante pour les chironomides mais il a semblé supporter les daphnies arctiques, ce qui a été suggéré par l'association entre leur densité et la concentration aqueuse de COD. Une étude indépendante qui a été réalisée récemment sur l'île Ellesmere confirme le rôle important du COD dans la distribution des daphnies (Strecker et al. 2008). Le COD stimule la production microbienne disponible pour la consommation par les daphnies (Hessen et al. 2004), mais il pourrait aussi réduire le stress physiologique causé par les rayons ultraviolets (Rautio et Korhola 2002; Strecker . et al. 2008). L'alimentation des copépodes

(*Limnocalanus macrurus*) n'a pas été examinée dans notre étude mais il est probable qu'ils se nourrissent principalement des algues planctoniques de plus grande taille (Peters et Downing 1984; Bertilsson et al. 2003; Rautio et Vincent 2006). Les anostracés sont des herbivores qui broutent les particules dans la colonne d'eau et se nourrissent également sur les substrats benthiques (Bertilsson et al. 2003; Rautio et Vincent 2006).

L'importance contrastante du COD comme source d'énergie pour les daphnies et les chironomides est possiblement liée à leurs modes d'alimentation. Les daphnies sont des herbivores généralistes qui broutent avec efficacité des particules de taille variable dans la colonne d'eau incluant les bactéries (< 1 µm à > 75 µm; Bertilsson et al. 2003). Les chironomides retrouvés à nos sites étaient surtout des collecteurs (qui consommaient les diatomées) et non-pas des filtreurs. De plus, la production par les algues benthiques est plus haute que celle des algues planctoniques, et peut-être, l'importance du carbone terrestre pour les daphnies reflète la contribution significative des bactéries dans la colonne des eaux plus humiques (Rautio et Vincent 2006).

Le type de nourriture semble avoir un effet sur la bioaccumulation chez les différents groupes de consommateurs primaires en Extrême Arctique. Dans les étangs et le lac Meretta, *Daphnia middendorffiana* avaient 3 à 5 fois plus de MeHg que les larves de chironomides (Figure 1A). Les anostracés, qui se nourrissent dans la colonne d'eau et également sur des substrats benthiques comme les chironomides, avaient des teneurs en MeHg intermédiaires. Cette observation suggère que l'alimentation dans la colonne d'eau, probablement sur les bactéries, augmentent la bioaccumulation du MeHg. Pickhardt et Fisher (2007) ont trouvé qu'une cyanobactérie de petite taille accumulait plus de MeHg que les plus grandes algues eucaryotes.
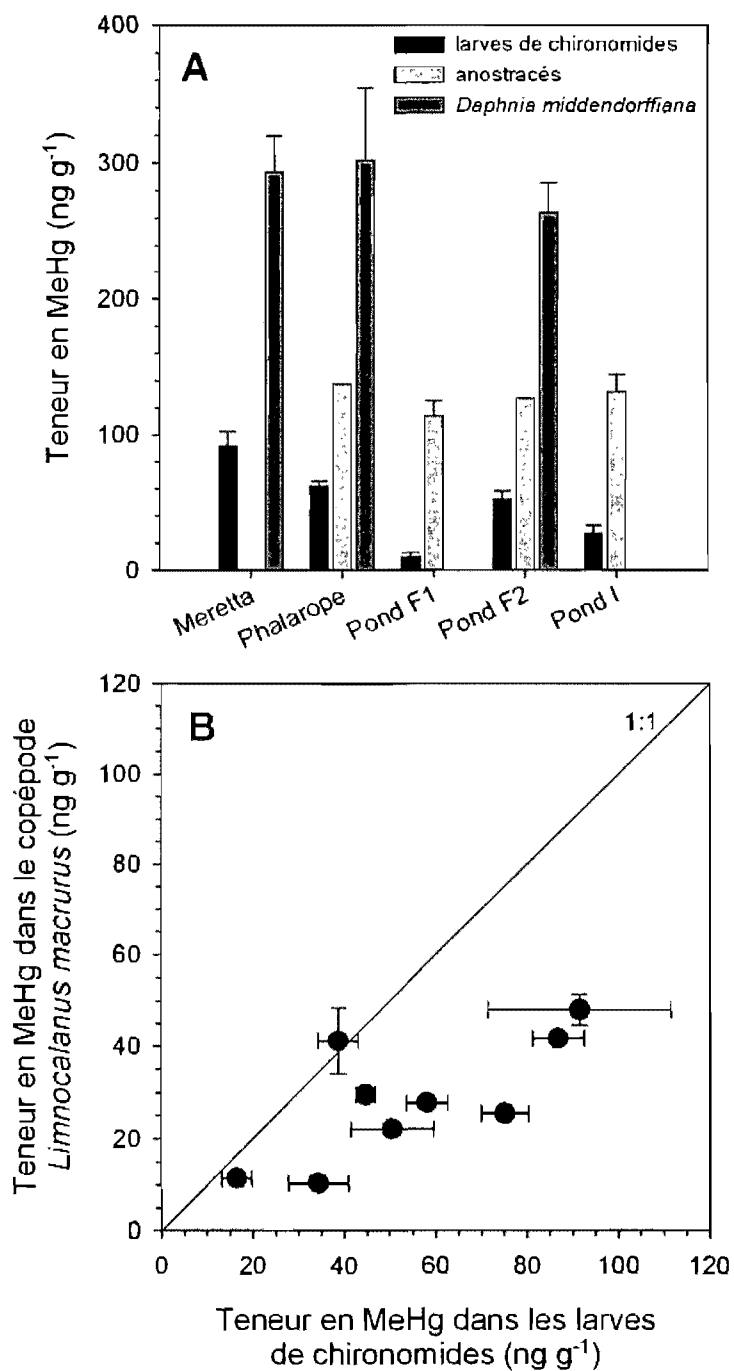
Figure 1. Comparaison de la teneur en MeHg dans différents consommateurs primaires

