UNIVERSITÉ DU QUÉBEC À MONTRÉAL

THE ROLE OF DISSOLVED ORGANIC CARBON AND ZOOPLANKTON COMMUNITY COMPOSITION ON METHYLMERCURY BIOACCUMULATION IN WESTERN ARCTIC LAKES

THESIS
PRESENTED
IN PARTIAL FULFILMENT OF REQUIREMENT FOR
THE DEGREE OF MASTER IN BIOLOGY

BY
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JUNE 17, 2019

UNIVERSITÉ DU QUÉBEC À MONTRÉAL

LE RÔLE DU CARBONE ORGANIQUE DISSOUS ET DE LA COMPOSITION DE LA COMMUNAUTÉ ZOOPLANCTONIQUE SUR LA BIOACCUMULATION DU MÉTHYLMERCURE DANS LES LACS DE L'ARCTIQUE DE L'OUEST

MÉMOIRE
PRÉSENTÉ
COMME EXIGENCE PARTIELLE
DE LA MAÎTRISE EN BIOLOGIE

PAR
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17 JUIN 2019

REMERCIEMENTS

Durant ces presque trois dernières années, j'ai côtoyé beaucoup de gens qui m'ont énormément aidé et appuyé dans la réalisation de ma maîtrise. J'ai eu la chance de faire plusieurs collaborations enrichissantes autant à l'international qu'au national. S'il y a bien une chose que j'aie apprise durant ces collaborations, c'est que peu importe d'où nous venons, des valeurs et des convictions de nos dirigeants ou bien de la langue que nous parlons, lorsque nous poursuivons les mêmes objectifs et que notre seule aspiration est d'apprendre, de découvrir et de rechercher, plus rien d'autre, mis à part les individus, n'a d'importance. C'est pour pouvoir remercier comme il se doit chacune de ces personnes qu'une partie de ces remerciements sera faite en anglais. Cela illustrera aussi très bien mes trois dernières années passées à jongler quotidiennement entre le français et l'anglais.

Tout d'abord, je tiens à remercier mille fois ma directrice de recherche, la professeure Alison Derry, pour son immense soutien, son temps et son encadrement lors de ces trois dernières années. Son dynamisme, son esprit novateur, son écoute ainsi que son intensité sont des qualités qui ont permis la réalisation de cette maîtrise. Merci d'avoir cru en moi et de m'avoir fait confiance avec ce projet ambitieux, mais au combien enrichissant. Je sortirai de cette expérience plus confiante et avec des souvenirs positifs en grande partie grâce à elle.

Thank you to my co-supervisor, Dr. Heidi Swanson for having included me into your lab and work. I particularly want to thank you for your support and kindness on our first field trip to Alaska. As a newly graduated undergrad, I was terrified to find myself alone for two weeks with people who did not speak my language, whom I barely knew while being in charge of so many things and being in such a remote area of the world. You have no idea how much you helped me build my self-confidence on that trip.

I also want to thank Kyra Simone who helped me sample and live picked zooplankton for many hours in the Yukon and in the Northwest Territories. Thank you for being there and for always giving your 100 % for this project that was not even yours and, above all, without ever complaining. Working with you made everything even easier and more special.

Thank you to Christian Zimmerman to have included me in the Alaska trip and to have helped and accompanied me during these long hours of sampling in the cold. Thank you to Brian Branfireun and the Biotron Laboratory for having welcomed and initiated me to the analytic procedures of mercury. Thank you to the Dehcho First Nation to have allowed me to be part of the Northwest Territories field season.

Je tiens à remercier Katherine Velghe et Simon Thibodeau pour leur aide, mais surtout pour leur présence dans le laboratoire durant ces nombreuses heures passées à l'identification des espèces de zooplancton. Il n'y a rien de plus rassurant et d'encourageant que d'avoir quelqu'un pour confirmer ce que nos yeux ont peine à voir. Merci à Louis Donelle pour son aide et sa disponibilité à m'aider lorsque je rencontrais un défi, un problème ou un message d'erreur incompréhensible dans R. A huge thank you to Matthew Yates for his tremendous helps and advice on statistical

questions, I would have not made it alive without you. You were a good teacher and helped me gain confidence in my statistic skills.

Je remercie tous les membres du laboratoire Derry ainsi que le GRIL-UQAM pour leur aide et leurs conseils apportés lorsque j'en avais besoin. Une mention spéciale à Martin Demers, mon partenaire de maîtrise. A special thank you to Gillian Martin who welcomed me and made me feel a part of the Derry Lab since day one. Thank you for your advice, but most of all, thank you for all these moments spent discussing everything and nothing. You have been a great colleague to work with, but especially an amazing friend from the beginning to the end.

Je tiens à remercier André Côté et Marie-Ève Houde, des personnes qui ignorent à quel point ils ont fait une différence dans les moments les plus difficiles de ce cheminement scolaire qui m'a mené jusqu'au cycle supérieur. Un énorme merci à ma famille et mes fidèles amies, Daphné et Geneviève, pour m'avoir accompagnée, soutenue, écoutée et encouragée durant les beaux et les moins beaux moments de cette aventure. Merci à Charles d'avoir égayé mon parcours, mais, surtout, merci pour ton soutien et ton appui inconditionnel durant ces dernières années. Finalement, le plus gros merci revient à mes chers parents qui ont toujours cru en moi (même lorsque je n'y arrivais pas moi-même) et qui m'ont appris à toujours donner mon 100 %. La réalisation de cette maîtrise n'aurait pas été possible sans vous derrière moi pour m'épauler ; une grande partie de ma réussite vous revient.

DÉDICACE

Je dédie ce travail à mes merveilleux parents. Merci pour votre soutien inconditionnel. Je n'y serais pas arrivée sans vous.

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Abs	Absorbance
AICc	Akaike information criterion corrected for small-sample-size
BASL	Biogeochemical Analytical Service Laboratory
BCECCR	Biotron center for Experimental Climate change Research
CO-t	Carbone organique d'origine terrestre
CFIRMS	Continuous flow isotope ratio mass spectrometer
Chl-a	Chlorophyll-a
CladPerL	Number of individual cladocerans found per L of water
Conduc	Conductivity
CVAFS	Cold Vapour Atomic Fluorescence spectrophotometry
DOC/COD	Dissolved organic carbon/Carbone organique dissous
DOM/MOD	Dissolved organic matter/Matière organique dissoute
EIL	Environmental Isotope Laboratory
FA	Fulvic acid
F.I.	Fluorescence Index
FMeHgW	Filtered methylmercury in the water
FTHgW	Filtered total mercury in the water
HA	Humic acid
Hg	Mercury

MeHg	Methylmercury
NWT	Northwest Territories
SO_4^{2-}	Sulfate
SRB	Sulfate-reducing bacteria
SUVA	Specific UV Absorbance
THg	Total mercury
TN	Total nitrogen
TP	Total phosphorus
U of A	University of Alberta
U of W	University of Waterloo
UFMeHgW	Unfiltered methylmercury in the water
UFTHgW	Unfiltered total mercury in the water
UQAM	Université du Québec à Montréal
WU	Western University
ZPerL	Number of individual crustacean zooplankton per L of water
$\delta^{13}C$	Stable carbon thirteen isotope ratios
$\delta^{15}N$	Stable nitrogen fifteen isotope ratios

LISTE DE SYMBOLES ET DES UNITÉS

°C	Degree celsius
‰	Parts per mil
C	Carbon
cm	Centimeter
g	Gram
Gg	Gigagrams
km^2	Square kilometer
L	Liter
m	Meter
mg	Milligram
ml	Milliliter
n	Frequency
ng	Nanogram
nm	Nanometer
SD	Standard deviation
SE	Standard error
µg	Microgram
µm	Micrometer

L'Arctique n'est qu'une sentinelle de la planète, un avertisseur, un vaste laboratoire naturel qui permet de mesurer les effets dévastateurs de nos comportements, et qui prouve que rien ne va plus.

— Jean Lemire, *L'Odyssée des illusions*

RÉSUMÉ

La fonte du pergélisol peut mobiliser du carbone, ainsi que des métaux liés à ce carbone, tel que le mercure, dans les systèmes aquatiques de l'Arctique. Cet apport est problématique puisque le méthylmercure (MeHg) peut se bioaccumuler et se bioamplifier dans la chaîne alimentaire et potentiellement atteindre des concentrations élevées dans la faune. Plusieurs études ont observé une relation unimodale entre la concentration en carbone organique dissous (COD) et la bioaccumulation du MeHg chez des organismes aquatiques. Toutefois, le rôle du COD dans la bioaccumulation du MeHg chez le zooplancton crustacé est peu compris. Nos objectifs sont de 1) déterminer si cette relation unimodale s'applique aussi au zooplancton, un maillon clé des chaînes alimentaires aquatiques ; et 2) déterminer si la composition de la communauté zooplanctonique est un facteur affectant la disponibilité du MeHg des niveaux trophiques supérieurs. Les communautés dominées par des filtreurs passifs, tels que les cladocères, devraient avoir une concentration en MeHg plus élevée comparativement aux copépodes qui ont une alimentation plus sélective. Nous avons échantillonné 11 lacs arctiques le long d'un gradient de concentration en COD sur une large échelle régionale. Les échantillons ont été séparés selon deux taxa ; les cladocères et les copépodes, puis analysés pour la teneur en MeHg. En accord avec d'autres études, sur des niveaux trophiques différents, nous avons trouvé une relation unimodale entre le COD et la bioaccumulation du MeHg dans le zooplancton, avec une concentration en carbone seuil de 8 mg-C-L^{-1}. Alors que la teneur en MeHg dans les tissus de la communauté entière était déterminée par les concentrations aqueuses de sulfate, celle des cladocères et des copépodes étaient déterminés par le pH et le COD respectivement. Comprendre comment certains processus écologiques affectant les niveaux trophiques inférieurs peuvent moduler le potentiel de bioaccumulation du MeHg en Arctique est essentiel, en particulier dans le contexte de changements climatiques où le dégel du pergélisol devrait augmenter.

Mots clés : méthylmercure, Arctique, biodisponibilité, bioaccumulation, gradient de concentration, COD, concentration seuil, zooplancton, composition de la communauté, sulfate, pH

INTRODUCTION

Les changements climatiques auront des effets marqués sur les écosystèmes lacustres de l'Arctique (ACIA, 2005; Prowse et al., 2009; Olsen et al., 2011; Vincent et al., 2011; Vincent et al., 2013). Alors que le réchauffement au niveau global se situait autour de 0,4 °C en 2005, celui de l'Arctique de l'Amérique du Nord était déjà de 2,1 °C (ACIA, 2005). En Amérique du Nord, le climat s'est réchauffé deux fois plus vite dans l'ouest de l'Arctique que dans l'est de l'Arctique alors que l'augmentation des précipitations dans l'est est beaucoup plus importante que dans l'ouest (Prowse et al., 2009). Le dégel du pergélisol pourrait être une source importante de carbone organique dissous (COD) auquel, un métal comme le mercure (Hg) peut se lier (Schuster et al., 2018). Lorsque le mercure inorganique n'est pas réduit puis réémis dans l'atmosphère, il devient biodisponible et peut être méthylé en MeHg (Lindberg et al., 2002). Ceci est un problème puisque la forme organique du Hg, le méthylmercure (CH_3Hg ; MeHg), est une neurotoxine pouvant engendrer de grands problèmes pour la santé humaine puisqu'il se bioaccumule (augmentation de sa concentration à l'intérieur de l'organisme dans le temps) et se bioamplifie (augmentation de sa concentration à chaque niveau trophique) le long de la chaîne alimentaire (Wiener et al., 2002; AMAP, 2011). La bioamplification se produit lorsqu'un contaminant n'est pas détruit ou excrété, mais qu'il s'accumule le long de la chaîne trophique (Poissant et al., 2008). L'homme est principalement exposé au MeHg par la consommation de poissons et cette exposition peut être particulièrement élevée dans les communautés du Nord (Mergler et al., 2007). La neurotoxicité du MeHg peut causer des dommages irréversibles au système nerveux central des fétus et peut engendrer une détérioration neurologique sévère chez l'adulte (Mergler et al., 2007). Au Canada, plus précisément au Yukon et dans les Territoires du Nord-Ouest

(T.N.-O.), il existe des avis de consommation de poissons d'eau douce qui sont publiés par les autorités sanitaires locales (Health and Welfare Canada, 1979, 1984). Le niveau de Hg retrouvé dans les poissons des T.N.-O, du Yukon et du nord du Québec dépasse fréquemment les limites permises pour la consommation et la vente de poissons (0.5 ug-g^{-1}) (Health and Welfare Canada, 1979, 1984). L'entrée du MeHg à la base de la chaîne alimentaire et son transfert subséquent vers les niveaux trophiques supérieurs sont souvent peu compris dans les systèmes naturels (Wiener et al., 2002). Ainsi, il est important de comprendre comment les processus écologiques, à l'intérieur de la communauté des niveaux trophiques inférieurs, peuvent affecter la bioaccumulation du Hg dans la chaîne alimentaire et ultimement la concentration en MeHg dans le poisson.

0.1 Le Mercure dans les Lacs Arctiques

Le mercure dans l'environnement provient de sources naturelles et de sources anthropiques (Pirrone et al., 2010; AMAP, 2011). Depuis la Révolution Industrielle, les activités industrielles ont mobilisé et redistribué dans l'environnement de grandes quantités de mercure (Poissant et al., 2008; AMAP, 2011). Les sources anthropiques comptent, entre autres, des processus industriels comme l'exploitation minière de l'or et de l'argent (Pacyna et al., 2010; Pirrone et al., 2010) et la combustion du charbon (Pacyna et al., 2010; Pirrone et al., 2010). Les propriétés chimiques et physiques du mercure font en sorte que ce métal est très ifficile à contenir et à récupérer dans l'environnement (Turner & Southworth, 1999). Ainsi, le mercure est un élément prisé dans les procédés industriels (Turner & Southworth, 1999).

Seulement une petite quantité du mercure retrouvé en Arctique provient de source régionale ou locale (AMAP, 2005). Le mercure est rapidement transporté jusqu'à

l'Arctique par des courants atmosphériques (AMAP, 2011) sous forme gazeuse (Hg^0; Hg(0)) (Wiener et al., 2002; Poissant et al., 2008). Dans l'atmosphère, le Hg(0) peut être oxydé et former du Hg(II) réactif (Lehnherr, 2014) et être efficacement déposé sous forme de dépôt humide ou sec, de l'atmosphère vers les bassins versants et les lacs (Mason & Sheu, 2002) (Figure 0.1). Des recherches récentes indiquent aussi que, dans l'Arctique, le Hg(0) se dépose directement dans l'environnement des toundras où il est ensuite repris par la végétation (Obrist et al., 2017). Une fois déposé, le mercure peut être séquestré dans le sol et les sédiments aquatiques ou être méthylé. Le Hg(II) peut être aussi réduit en Hg(0) par des mécanismes biotiques (Marvin-DiPasquale & Oremland, 1998) et photochimiques (Amyot et al., 1994) puis réémis dans l'atmosphère (Lehnherr, 2014).

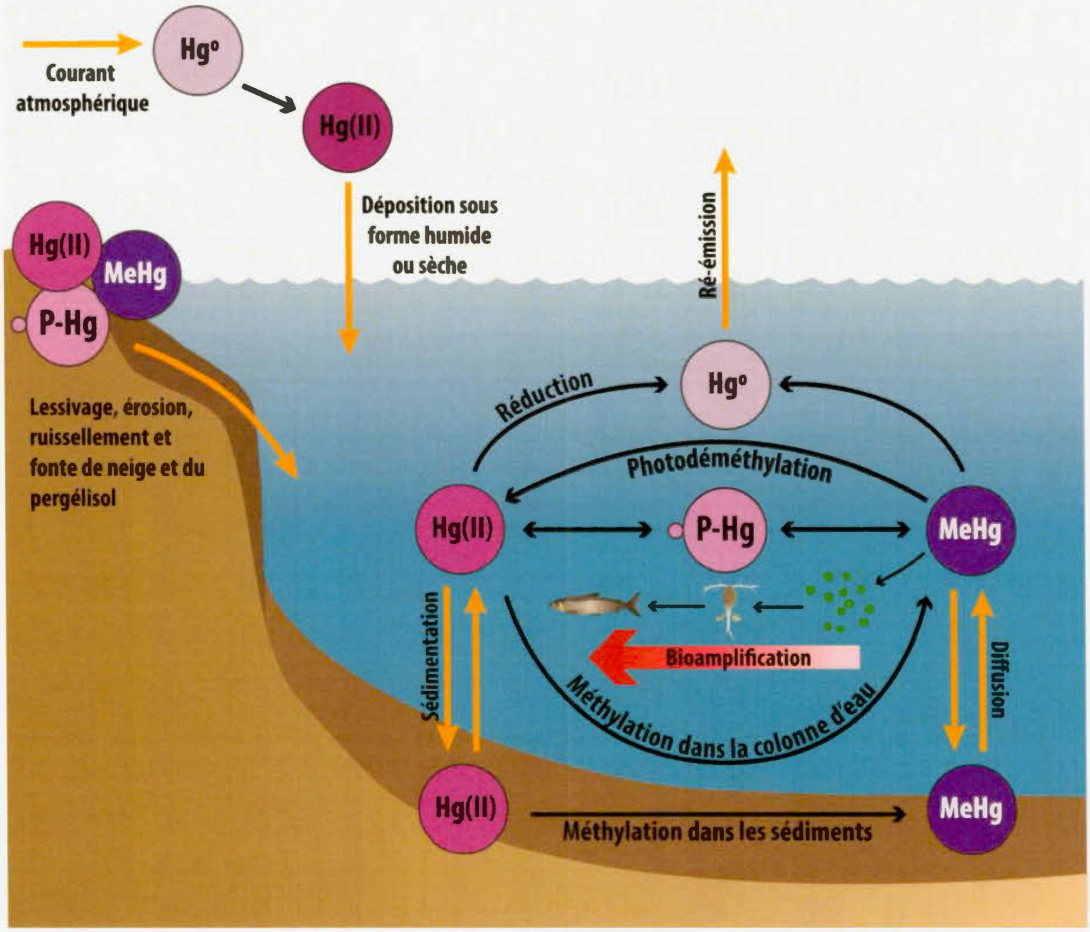

Figure 0.1. Simplification du cycle du mercure (Hg) dans les lacs de l'Arctique. Traditionnellement, il était pensé que le Hg entrait dans les écosystèmes arctiques principalement sous forme inorganique (Hg(II)) par déposition atmosphérique et/ou par transport dans le bassin versant. Toutefois, des études récentes indiquent que le dépôt direct de Hg élémentaire gazeux (Hg(0)) ainsi que son absorption subséquente par la végétation sont d'important processus d'entrée dans l'environnement des toundras de l'Arctique. La méthylation du Hg est le processus le plus important du point de vue écotoxicologique (figure modifiée de Wiener et al. (2002)).

0.2 La Méthylation du Mercure

Dans les écosystèmes d'eau douce, la production de MeHg peut prendre place dans les sédiments (Gilmour & Riedel, 1995), dans la zone anoxique de l'hypolimnion (Eckley & Hintelmann, 2006), ainsi que dans le périphyton (Paranjape & Hall, 2017). Dans les lacs, il est généralement accepté que la méthylation du Hg se déroule principalement au niveau de l'interface eau-sédiment (Ullrich et al., 2001) et dans une moindre mesure dans la colonne d'eau (Xun et al., 1987). Dans les lacs boréaux, les bassins versants sont aussi une source importante de MeHg (Bravo et al., 2017).

Les Processus de Méthylation et de Déméthylation

En Arctique, la concentration en MeHg dans les milieux aquatiques dépend de deux processus opposés soit la méthylation du Hg et la déméthylation du MeHg dans la colonne d'eau (Lehnherr, 2014). Le processus de méthylation peut se faire par des mécanismes biotiques et abiotiques (Ullrich et al., 2001). Toutefois les mécanismes abiotiques sont considérés comme étant de faibles importances comparativement aux mécanismes biotiques puisqu'ils nécessitent la présence de donneurs de groupement méthyle directement dans le milieu (Ullrich et al., 2001). Les substances humiques peuvent jouer le rôle d'agent méthylant dans l'environnement (Talmi & Mesmer, 1975). La transformation biotique active du Hg en MeHg nécessite la présence de bactéries possédant le groupement de gènes *hgcAB* (Gilmour et al., 2013; Parks et al., 2013). Ces gènes permettent l'assemblage du Hg avec un groupement méthyle grâce à l'encodage de protéines à corrinoïde et à ferrédoxine (HgcA et HgcB respectivement) (Parks et al., 2013). La méthylation biotique est associée à trois principaux types de bactéries, soit les bactéries sulfato-réductrices (Gilmour et al., 1992; AMAP, 2011), les bactéries réductrices de fer (Parks et al., 2013), les

archéobactéries méthanogènes (Hamelin et al., 2011) et potentiellement les phototrophes (Grégoire & Poulain, 2014). Il se pourrait aussi qu'il y ait une modification, associé aux changements des saisons, dans la dominance des agents microbiens responsables de la méthylation (Lázaro et al., 2018).

Tout comme les mécanismes de méthylation, les mécanismes de déméthylation peuvent être réalisés de façon biotique ou de façon abiotique (Wiener et al., 2002; Lehnherr et al., 2012). La déméthylation biotique du MeHg nécessite des bactéries possédant l'opéron *mer* (Schaefer et al., 2004), qui, à l'aide d'une lyase organomercuriale, est capable de séparer le Hg du groupement méthyle auquel il est associé (Barkay et al., 2003). La déméthylation biotique est probablement réalisée par des archéobactéries méthanogènes et bactéries sulfato-réductrices (Marvin-DiPasquale & Oremland, 1998). Le MeHg peut aussi être réduit par photolyse (c.-à-d. abiotiquement) par les radiations solaires à la surface de l'eau (Lehnherr & St. Louis, 2009). La photodéméthylation est possible grâce à un processus intramoléculaire par lequel la lumière est absorbée par le COD puis l'énergie résultante est transférée afin de briser le lien entre le carbone et le Hg (Jeremiason et al., 2015). Cette photodéméthylation aboutit en la conversion du MeHg en Hg(II) et en Hg(0) (Lehnherr et al., 2012; Lehnherr, 2014) et elle peut constituer un agent important de contrôle du MeHg (Hammerschmidt et al., 2006; Lehnherr, 2014). Toutefois, l'importance relative de ce mécanisme n'est pas la même dans tous les lacs et cela est probablement dû à la concentration aqueuse en COD (Girard et al., 2016).