en Extrême Arctique. L'intervalle d'erreur est l'écart type de la moyenne.

Dans les lacs, le copépode *Limnocalanus macrurus* avait environ la moitié de MeHg comparé aux larves de chironomides (Figure 1B). Si nous supposons que ces copépodes consomment généralement les algues planctoniques de plus grande taille, les différences pourraient refléter l'assimilation variable de MeHg par les algues planctoniques et benthiques. Une étude plus approfondie est nécessaire pour élucider l'assimilation variable de MeHg par les différents groupes microbiens (les algues et les bactéries planctoniques, les algues benthiques) et l'importance des bactéries planctoniques dans le transfert du MeHg.

Bioaccumulation du MeHg entre les habitats des lacs tempérés

Notre étude au Québec montre (comme en Arctique) que des différences existent dans la bioaccumulation du MeHg entre les macroinvertébrés littoraux et le zooplancton pélagique, en particulier dans les lacs acides et les lacs humiques. Dans ces lacs tempérés, le zooplancton et les macroinvertébrés littoraux sont tous les deux des proies importantes qui peuvent transférer des quantités différentes de MeHg aux poissons. Cette différence n'est pas insignifiante, et elle peut être du même ordre de grandeur ($\sim$ 40–160 ng g^{-1}) que la variabilité entre des lacs contaminés et non-contaminés. La variabilité observée entre les habitats lacustres est possiblement causée par le degré d'assimilation du MeHg par les ressources d'alimentation pour les macroinvertébrés et le zooplancton, le niveau d'exposition au MeHg aqueux, ou les différences bioénergétiques entre ces deux groupes d'invertébrés. Notre recherche implique que les chaînes alimentaires pélagiques et littorales ne répondent pas nécessairement de façon égale aux perturbations du cycle du mercure.

Comparaison de la bioaccumulation du MeHg entre les lacs tempérés et arctiques

D'après nos études réalisées en régions tempérées et arctiques, il y a quelques différences notables dans le mouvement du mercure entre ces latitudes. Tout d'abord, les conditions environnementales sont très différentes; spécifiquement, la quantité de matière organique est appauvrie dans les eaux et les sédiments arctiques, les concentrations aqueuses de chlorophylle, de phosphore total et de COD sont également appauvries en Arctique, et la gamme des conditions est beaucoup plus variable parmi les lacs tempérés (Tableau 1). Les concentrations de mercure total et de MeHg dans l'eau sont, en moyenne, 3 à 4 fois plus élevées dans les lacs tempérées, et les différences pour le mercure dans les sédiments littoraux sont encore plus contrastées (Tableau 1). Les plus basses concentrations de mercure en Extrême Arctique sont probablement liées aux faibles quantités de matière organique qui empêchent la rétention du mercure dans l'écosystème, aux conditions défavorables pour la méthylation bactérienne, et aux plus bas apports de mercure provenant de l'atmosphère et du bassin versant (Semkin et al. 2005).