0.3 Facteurs Affectant la Méthylation dans l'Environnement

Le processus de méthylation du Hg dépend de l'activité microbienne et de la biodisponibilité du Hg, laquelle dépend à son tour de plusieurs facteurs tels que le pH,

la température, des conditions d'oxydoréduction, de la concentration en COD et de la présence de sulfate (Lehnherr, 2014). La fonte prévue de 30 à 99 % du pergélisol d'ici 2100 (Koven et al., 2013) pourrait aussi être une source importante de COD auquel un métal comme le Hg peut se lier (Schuster et al., 2018). Même si la quantité de Hg qui sera relâchée suite à cette fonte dépend de la concentration en Hg retrouvé dans le pergélisol (AMAP, 2011) des recherches suggèrent que cet apport pourrait surpasser celui du flux atmosphérique (Klaminder et al., 2008). Des études récentes évaluent qu'environ 1656 ± 962 Gg de Hg serait présentement emprisonné dans le pergélisol de l'hémisphère Nord ; une concentration représentant près du double de la quantité de Hg retrouvé dans tous les autres compartiments combinés (Schuster et al., 2018). St. Pierre et al. (2018) estiment qu'environ 5 % du Hg emprisonné dans le pergélisol de l'hémisphère Nord, soit environ 88 Gg, est présentement à risque d'être relâché dans l'environnement.

Le Carbone Organique Dissous

Le COD est, entre autres, composé de substances humiques définies comme étant une série de molécules colorées relativement lourdes (Aitkenhead-Peterson et al., 2003). La majorité de ces substances humiques se retrouvent sous forme d'acides fulviques (Schnitzer & Neyroud, 1975) et le reste se trouve sous forme d'acides humiques (Aitkenhead-Peterson et al., 2003). Habituellement, il est considéré que les acides fulviques sont plus labiles que les acides humiques (Pitter & Chudoba, 1990). Le Hg est considéré comme un acide mou ce qui lui permet de former des complexes stables avec des bases molles comme les thiols, les sulfures et d'autres ligands contenant des atomes de soufre réduits (Lehnherr, 2014). Ainsi, le Hg peut former des associations particulièrement fortes avec la matière humique, en se liant probablement à un groupement thiol (-RSH) (Lindqvist et al., 1991). Aussi appelés mercaptan (« *qui*

capte le mercure »), les groupements thiols jouent des rôles essentiels dans plusieurs réactions cellulaires (Pompella et al., 2002). L'affinité du Hg pour les groupements thiols ainsi que sa nature lipophile (Harris et al., 2003), favorise sa rétention autant dans les muscles que dans les tissus gras (Lehnherr, 2014). Ainsi, le Hg peut se lier à des particules biogéniques comme des bactéries, des algues et même le phytoplancton (Ullrich et al., 2001). Les organismes unicellulaires sont donc un point d'entrée important pour le MeHg dans les chaînes alimentaires aquatiques (AMAP, 2011). La matière organique dissoute (MOD) peut affecter le taux de méthylation et de déméthylation du Hg dans un lac de plusieurs façons. Certaines formes de COD terrestre peuvent être des sources de carbone décomposables pour la population microbienne (Hammerschmidt & Fitzgerald, 2004) et une augmentation en COD pourrait stimuler l'activité microbienne et augmenter indirectement la méthylation du Hg (Miskimmin et al., 1992). La MOD peut servir de véhicule de transport au Hg vers les sites de méthylation (Hill et al., 2009; AMAP, 2011). Bravo et al. (2017) ont démontré que lorsque les sédiments sont concentrés en MOD d'origine terrestre, la concentration en MeHg peut être augmentée même si le taux de méthylation reste bas. Ainsi, l'ingestion de MOD transportant du Hg par les macroinvertébrés benthiques peut aussi être une voie d'entrée du MeHg dans les chaines alimentaires aquatiques. La MOD peut aussi favoriser et défavoriser le processus de photodéméthylation (Girard et al., 2016). Les groupements thiol de la MOD, auxquels le MeHg s'associe de préférence, peuvent favoriser la photodéméthylation (Zhang & Hsu-Kim, 2010). Le niveau d'aromaticité des groupements thiols influencera la vitesse de photodéméthylation, avec une vitesse plus rapide associée au groupement plus aromatique (Qian et al., 2014). La photodéméthylation pourrait être modulée par la présence d'espèces réactive à l'oxygène (*reactive oxygen species*; *ROS*) (Hammerschmidt & Fitzgerald, 2010) créés avec la matière organique par photoproduction dans la zone photique (Zhang & Hsu-Kim, 2010). Toutefois, une augmentation de la quantité de composés de MOD colorés et photoactifs causera le brunissement de l'eau (Ask et al., 2012) ce qui peut diminuer la concentration de

photon libre dans le lac qui serait autrement disponible pour la photodéméthylation (Hammerschmidt et al., 2006). Girard et al. (2016) ont proposé qu'il existait une concentration seuil après quoi le COD inhiberait la photodéméthylation. À faible concentration de COD, la photodéméthylation serait limitée par la concentration en *ROS*, alors que l'atténuation des UV et la complexation seraient plus importantes à haute concentration en COD (Girard et al., 2016). Ainsi, alors que la photodéméthylation peut être un mécanisme important de contrôle du MeHg aqueux dans les lacs tempérés (Hammerschmidt et al., 2006; Lehnherr, 2014), il est possible qu'elle soit de moindre importance dans certains lacs Arctiques dont la concentration en COD est faible (Girard et al., 2016). Il faut toutefois tenir compte, qu'avec le réchauffement climatique prévu, la saison sans neige, où la photodéméthylation est possible, pourrait être prolongée, augmentant tout de même la quantité de MeHg pouvant être photodéméthylé (Hammerschmidt et al., 2006). La brunification de l'eau par la MOD peut aussi favoriser la production bactérienne par rapport à la production algale résultant en une plus grande concentration de ressource bactérienne moins nutritive pour le zooplancton (Jansson et al., 2007). En effet, en plus de favoriser la production bactérienne, il a été démontré que le COD avait un effet inhibiteur sur la photosynthèse du phytoplancton (del Giorgio & Peters, 1994) puisqu'il peut diminuer de façon importante la profondeur de la couche à laquelle les radiations solaires peuvent pénétrer (von Einem & Granéli, 2010).

La MOD peut aussi affecter le taux de méthylation, car les acides fulviques et les acides humiques, composant le COD, peuvent directement méthyler le Hg de façon abiotique et ce processus pourrait être augmenté avec un enrichissement en MOD (Ullrich et al., 2001). Finalement, le Hg et le MeHg peuvent être fortement liés au COD, et cette liaison peut réduire la biodisponibilité du Hg et par conséquent diminuer autant le taux de production de MeHg que la biodisponibilité du MeHg (Miskimmin et al., 1992; Tsui & Finlay, 2011). Plusieurs recherches ont démontré

que le COD pouvait à la fois promouvoir et inhiber la bioaccumulation du MeHg (relation unimodale) de plusieurs organismes dans les écosystèmes lacustres (Figure 0.2), tels que chez les bactéries (Chiasson-Gould et al., 2014), les amphipodes (French et al., 2014), les insectes émergeant (Chaves-Ulloa et al., 2016) et les perchaudes (*Perca flavescens*) (Driscoll et al., 1994). Ces études ont trouvé qu'à basse concentration de COD, la biodisponibilité du Hg était augmentée, et ce, jusqu'à l'atteinte d'une concentration seuil en COD ou la bioaccumulation était maximale. Toutefois, lorsque cette concentration seuil en COD était dépassée, la bioaccumulation du MeHg dans ces organismes se voyait diminuée (Figure 0.2). D'autres études ont plutôt démontré l'existence d'une relation négative entre la concentration aqueuse en COD et la concentration en MeHg chez le seston (Tsui & Finlay, 2011), le phytoplancton (Gorski et al., 2008) et les libellules (Jeremiason et al., 2016). Braaten et al. (2018) ont observé que la concentration en MeHg de la Perche commune (*Perca fluviatilis*) pouvait suivre une relation unimodale et une relation négative avec la concentration aqueuse en COD.

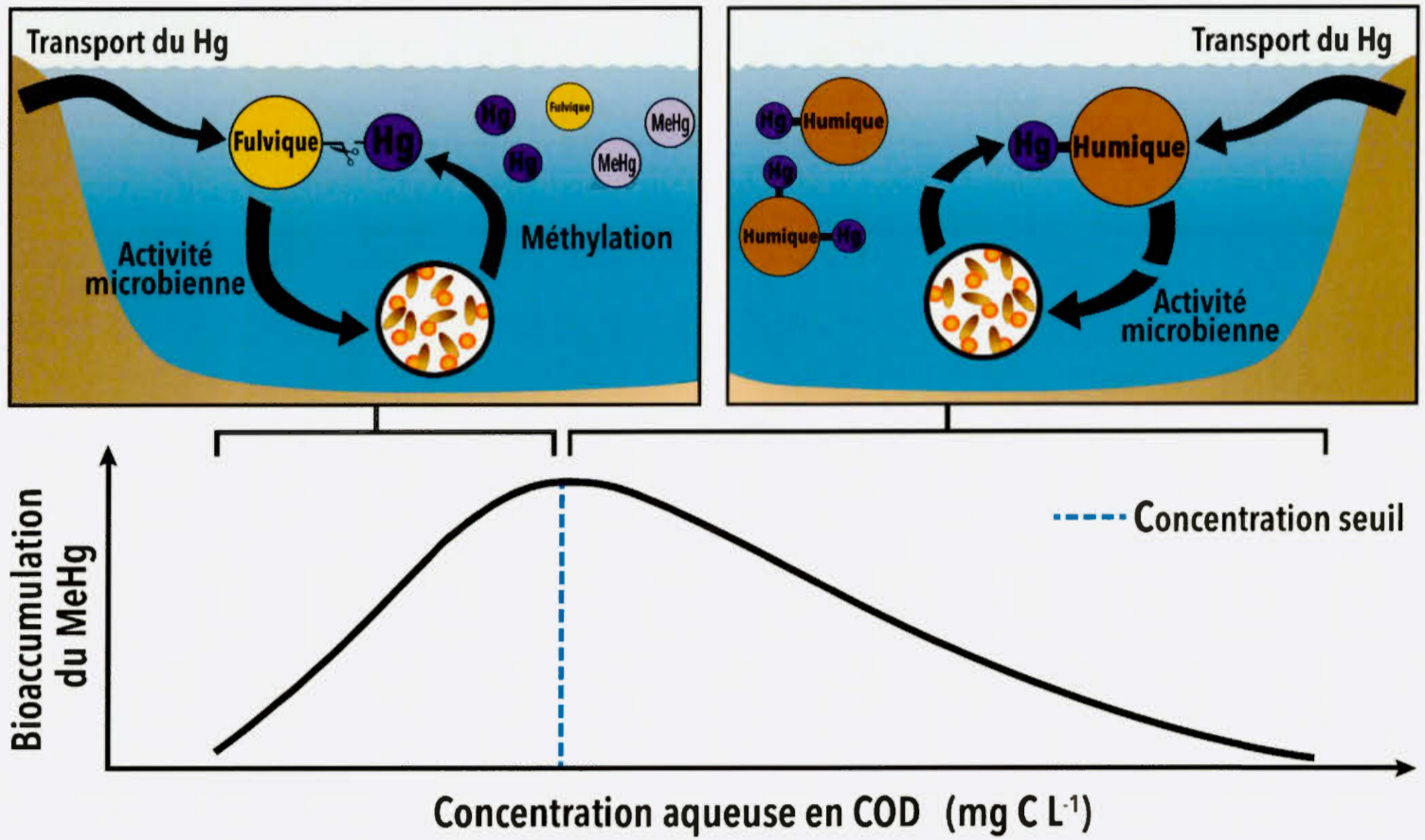

Figure 0.2. Relation unimodale entre la concentration aqueuse de carbone organique dissous (COD) et la bioaccumulation du MeHg chez des amphipodes de l'Arctique de l'Ouest (French et al., 2014). La ligne pointillée bleue représente la concentration seuil en COD (mg-C-L^{-1}) après laquelle la bioaccumulation du MeHg commence à diminuer.

La portion gauche de la courbe unimodale, où la bioaccumulation du MeHg augmente avec la concentration aqueuse en COD, peut être expliquée par plusieurs mécanismes (Figure 0.2). À mesure que le Hg est transporté avec le COD vers les lacs (Hill et al., 2009), le COD peut promouvoir la bioaccumulation du MeHg en augmentant l'approvisionnement de Hg aux lacs et en stimulant l'activité hétérotrophique microbienne responsable de la dégradation du COD qui aboutira en la libération des ions Hg qui y sont liés (Porcal et al., 2009). La diminution de la biodisponibilité du Hg dans les lacs riches en COD (Figure 0.2; section droite de la courbe) est probablement due à la formation d'espèces de Hg qui ne sont pas facilement disponibles pour l'assimilation directe du Hg dans l'eau par les organismes (bioconcentration), le premier mode d'assimilation du Hg pour les niveaux trophiques inférieurs et intermédiaires (Barkay et al., 1997). Aussi, la bioaccumulation du Hg est élevée lorsque le Hg est principalement associé avec de l'acide fulvique, mais est dramatiquement réduite lorsque la concentration en COD atteint la concentration seuil et que le Hg devient principalement associé avec de l'acide humique moins labile (French et al., 2014). Il existe toutefois des dissemblances, selon les études et selon les organismes, quant à la valeur exacte de cette concentration seuil en COD. Certaines études ont observé une relation négative entre la bioaccumulation du MeHg et la concentration aqueuse en COD avec une bioaccumulation maximale lorsque la concentration aqueuse en COD était égale à ~5 mg-C-L^{-1} (Gorski et al., 2008; Tsui & Finlay, 2011; Chaves-Ulloa et al., 2016; Braaten et al., 2018). D'autres études ont plutôt trouvée qu'une concentration aqueuse égale ~8 mg-C-L^{-1} était la concentration en COD aqueux qui favorisait le plus la bioaccumulation du MeHg (Driscoll et al., 1994; French et al., 2014). Il est donc possible de penser que la bioaccumulation du MeHg dans les systèmes lacustres serait favorisée lorsque la concentration en COD se situe entre 5 et 8 mg-C-L^{-1}, et qu'elle serait potentiellement inhibée lorsque la concentration en COD est plus faible ou plus élevée que 8 mg-C-L^{-1}.

Le Sulfate

Bien que les résultats de MacMillan et al. (2015) laissent suggérer que les archéobactéries méthanogènes pourraient être des agents méthylant importants dans l'Arctique canadien de l'Est, les bactéries sulfato-réductrices sont généralement acceptées comme étant les principaux agents de méthylation du Hg dans les sédiments (Compeau & Bartha, 1985; Paranjape & Hall, 2017). Les bactéries sulfato-réductrices auront un avantage compétitif sur les méthanogènes, puisque les méthanogènes utilisent un nombre limité de substrats pour leur croissance, alors que les bactéries sulfato-réductrices utilisent de gros groupements d'acide organique (Weijma et al., 2002). Au contraire, les composés utilisés par les méthanogènes ont besoin d'être préalablement dégradés par d'autres groupes de bactéries avant de pouvoir être utilisés. Ainsi, les méthanogènes peuvent dépendre d'interactions syntrophiques (Bogard et al., 2014). Toutefois, il existe une relation unimodale entre la quantité de MeHg créé par les bactéries sulfato-réductrices et la concentration aqueuse en sulfate (Gilmour & Henry, 1991). À trop base concentration de sulfate, la méthylation par les bactéries sulfato-réductrices est limitée par le manque de substrat (Gilmour & Henry, 1991) alors, qu'à haute concentration, les sous-produits de la respiration des bactéries (les sulfures) vont interférer avec la méthylation du Hg en formant des complexes avec ce dernier (Gorski et al., 2006). Dans la MOD, il est possible de retrouver le soufre sous sa forme oxydée (sulfate (SO_4^{2-}), sulfonate), et réduite (sulfure (S^{2-}), thiol) (Ravichandran, 2004). Toutefois, il semble que seulement le sulfure soit d'importance pour la complexation du Hg avec la MOD (Ravichandran, 2004). Gilmour & Henry (1991) ont observé un taux de méthylation optimal par les bactéries sulfato-réductrices lorsque la concentration en SO_4^{2-} se trouvait entre 20 et 50 mg-L^{-1}. Selon Lovley & Klug (1983), une concentration en SO_4^{2-} inférieur à 10 mg-L^{-1} peut commencer à réellement limiter l'activité des bactéries sulfato-réductrices. Ces microorganismes peuvent toutefois rester actifs même à des concentrations en SO_4^{2-} aussi basses que 3 mg-L^{-1} puisqu'ils sont de meilleurs

compétiteurs que les méthanogènes (Lovley & Klug, 1983). L'augmentation de l'érosion des bassins versants avec le réchauffement climatique libèrera des ions incluant des ions SO_4^{2-} dans les milieux aquatiques (Capone & Kiene, 1988). Ceci pourrait potentiellement augmenter la méthylation du Hg par les bactéries sulfato-réductrices dans les lacs ou le SO_4^{2-} est limitant (Hammerschmidt et al., 2006). Ce facteur pourrait être potentiellement important dans les lacs arctiques souvent limités en SO_4^{2-} (Gilmour & Henry, 1991).

Les conditions d'oxydoréduction

Les conditions oxiques favorisent généralement la sédimentation du Hg et du MeHg, alors que les conditions anoxiques favorisent la production de MeHg causant une plus grande concentration de MeHg diffusant vers la colonne d'eau (Regnell et al., 1996). Même si la méthylation du Hg peut avoir lieu autant dans des environnements aérobiques que dans des milieux anaérobiques, cette dernière se déroule principalement en conditions anaérobiques (Compeau & Bartha, 1985; Matilainen et al., 1991; Ullrich et al., 2001). Les conditions anaérobiques promeuvent la stabilité du MeHg (Compeau & Bartha, 1985), alors que les conditions aérobiques réduisent l'activité des bactéries sulfato-réductrices provoquant un taux de méthylation lent (Ullrich et al., 2001) et favorisant la déméthylation du MeHg (Compeau & Bartha, 1985).

La méthylation anaérobique semble être favorisée par la présence de grandes concentrations de matière organique, possiblement due à son effet sur la croissance microbienne (Compeau & Bartha, 1985). À l'opposé, la méthylation aérobique ne semble pas être modulée par la faune microbienne et semble être réduite en présence de grande concentration de matière organique, de particules en suspension et de

composé humique (Matilainen et al., 1991). La méthylation aérobique dans les sédiments superficiels riches en composés organiques est abiotique et elle est considérée comme lente comparativement à la méthylation anaérobique (Matilainen et al., 1991). Elle peut toutefois être augmentée par la présence de minéraux dans les sédiments, tels que le Fer et le Manganèse (Matilainen et al., 1991). Ces métaux interagiraient avec le soufre aqueux présent dans les sédiments et diminueraient les interactions entre le Hg et le soufre résultant en une plus grande quantité de Hg libre et disponible pour la méthylation (Matilainen et al., 1991). Le taux maximal de méthylation biotique dans les sédiments serait observé directement sous l'interface eau-sédiments, où les conditions anaérobiques sont modérées (Bubb et al., 1993). En effet, la surface oxygénée des sédiments serait dominée par la déméthylation biotique du MeHg, alors que dans les couches plus profondes des sédiments, la présence d'espèces réduites de soufre limiterait la disponibilité de Hg pour la méthylation (Bubb et al., 1993). Dans la colonne d'eau, la production de MeHg est aussi associée aux zones de faibles concentrations en oxygène (Bloom et al., 1991). D'autre facteurs environnementaux, tel que le pH et la matière organique peuvent interagir avec les conditions d'oxydoréduction (Ullrich et al., 2001).

L'acidité

Le pH est souvent mentionné comme facteur important contrôlant le taux de méthylation (Miskimmin et al., 1992), et la concentration en MeHg chez les poissons et les invertébrés (Wiener et al., 1990; Watras et al., 1998; Kainz & Mazumder, 2005). En effet, un pH plus acide changera les propriétés chimiques du COD en réduisant sa capacité de liaison avec le Hg, entrainant une augmentation de la concentration en Hg (II) libre dans l'eau (Davis et al., 1985; Hintelmann et al., 1995; Kelly et al., 2003; Stenzler et al., 2017). Ceci augmentera la quantité de Hg biodisponible pour la

méthylation ainsi que pour l'absorption par la faune (Miskimmin et al., 1992; Ullrich et al., 2001; Jardim et al., 2010). Une diminution en pH de 7 à 5 est suffisante pour augmenter significativement la quantité de MeHg relâché des sédiments vers la colonne d'eau (Miller & Akagi, 1979; Ullrich et al., 2001). Un faible pH peut aussi favoriser l'activité de certaines espèces bactériennes et les voies biochimiques affectant la méthylation du Hg (Miskimmin et al., 1992). Ainsi, la solubilité et la mobilité du Hg et du MeHg sont dépendantes du pH et les pluies acides pourraient augmenter l'apport aux lacs en Hg provenant des bassins versants (Lee & Hultberg, 1990). L'apport en substance humique provenant du COD a aussi un effet d'acidification naturelle (de Wit et al., 2012; Braaten et al., 2014). Le pH pourrait donc jouer un rôle important dans la bioaccumulation du Hg chez le zooplancton. Les résultats de Clayden et al. (2014) appuie ce fait, car ils ont démontré que l'accumulation du MeHg chez les macroinvertébrés était plus importante dans les environnements acides où l'approvisionnement en MeHg est généralement élevé.