Il y a un paradoxe dans ces observations parce que même si le mercure est moins concentré dans l'environnement en Extrême Arctique, la teneur en MeHg dans les invertébrés aquatiques des deux régions est néanmoins relativement semblable (Tableau 1). Des facteurs de bioconcentration ont été calculés pour examiner le rapport entre le MeHg dans la colonne d'eau et la teneur dans les invertébrés (MeHg$_{biomasse}$ [ng kg^{-1}] /MeHg$_{aqueux}$ [ng L^{-1}]). La bioconcentration du MeHg était, en moyenne, plus élevée dans le zooplancton et les larves de chironomides en Extrême Arctique que pour les consommateurs primaires littoraux dans les lacs tempérés (Figure 2).

Tableau 1. Comparaison des caractéristiques de la colonne d'eau et de la teneur en mercure dans les sédiments littoraux et dans les invertébrés aquatiques entre les sites de l'Extrême Arctique et du Québec.

Caractéristique	Sites arctiques ($n = 22$)§		Sites tempérés ($n = 8$)	
	Moyenne	Min–Max	Moyenne	Min–Max
Eau				
pH	8,2	7,8–8,6	6,9	5,2–8,1
Température (°C)	5,0	2,1–8,9	19,5‡	15,4–24,2
Conductivité (μS cm^{-1})	159	96–252	90	13–182
Stratification thermique (no. de lacs)	0	---	6	---
Carbone organique dissous (mg L^{-1})	1,7	< 0,6–7,4	6,6	3,3–10,5
Phosphore total (μg L^{-1})	3,4	1,2–11,8	16,4	6,2–38,7
Chlorophylle *a* (μg L^{-1})	0,3	0,1–0,4	6,1	0,9–22,9
THg (ng L^{-1})	0,62	0,07–1,39	1,87	0,44–3,35
MeHg (ng L^{-1})	0,04	< 0,02–0,15	0,16	0,04–0,57
Sédiments littoraux				
THg (ng g^{-1})	6	3 – 12	138	14–275
MeHg (ng g^{-1})	0,13	< 0,04–0,64	0,91	0,14–1,51
Matière organique (%)	4	1–12	26	3–39
Invertébrés				
MeHg – zooplancton (ng g^{-1})†	78	10–269	119	20–388
MeHg – macroinvertébrés (ng g^{-1})¥	48	10–92	75	22–224

§ Les sites comprennent les 17 lacs et 5 étangs.

‡ Température de l'épilimnion

† Mesurés sur des échantillons « en vrac »

¥ Les valeurs de l'Arctique sont pour les larves de chironomides et celles des lacs tempérés sont pour des macroinvertébrés de la zone littorale (consommateurs primaires seulement).
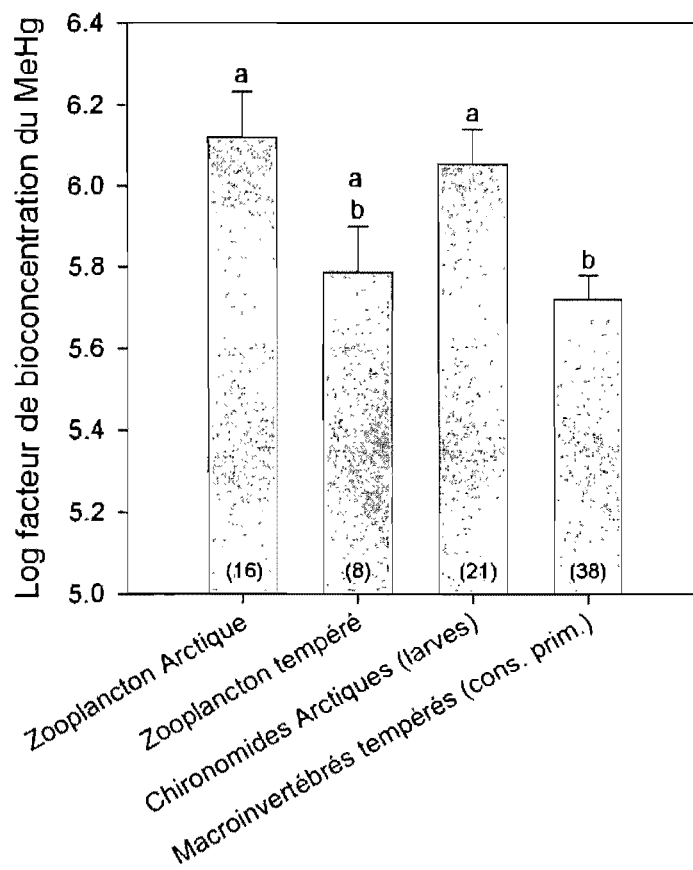
Figure 2. Facteurs de bioconcentration du MeHg entre l'eau et les consommateurs primaires (cons. prim.) dans les eaux tempérées et polaires. Chaque facteur a été calculé pour la moyenne d'un groupe d'invertébrés dans un lac ou un étang, et le nombre de facteurs est entre parenthèses. Les moyennes avec les mêmes lettres ne sont pas différentes selon une comparaison avec la correction de Holms (ANOVA; $F_{3,82} = 5,76$; $p = 0,001$; $n = 83$).

Les facteurs de bioconcentration du MeHg pour le zooplancton tempéré étaient, en général, bas comparé aux invertébrés en Extrême Arctique mais la différence n'était pas significative (Holms $p = 0,099$; Figure 2).

Nous suggérons que la biodisponibilité du mercure aqueux et la longueur des cycles de vie pourraient expliquer la tendance d'une forte bioconcentration du MeHg en Extrême Arctique. Nous avons trouvé une influence négative du COD envers la teneur en MeHg dans les chironomides, et donc, le MeHg est possiblement plus biodisponible dans les eaux très claires à cause du manque de matière organique. En milieu marin sur la côte de l'île Cornwallis, les bactéries expriment des gènes de résistance contre le mercure ce qui suggère le mercure est très biodisponible en Arctique malgré des concentrations basses dans l'environnement (Poulain et al. 2007). Une autre possibilité est que les longs cycles de vie des daphnies et des chironomides jouent un rôle. Les chironomides arctiques nécessitent au moins 2–3 ans pour compléter leur cycle (Welch 1976), et les daphnies deviennent matures après environs 20–24 jours (Yurista et O'Brien 2001), ce qui est environ le double du temps nécessaire pour la maturation en régions tempérées. Un taux de croissance réduit augmente la bioaccumulation du MeHg chez les invertébrés (Karimi et al. 2007).

Une autre distinction entre les latitudes est le rôle plus apparent des processus géochimiques dans la bioaccumulation du MeHg en lacs tempérés. Le COD était un vecteur clé dans le transport du mercure total vers les lacs tempérés, et le pH de l'eau a expliqué la majorité de la variance des concentrations de MeHg dans les invertébrés. Cette association reflète l'effet de l'acidité sur la biodisponibilité du mercure et sur la méthylation bactérienne (Gilmour et al. 1992; Kelly et al. 2003) et démontre un contrôle dominant de ces processus dans le transfert du MeHg aux chaînes alimentaires. En

Extrême Arctique, toutes les eaux étaient alcalines et donc, il n'y avait pas une influence importante du pH entre les sites. Ceci est représentatif de l'Extrême Arctique car la majorité des eaux douces à travers l'archipel Arctique sont alcalines (pH ~8), sauf dans certaines régions comme l'île Baffin où les eaux sont plus acides à cause de la géologie locale (Hamilton et al. 2001).

Avenues de recherche

Nous avons montré que le lien est faible entre la bioaccumulation du MeHg dans les invertébrés aquatiques en Extrême Arctique et les apports de mercure, provenant surtout de la déposition atmosphérique. De plus, nous avons identifié des facteurs biologiques et écologiques qui influencent leur teneur en MeHg comme la métamorphose chez les chironomides et la taxonomie du zooplancton. Cette recherche fournit les premières données publiées sur le mouvement du MeHg dans les chaînes alimentaires aquatiques pour cette région polaire, et elle identifie certains processus qui méritent plus d'étude.

En premier, le faible potentiel de méthylation bactérienne dans les lacs de l'Extrême Arctique reste spéculatif, et des mesures directes du taux de production du MeHg dans ces lacs sont fondamentales à une meilleure compréhension de son mouvement. Les facteurs géochimiques qui contrôlent la biodisponibilité du MeHg semblent être critique également, selon la forte bioconcentration du MeHg comparé aux lacs tempérés. Le rôle des bactéries comme une voie de contamination mérite plus d'étude pour expliquer la concentration élevée de MeHg dans les daphnies. Une portion considérable de la variance en MeHg dans les chironomides reste inexpliquée, et des teneurs plus fortes dans le groupe Diamesinae suggèrent qu'une influence taxonomique est pertinente.