La Température

La température affecte principalement la méthylation du Hg en affectant directement l'ensemble de l'activité microbienne (Bisogni & Lawrence, 1975). Une augmentation en température suite au réchauffement climatique favorisera la production de MeHg en Arctique en augmentant la période durant laquelle la méthylation peut avoir lieu (Hintelmann, 2010). Les changements climatiques pourraient aussi modifier la production de MeHg en modifiant la distribution des milieux humides ou en augmentant la quantité de Hg qui sera relâchée par le pergélisol (Macdonald et al., 2005; Schuster et al., 2018; St. Pierre et al., 2018). Toutefois, certains chercheurs ont démontré que la méthylation du Hg par l'activité microbienne dans les régions plus froides était déjà très efficace (Barkay et al., 2011) et il semble aussi que la

température ait un effet positif sur le taux de déméthylation (Matilainen et al., 1991). L'effet de la température sur la production de MeHg reste incertain et pourrait être spécifique au milieu (Lehnherr, 2014).

0.4 Facteurs Affectant La Bioaccumulation chez le Zooplancton

Alors que certains facteurs environnementaux, tels que le pH, le COD, le sulfate et les conditions d'oxydoréduction affecteront la quantité de MeHg biodisponible, certains facteurs affecteront directement la bioaccumulation chez les organismes. De plus, certains groupes d'organismes, tels que le seston, affecteront plus fortement la quantité de MeHg retrouvé au sommet de la chaîne trophique (Wu et al., 2019b). Le zooplancton occupe une position intermédiaire dans la chaîne trophique et joue donc un rôle critique dans le transfert du MeHg de la base de la chaîne vers les niveaux supérieurs (Todorova et al., 2015). Un changement dans l'accumulation du MeHg chez le zooplancton affectera la concentration du MeHg retrouvé dans les poissons (Todorova et al., 2015). Ainsi, considérant la position du zooplancton dans la chaîne trophique, des pressions *top-down*, tels des changements dans la communauté ichtyenne, et des pressions *bottom-up*, tel un changement dans la densité de phytoplancton, peuvent altérer la structure de la communauté zooplanctonique ce qui affectera en retour l'accumulation du MeHg (Todorova et al., 2015). Comprendre ce qui peut influencer l'accumulation chez le zooplancton est donc critique afin d'avoir une meilleure vue d'ensemble sur le niveau de MeHg retrouvé dans les poissons consommés par l'homme.

Outre la concentration en MeHg dans l'environnement lui-même (Lehnherr et al., 2012), d'autres facteurs peuvent influencer la bioaccumulation du MeHg chez le zooplancton, comme la productivité (Karimi et al., 2007), le taux de croissance des

individus (Lehnherr et al., 2012), la composition de la communauté (Watras et al., 1998; Chételat & Amyot, 2009; Lehnherr et al., 2012; Todorova et al., 2015) et la source alimentaire (Kainz & Mazumder, 2005; de Wit et al., 2012; Berggren et al., 2014). En plus d'influencer le taux de méthylation, la température aura aussi un grand impact sur la bioaccumulation du MeHg dans les organismes puisqu'elle aura un effet sur la croissance des organismes (Simoneau et al., 2005) ainsi que sur la composition de la communauté (Schindler, 1990). La bioamplification du Hg dans les réseaux trophiques est plus élevée dans les environnements froids et peu productifs (Lavoie et al., 2013). Un taux de croissance faible relativement à la consommation alimentaire dans les climats plus froids favorisera de plus grandes concentrations en MeHg dans les organismes comme le zooplancton (Simoneau et al., 2005). À l'opposé, des températures plus chaudes vont augmenter le taux de croissance des organismes ce qui diminuera la quantité de Hg par unité de masse corporelle (biodilution par la croissance) (Karimi et al., 2007). De plus, des températures basses diminuent le taux d'excrétion du MeHg chez les organismes ce qui favorise sa rétention et sa bioaccumulation (Trudel & Rasmussen, 1997).

En général, les lacs riches en nutriment produisent plus de biomasses algales et augmentent le taux de croissance du zooplancton (Pickhardt et al., 2005) entrainant un transfert de MeHg plus faible vers les niveaux supérieurs à cause de l'effet de biodilution (Pickhardt et al., 2002; Chen & Folt, 2005; Pickhardt et al., 2005). La biodilution survient lorsque la quantité de Hg aqueux biodisponible est divisée en un plus grand nombre d'individus ou de cellules algales (Pickhardt et al., 2002). Un taux de croissance plus élevé chez le zooplancton réduit la quantité de MeHg accumulé puisqu'une plus grande quantité de biomasses est produite par unité de Hg consommé (Karimi et al., 2007). De plus, avec les changements climatiques, le nombre de jours où la croissance sera possible risque d'augmenter (Shuter & Ing, 1997). Une augmentation de la productivité pourrait avoir des effets importants sur la

bioaccumulation du Hg dans la communauté zooplanctonique (Chételat & Amyot, 2009). En effet, la faible productivité de certains lacs de l'Arctique limiterait la présence de certaines espèces de cladocères riches en Hg comme les *Daphnia* ce qui diminuerait la concentration en MeHg moyenne de la communauté de zooplancton (Chételat & Amyot, 2009). Chételat & Amyot (2009) ont associé de grandes concentrations en MeHg mesuré dans le zooplancton, entre autres, à la présence de l'espèce *Daphnia middendorffiana* plutôt qu'à la concentration en MeHg dans l'eau. Des résultats similaires ont été observés par Pickhardt et al. (2005), mais pour l'espèce *Daphnia mendotae*. Dans ces deux études, la concentration en MeHg de la communauté zooplanctonique était jusqu'à cinq fois plus élevée, lorsque les *Daphnia* étaient présentes dans la communauté de zooplancton, que dans les communautés où les copépodes dominaient (Pickhardt et al., 2005; Chételat & Amyot, 2009). L'effet des *Daphnia* sur la concentration en Hg des communautés zooplanctoniques n'est toutefois pas généralisé. En effet, certaines études ont plutôt démontré une plus faible absorption de Hg chez les *Daphnia* comparativement à d'autres taxa (Masson & Tremblay, 2003; Long et al., 2018). Masson & Tremblay (2003) ont plutôt associé les concentrations élevées en Hg à la présence du cladocère *Holopedium gibberum*.

Puisque l'alimentation est la source principale de contamination en MeHg pour le zooplancton (Tsui & Wang, 2004), la disparité des concentrations retrouvées chez les cladocères comparativement aux copépodes ainsi qu'entre les *Daphnia* et *H. gibberum* pourrait être due à des stratégies d'alimentation différente (Figure 0.3) (Chételat & Amyot, 2009). En général, le zooplancton se nourrit en faisant passer de l'eau et des particules à travers son corps et son efficacité à le faire est proportionnelle à sa longueur (Wetzel, 2001). Les cladocères sont des filtreurs efficaces se nourrissant de petites cellules comme des bactéries, des algues et des détritus particulaires dans la colonne d'eau, alors que les copépodes se nourrissent activement sur de plus grandes proies comme des cellules algales et/ou de petits

zooplanctons (Bertilsson et al., 2003; Karlsson et al., 2003). Alors que les *Daphnia* consomment avec une efficacité équivalente les cellules algales et bactériennes, *H. gibberum* possède une alimentation plus orientée et spécialisée dans les macro-particules et il possède aussi un taux d'alimentation plus élevé que les *Daphnia* (Hessen, 1985). Ces caractéristiques pourraient augmenter l'exposition au Hg chez *H. gibberum* (Masson & Tremblay, 2003). Dans tous les cas, les bactéries pourraient être une voie importante pour le transfert du Hg chez le zooplancton puisqu'elles consomment des substances organiques dissoutes dans la colonne d'eau avec qui le MeHg peut se lier (Chételat & Amyot, 2009). Il a aussi été démontré que certaines espèces de *Daphnia* se nourrissaient à l'interface eau-sédiment, où la concentration en MeHg peut parfois être plus élevée (Rautio & Vincent, 2006). Puisque les *Daphnia* ont un taux d'alimentation plus élevé que les copépodes (Bertilsson et al., 2003) et qu'elles sont préférées par plusieurs poissons (Mittelbach et al., 1995), elles représentent potentiellement des espèces clés dans le transfert trophique de MeHg vers les poissons (Folt et al., 2002).

Figure 0.3. Composition de la communauté et stratégies alimentaires : deux facteurs pouvant affecter la bioaccumulation du MeHg des communautés zooplanctoniques en Arctique.

0.5 Objectifs du Mémoire

L'Arctique couvre une grande proportion du Canada et bien qu'il soit vulnérable aux changements climatiques et à la contamination par le Hg, il existe encore beaucoup de lacunes dans nos connaissances concernant le comportement de ce contaminant dans cet écosystème vulnérable (Government of Canada, 2017). En 2017, le département d'*Environnement et Changement Climatique Canada* précisait dans un rapport sur l'évaluation de l'état du Hg au Canada que la plus grosse lacune dans nos connaissances concernait l'impact qu'auraient les changements climatiques sur le cycle du Hg au Canada. Ce rapport soulignait également l'insuffisance de nos connaissances quant à l'impact de la température, de l'acidité et de la matière organique sur la production et la bioaccumulation du MeHg dans les systèmes

aquatiques d'eau douce de l'Arctique (Government of Canada, 2017). Les mécanismes associés à la mobilisation, la formation ainsi que la bioaccumulation du MeHg en Arctique sont nombreux, complexes et souvent corrélés. Toutefois, certaines variables environnementales telles que la concentration aqueuse en COD semblent avoir un impact généralisé sur le cycle du Hg (Figure 0.4).

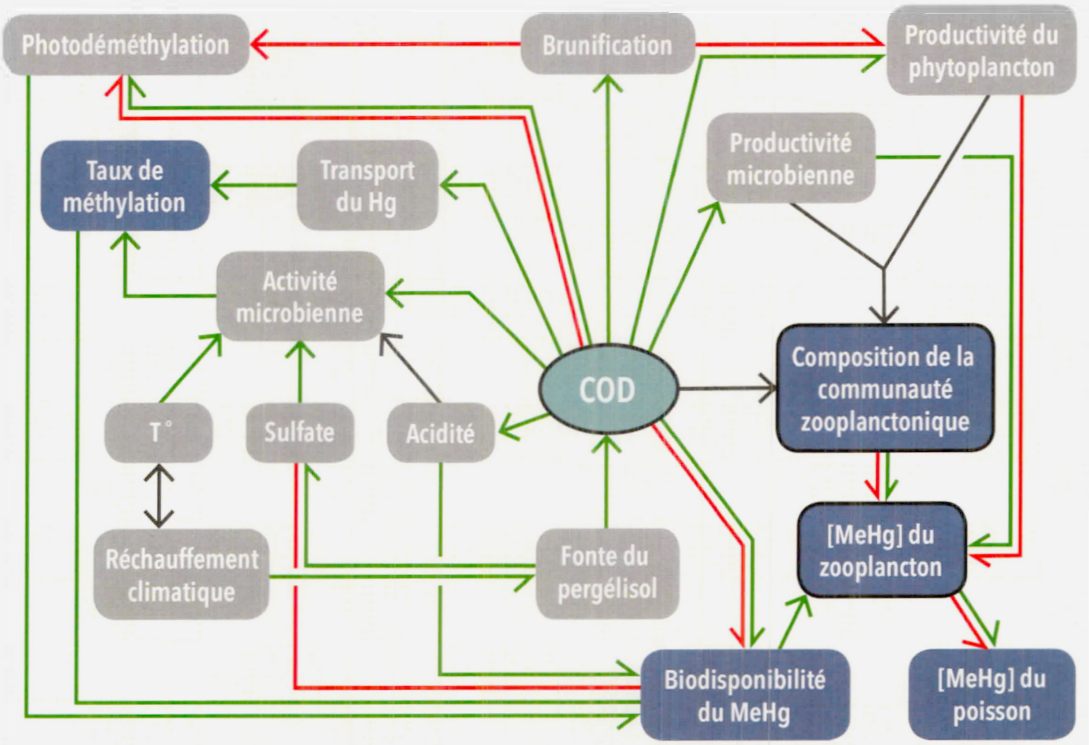

Figure 0.4. Résumé non exhaustif des facteurs pouvant affecter le cycle du Hg en Arctique, sa méthylation, ainsi que sa bioaccumulation subséquente chez le zooplancton avec comme point central, l'effet du carbone organique dissous (COD). Flèches vertes : effets positifs ou augmentation; Flèches rouges : effets négatifs ou diminution; Flèches noires : effet général du processus. Les compartiments encadrés en gras sont les composantes principales étudiées dans ce mémoire.

Il est possible de constater avec la Figure 0.4 que la concentration aqueuse de COD est au cœur de plusieurs interactions favorisant ou défavorisant le transport et la biodisponibilité du MeHg dans les lacs en Arctique. Toutefois, la relation entre le COD et la bioamplification du MeHg dans les chaînes trophiques de l'Arctique est

complexe et cette complexité est amplifiée par la maigre compréhension des facteurs affectant la bioaccumulation du MeHg dans les niveaux trophiques inférieurs. Le zooplancton crustacé occupe une position intermédiaire dans la chaîne trophique faisant de lui un acteur important dans le transfert du MeHg vers les niveaux trophiques supérieurs. Comprendre ce qui peut influencer l'accumulation du Hg chez le zooplancton est donc critique afin d'avoir une meilleure vue d'ensemble sur le niveau de MeHg retrouvé dans les poissons qui sont consommés par l'Homme.

Les objectifs de ce mémoire étaient de 1) examiner et quantifier l'effet de la concentration en COD aqueuse sur la bioaccumulation du MeHg chez le zooplancton crustacé; et 2) déterminer si la composition de la communauté zooplanctonique est un facteur important pouvant influencer la concentration en MeHg qui sera disponible pour les niveaux trophiques supérieurs. Les hypothèses de départ étaient qu'il existerait effectivement une relation unimodale entre le COD aqueux et la bioaccumulation du MeHg zooplanctonique et que cette bioaccumulation serait maximale dans les lacs à concentration intermédiaire en COD. De plus, nous avons supposé que la dominance de certains taxa (cladocère ou copépode) ou de certaines espèces, comme les *Daphnia*, pourrait augmenter ou diminuer la quantité totale de MeHg retrouvée dans la communauté zooplanctonique due aux différentes stratégies alimentaires exprimées par ces taxa.

Pour réaliser ces objectifs, la concentration en MeHg des communautés zooplanctoniques ainsi que celle de deux taxa spécifiques, les cladocères et les copépodes, ont été analysées pour 11 lacs répartis sur trois régions (Arctique : Alaska, États-Unis d'Amérique; subarctique : Yukon et Territoires du Nord-Ouest, Canada). Ces 11 lacs couvraient un gradient de concentration en COD aqueux allant de 0.3 à 18.8 mg-C-L^{-1}. Plusieurs variables ont aussi été collectées à chaque site, afin de

déterminer quels facteurs environnementaux modulaient le plus fortement la concentration en MeHg de la communauté entière ainsi que celle des taxa spécifiques.

Ce mémoire est composé d'un seul article présenté au chapitre I. Cet article est le produit des résultats obtenus à la suite d'un échantillonnage effectué en Alaska à l'été 2016 et au Yukon et aux Territoires du Nord-Ouest à l'été 2017. Cette introduction a pour objet de présenter des notions de base quant au sujet de notre étude et de démontrer la complexité du cycle du Hg et des processus de bioaccumulation qui l'accompagne dans les milieux arctiques. Elle met aussi l'accent sur la nécessité de mieux comprendre les facteurs affectant la bioaccumulation dans les niveaux trophiques inférieurs tels que le zooplancton crustacé. Le chapitre I est suivi d'une conclusion générale mettant en lumière les points importants de l'étude et présente une piste de recherche intéressante pour de futurs travaux.

CHAPITRE I

ABIOTIC AND BIOTIC DETERMINANTS OF METHYLMERCURY BIOACCUMULATION IN ZOOPLANKTON FROM WESTERN ARCTIC LAKES

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1.1 Abstract

Methylmercury (MeHg) in Arctic aquatic ecosystems is problematic because it can bioaccumulate and biomagnify in food webs, potentially reaching high concentrations in mammals and fish consumed by northern communities. Dissolved organic carbon (DOC) can bind metals, such as mercur, and the role of DOC in determining MeHg bioaccumulation at key intermediate trophic levels in aquatic food webs, such as in crustacean zooplankton, is still poorly understood. Our goals were twofold: 1) to investigate the relationship between lakewater DOC concentration and MeHg bioaccumulation in crustacean zooplankton, and 2) to assess if zooplankton community composition influences availability of MeHg in aquatic food webs. We predicted that zooplankton communities dominated by passive filter feeders, such as Cladocera, would have higher concentrations of MeHg, compared to selectively-feeding copepods. Cladocera have higher feeding rates and their diet contains a larger proportion of bacteria, which can have relatively high levels of MeHg. We collected zooplankton from 11 Arctic lakes along a broad landscape gradient that spanned high (Northwest Territories), intermediate (Alaska) and low (Yukon) lakewater DOC concentrations. Samples were separated into two major taxa, Cladocera and Copepoda, and tested for MeHg. We found support for a unimodal relationship between DOC and MeHg bioaccumulation in zooplankton, with a peak threshold around 8 mg-C-L^{-1}. While MeHg tissue content of bulk communities was best explained by sulphate concentrations in water, MeHg tissue content of taxon-specific groups of cladocerans and copepods were best explained by pH and DOC, respectively. These results are important to consider in the context of climate change, because inputs of MeHg and lake water chemistry, including concentrations of DOC and ions, are expected to increase, and potentially change the bioavailability of MeHg across a range of trophic levels in freshwater ecosystems.

Keywords: methylmercury, Arctic, bioavailability, bioaccumulation, concentration gradient, DOC, threshold, zooplankton, community composition, sulfate, pH

1.2 Introduction

MeHg is a potent neurotoxin that can bioaccumulate and biomagnify in aquatic food webs and reach harmful concentrations in predatory fish eaten by wildlife and humans (AMAP, 2011). Arctic freshwater ecosystems are particularly vulnerable to increases in mercury (Hg) as a result of warming climate because thawing permafrost is predicted to release large amounts of dissolved organic carbon (DOC) and bound mercury (Hg) into rivers and lakes (Jonsson et al., 2017; Schuster et al., 2018). In certain regions of Canada, such as the Yukon Territory, the Northwest Territories (hereafter called NWT), and northern Quebec, local consumption guidelines have been issued by regional health authorities for fish consumption (Poissant et al., 2008) because Hg levels in fish frequently exceed the permitted limits of 0.5 $\mu g\text{-}Hg\text{-}g^{-1}$ (Health and Welfare Canada, 1979, 1984). Given our incomplete understanding of effects of DOC on bioacumulation of MeHg at lower trophic levels, and climate-induced increases in DOC and MeHg loading to Arctic lakes, there is an urgent need to investigate relationships between DOC and MeHg in zooplankton of Arctic lakes.

Dissolved organic carbon (DOC) concentrations in lakes can strongly influence Hg bioavailability and MeHg bioaccumulation in aquatic organisms. Several studies have explored MeHg bioaccumulation along DOC gradients in freshwater benthic macroinvertebrates (amphipods in western Arctic lakes (French et al., 2014), emerging insects (Chaves-Ulloa et al., 2016)), phytoplankton (Gorski et al., 2008), bacteria (Chiasson-Gould et al., 2014), seston (Tsui & Finlay, 2011) and fish (Yellow perch (Driscoll et al., 1994) and European perch (Braaten et al., 2018)). While some of these studies found that MeHg bioaccumulation followed unimodal relationships along a DOC gradient (Driscoll et al., 1994; Chiasson-Gould et al., 2014; French et al., 2014; Chaves-Ulloa et al., 2016), others have found a negative relationship (Gorski et al., 2006; Tsui & Finlay, 2011; Jeremiason et al., 2016). Braaten et al.

(2018), for example, found both a unimodal and a negative relationship between fish mercury concentration and aqueous DOC concentration. A unimodal relationship between MeHg bioaccumulation and DOC concentration is explained by several mechanisms. At lower to intermediate DOC concentrations (2.2 – 8.5 mg-C-L^{-1}; French et al. (2014)), DOC can enhance Hg bioaccumulation by a) increasing the Hg transport from land to lakes, b) stimulating microbial activity, and c) through a combination of these processes, releasing bound Hg available for subsequent methylation (Porcal et al., 2009). At higher DOC concentrations (8.6 – 23.1 mg-C-L^{-1}; French et al. (2014)), DOC can inhibit MeHg bioaccumulation via formation of large, less labile Hg-DOC complexes that are less available for direct biological uptake and methylation (Barkay et al., 1997; Tsui & Finlay, 2011). The unimodal relationship between MeHg bioaccumulation with DOC is also influenced by the composition and lability of DOC, and its association with Hg (Pitter & Chudoba, 1990; French et al., 2014). In French et al. (2014), Hg was primarily associated with a lighter, more labile DOC molecule known as fulvic acid (FA) at lower DOC concentrations. By contrast, refractory humic acid (HA) DOC molecules dominated at higher DOC concentrations (French et al., 2014). French et al. (2014) found that Hg bioaccumulation in amphipods was highest at an intermediate DOC concentration (8.5 mg-C-L^{-1}), because the FA:HA ratio was relatively low (thus, DOC was labile), and therefore, Hg was readily available for methylation and biological uptake (French et al., 2014). However, the degree of generality in the unimodal relationship between DOC and MeHg bioaccumulation in other freshwater organisms is unknown, and has not been specifically tested and compared among specific taxonomic groups of zooplankton.

In crustacean zooplankton, the community composition and/or the prevalence of specific taxonomic groups with different feeding strategies can potentially modulate how MeHg is bioaccumulated along DOC gradients. For example, Todorova et al. (2015) detected a relationship between zooplankton community composition and the

overall MeHg concentration of the community; high concentrations of MeHg were associated with larger zooplankton species, such as *Daphnia*. Similar results were observed by other researchers: two to five-times higher MeHg concentrations were found in *Daphnia*-dominated communities compared to copepod-dominated communities (Pickhardt et al., 2005; Chételat & Amyot, 2009). These taxon-specific differences in zooplankton MeHg concentrations (Cladocera vs. Copepoda) can be explained by differences in feeding strategies (Todorova et al., 2015). Cladocera (Crustacea, Branchiopoda), especially *Daphnia* sp., are highly efficient yet passive filtering grazers (Bertilsson et al., 2003; Riisgård, 2015). As a result, *Daphnia* can have high feeding rates on seston, and may consume a high concentration of bacterial cells in the process (Bertilsson et al., 2003). Copepods (Crustacea, Maxillopoda) tend to use raptorial feeding strategies (Riisgård, 2015), and are efficient at selectively feeding on larger prey such as larger phytoplankton cells, while being inefficient at feeding on bacteria (Bertilsson et al., 2003). Since bacteria are responsible for the degradation of organic matter in the water column, and because organic matter in the water column can strongly bind Hg, it has been suggested that consumption of bacteria by zooplankton is likely an important entry point for MeHg into aquatic food webs (Chételat & Amyot, 2009; AMAP, 2011).

Our objectives were two-fold: 1) to investigate the relationship between lakewater DOC concentration and MeHg bioaccumulation in a pelagic basal component of the aquatic food web, the crustacean zooplankton, and 2) to evaluate how MeHg bioaccumulation in zooplankton taxonomic groups with different feeding strategies (Cladocera vs. Copepoda) varied along a lakewater DOC gradient, in relation to other known factors that influence MeHg concentration in zooplankton. Our study was conducted in lakes that span three Arctic regions in northwestern North America (Yukon Territory, north slope of Alaska, and NWT). For the first objective, we predicted that pelagic crustacean zooplankton would follow a unimodal response

between lakewater DOC concentration and MeHg bioaccumulation (Driscoll et al., 1994; Chiasson-Gould et al., 2014; French et al., 2014; Chaves-Ulloa et al., 2016; Braaten et al., 2018), and that cladocerans response would present a higher maximal MeHg bioaccumulation peak compared to copepods. For the second objective, we predicted that cladoceran-dominated zooplankton communities would have higher total community MeHg concentration compared to copepod-dominated communities, as a result of their differences in feeding strategies (Pickhardt et al., 2005; Chételat & Amyot, 2009; Todorova et al., 2015). Understanding how lower trophic ecological processes affect MeHg bioaccumulation in Arctic aquatic food webs is vital, especially in the context of climate change and accelerated permafrost thawing.

1.3 Methods

1.3.1 Study Sites and DOC Gradient

Eleven study lakes were selected across a northern landscape to represent a broad gradient of DOC concentrations in subarctic and arctic environments, ranging from 0.3 to 18.8 mg-C-L^{-1}. Limnological sampling and zooplankton tissue collection for isotope and MeHg analyses were conducted over two summers. In 2016, six arctic lakes were sampled in Alaska, USA. In 2017, two subarctic lakes were sampled in Yukon, Canada and three subarctic lakes were sampled in the Northwest Territories (NWT), Canada (Table 1.1; Figure 1.1). With the exception of Kluane Lake (Yukon), where we sampled two different sites with known contrasting environmental conditions, we sampled one site per lake. The three lake regions occurred along a continuous subarctic/arctic regional gradient in aqueous DOC concentration: Yukon: from 0.3 to 3.1 mg-C-L^{-1}, Alaska: from 3.2 to 8.1 mg-C-L^{-1}, and NWT: from 10.0 to 18.8 mg-C-L^{-1}.

Table 1.1. Coordinates and various physicochemical information that could be of interest in understanding MeHg bioaccumulation in crustacean zooplankton for each study lake from the Yukon, Alaska, and the Northwest Territories.

Region	Lake name	Latitude	Longitude	Depth (m)	Surface area (km^2)	DOC (mg C L^{-1})	pH	Chl-a ($\mu g\ L^{-1}$)	SO_4^{2-} (mg L^{-1})
Yukon, CA	Kluane M	61.335163	-138.822253	91	433.19	0.8	7.8	0.29	53.81
	Kluane B	61.435191	-139.013320	91	433.19	4.8	8.3	3.19	35.20
	Kathleen	60.585277	-137.320815	111	32.88	0.3	7.9	0.34	54.43
Alaska, USA	ATQ200	70.454750	-156.947900	2.6	2.49	3.2	7.0	4.59	—
	ATQ201	70.327230	-156.806550	3.0	1.38	4.9	7.3	6.51	0.20
	ATQ206	70.415570	-156.981280	3.0	1.73	4.2	7.5	3.51	0.05
	RDC308	69.986350	-156.424450	4.1	0.72	8.1	8.0	2.63	4.51
	RDC309	70.024590	-156.566520	2.1	0.51	8.1	7.4	3.40	0.38
	RDC311	69.996140	-156.689120	2.6	0.66	6.0	8.1	3.34	0.80
Northwest Territories, CA	Big Island	62.093267	-119.866174	—	18.36	10.0	7.7	4.98	3.51
	Sanguez	61.258904	-120.497490	17.8	1.66	17.8	6.9	5.08	13.31
	Ekali	61.291570	-120.593369	10.0	1.94	18.8	7.6	8.72	11.23

The Alaskan lakes were distributed between two local regions: Atqasuk (ATQ), and Reindeer Camp (RDC). Depth (m) represents maximum depth according to literature for Kluane lake. (Barker et al., 2014), Kathleen lake (Mackenzie-Grieve & Post, 2006), Sanguez and Ekali lake (Evans et al., 2005). Depth for Alaskan lakes represent depth recorded on the field in this study. Lake surface area was estimated using the program ImageJ (Rasband, 2011) and satellite image provide by Google Maps (Kluane (2 sites; Kluane M located in the central basin of the lake, near Jacquot Island, and Kluane B located in one of the two arms of Kluane Lake, Brooks Arm; Google (2019f)); Kathleen (Google, 2019g); ATQ200 (Google, 2019a); ATQ201 (Google, 2019j); ATQ206 (Google, 2019c); RDC308 (Google, 2019d); RDC309 (Google, 2019i); RDC311 (Google, 2019b); Big Island (Google, 2019e); Sanguez (Google, 2019h); Ekali (Google, 2019k)).

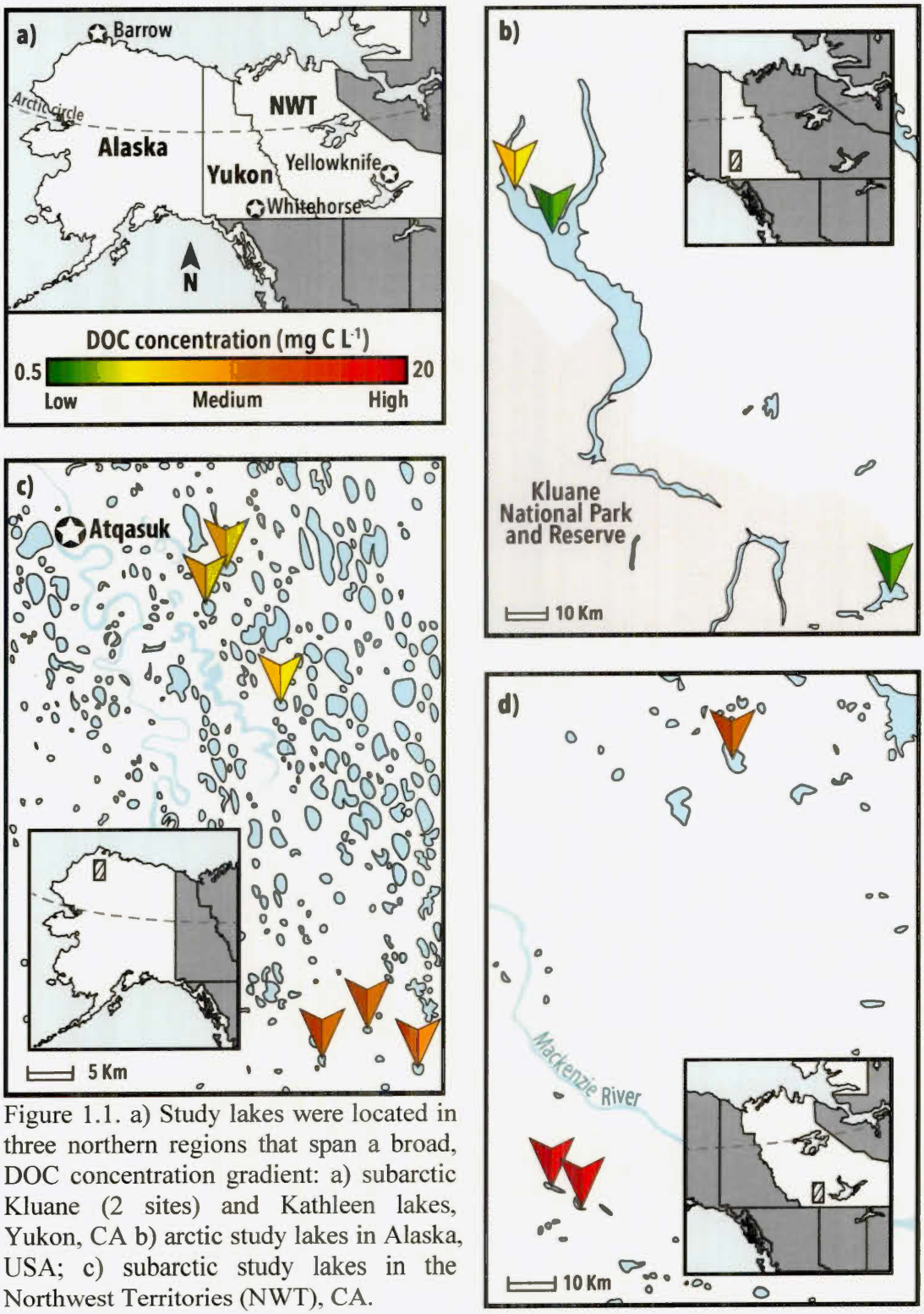


Figure 1.1. a) Study lakes were located in three northern regions that span a broad, DOC concentration gradient: a) subarctic Kluane (2 sites) and Kathleen lakes, Yukon, CA b) arctic study lakes in Alaska, USA; c) subarctic study lakes in the Northwest Territories (NWT), CA.

The Yukon study lakes (n=2) had the lowest aqueous DOC concentrations (0.3 to 3.1 mg-C-L^{-1}) in this study. The two sampling sites within Kluane Lake were spatially distant (~8 km) and differed strongly in hydrology and physicochemical conditions (Barker et al., 2014). Kluane lake is located at the limits between extensive discontinuous permafrost (50 – 90 % of land area underlain by permafrost) and sporadic discontinuous permafrost (10 – 50 % of land area underlain by permafrost) (Canada Center for Mapping. National Atlas information Service, 1995). Kluane Lake is part of the White watershed and is the largest lake contained entirely within Yukon Territory, with a surface area of greater than 400 km^2, mean depth of 31 m and maximum depth of 91 m (Barker et al., 2014). The Kluane M site was located in the central basin of the lake, near Jacquot Island, where the water is clear (0.5 mg-C-L^{-1}). The Kluane B site was located in one of the two arms of Kluane Lake, Brooks Arm, where the water is shallower, warmer, and more tannic (3.1 mg-C-L^{-1} (McKnight, 2017); this study) (Barker et al., 2014). Kluane Lake is underlain by metamorphic bedrock (Lockhart et al., 2005). Given the environmentally divergent conditions and spatial distance between these two study sites within Kluane Lake, we considered Kluane M and Kluane B sites as separate, distinct lake sites for passively-dispersing zooplankton. Kathleen Lake is in a sporadic discontinuous permafrost area, and is part of Alsek watershed (Canada Center for Mapping. National Atlas information Service, 1995). Kathleen Lake is a large, deep lake with clear water (surface area = 33.76 km^2, mean depth = 55.2 m, max depth = 111 m, Secchi depth = 20 to 23 m (Mackenzie-Grieve & Post, 2006); Secchi depth = 13 m (this study)), and represents the lake with the lowest DOC concentration within and among regions in our study. Yukon study lakes are parts of the physiographic region of the Boreal Cordillera (Marshall et al., 1999).

The Alaskan study lakes (n=6) are located on the tundra of the Arctic Coastal Plain. All lakes are part of the Meade River watershed and are in an area of continuous

permafrost (Brown et al., 2000) (90 – 100 % of the land area is underlain by permafrost; Canada Center for Mapping. National Atlas information Service (1995)). The Alaskan lakes are small thermokarst lakes that have formed from degradation of permafrost, and have a mean surface area of 1.25 km^2 (min: 0.51; max: 1.73) (Grosse et al., 2013). The Alaskan study lakes were evenly distributed between two local regions (Atqasuk (ATQ) and Reindeer Camp (RDC)), which are separated by a distance of ~0.5 degree of latitude.

The study lakes in the NWT (n=3) are located in the Dehcho region of the Northwest Territories, near Jean Marie River. These lakes are part of the Upper Mackenzie watershed, and are located in the Taiga Plains physiographic region (Marshall et al., 1999). While Sanguez and Ekali lakes are in an area of sporadic discontinuous permafrost (Canada Center for Mapping. National Atlas information Service, 1995) and are similar in size (1.94 and 1.66 km^2 respectively), Big Island Lake is in an area of extensive discontinuous permafrost (Canada Center for Mapping. National Atlas information Service, 1995) and is much larger in size (18.36 km^2). Ekali and Sanguez lakes have a maximum depth of 10.0 and 17.8 m, respectively (Evans et al., 2005) and both are underlain by sedimentary bedrock (Lockhart et al., 2005).

1.3.2 Physicochemical Water Conditions

The vertical stratification of each study lake was characterised by measuring in-situ vertical profiles of temperature (°C), conductivity (Conduc.; $\mu S\text{-}cm^{-1}$), pH, and dissolved oxygen (DO; $mg\text{-}L^{-1}$) at each study lake site with a multiparameter meter (YSI 6600 Sonde). Surface water samples were collected from each lake site: Chlorophyll-a (Chl-a; $\mu g\text{-}L^{-1}$), DOC ($mg\text{-}C\text{-}L^{-1}$), MeHg ($ng\text{-}L^{-1}$), sulfate ($SO_4^{2-}$; $mg\text{-}L^{-1}$), total Hg (THg; $ng\text{-}L^{-1}$), total nitrogen (TN; $\mu g\text{-}L^{-1}$) and total phosphorus (TP; $\mu g\text{-}L^{-1}$). Analyses of TP, TN and Chl-a were conducted at University of Alberta

Biogeochemical Analytical Service Laboratory (U of A – BASL; Edmonton, Alberta, Canada). TP and TN analyses were performed by Flow Injection Analysis (Lachat QuikChem 8500 FIA automated ion analyser) and Chl-a was extracted with 95 % ethanol on a filter overnight and measured with a Fluorophotometer (ShimadzuRF-1501 spectrofluorophotometer). pH values used in statistical analyses were determined by an autotitrator (Man-Tech PC-Titrate with conductivity probe at U of A – BASL). DOC concentrations of lakewater were measured by persulphate oxidation on a Aurora 1030W (OI Analytical, Texas) at the Biotron Center for Experimental Climate Change Research at Western University (WU – BCECCR; London, Ontario, Canada). For DOC, we also quantified water absorbance at 254-nm (Abs), Fluorescence Index (F.I.) (calculated according to McKnight et al. (2001)), and Specific UV Absorbance (SUVA) (calculated with water Abs and DOC concentration according to Weishaar et al. (2003)). An Aqualog spectrophotometer was used for these analyses (HORIBA Scientific, New Jersey). SO_4^{2-} concentrations in lakewater were analysed by ion chromatography with a DIONEX ion chromatograph combined with an AS14 analytical column at the University of Waterloo Biogeochemistry Lab (Waterloo, Ontario, Canada).

Water samples for total and methyl mercury analyses were collected using the "clean hands-dirty hands" method (US EPA method 1669, 1996). All samples for mercury analyses in water were preserved with ultra-trace HCl (1 % by volume). Unfiltered water samples for mercury analyses were collected from just below the surface (grab sampling) using "clean-hands, dirty hands" technique. Filtered water samples were collected by pumping water with a peristaltic pump through an in-line quartz filter (nominal pore size of 0.4 μm) that was muffled at 500 °C for 15 minutes. Teflon lines, c-flex tubing, and filter cartridges were acid-cleaned with HCl prior to use, and clean lines, filters, and filters were used at each site. Total Hg and MeHg concentrations in lakewater were measured at WU – BCECCR (BCECCR is a CALA-accredited and

ISO-accredited lab; Method Ref. modified from U.S. Environmental Protection Agency method 1631 (THg; EPA (1999)) and method 1630 (MeHg; EPA (1998))). For NWT and Alaskan lakes, one filtered and one unfiltered duplicate were collected for analysis of both total Hg and MeHg aqueous concentration. Variance between duplicates was 1.624×10^{-3} ng-L^{-1} for unfiltered total Hg, 3.211×10^{-3} ng-L^{-1} for filtered total Hg, 6.413×10^{-6} ng-L^{-1} for unfiltered MeHg, and 1.587×10^{-5} ng-L^{-1} for filtered MeHg. Additionally, one field blank and two filter blanks, both for total Hg and MeHg aqueous concentration, were performed for the Alaskan lakes only. No MeHg was detected in either the field or filter blank. For total Hg, filter blanks were below detection limits whereas the field blank total Hg concentration was 0.140 ng-L^{-1}. The method reporting limits were 0.10 ng-L^{-1} for THg and 0.02 ng-L^{-1} for MeHg. A summary table of all analysed parameters with methods and instruments are briefly described in Table A1.

1.3.3 Crustacean Zooplankton

1.3.3.1 Community Composition of Taxonomic and Functional Groups

Field sampling. Crustacean zooplankton community samples were collected from each study lake. In Alaska, the zooplankton were collected at 1-m depths from the center of each lake by filtering 60 L of water through 54 µm mesh Nitex. This sampling approach was employed in the Alaskan study lakes because these ecosystems are shallow (~3 m), and vertical net hauls with our Wisconsin net would have disturbed bottom sediments. The zooplankton samples collected from the Alaskan study lakes are representative of the zooplankton community in the entire water column that is present in these shallow lakes. In Yukon and NWT lakes, a 35 cm-diameter, 54 µm mesh Nitex Wisconsin net was deployed to vertically collect the zooplankton throughout the water column at the center of each lake. In the Yukon

and NWT, the deeper lake depths required vertical sampling with a Wisconsin net to ensure that the water column to at least 5 m below the photic zone was sampled. The exceptions were Kluane B and Big Island, where extreme weather conditions at Big Island and the shallow depth of Kluane B (~3 m) precluded vertical tows. In these two lakes, in place of a vertical tow, we did a horizontal tow by lowering the net at 0.5 m under the surface water and pulling it with the boat at a known speed for a known amount of time (Table A2). In cases where vertical tows were not possible, zooplankton sampling was considered representative of the water column because the lakes were not thermally stratified (Table A2). Following collection, zooplankton were anesthetized with carbon dioxide by adding citrate sodium powder, and preserved with 95 % ethanol.

Taxonomic identification and enumeration. Crustacean zooplankton were identified to the lowest taxonomic level possible, and the relative abundance of taxonomic units was enumerated using the combination of a high-resolution dissecting microscope (Olympus SZX10) and an inverted microscope (Olympus CKX41) (Olympus Canada Inc., Richmond Hill, Ontario, Canada) in the laboratory at the Université du Québec à Montréal (Montréal, QC, Canada). The following taxonomical keys were used; Edmondson (1959) and Thorp & Covich (2010) for general identification, Sandercook & Scudder (1996) and Lesko et al. (2003) for calanoid copepods, Hudson et al. (2003a) for cyclopoid copepods, Hebert (1995) and Brooks (1957) for cladocerans, and Aliberti et al. (2013) as a visual general key. The counting protocol that we used was focused on targeting mature individuals, while allowing for detection of rare species (Girard & Reid, 1990). For this counting protocol, at least 250 individuals were counted so that no more than 50 copepodids per order (cyclopoids and calanoids), no more than 50 individuals per species and no more than 30 nauplii (calanoid and cyclopoid nauplii were combined) were included in the sum to 250 individuals, even though more were counted. Through this protocol, the

volume of subsamples varied between samples, depending on zooplankton density from each lake, and this was subsequently accounted for in our calculations of zooplankton abundance per unit L of water filtered (Indiv.-L^{-1}) from each lake.

Classification of functional groups. To classify zooplankton taxonomic species according to groups of ecological function, we collected functional trait information on almost every species from our study lakes, which included trophic group (carnivore, herbivore, omnivore, omnivore with a preference for herbivory (omni-herbivore), parasitic and immature) and mean body length (Table A3). Functional groups of zooplankton were generated with a dendrogram based on these functional traits, which also included taxon group and order/family as separate criteria (with the exception of *Ceriodaphnia lacustris* that was not included in the Daphniidae family; Figure A1). Cyclopoid and calanoid copepedites were combined as a functional group. Due to its unique trophic group as a parasitic copepod, *Ergasilus sp.* was analyzed as a unique group. Only family and mean body size were used to create functional groups for Cladocera, because with the exception of the predator *Leptodora kindti*, all species within this group were herbivores.

1.3.3.2 Live Animal Tissue Collection

Live zooplankton tissue was collected and frozen in the field for subsequent isotope and MeHg analyses. The same field collection methods used to collect preserved zooplankton for community analyses were used to collect live zooplankton for tissue analyses. To keep the zooplankton alive during transport from the lake to the field laboratory at each regional camp, the live zooplankton were stored in 1 L Nalgene bottles with lake-water and were kept cool and out of direct sunlight on icepacks in coolers. Live zooplankton from the Nalgene bottles was concentrated using a 54 μm

mesh and placed in a 100 ml sample jar to represent a whole community sample (hereafter called Bulk zooplankton sample) that included crustacean zooplankton, rotifers, protozoans, phytoplankton and bacteria. These Bulk zooplankton samples were frozen upon arrival from each lake at the field camp. Animals were not depurated in clean water before being frozen because potential zooplankton MeHg contribution to higher trophic level was of interest.

Additional live zooplankton were collected and stored in Nalgene bottles on ice in coolers for subsequent analysis of isotopic and MeHg tissue content according to taxonomic group. At the field camp, live zooplankton was separated into broad taxonomic groups for each lake. Taxa-selective picking was performed with the aid of a dissecting stereo-microscope (Olympus SZ61TR), with pipettes or tweezers for bigger or floating zooplankton. Zooplankton were manually separated in two major taxa: Cladocera and Copepoda. Individuals from the same taxon were placed in a 2 ml sample tube, while being careful to minimize the inclusion of phytoplankton, rotifers and/or water. When lake zooplankton concentrations were sufficiently dense, two sample tubes of live-picked tissue per taxa were collected. All samples were frozen at -20 °C until laboratory analyses. Samples were subsequently freeze-dried and ground to a fine powder at University of Waterloo (Waterloo, Ontario, Canada).