Notre recherche au Québec (mais aussi en Extrême Arctique) montre que la teneur en MeHg dans les invertébrés peut varier entre les habitats d'un lac, et dans certains cas, ces différences peuvent être aussi importantes que la variabilité entre lacs. L'étude du mouvement de MeHg à l'échelle de l'habitat lacustre mérite plus d'attention parce que cette variabilité pourrait affecter le transfert aux poissons. Les facteurs qui contrôlent la bioconcentration du MeHg dans les bactéries et les algues de différents types (e.g., le périphyton versus le phytoplancton) sont mal connus. Une plus forte accumulation du MeHg dans le zooplancton de lacs acides et de lacs humiques est possiblement liée aux concentrations élevées dans l'eau de l'hypolimnion mais cette voie de contamination est spéculative. Le rôle du détritus pour diminuer le transfert du MeHg dans la chaîne alimentaire littorale est une autre avenue de recherche potentielle.

Le réchauffement climatique est en cours de changer rapidement l'écologie de l'Arctique (Smol et al. 2005; Prowse et al. 2006), et il y aura certainement un impact sur le cycle de mercure. Notre recherche met en évidence comment un élargissement de la distribution des daphnies pourraient modifier le transfert du mercure aux poissons mais cette hypothèse considère seulement un des effets possibles du réchauffement climatique, une conséquence à long terme des changements dans la composition des communautés aquatiques. D'autres effets plus rapides sur les processus biogéochimiques incluent possiblement une augmentation des apports de mercure par le dégel du pergélisol, une stimulation de la méthylation dans les sédiments lacustres suite aux plus grands apports de matière organique terrestre et au réchauffement de l'eau, ou une réduction dans la photodécomposition du MeHg aqueux par des apports plus élevés en COD aux lacs (Hammerschmidt et al. 2006). Pour les poissons, le stress métabolique induit par le réchauffement des eaux douces pourrait possiblement amplifier

l'accumulation des métaux traces (Reist et al. 2006). Les changements observés dans le cryosphère arctique durant la dernière décennie sont sans précédent dans l'histoire récente (NSIDC 2008), en particulier l'intensité de la fonte de neige et de glace, et l'étude de ces impacts sur le cycle de mercure est une problématique de grande actualité.

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ANNEXE 1 – PHOTOS DE LACS ÉCHANTILLONNÉS EN EXTRÊME

ARCTIQUE, NUNAVUT, CANADA

Oasis polaire aux basses terres de Truelove, île Devon (75 '40' N, 84°33' W)

Lac Immerk, île Devon, oasis polaire (75°40'48" N, 84°33'36" W)

Phalarope (un étang), île Devon, oasis polaire (75°39'36" N, 84°36'36" W)

Lac Middle Beschel, île Devon, oasis polaire (75°39'00" N, 84°28'12" W)

Ruisseau qui alimente le lac Char, île Cornwallis, désert polaire (74°42'36" N, 94°53'24" W)

Lac Char, île Cornwallis, désert polaire (74°42'16" N, 94°52'56" W)

Lac Titti, île Devon, désert polaire (74°40'48" N, 84°22'48" W)

Lac Amituk, île Cornwallis, désert polaire (75°02'44" N, 93°47'15" W)

ANNEXE 2 – MESURES DE LA TENEUR EN MÉTHYLMERCURE

DANS LES INVERTÉBRÉS AQUATIQUES APRÈS LA DÉPURATION

Tableau 1. La teneur en méthylmercure (MeHg) dans les invertébrés aquatiques après la dépuration.

Organisme	Lac	Individus non-dépurés		Individus dépurés			Temp. de l'eau (°C)	No. d'individus par échantillon	Faux plancher§	Autres détails
		MeHg (ng g^{-1})‡	n†	MeHg (ng g^{-1})‡	n†	Heures				
Isopodes	Morency	71 ± 3	2	67 ± 0.3	2	19	4	15	Oui	Eau de lac filtrée
		---	---	82 ± 4	2	43	4	15	Oui	Eau de lac filtrée
Amphipodes	Morency	26 ± 3	2	25 ± 1	2	24	4	~ 20	Oui	Eau de lac filtrée
Demoiselles	Triton	76 ± 7	2	87 ± 2	2	48	4	~ 8	Oui	Eau de lac filtrée
Chaoborus	Croche	15 ± 1	2	15 ± 3	2	24	4	~ 20	Non	Eau de lac filtrée
Éphémères	Parker	66	1	65 ± 6	2	9	~ 20	16	Oui	Eau de lac non-filtrée
Demoiselles	Parker	69	1	69 ± 5	2	9	~ 20	8	Oui	Eau de lac non-filtrée
Trichoptères	Blanc	338 ± 57	2	305	1	24	~ 20	10-15	Oui	Eau de lac non-filtrée

‡ Moyenne ± 1 écart type

† Nombre d'échantillons

§ Un faux plancher à été construit en dessous du contenant avec du matériel de filet (maille de 500 µm) pour éviter la coprophagie.