1.3.3.3 Stable Isotope Analysis

Analyses of stable isotope ratios in zooplankton ($\delta^{13}C$ and $\delta^{15}N$ were performed at the University of Waterloo – Environmental Isotope Laboratory (U of W – EIL; Waterloo, Ontario, CA). This was done by combustion conversion of sample material to gas through a 4010 Elemental Analyzer (Costech Instruments, Italy) coupled to a Delta Plus XL (Thermo-Finnigan, Germany) continuous flow isotope ratio mass

spectrometer (CFIRMS). The average sample mass was ~0.33 mg, and duplicates were run every 10 samples. We present stable isotope ratios as delta values ($\delta^{13}C$; $\delta^{15}N$) in parts per mil (‰) relative to international standards (Pee-Dee Belmnite and N_2 gas, respectively).

1.3.3.4 Mercury Analysis

Methylmercury analysis was performed at WU – BCECC. Analyses were completed in accordance with a modified version of U.S. Environmental Protection Agency method 7473 (EPA, 2007), Lab Method ID – TM.0812. The average sample mass was 15 mg (min: 1.2 mg, max: 36.1 mg). At least one sample per run had an analytical duplicate but most samples had two or more analytical replicates each when enough biomass was availabl. A total of 54 samples were analysed; 15 samples had triplicates and 7 samples had duplicates). Average variance between duplicate and between each runs was 5.366 ng-g^{-1}. A certified reference material (DORM-4; fish protein certified reference material for trace metals from the National Research Council, Ottawa, Ontario) was analysed after every ~11 samples along with duplicate of spiked reference material (mean recovery: 91.1% ± 11.2 SD, n=20). Blanks were analysed at the beginning of each run and following every ~15 samples (n=12). The method reporting limit was 0.024 ng-L^{-1} MeHg and the detection limit was 3.6 ng-L^{-1} MeHg for a 10 mg sample. All zooplankton MeHg tissue concentrations are expressed as ng-g^{-1} dry weight.

1.3.4 Statistical Analyses

1.3.4.1 Zooplankton MeHg Bioaccumulation Factor (BAF)

To determine the DOC threshold concentration at which point MeHg bioaccumulation was maximal, the MeHg bioaccumulation factor (BAF) from water for each zooplankton taxa category was calculated by dividing the MeHg concentration in zooplankton (ng-kg^{-1}) by the unfiltered MeHg concentration in water (ng-kg^{-1}). Aqueous filtered MeHg concentration in the water (FMeHgW) is typically used to calculate BAF for contaminants. However, most concentrations of MeHg in filtered water were lower then detection limits, including those for ATQ201, ATQ206, ATQ200, Kluane M and Kathleen lakes (See Appendix B for more information). Using filtered concentrations of MeHg to calculate BAF would therefore have reduced our number of observations from 12 to 8, and thus unfiltered MeHg concentrations were used to calculate BAF. A three-factor Lorentzian model was performed to assess MeHg bioaccumulation in each of the zooplankton taxon-specific groups (Bulk, Cladocera, and Copepoda) in each of the lakes (French et al. 2014):

$$BAF = \frac{a}{1 + \left(\frac{([DOC]_{water} - X0)}{e^{b}}\right)^{2}}$$

In this equation, a is the inflection point of the curve on the y-axis, $X0$ is the DOC concentration at the inflection point on the x-axis (or the DOC threshold concentration (DOC T_c)), and b is a measure of the spread of the curve. For all three groups of taxa (Bulk zooplankton community, Cladocera and Copepoda), non-linear least squares models were performed using R, version 3.3.3 (R Core Team, 2017) to test the relationship between zooplankton BAF along the DOC gradient. NLS iterations starting values for each taxa-specific parameter estimation were set at the

maximum BAF value for *a*, the maximum DOC value for *X0* and a fixed value of 5 for *b* using separate data sets for each group of taxa. We excluded Kluane M Lake and Kathleen Lake from DOC threshold analyses because results on 2 duplicate samples were either below the method detection limit (0.006 ng-L^{-1}) or at the detection limit; both were 3 times lower than the reporting limit (0.018 ng-L^{-1}).

To assess if model parameters were different between groups of taxa, we compared mean values and the range of confidence intervals. Confidence intervals for each taxon-specific parameter was determined using SAS© software (Version 9.4, SAS Institute Inc. (2015)) with the *NLIN* Procedure. Parameter comparison was determined with a likelihood ratio test using the *TEST* statement in the SAS© software *MODEL* Procedure. If taxon-specific parameters (e.g., $X0_{clado}$ versus $X0_{bulk}$) were not different from each other ($P \geq 0.05$), these were subsequently combined as a unique parameter (e.g., $X0_{bulk+clado}$), and the model was recomputed with the unique combined parameter for taxa groups. Paired comparisons revealed that *a* for Bulk zooplankton was not different from *a* for Cladocera ($p = 0.1597$) or from *a* for Copepoda ($p = 0.0642$). The spread of the unimodal curve (*b*) for Bulk zooplankton (3.99 ± 2.05 S.E.) did not differ from *b* for Cladocera ($p = 0.9782$) or from *b* for Copepoda ($p = 0.2546$) but *b* for Copepoda was different from *b* for Cladocera ($p = 0.0148$). We did not detect differences in DOC threshold concentration (DOC T_c) between Copepoda (8.05 ± 0.43 mg-C-L^{-1}), Cladocera (7.39 ± 2.22 mg-C-L^{-1}), and Bulk zooplankton (5.44 ± 3.78 mg-C-L^{-1}) ($p = 0.7754$) (Table C1; Figure C1 and C2). Consequently, all taxa should have the same value for *X0*. All other parameter estimates were recalculated based on this adjusted DOC T_c, and are shown in Table 1.2 (F value = 20.77; $p < 0.001$). A similar model (three-factor Lorentzian model) was also used to test for a unimodal relationship between water SO_4^{2-} concentration and unfiltered MeHg water concentration, which has been previously shown by Gilmour & Henry (1991) (Figure C3).

1.3.4.2 Regional and Environmental Determinants of Zooplankton MeHg Tissue Concentration

We employed linear regression models to test for environmental variables that were important in explaining zooplankton taxon-specific MeHg tissue concentration. As a first step, we performed Pearson correlation analyses between taxon-specific MeHg concentration (ng-g^{-1}) and all measured environmental variables (Abs, Chl-a, Conduc, DOC, F.I., pH, SO_4^{2-}, SUVA, TP, TN, unfiltered and filtered MeHg in the water (UFMeHgW and FMeHgW respectively), unfiltered and filtered total Hg in the water (UFTHgW and FTHgW respectively), $\delta^{13}C$, and $\delta^{15}N$). We also tested for correlations of taxon-specific MeHg tissue concentration with i) ratio of UFMeHgW:DOC (Chételat et al. 2018), ii) the number of crustacean zooplankton per L (ZPerL), and iii) the number of Cladocera per L (CladPerL). The following variables were *ln* transformed following Shapiro-Wilk tests for normality and analyses of residual plots: SO_4^{2-}, UFTHgW, FTHgW, UFMeHgW, FMeHgW, TN, MeHgW:DOC, ZPerL, CladPerL, Abs., and zooplankton MeHg tissue concentration. Each variable was tested and plotted against taxon-specific untransformed and transformed zooplankton MeHg tissue concentration. If there was a significant correlation or if graph plots suggested a relationship, the variable was included in a multiple regression model set. We searched for outliers, and if a correlation was driven solely by one lake, the variable was not included in the model set (see Appendix B, supplementary statistical methods for these and other data exclusions and limitations (e.g., not enough sample mass for analysis)). Correlation and multiple linear regression model analyses were performed with 11 lakes for Bulk zooplankton (n=11), 9 lakes for Cladocera (n=9), and 8 lakes for Copepoda (n=8).

Bulk zooplankton models included up to six environmental variables (SO_4^{2-}, Conduc., CladPerL, SUVA, and TN). Cladocera models included up to two environmental variables (pH and $\delta^{15}N$). Copepoda models also included up to two environmental

variables (DOC and Abs.). Ratios of unfiltered MeHg in water:DOC (Chételat et al. 2018) was not identified as a significant variable in the correlation analysis, and thus was not included in the model set (see Appendix B for statistical significance of each variable and information on variable exclusion). Similarly, $\delta^{13}C$ was not identified as a significant variable in the correlation analysis for any of the taxa (Figure C4). All candidate model sets are shown in Table 1.4, 1.5 and 1.6. Since aqueous MeHg concentrations can be a strong driver of MeHg in organism, we also tested for correlations between unfiltered MeHg in water and taxa-specific MeHg tissue concentration. Linear regression models were run with R for each taxon-specific group. For each series of taxon-specific models, a null model was included in the model pool. Akaike information criterion corrected for small-sample-size (AICc) and model weights (ω_i) were generated for each model and used in model selection. Variance Inflation Factor and Condition Index were checked for each model to assess for multicollinearity, and residuals were checked for normality. Only one final model had non-normal residuals (Shaprio-Wilk, $W = 0.8022$, $p = 0.0154$), but plots of residuals did not raise concern (see Figure C6), so this model was retained. The final model selected for each taxon-specific group is presented in Figure 1.7, and had the lowest AICc and the highest ω_i.

1.3.4.3 Influence of Zooplankton Communities on MeHg Bioavailability in Aquatic Food Webs

Nonmetric multidimensional scaling (NMDS) community analyses were performed on each of zooplankton taxonomic species abundance and on zooplankton functional group abundance among study lakes for a series of regional and environmental comparisons. Within each taxon-specific group (Bulk zooplankton, Cladocera, and Copepoda), the environmental comparisons for taxonomic and functional group community assemblages were the environmental variables that had been selected in the final zooplankton MeHg tissue concentration multiple regression models: SO_4^{2-}

for Bulk zooplankton, pH for Cladocera, and DOC for Copepoda. For each environmental variable, lakes were categorized as high or low concentration for ellipse categories. High or low concentration categories were determined at the midpoint of the gradient for each of these environmental variables. Region and environmental variables were plotted as ellipses on the NMDS, and differences between ellipses were tested with permutational MANOVA ($P < 0.05$) (Adonis function, *vegan* package in R, number of permutation = 9999; Oksanen et al. (2018)).

1.4 Results

1.4.1 Analysis of Environmental Determinants of MeHg Concentrations in Lakewater

Unfiltered MeHg concentrations in lakewater (UFMeHgW; *ln*-ng-L^{-1}) ranged from 0.011 to 0.079 ng-L^{-1} (mean = 0.029 ng-L^{-1}), and linearly increased with many environmental variables of lakewater, including water colour (Abs, $p = 0.0022$; $R^2 = 0.6289$), Chl-a ($p = 0.0016$; $R^2 = 0.6543$), DOC ($p = 0.0004$; $R^2 = 0.7402$), TN ($p = 0.0001$; $R^2 = 0.7992$), and TP ($p = 0.0208$; $R^2 = 0.4058$) (Figure 1.2). UFMeHgW increased with DOC concentration across the gradient of study lakes (Figure 1.2d). Many of these explanatory variables were collinear, which can make their interpretation difficult. DOC increased linearly with Chl-a ($p = 0.0069$), TN ($p = < 0.0001$) and Abs ($p = < 0.0001$) (Figure 1.3a, b and d). Chl-a also increased linearly with TN ($p = 0.0013$), TP ($p = 0.0015$) and Abs ($p = 0.0194$) (Figure 1.3e, f and g), while TN linearly increased with TP ($p = 0.0169$) and Abs ($p = 0.0012$) (Figure 1.3h and i). SO_4^{2-} decreased linearly with TN ($p = 0.02828$, $R^2 = 0.3675$) and Chl-a ($p = 0.0395$, $R^2 = 0.3238$). We detected a unimodal relationship between SO_4^{2-} concentration and UFMeHgW, with a visual threshold concentration of aqueous SO_4^{2-} of 12.35 mg-L^{-1} (Figure C3).

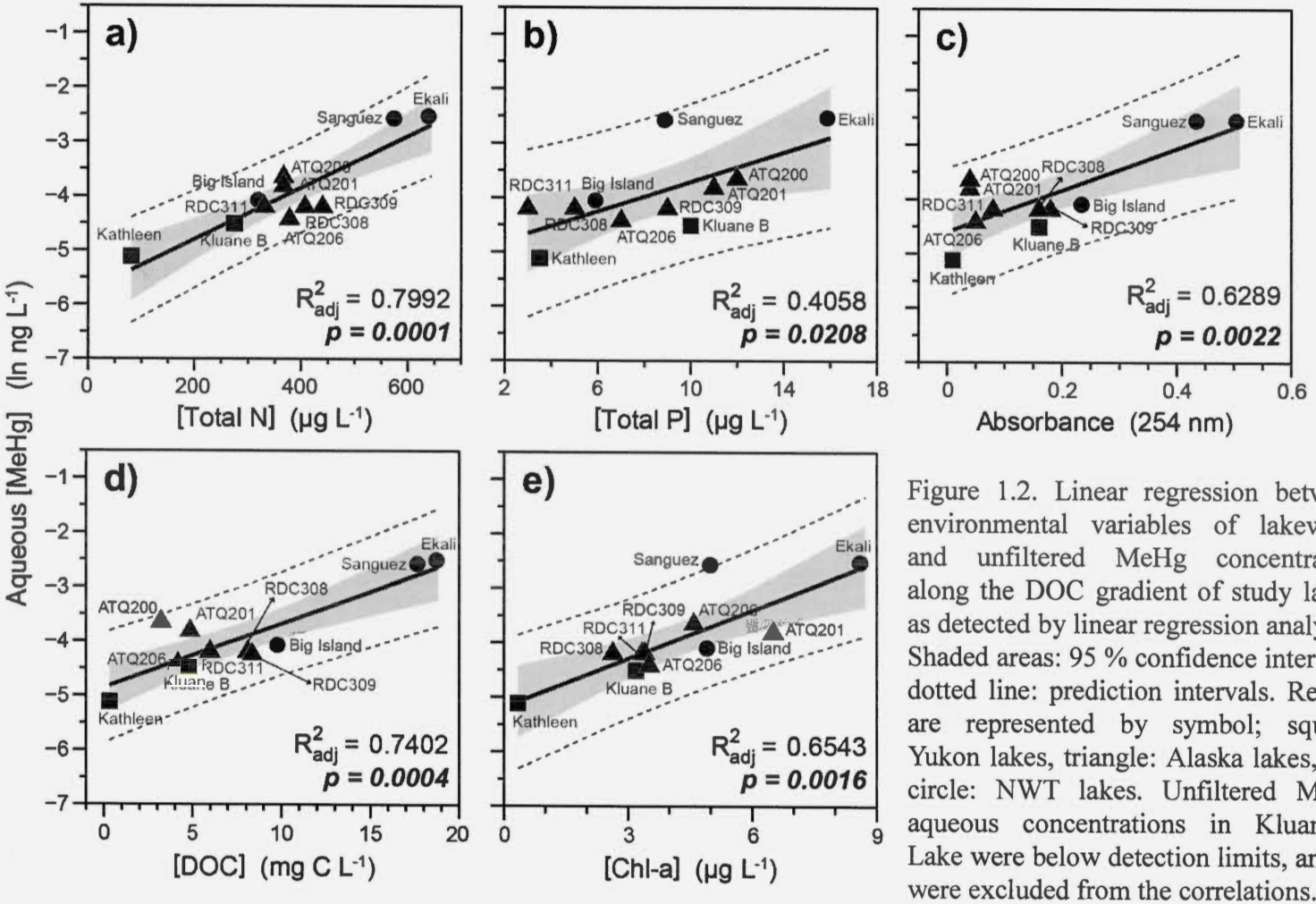


Figure 1.2. Linear regression between environmental variables of lakewater and unfiltered MeHg concentration along the DOC gradient of study lakes, as detected by linear regression analyses. Shaded areas: 95 % confidence intervals, dotted line: prediction intervals. Region are represented by symbol; square: Yukon lakes, triangle: Alaska lakes, and circle: NWT lakes. Unfiltered MeHg aqueous concentrations in Kluane M Lake were below detection limits, and so were excluded from the correlations.

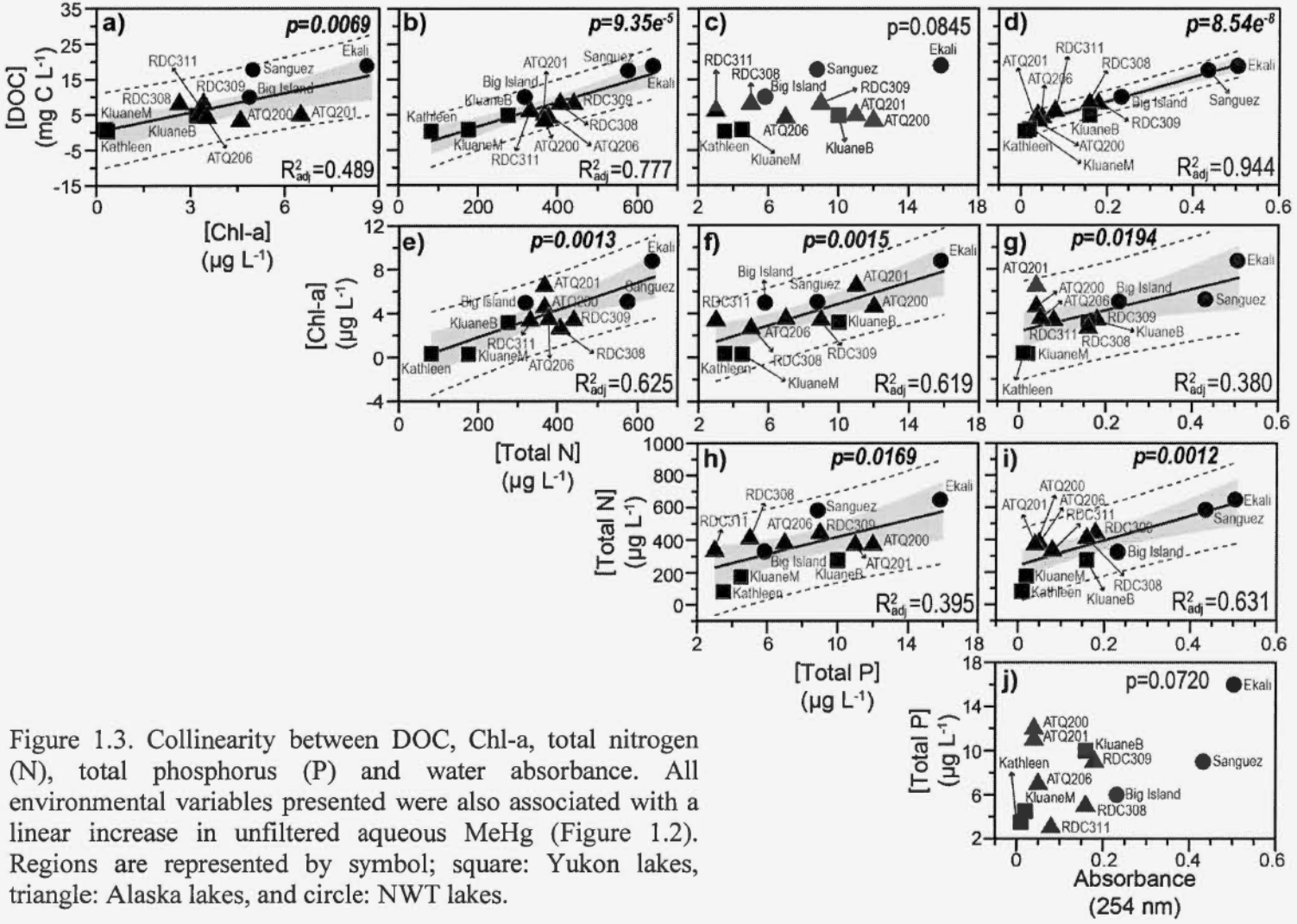


Figure 1.3. Collinearity between DOC, Chl-a, total nitrogen (N), total phosphorus (P) and water absorbance. All environmental variables presented were also associated with a linear increase in unfiltered aqueous MeHg (Figure 1.2). Regions are represented by symbol; square: Yukon lakes, triangle: Alaska lakes, and circle: NWT lakes.

1.4.2 Zooplankton MeHg Bioaccumulation Factor (BAF) and Tissue Concentration

As predicted, the zooplankton MeHg bioaccumulation factor (BAF) followed a unimodal response along the DOC gradient that ranged from 3.22 to 18.80 mg-C-L^{-1} across three northern regions of the western Arctic (Table 1.2; Figure 1.4). Within each taxon-specific group, BAF varied from 8.87 to 112.01 for Bulk zooplankton (mean = 55.29), 38.54 to 221.67 for Cladocera (mean = 117.69), and 7.12 to 428.70 for Copepoda (mean = 136.24). For all taxon-specific groups, the highest MeHg BAF in zooplankton occurred at intermediate DOC concentrations in the Alaskan study lakes (3.22 to 8.10 mg-C-L^{-1}). DOC threshold concentrations (*X0* in the model; DOC T_c in Figure 1.4; mg-C-L^{-1}) were similar between taxon-specific groups (see methods, Table C1; Figure C1 and C2), and converged on 8.01 ± 0.37 S.E. mg-C-L^{-1} (Table 1.2).

Table 1.2. Estimated parameters and statistics for three-factor Lorentzian models of taxon-specific zooplankton groups, based on all taxon having the same value for *X0*.

Taxa	Model Parameter	Parameter Estimate	Std. Error	Confidence Limits	*T*	*p*
Bulk zooplankton	a	66.66	23.43	± 48.58	2.846	**0.009**
	b	4.32	2.10	± 4.28	2.054	0.052
Cladocera	a	153.80	26.41	± 54.75	5.824	**< 0.001**
	b	4.10	0.91	± 1.89	4.503	**< 0.001**
Copepoda	a	343.60	35.19	± 72.90	9.766	**< 0.001**
	b	1.15	0.36	± 0.75	3.157	**0.005**
All taxa	X0	8.01	0.37	± 0.77	21.462	**< 0.001**

Properties of the unimodal response curve: a: curve inflection point on the y-axis; X0: DOC concentration at the inflection point (DOC threshold concentration (DOC Tc)); b: measure of the spread of the curve. Confidence intervals were set at 95 %. Parameters statistical difference (see methods and Figure C2): all taxa statisticaly converged for parameter X0 while parameters a and b were statistically different for each taxa. Response parameters for taxon-specific groups, as estimated with independent X0 for each group, are shown in Table C1 and Figure C1).

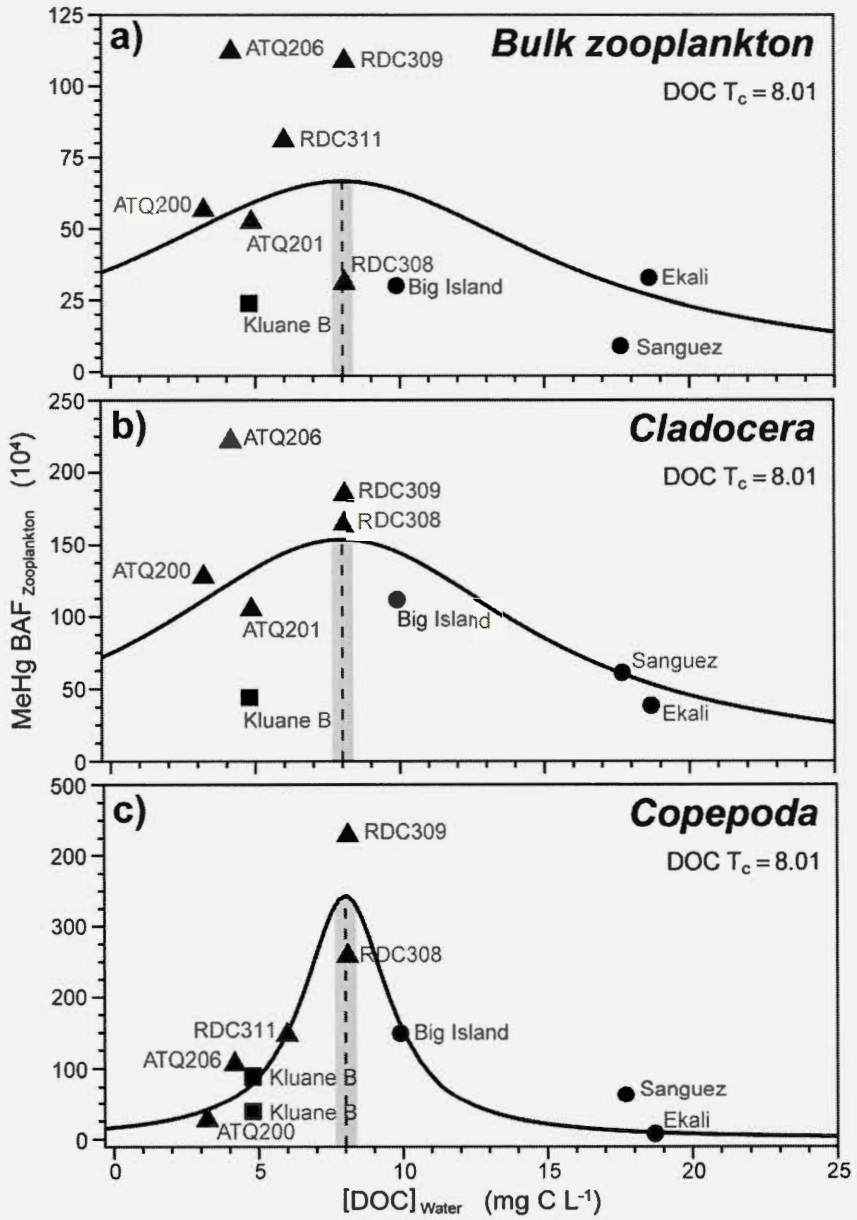


Figure 1.4. Zooplankton MeHg bioaccumulation factor (BAF) in relation to a freshwater gradient in DOC concentration among lakes across three regions of the western Arctic. BAF is the ratio of MeHg zooplankton tissue content (ng-kg^{-1}) to aqueous MeHg concentration (ng-kg^{-1}). A three-factor Lorentzian model was used (French et al. 2014) to determine the DOC threshold concentration (DOC Tc; dashed line; mg-C-L^{-1}) past which MeHg BAF begans to decline in zooplankton along this gradient. The shaded region represents the standard error for DOC Tc. Regions are represented by different symbols, square: Yukon lakes, triangle: Alaska lakes, and circle: NWT lakes. Model parameter statistics are shown in Table 1.2.

The DOC concentration at which MeHg BAF peaked was similar among zooplankton taxa, but other aspects of the unimodal response of MeHg BAF to the DOC gradient differed among zooplankton taxon-specific groups (Table 1.2; Figure 1.4). The amplitude of the unimodal response (*a*) was more pronounced for Copepoda (343.60 ± 35.19 S.E.) compared with Cladocera (153.80 ± 26.41 S.E.) (MeHg BAF; Figure 1.4). This higher maximal MeHg BAF could potentially be explained by differences in trophic levels among taxa (see Figure 1.5), since $\delta^{15}N$ (‰) was most elevated in Copepoda, followed by Bulk zooplankton, and lowest in Cladocera for the same lakes. Moreover, the Lorentzian curve was narrower for Copepoda, with a *b* estimate of 1.16 ± 0.41 S.E., compared with Cladocera (4.09 ± 1.22 S.E.) (Table 1.2). This narrower fit could potentially be explained by the smaller range in Copepoda $\delta^{15}N$ (‰) values compared to Bulk zooplankton and Cladocera. Difference between maximum and minimum $\delta^{15}N$ (‰) values were 2.71, 4.52 and 7.66 for Copepoda, Bulk zooplankton and Cladocera respectively. The unimodal relationships for bulk zooplankton and Cladocera were similar in shape. However, this is not explained by a predominance of Cladocera in the Bulk zooplankton sample (see Figure 1.8). Therefore, our prediction of a unimodal response between zooplankton MeHg BAF and lakewater DOC concentration was supported, but our taxon-specific group finding was opposite to what we had predicted; the amplitude of the unimodal BAF response was higher but narrower in Copepoda compared to Cladocera.

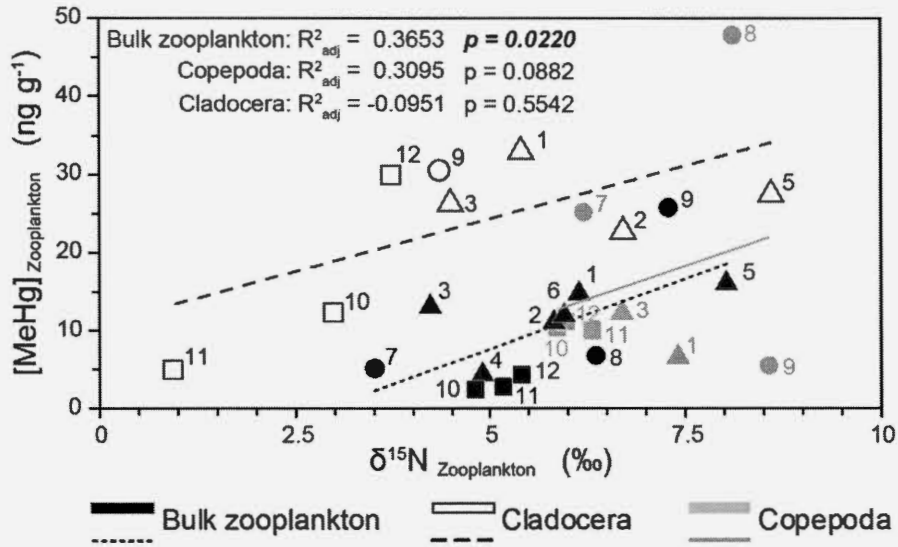


Figure 1.5. Nitrogen isotope ratio ($\delta^{15}N$; ‰) for each taxa in each lake in relation to their respective MeHg tissue concentration (ng-g^{-1}) to show difference in trophic position. Regions are represented by symbols, square: Yukon; triangle: Alaska; and circle: NWT. Lakes are numbered as followed: **1.** ATQ200, **2.** ATQ201, **3.** ATQ206, **4.** RDC308, **5.** RDC309, **6.** RDC311, **7.** Big Island, **8.** Sanguez, **9.** Ekali, **10.** Kluane M, **11.** Kluane B, and **12.** Kathleen. Higher $\delta^{15}N$ values indicate higher trophic position while lower $\delta^{15}N$ values indicate lower trophic level.

Zooplankton MeHg tissue concentration varied from 2.54 to 25.64 ng-g^{-1} in Bulk zooplankton samples (mean = 9.97 ng-g^{-1}), from 4.86 to 46.74 ng-g^{-1} in Cladocera samples (mean = 25.30 ng-g^{-1}), and from 4.28 to 64.31 ng-g^{-1} in Copepoda samples (mean = 21.57 ng-g^{-1}) (Figure 1.6). Within Alaskan lakes, Cladocera in the ATQ lakes had higher MeHg tissue concentrations than the Copepoda, while in the RDC lakes, the opposite was observed (i.e. higher MeHg tissue concentration in Copepoda than in Cladocera). High MeHg tissue concentration did not always result in high BAF. In the NWT lakes, zooplankton MeHg tissue concentrations were high in Ekali and Sanguez lakes, but zooplankton MeHg BAF in these two lakes were among the lowest observed, because of relatively high MeHg concentrations in water (Figure 1.6a, b). Kluane M and Kathleen Lake (Yukon) were excluded from DOC threshold models because of uncertainty in UFMeHgW concentration that were below analytical detection limits (see methods). Although we were unable to quantify BAFs

in Kathleen Lake, tissue MeHg concentrations in Cladocera were high. This was especially notable given the very low DOC concentration (Figure 1.6a, b).

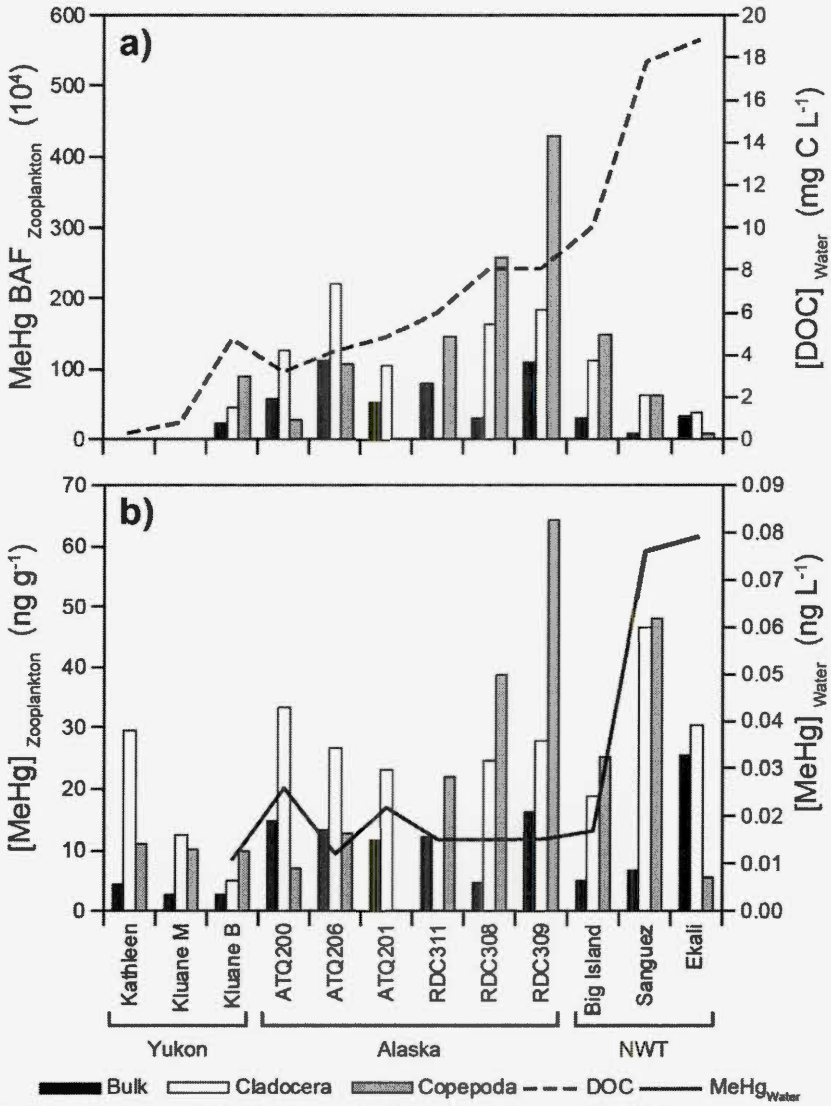


Figure 1.6. Zooplankton MeHg bioaccumulation factor (BAF) compared to lake DOC concentration (dashed line) (a), and zooplankton MeHg concentration compared to unfiltered aqueous MeHg concentration (UFMeHgW; solid line) (b) among lakes. UFMeHgW concentration is following a similar pattern as DOC concentration, increasing as DOC increase. Uncertainty in UFMeHgW concentration in Kluane M and Kathleen lakes did not allow calculation of BAFs in these lakes. Lakes are presented according to a region-specific DOC gradient.

Aqueous MeHg concentration was not a significant predictor for MeHg concentration for any taxa (all p-value > 0.09; Table 1.3; Figure C5). Only one environmental variable was retained for explaining zooplankton MeHg tissue concentration (ng-g^{-1}) in the final regression model for each taxon-specific group (Table 1.4, 1.5 and 1.6): SO_4^{2-} for Bulk zooplankton, pH for Cladocera, and DOC for Copepoda (Figure 1.7). Bulk zooplankton MeHg concentration was best predicted by a negative relationship with SO_4^{2-} water concentration (slope = -0.24, R^2_{adj} = 0.77), such that higher MeHg concentration in Bulk zooplankton samples were associated with lower lakewater SO_4^{2-} concentrations (Figure 1.7a.). A negative linear relationship was also observed between lakewater pH and Cladocera MeHg concentration (slope = -1.08; R^2_{adj} = 0.47; Figure 1.7b.). However, MeHg concentration in Copepoda (*ln*-ng-g^{-1}) was positively linearly related with lakewater DOC concentration (mg-C-L^{-1}; slope = 0.099; R^2_{adj} = 0.76; Figure 1.7c.), suggesting that higher DOC concentration may promote higher MeHg concentration in Copepoda, but not necessarily in Cladocera.

Table 1.3. Aqueous unfiltered MeHg concentration and environmental predictors of zooplankton MeHg tissue concentration, as determined by model selection for multiple regression analyses.

Model	Variable	Err df	Mod df	R^2_{adj}	F	p
Bulk zooplankton	UFMeHgW	7	3	-0.13	0.07	0.804
Cladocera	UFMeHgW	5	3	0.35	4.27	0.094
Copepoda	UFMeHgW	4	3	0.18	2.09	0.222

Zooplankton tissue MeHg concentration, aqueous unfiltered MeHg (UFMeHgW) and variables indicated by * were *ln* transformed. RDC309 was excluded from both Cladocera and Copepoda, RDC311 was exclude only from Cladocera and RDC308 and ATQ201 were exclude from Copepoda. Visual representation are presented in Figure C5.

Table 1.4. Model selection for best environmental variables explaining Bulk methylmercury concentration in crustacean zooplankton samples.

Model	Variable	Err df	Mod df	AICc	ΔAICc	-2 log likelihood	ω_i	R^2_{adj}	F	*p*
1	SO_4^{2-}	8	3	13.55	0	0	0.74	0.77	31.61	**0.0005**
7	SO_4^{2-} + Conduc.	7	4	18.61	5.06	2.20	0.06	0.76	15.54	**0.0027**
8	SO_4^{2-} + TN	7	4	18.76	5.22	2.27	0.05	0.76	15.24	**0.0028**
6	SO_4^{2-} + SUVA	7	4	19.11	5.56	2.41	0.05	0.75	14.61	**0.0032**
9	SO_4^{2-} + CladPerL	7	4	19.40	5.86	2.54	0.04	0.74	14.08	**0.0035**
3	Conduc.	9	3	20.79	7.24	3.14	0.02	0.58	14.55	**0.0041**
5	CladPerL	9	3	21.69	8.14	3.54	0.01	0.54	12.69	**0.0061**
15	TN + CladPerL	8	4	22.99	9.44	4.10	0.01	0.64	9.794	**0.0071**
14	Conduc. + CladPerL	8	4	23.35	9.80	4.26	0.01	0.63	9.344	**0.0081**
2	SUVA	9	3	23.39	9.84	4.27	0.01	0.46	9.585	**0.0128**
12	SUVA + CladPerL	8	4	24.06	10.52	4.57	$3.83e^{-3}$	0.60	8.506	**0.0105**
10	SUVA + Conduc.	8	4	25.19	11.65	5.06	$2.18e^{-3}$	0.56	7.287	**0.0158**
13	Conduc + TN	8	4	25.32	11.78	5.11	$2.04e^{-3}$	0.55	7.154	**0.0165**
19	SO_4^{2-} + Conduc. + TN	6	5	26.29	12.74	5.53	$1.26e^{-3}$	0.76	10.41	**0.0086**
11	SUVA + TN	8	4	27.07	13.52	5.87	$8.55e^{-4}$	0.48	5.521	**0.0312**
21	SO_4^{2-} + TN + CladPerL	6	5	27.14	13.59	5.90	$8.25e^{-4}$	0.74	9.403	**0.0110**
16	SO_4^{2-} + SUVA + Conduc.	6	5	27.15	13.61	5.91	$8.18e^{-4}$	0.74	9.384	**0.0111**
17	SO_4^{2-} + SUVA + TN	6	5	27.28	13.73	5.96	$7.68e^{-4}$	0.73	9.342	**0.0115**
0	—	10	2	27.44	13.89	6.03	$7.09e^{-4}$	—	—	—
20	SO_4^{2-} + Conduc. + CladPerL	6	5	27.54	13.99	6.08	$6.74e^{-4}$	0.73	8.953	**0.0128**
4	TN	9	3	28.04	14.49	6.29	$5.24e^{-4}$	0.18	3.176	0.1084
18	SO_4^{2-} + SUVA + CladPerL	6	5	28.05	14.50	6.30	$5.22e^{-4}$	0.71	8.405	**0.0144**
24	SUVA + TN + CladPerL	7	5	28.62	15.08	6.55	$3.92e^{-4}$	0.65	7.055	**0.0160**
25	Conduc. + TN + CladPerL	7	5	28.78	15.23	6.61	$3.63e^{-4}$	0.64	6.924	**0.0168**

Table 1.4 (*continued*)

Model	Variable	Err df	Mod df	AICc	ΔAICc	ω_i	-2 log likelihood	R^2_{adj}	F	*p*
23	SUVA + Conduc. + CladPerL	7	5	30.07	16.53	$1.90e^{-4}$	7.18	0.59	5.894	**0.0250**
22	SUVA + Conduc. + TN	7	5	31.81	18.26	$7.98e^{-5}$	7.93	0.53	4.696	**0.0422**
30	SUVA + Conduc. + TN + CladPerL	6	6	39.18	25.63	$2.00e^{-6}$	11.13	0.60	4.784	**0.0447**
29	SO_4^{2-} + Conduc. + TN + CladPerL	5	6	40.73	27.18	$9.23e^{-7}$	11.80	0.73	6.956	**0.0283**
26	SO_4^{2-} + SUVA + Conduc. + TN	5	6	40.77	27.22	$9.03e^{-7}$	11.82	0.73	6.919	**0.0286**
28	SO_4^{2-} + SUVA + TN + CladPerL	5	6	41.86	28.31	$5.23e^{-7}$	12.30	0.69	6.075	**0.0370**
27	SO_4^{2-} + SUVA + Conduc. + CladPerL	5	6	42.14	28.60	$4.55e^{-7}$	12.42	0.68	5.872	**0.0395**
31	SO_4^{2-} + SUVA + Conduc. + TN + CladPerL	4	7	70.42	56.87	$3.30e^{-13}$	24.70	0.67	4.618	0.0817

Environmental variables included in each model were selected fallowing correlation and graphs analyses. Error degree of freedom (Err df) and model degree of freedom (Mod df) are shown. MeHg in Bulk zooplankton, SO_4^{2-} and CladPerL were *ln* transformed for all models. Ekali lake was excluded from all models. SO_4^{2-} concentration was lower than detection limits for ATQ200 (See Appendix B). Models are presented from the lowest to the highest ΔAICc score.

Table 1.5. Model selection for best environmental variables explaining Cladocera methylmercury concentration.

Model	Variable	Err df	Mod df	AICc	ΔAICc	ω_i	-2 log likelihood	R^2_{adj}	F	*p*
1	pH	7	3	20.86	0	0.63	0	0.47	8.156	**0.0245**
0	—	8	2	23.01	2.15	0.22	0.94	—	—	—
2	$\delta^{15}N$	4	3	23.71	2.85	0.15	1.24	0.58	7.822	**0.0490**
3	pH + $\delta^{15}N$	3	4	53.52	32.67	$5.10e^{-8}$	14.19	0.45	3.073	0.1878

MeHg in Cladocera was *ln* transformed for all models. Error degree of freedom (Err df) and model degree of freedom (Mod df) are shown. Ekali, RDC309 and RDC311 lakes were excluded from all models. $\delta^{15}N$ data were not available for RDC308, Big Island and Sanguez lakes (See Appendix B for more information). Models are presented from the lowest to the highest ΔAICc score.

Table 1.6. Model selection for best environmental variables explaining Copepoda methylmercury concentration.

Model	Variable	Err df	Mod df	AICc	ΔAICc	ω_i	-2 log likelihood	R^2_{adj}	F	*p*
1	DOC	6	3	13.85	0	0.92	0	0.76	22.65	**0.0031**
2	Abs.	6	3	20.66	6.81	0.03	2.96	0.43	6.23	**0.0468**
0	—	7	2	20.75	6.91	0.03	3.00	—	—	—
4	DOC + Abs.	5	4	21.87	8.02	0.02	3.48	0.75	11.56	**0.0133**

MeHg in Copepoda and Absorbance (Abs.) were *ln* transformed for all models. Error degree of freedom (Err df) and model degree of freedom (Mod df) are shown. Ekali, RDC309, RDC308 and ATQ201 lakes were excluded from all models. Filtered MeHg concentration in the water (FMeHgW) was also a variable of interest, but since FMeHgW concentrations were lower than detection limits for ATQ200, Kluane M and Kathleen lakes (See Appendix B for more information) we did not have enough data to include FMeHgW in the model set. Model are presented from the lowest to the highest ΔAICc score.

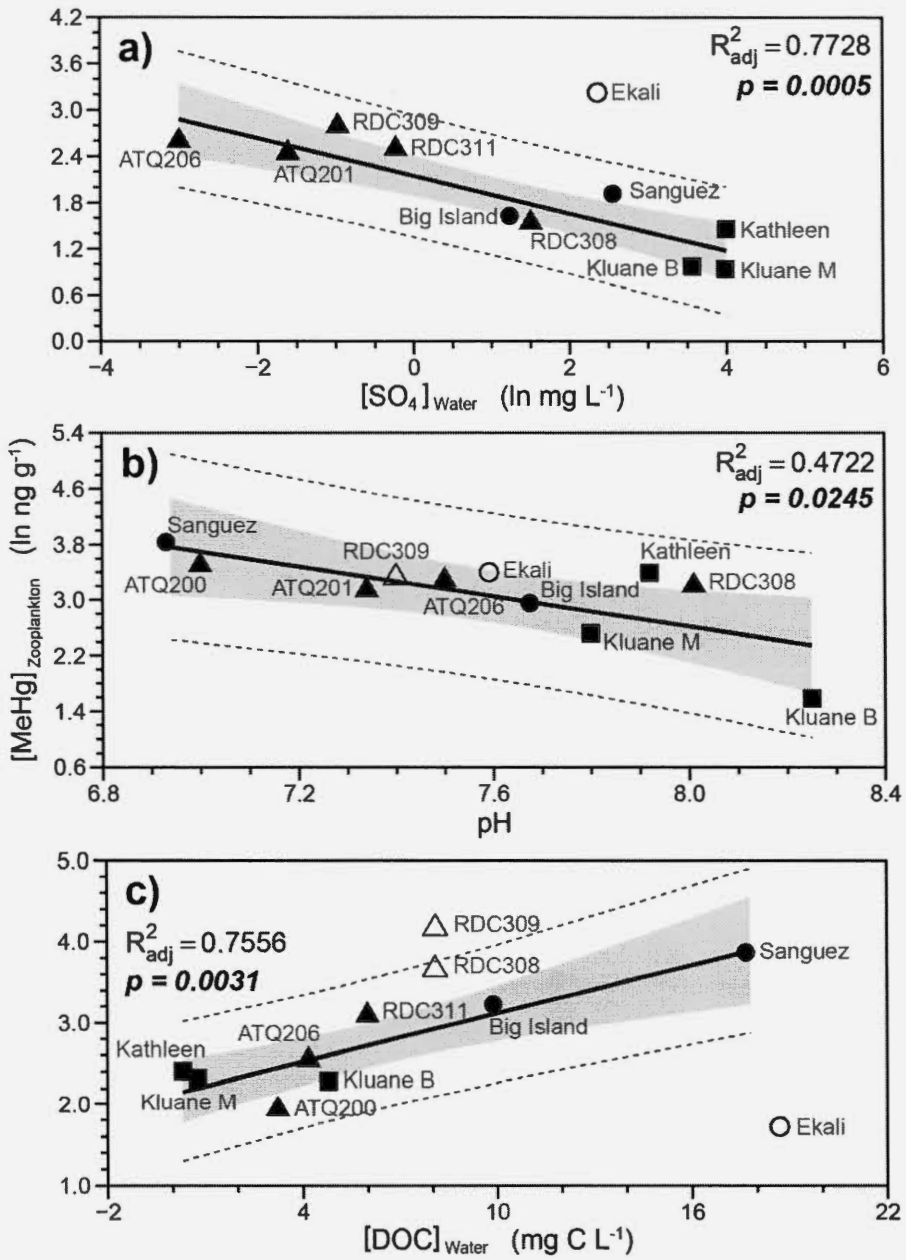


Figure 1.7. Linear regression models for relationships between a) Bulk zooplankton, b) Cladocera and c) Copepoda MeHg tissue concentration and model-selected environmental variables. Shaded areas: 95 % confidence intervals, dotted line: prediction intervals. Regions are represented by different symbols, square: Yukon lakes, triangle: Alaska lakes, and circle: NWT lakes. Lakes represented by open symbols are lakes that were *a priori* excluded from regression models, but included on the graphs for comparative purposes (see data exclusions in Appendix B).

1.4.3 Influence of Zooplankton Communities on MeHg Bioavailability in Aquatic Food Webs

Most lakes were dominated by Copepoda, with the exception of ATQ206, ATQ201 and RDC309 that were dominated by cladocerans. Of these three cladoceran-dominated lakes, two of the lakes, ATQ206 and RDC309, had high MeHg BAF in Bulk zooplankton (Figure 1.8). All three of the cladoceran-dominated lakes had an abundance of the cladoceran *Bosmina longirostris* (ATQ206: 89 %, ATQ201: 95 %, RDC309: 86 %; Figure C7b, c and e). Lakes in the NWT,, as well as RDC308 and Kluane B, were dominated by Copepoda, and had lower MeHg BAF in Bulk zooplankton. With the exception of Kluane B, copepod assemblages in these copepod-dominated lakes were represented by larval stage, nauplii (RDC308: 80 %, Ekali: 89 %, Sanguez: 97 %, Big Island: 90 %; Figure 1.8). Both RDC311 and RDC308 were also dominated by nauplii (78 % and 80 % respectively). In Kluane B, 78 % of the copepod assemblages were immature stage copepodites (included in the Copepoda category in Figure 1.8; Figure C7h). All zooplankton communities in lakes in the Yukon were dominated by copepodites (Kluane M: 77 %, Kluane B: 78 %, Kathleen: 76 %; Figure C7g, h, and i), with a higher percentage of cyclopoid copepodites in both Kluane M and Kluane B (41 % and 54 % respectively), whereas calanoid copepodites represented 51 % of the zooplankton community in Kathleen Lake. Lakes in Alaska had a lower number of crustacean zooplankton species (mean = 4.8) than lakes in either Yukon or NWT (mean = 9 and 8 respectively) (Figure C7).

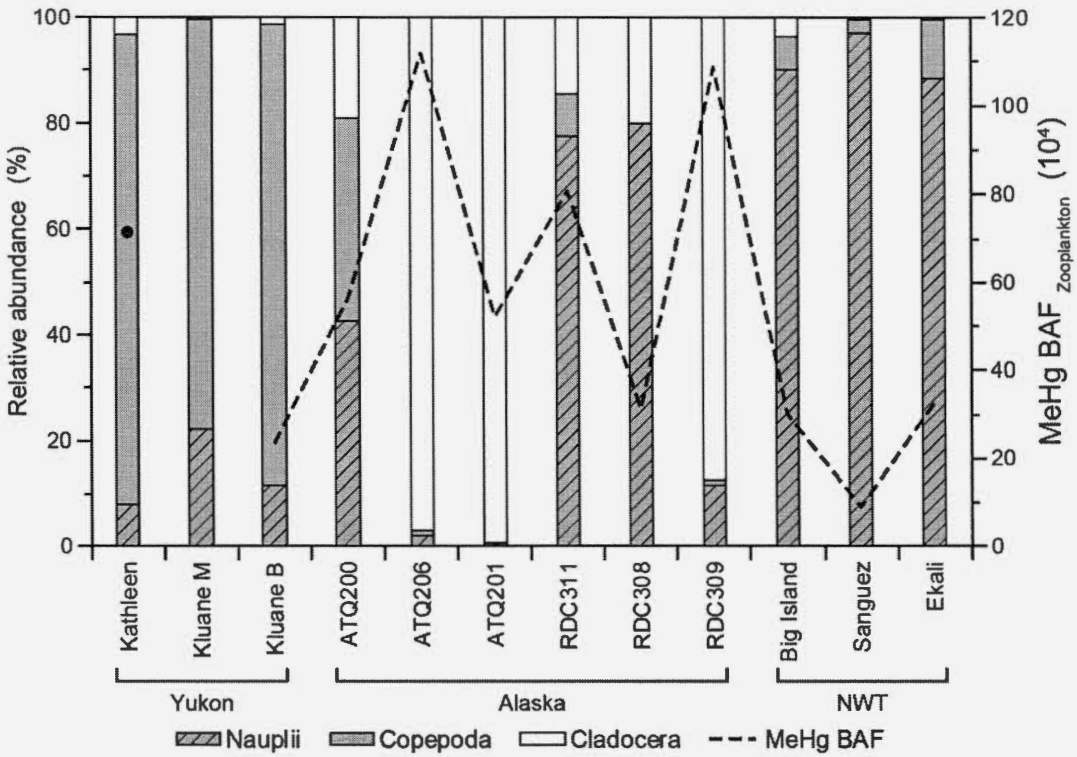


Figure 1.8. Percentage of the zooplankton community comprised by Copepoda and the Cladocera for each lake, and compared to Bulk zooplankton MeHg BAF (dashed line). The dashed region for taxa Copepoda represents the percentage of the crustacean zooplankton community that was nauplii, the larval stage of Copepoda. Copepodites, the immature stage of Copepoda, are included in the category Copepoda in this figure. The dashed line represents the MeHg BAF (10^4) for Bulk zooplankton. Species-specific relative abundances are presented in Figure C7.

Zooplankton communities along the DOC study gradient differed by region, both taxonomically ($p = 0.008$) and according to functional group ($p = 0.007$; *PERMANOVA*; Figure 1.9a,b). Of the 30 identified species, only three species were found in all three regions (*Leptodiaptomus pribilofensis*, *Daphnia longiremis* and *Chydorus sphaericus*). Four species were found in two of the three regions (*Cyclop scutifer*, *Bosmina longirostris*, *Alona sp.* and *Diaphanosoma branchyurum*), and all other species were unique to their region (Figure C7). For functional groups of zooplankton, the majority of taxa were herbivores. There was at least one representive of each trophic feeding group in each region, except for the parasitic

species *Ergasilus sp.* that was only found in Ekali Lake in the NWT (Figure C7). However, each region had different combinations of functional traits, resulting in divergence in the distribution of zooplankton functional groups among regions (Figure 1.9b).

Because the concentration of SO_4^{2-} in lakewater explained Bulk zooplankton MeHg tissue concentration (Figure 1.7a), we compared zooplankton communities between lakes with low (from 0 to 27.49 mg-L^{-1}) and high (from 27.50 to 55 mg-L^{-1}) SO_4^{2-} concentrations (NMDS, Figure 1.9c, d). Although SO_4^{2-} concentration in lakewater was important for explaining the distribution of taxonomic ($p = 0.016$, *PERMANOVA*, Figure 1.9c) and functional groups ($p = 0.017$, *PERMANOVA*, Figure 1.9d) of zooplankton among lakes, these patterns were likely explained by a combination of both region and SO_4^{2-}, because all lakes with high SO_4^{2-} concentrations were in the Yukon. Our findings suggest that MeHg tissue concentrations in Bulk zooplankton samples are more likely explained by physicochemical processes that affect SO_4^{2-} and MeHg than by zooplankton community composition (Figure 1.9a,b).

Lakewater pH best explained MeHg tissue concentration in Cladocera MeHg (Figure 1.7b), so we compared cladoceran assemblages from lakes with lower (6.90 to 7.57) and higher (7.58 to 8.25) pH (NMDS, Figure 1.9e,f). Lakewater pH did not structure taxonomic composition of cladoceran species among study lakes ($p = 0.102$, *PERMANOVA*, Figure 1.9e). However, lakewater pH explained among-lake differences in the distribution of cladoceran functional groups ($p = 0.016$, *PERMANOVA*, Figure 1.9f). Species detected in the lower-pH category were mainly non-*Daphnia* species. The functional group uniting *Daphnia pulex/pluricaria* and *Daphnia mandotae* (functional group 40 in Figure 1.9f) was the only group including *Daphnia* that was included within the lower-pH ellipse. Therefore, daphniid-dominated cladoceran assemblages in higher-pH lakes had lower MeHg tissue

content while cladoceran assemblages that were dominated by non-daphniids in lower-pH lakes had higher MeHg tissue content (Figure 1.7b, Figure 1.9f). Our findings suggest that both pH and the composition of functional cladoceran groups in lake zooplankton communiites could influence MeHg tissue concentration in Cladocera.

Lakewater DOC concentration best explained Copepoda MeHg tissue concentration (Figure 1.7c), and so we compared copepod assemblages from lakes with lower (0 to 9.49 mg-C-L^{-1}) and higher (9.50 to 19 mg-C-L^{-1}) DOC concentrations. However, DOC was not an important determinant of taxonomic or functional group composition of Copepoda among lakes (Figure C8). This finding suggests that DOC concentration did not affect Copepoda MeHg tissue concentration through species or functional group community composition, but rather through interactions between DOC and Hg.

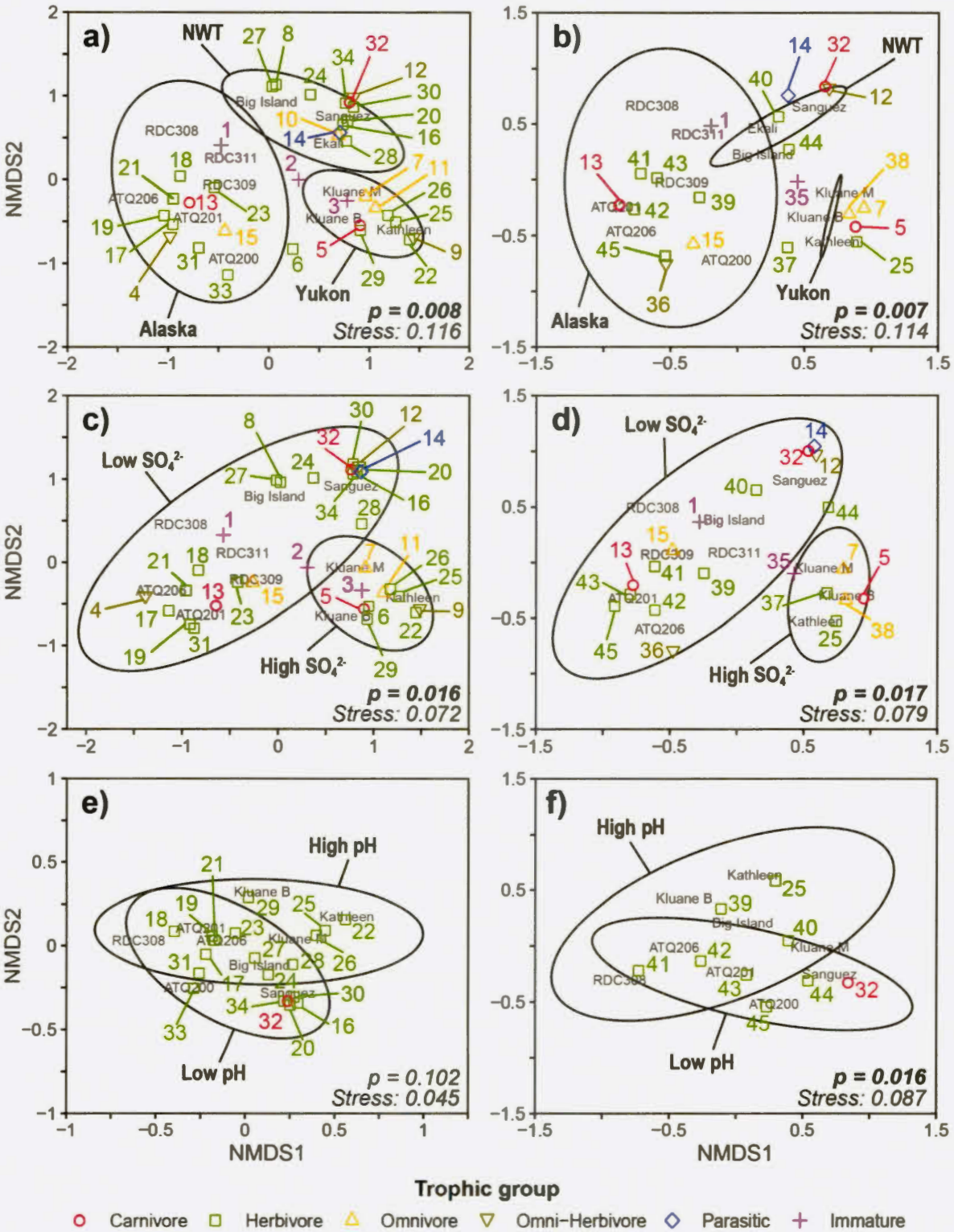

a)
NWT
Alaska
Yukon
p = 0.008
Stress: 0.116
b)
NWT
Alaska
Yukon
p = 0.007
Stress: 0.114
c)
Low SO4 2-
High SO4 2-
p = 0.016
Stress: 0.072
d)
Low SO4 2-
High SO4 2-
p = 0.017
Stress: 0.079
e)
High pH
Low pH
p = 0.102
Stress: 0.045
f)
High pH
Low pH
p = 0.016
Stress: 0.087
NMDS1
NMDS2
Big Island
Sanguez
Ekali
Kluane M
Kluane B
Kathleen
RDC308
RDC311
RDC309
ATQ206
ATQ201
ATQ200
Trophic group
Carnivore
Herbivore
Omnivore
Omni-Herbivore
Parasitic
Immature

Figure 1.9. NMDS biplots of freshwater zooplankton community composition among lakes across three western Arctic regions according to taxonomic species abundance (left panels: a, c, e) and functional group abundance (right panels: b, d, f). The distribution of species and functional groups in whole zooplankton communities, representative of the composition of Bulk zooplankton MeHg samples, was determined by region (a, b) and by SO_4^{2-} concentration (c, d). The distribution of functional groups (f), but not species (e), in cladoceran assemblages was determined by pH. Species ordination positions are represented by numbers: ***Juvenile copepod stages:*** **1.** Nauplii, **2.** Copepedite calanoida, **3.** Copepedite cyclopoida; ***Calanoid copepods:*** **4.** *Eurytemora sp.*, **5.** *Heterocope septentrionalis*, **6.** *Leptodiaptomus pribilofensis,* **7.** *Leptodiaptomus sicilis*, **8.** *Leptodiaptomus siciloides,* **9.** *Senecella calanoides*; ***Cyclopoid copepods: 10.*** *Acanthocyclops robustus/vernalis,* **11.** *Cyclops scutifer*, **12.** *Eucyclops agilis*, **13.** *Microcyclops rubellus*; ***Other copepods:*** **14.** *Ergasilus sp.*, **15.** *Herpacticoida sp.*; ***Cladocerans :*** **16.** *Acroperus harpae*, **17.** *Alona sp.*, **18.** *Bosmina longirostris*, **19.** *Camptocercus sp.*, **20.** *Ceriodaphnia lacustris*, **21.** *Chydorus sphaericus*, **22.** *Daphnia ambigua*, **23.** *Daphnia longiremis*, **24.** *Daphnia mendotae*, **25.** *Daphnia middendorffiana*, **26.** *Daphnia parvula*, **27.** *Daphnia pulex/pluricaria*, **28.** *Diaphanosoma branchyurum*, **29.** *Eubosmina longispina*, **30.** *Graptoleberus testudinaria*, **31.** *Holopedium gibberum*, **32.** *Leptodora kindti*, **33.** *Macrothrix sp.,* and **34.** *Sida crystallina*. Numbers over 34 represent species groups that were clustered according to ***functional traits:*** Order/Family, trophic feeding group, and mean body length (see Table A3 and Figure A1): **35.** *2* and *3*, **36.** *4* and *9*, **37.** *6* and *8*, **38.** *10* and *11*, **39.** *22*, *23* and *26*, **40.** *24* and *27*, **41.** *18* and *29*, **42.** *17*, *21* and *30*, **43.** *16* and *19*, **44.** *20*, *28* and *33*, and **45.** *31* and *34*. Trophic groups are represented by shape; circles for carnivore, square for herbivores, triangles for omnivore, upside down triangle for omnivore with herbivory preferences, diamond for parasites and cross for immature. In a) and b), all lakes were included in the analyses. As for the model-selected environmental variables Ekali and ATQ200 lakes were excluded from the analyses in c) and d) because Ekali Lake qualified as an outlier for MeHg concentration in Bulk zooplankton and was uniquely dominated by parasitic copepods and because SO_4^{2-} was below detection limit in ATQ200 Lake. Similarly, Ekali, RDC309 and RDC311 were excluded from the analyses in e) and f), because Cladocera from Ekali and RDC309 lakes represented a mixed sample of inshore and offshore individuals and because lack of sufficient cladoceran biomass in RDC311 Lake did not allow MeHg tissue analyses.

1.5 Discussion

We provide a first study to address MeHg bioaccumulation in taxon-specific crustacean zooplankton in Western Arctic lakes across a DOC gradient (Figure 2.1), and consider the potential role of community composition in determining MeHg content of tissue samples. Consistent with our prediction, we detected a unimodal relationship between crustacean zooplankton MeHg bioaccumulation and DOC concentration; MeHg bioaccumulation peaked at a threshold of 8 mg-C-L^{-1}. Our taxon-specific group findings were opposite to what we had predicted – the amplitude of the unimodal BAF response was higher, but narrower, in Copepoda compared to Cladocera along DOC lake gradient that we examined. Our stable isotope data indicated that this difference in amplitude was likely because of differences in trophic position, rather than because of passive versus selective feeding strategy differences between Cladocera and Copepoda. Lakewater DOC was positively correlated with aqueous MeHg concentration and best explained Copepoda MeHg tissue concentration, but DOC was not a significant predictor of either Cladocera or Bulk zooplankton MeHg tissue concentrations. Instead, pH best explained Cladocera MeHg tissue concentration and the distribution of cladoceran functional groups among lakes: daphniid-dominated cladoceran assemblages in higher-pH lakes had lower MeHg tissue content while cladoceran assemblages that were dominated by non-daphniids in lower-pH lakes had higher MeHg tissue content. Not surprisingly, Bulk zooplankton tissue samples that were comprised of all crustacean taxonomic groups, as well as rotifers, protozoans, phytoplankton and bacteria, had a lower MeHg BAF compared to the taxon-specific groups. Bulk zooplankton tissue MeHg concentrations were explained by regional differences in lakewater SO_4^2 concentrations, rather than by regional differences in zooplankton species or functional group distributions. MeHg bioaccumulation at lower trophic levels in aquatic food webs is poorly understood, especially in the face of climate change;

northern lakes are predicted to become more enriched in terrestrial DOC. Our study underscores the importance of considering lake DOC gradients in zooplankton MeHg bioaccumulation, as well as the distribution of functional groups among zooplankton communities, for improving predictions of MeHg bioavailability to higher vertebrate consumers.

1.5.1 Environmental Determinants of MeHg Concentrations in Lakewater

MeHg concentrations in unfiltered lake water were significantly and positively correlated with absorbance, and concentrations of chlorophyll-a, DOC, TN and TP. MacMillan et al. (2015) also found a positive correlation between aqueous MeHg concentration in thaw ponds and DOC, water absorbance (320 nm), and both TN and TP. An increase in DOC can increase lake browning, resulting in reduced phytoplankton production and subsequently decreased photodemethylation rates, which can result in higher MeHg concentration (Hammerschmidt et al., 2006). On the other hand, DOC can also promote microbial activity (Jonsson et al., 2017), which can augment Hg methylation by bacteria, and increase the MeHg concentration in freshwater ecosystems (Benoit et al., 2002). However, at high concentrations, DOC can decrease Hg bioavailability by creating complexes that decrease bioavailability by preventing Hg uptake across cellular membrane (AMAP, 2011; Tsui & Finlay, 2011; French et al., 2014). DOC will also strongly influence water absorbance (Kritzberg & Ekström, 2012) and it is probably because of the underlying relationship between DOC and Abs that we see a relationship between aqueous MeHg and Abs.

Long et al. (2018) suggested that an increase in TP concentration could promote MeHg bioaccumulation in zooplankton by the phosphorus association with particulate matter. Suspended particulates can adsorb both inorganic Hg and TP

(Razavi et al., 2015). Accordingly, the positive correlation between TP and MeHg could be explained by the positive correlation existing between TP and particulate matter (Lindström, 2001) and the high affinity of Hg and MeHg for particulate matter (Long et al., 2018).

Despite previous findings of a positive correlation of increases in nutrient on aqueous MeHg concentration (Braaten et al., 2014; MacMillan et al., 2015; Chételat et al., 2018), the effect of TN on MeHg concentrations in water is still, to our knowledge, unclear. Chételat et al. (2018) found that TN can affect lake sensitivity (defined as "the ability of an ecosystem to transform inorganic mercury loads to methylmercury in biota" by Munthe et al. (2007)). Braaten et al. (2014) found that TN can also increase methylation, but without any clear explanation of how. The positive correlation could be related to methylation from methanogenic archaea, since both Lehnherr et al. (2012) and MacMillan et al. (2015) found a positive correlation between MeHg concentration and TN and between MeHg concentration and aqueous dissolved methane.

We also found a unimodal relationship between SO_4^{2-} and lakewater unfiltered MeHg concentration, which is consistent with prevous findings (Gilmour & Henry, 1991). At low SO_4^{2-} concentrations, methylation processes by sulfate-reducing bacteria (SRB) is limited by lack of substrate (Gilmour & Henry, 1991) while, at high concentration, byproducts of SO_4^{2-} respiration (sulfide) interferes with Hg methylation (Gorski et al., 2006). However, the threshold concentration for SO_4^{2-} for our study lakes was lower (~12 mg-L^{-1}) than expected. Gilmour & Henry (1991) found that the optimal SO_4^{2-} concentration for SRB was between 20 and 50 mg-L^{-1}. In our study, only one lake (Kluane B) had a SO_4^{2-} concentration in this range (35.2 mg-L^{-1}), while other Yukon lakes had higher concentrations (~54 mg-L^{-1}), and Alaska and NWT lakes all had relatively low SO_4^{2-} concentration (min = 0.05 mg-L^{-1}

ATQ206; max = 13.31 mg-L^{-1} Sanguez). The gradient in SO_4^{2-} concentration used by Gilmour & Henry (1991) was also wider than the gradient used in this study (0.3 to 104.0 mg-L^{-1}). It is also important to mention that inter-correlation between many variables make interpretation, in terms of relative importance, difficult. All variables we measured, except for TP and SO_4^{2-}, were positively and significantly correlated with DOC, Chl-a was also positively correlated with both TN and TP, and SO_4^{2-} was negatively correlated with Chl-a and TN.

1.5.2 Unimodal MeHg Bioaccumulation along a DOC Gradient

We detected a unimodal relationship between lakewater DOC concentration and MeHg bioaccumulation in crustacean zooplankton. This finding is consistent with other studies that have addressed other trophic levels, such as bacteria (Chiasson-Gould et al., 2014), macroinvertebrates (French et al., 2014; Chaves-Ulloa et al., 2016), and fish (Driscoll et al., 1994; Braaten et al., 2018). The DOC threshold of ~8 mg-C-L^{-1} for crustacean zooplankton estimated in our study (Bulk zooplankton samples, Cladocera, and Copepoda) has also been reported for yellow perch (*Perca flavescens*; Driscoll et al. (1994)) and amphipods (French et al., 2014). However, other researchers have found DOC threshold concentrations closer to ~5 mg-C-L^{-1} for a diversity of trophic levels in aquatic food webs that include seston (Tsui & Finlay, 2011), phytoplankton (Gorski et al., 2008), macroinvertebrates (Chaves-Ulloa et al., 2016), and European perch (*Perca fluviatilis*; Braaten et al. (2018)). Not all investigators have detected a unimodal relationship between DOC water concentration and MeHg bioaccumulation. For example, Jeremiason et al. (2016) observed a decrease in BAF in dragonfly larvae with increased DOC concentrations. However, this finding may be explained because all DOC concentrations in this study were greater than 9.60 mg-C-L^{-1}. Similarly, Gorski et al. (2006) and Tsui & Finlay

(2011) found a decrease in MeHg bioaccumulation of algae and seston respectively when aqueous DOC concentration exceed ~5 mg-C-L^{-1}. Consistent with the DOC threshold of ~8 mg-C-L^{-1} for MeHg bioaccumulation in aquatic organisms (Driscoll et al. 1994; French et al. 2014; this study), Girard et al. (2016) proposed a unimodal relationship between DOC concentration and photodemethylation processes, with a breaking point when DOC concentrations were between 5 and 10 mg-C-L^{-1}. Therefore, the unimodal relationship between lakewater DOC and crustacean zooplankton MeHg BAF, with a DOC threshold of ~8 mg-C-L^{-1}, is consistent with other studies that have addressed this relationship in other taxa at other trophic levels of aquatic food webs.

Our findings suggest that it is important to consider taxon-specific groups when considering MeHg bioaccumulation in zooplankton, and subsequent bioavailability of MeHg for higher trophic levels in aquatic food webs. We found that using Bulk zooplankton samples, which includes all crustacean groups as well as rotifers and seston, could result in an underestimation of potential MeHg bioaccumulation in this organismal group. One possible explanation for higher BAF in Cladocera and Copepoda than in Bulk zooplankton samples could be that the Bulk zooplankton samples also included rotifers and phytoplankton, which may have diluted the MeHg bioaccumulation signal from the crustacean zooplankton. Consistent with this explanation, Long et al. (2018) found that MeHg bioaccumulation increased from micro- to meso- to macro-zooplankton. Contrary to our taxon-specific group prediction for MeHg BAF, we did not find that cladocerans had higher BAF along the DOC gradient compared to copepods. Instead, Copepoda had a higher but narrower BAF in response to the DOC gradient than Cladocera. Our stable isotope data suggested that the Copepoda in our study occupied a slightly higher trophic level than both Cladocera and Bulk zooplankton (Figure 1.5). Out of 12 species of Copepoda found in our lakes, only 2 species have a strictly herbivorous diet and 3 have an

omnivorous diet with a herbivorous preference (Table A3). All other species have either an omnivorous diet (n=4), a carnivorous diet (n=2), or a parasitic diet (n=1) (Table A3). Contrariwise, out of 19 species of Cladocera found in our lakes all except one (*Leptodora kindti*; carnivorous diet) have a herbivorous diet (Table A3). These differences in diet preference proportion between Copepoda and Cladocera could explain why copepods occupied a higher trophic level in our study. This difference in trophic position may explain the higher MeHg bioaccumulation in the copepods compared to the cladocerans, despite the fact that many cladocerans have a passive feeding strategies that could potentially allow for greater accumulation of methylating bacteria in their diet (Bertilsson et al., 2003; Chételat & Amyot, 2009).

The unimodal relationships between MeHg bioaccumulation and DOC concentration that we detected can be explained through a series of mechanisms. It is well known that dissolved organic matter (DOM; often calculated as DOC) affects Hg mobility and bioavailability in freshwater systems. At lower concentrations, DOC can enhance Hg bioaccumulation by a) increasing the Hg pool through transport of Hg from the surrounding environment b) stimulating DOC degradation by microbial activity and thus methylation, and c) through a combination of these processes, releasing bound Hg available for subsequent methylation (Porcal et al., 2009). DOC can act as a complexing agent because it possesses reduced thiols group to which Hg has high affinity for (Ravichandran, 2004). Higher bioavailability at lower DOC concentrations is explained by the binding of Hg to a fraction of the DOM pool that is more easily internalized by bacteria, such as fulvic acids (FA) (Chiasson-Gould et al., 2014; French et al., 2014). Presence of fulvic acids can increase Hg bioaccumulation in food webs because fulvic acids are relatively light, with more labile carbon that is less costly to process by bacteria (French et al., 2014). Chiasson-Gould et al. (2014) also proposed that Hg could be directly internalized by bacteria (without the DOC particle) following ligand exchange between DOC and the bacterial cell wall.

At higher DOC concentrations, refractory humic acid (HA) DOC molecules dominate. Resulting Hg-DOC complexes are less available for direct biological uptake and methylation (Barkay et al., 1997; Tsui & Finlay, 2011). These HA compounds are more stable and reduce the aqueous concentration of free Hg (Koukal et al., 2003). It has also been demonstrated that HA can be adsorbed onto algal cell walls, reducing potential contact with free metal ions and subsequent internalization (Koukal et al., 2003). At intermediate DOC concentrations, where the FA:HA ratios is still relatively low, MeHg bioaccumulation is highest, because of DOC-mediated Hg transport, and enhancement of biotic methylation (Porcal et al., 2009).

Although we were unable to quantify BAFs for MeHg in Kluane M and Kathleen lakes, MeHg concentrations in cladocerans from Kathleen Lake were relatively high, especially when considering the relatively high pH and low DOC concentration observed in this lake. This could be because the cladoceran community in Kathleen Lake was dominated by large-bodied Daphniidae, *Daphniia middendorfiana*. Previous researchers have reported up to five times more MeHg has in communities dominated by *Daphnia* species compared to communities dominated by Copepoda (Pickhardt et al., 2005; Chételat & Amyot, 2009), and high MeHg was mainly associated with the presence of *D. middendorfiana* in Chételat & Amyot (2009). To our knowledge, no other study has examined the relationship between MeHg in zooplankton and DOC along a DOC gradient that included DOC concentrations as low as 0.34 mg-C-L^{-1} (Kathleen Lake) (Gorski et al. (2008): 1.2 to 38.3 mg-C-L^{-1}; Driscoll et al. (1994): 3.4 to 26.5 mg-C-L^{-1}; French et al. (2014): 2.2 to 23.1 mg-C-L^{-1}; Chiasson-Gould et al. (2014): 0.8 to 38.1 mg-C-L^{-1}; Braaten et al. (2018): 3.6 to 20.1 mg-C-L^{-1}). Our results, and the lack of studies that include lakes with very low DOC concentration, such as Kathleen and Kluane M lakes, highlight the need for further study on MeHg bioaccumulation in very clear lakes.

1.5.3 Influence of Zooplankton Communities and Environmental Characteristics on MeHg BAF and Tissue Concentrations

Our study is one of the first that we are aware of to address the role of community composition in determining MeHg tissue concentration in crustacean zooplankton for the western Arctic. We found that Bulk zooplankton samples of zooplankton, which are traditionally collected for MeHg in aquatic studies, could underestimate MeHg bioaccumulation in zooplankton. Bioaccumulation factors and MeHg concentrations in copepods were best explained by lakewater DOC concentration. The reason why DOC best explained variability in MeHg BAF and concentration in copepods, but not in cladocerans, is not yet clear and may be related to species composition and the trophic position of functional feeding groups present in different lakes.

Although the relationship between MeHg BAF and DOC has shown to be unimodal for many taxa that span several trophic levels of aquatic food webs (Driscoll et al., 1994; Gorski et al., 2008; Tsui & Finlay, 2011; Chiasson-Gould et al., 2014; French et al., 2014; Chaves-Ulloa et al., 2016; Braaten et al., 2018), other environmental factors were important for determining MeHg tissue content in Bulk zooplankton and Copepoda in this study. A negative relationship between SO_4^{2-} concentration in the water column and Bulk zooplankton MeHg concentration suggests that SRB, or some other group of sulphur reducing organisms such as archaea, is playing an important role in Hg methylation in our study lakes. It could also reflect difference in capacity of methylmercury production between lakes (Bailey et al., 2017). Other research has shown that Hg methylation can be enhanced after an artificial increase of SO_4^{2-} in temperate lakes (Gilmour et al., 1992). However, a unimodal relationship between SO_4^{2-} and Hg methylation has also been reported, in which Hg methylation increases up to a certain concentration of SO_4^{2-}, after which SRB byproducts (reduce sulfide species) form complexes with Hg, reducing its bioavailability (Gorski et al., 2006;

Aiken et al., 2011). Jeremiason et al. (2016) found lower MeHg concentration in dragonfly larvae at sites with higher SO_4^{2-} concentration (29 ng-MeHg-g^{-1}; 250 mg-SO_4^{2-}-L^{-1}) compared to sites with lower SO_4^{2-} concentration (187 ng-MeHg-g^{-1}; 4.59 mg-SO_4^{2-}-L^{-1}). While our SO_4^{2-} gradient did not reach as high concentrations as those observed in Jeremiason et al. (2016) (maximum SO_4^{2-} concentration 54 mg-L^{-1}), our results were generally consistent with those of Jeremiason et al. (2016); across a SO_4^{2-} water concentration gradient we found higher MeHg concentrations in Bulk zooplankton at sites with lower SO_4^{2-} (e.g., ATQ206) compared to those with higher SO_4^{2-} (Kathleen and Kluane M). The absence of a relationship between SO_4^{2-} and MeHg tissue concentration in the other taxa tested in this study (Cladocera and Copepoda) suggests that the effect of SO_4^{2-} may be associated with smaller organisms, such as rotifers and/or phytoplankton. This requires further study.

Although our pH gradient was limited in magnitude (6.9 to 8.3), we detected a negative relationship between pH and cladoceran MeHg concentration. Lakewater pH best explained Cladocera MeHg tissue concentration and the distribution of cladoceran functional groups among lakes: daphniid-dominated cladoceran assemblages in higher-pH lakes had lower MeHg tissue content while cladoceran assemblages that were dominated by non-daphniids in lower-pH lakes had higher MeHg tissue content. Low pH has been reported as an important variable in controlling methylation rate (Miskimmin et al., 1992), and MeHg content in fish and invertebrates (Wiener et al., 1990; Watras et al., 1998; Kainz & Mazumder, 2005). Lower pH induces a change in DOC chemical properties, which in turn favours the release of metal ions, such as Hg, from Hg—DOC complexes (Davis et al., 1985; Hintelmann et al., 1995). This increases the amount of free Hg available for uptake and methylation (Miskimmin et al., 1992; Ullrich et al., 2001; Jardim et al., 2010). A decrease in pH from 7.0 to 5.0 has been shown to significantly increase the amount of MeHg released from sediment (Miller & Akagi, 1979; Ullrich et al., 2001). Certain

species of Cladocera, such as *D. middendorfiana,* have been found to feed at the sediment-water interface (Rautio & Vincent, 2006). This species was found in two of our lakes, including Kathleen Lake, and may be part of the reason why cladocerans in Kathleen Lake had relatively high MeHg concentrations. High-filtering species such as *Holopedium gibberum* (Hessen, 1985) were present in some lakes with high Cladocera MeHg concentrations, and this dominance by Holopedium in the cladoceran community in our lower-pH study lakes could also help explain why pH was correlated with cladoceran MeHg concentration and not other taxa. This is consistent with the literature as it is known that *H. gibberum* presence is accosiated with low pH lakes (Hamilton, 1958; Hutchinson, 1967). While Daphnia can consume, at approximately the same efficiency rate, algal and bacterial cells, *H. gibberum* is thought to specialize more on macro particles, and have a higher filtering rate than *Daphnia* (Hessen, 1985). This could mean a higher ingestion rate and a higher Hg exposure in *H. gibberum* than in *Daphnia* species (Masson & Tremblay, 2003). Given that the study lakes were selected to maximize a gradient in DOC concentration, the findings of taxa-specific relationships between MeHg and pH (Cladocera) and SO_4^{2-} (Bulk zooplankton) require further investigation across broader ranges of environmental variables that covaried with DOC. Whether or not pH and SO_4^{2-} are driving MeHg concentrations in specific taxa cannot be fully assessed from our data.

The western Arctic is warming at a faster rate than the global average, and warming could disrupt zooplankton community composition (Deasley et al., 2012; Thienpont et al., 2015) and have an impact on MeHg concentration in the community. It has been found that warming periods are associated with an increase in relative abundance of more specialized cladoceran taxa, at the expense of more generalist taxa (Thienpont et al., 2015). More precisely, generalist littoral species can be replaced by open-water specialist species, such as *Bosmina sp.* in western Arctic lakes in North

America (Thienpont et al., 2015). Increases in *Bosmina* abundance following warmer periods have also been observed in other regions of the world (Italy: Manca et al. (1996), Austrian Alps: Nevalainen et al. (2013)). This has been suggested to be facilitated by increased primary production that results from a shorter ice cover season (Thienpont et al., 2015). This could be a concern, because our results showed that lakes with high Bulk zooplankton MeHg BAF were dominated by Cladocera taxa, and more precisely *Bosmina longirostris* (ATQ206 = $112x10^4$ and RDC309 = $108x10^4$). Thus, Arctic warming could potentially result in higher food availability for zooplankton over a longer open-water season, and could favour open-water specialist species found in pelagic areas of lakes, such as *Bosmina sp.*. Since higher Bulk zooplankton MeHg BAF was associated with high *Bosmina* abundance in our study, and because western Arctic lakes have shorter periods of ice cover as a result of climate change (Prowse et al., 2009), MeHg concentration could potentially increase in zooplankton communities in Arctic lakes in the future. There is a need to consider regional differences in zooplankton community composition across Arctic regions from a taxonomic and functional perspective as biotic influences may modulate MeHg bioaccumulation at lower trophic levels in response to climate change in aquatic environments across the Arctic.

Caveats

An important caveat in our study is the large spatial scale at which we collected our data, covering three distant geographic regions of western Arctic lakes with different zooplankton communities. We predicted that optimal BAF in zooplankton would be observed in lakes with intermediate DOC concentrations, which, in our case, were found in Alaska. This hypothesis was confirmed by our results for all taxa analyzed (Figure 1.4). However, it has also been shown that latitude is positively correlated with MeHg biomagnification in freshwater systems, suggesting that the lower

temperatures and lower productivity found in high-latitude lakes promotes MeHg biomagnification (Lavoie et al., 2013). Consequently, latitude could have been a factor in our study, due to the fact that lakes where we found high bioaccumulation were also high latitude lakes located in Alaska. However, our prediction that higher DOC concentrations would be associated with higher aqueous MeHg concentrations because DOC acts as a carrier of MeHg into lakes and as a substrate for methylation (Porcal et al., 2009) was supported. We found that high DOC lakes (NWT) also had the highest aqueous MeHg concentration (Figure 1.6). Furthermore, this increase in aqueous MeHg did not translate to an increase in BAF but with lower BAF, as would be predicted with a unimodal response (French et al., 2014). Strong regional differences in community composition did not allow us to fully assess community composition effect on MeHg bioaccumulation. Also, our study involved a total of 11 lakes; additional lakes would have improved the power of our models and the representation of abiotic and biotic variation in lakes across this broad spatial scale.

Spurrious correlations are known to potentially complicate statistical analyses of relationships between DOC and MeHg BAF (Pollman & Axelrad, 2014). Indirect spurious correlation can arise when one of the variables used in a ratio calculation of MeHg BAF (e.g., aqueous MeHg) is strongly correlated with the variables that it is tested against (e.g., DOC) (Pollman & Axelrad, 2014), which is the case in this study (Figure 1.2). In presence of a spurious correlation, there can be potentially misleading interpretations of the relationship between DOC and BAF, which may rather be driven by the correlation between DOC and aqueous MeHg (Pollman & Axelrad, 2014). A spurious correlation could explain why Copepoda threshold model (Figure 1.4) had a narrower spread for the unimodal curve than the other taxa. However, only the denominator (aqueous MeHg concentration) in the Copepoda BAF calculation was linearly correlated with DOC concentration. This was also the case for Bulk zooplankton and cladoceran samples. Furthermore, Bulk zooplankton and Cladocera

numerator values (zooplankton MeHg tissue concentration) were not linearly correlated with aqueous DOC concentration. Although Pollman & Axelrad (2014) suggest the use of multivariate analyses with zooplankton MeHg concentration, aqueous MeHg concentration and DOC concentration could be used to avoid spurious correlation, this approach was inappropriate for our study. A multivariate solution to spurious correlation would have been problematic in our study because of collinearity between DOC and aqueous MeHg concentration in the same model. The same problem would also arise with the use of linear model with interaction, in addition to the fact that we would not have enough power to perform such tests with confidence (Bulk: n=11 lakes; Cladocera: n=9 lakes; Copepoda: n=8 lakes;). Moreover, the goal of our study was to compare the trend of MeHg BAF along a DOC gradient, and to do so, we choose to assess our question in the same way other studies with a similar question as ours have done, with a unimodal curve using a Lorentzian model (French et al., 2014; Braaten et al., 2018).

1.5.4 Implications

Our study underscores the importance of considering lake DOC concentrations, and to some extent zooplankton community composition, in crustacean zooplankton MeHg bioaccumulation in northern lakes. Our results suggest that higher zooplankton MeHg bioaccumulation could occur in lakes with intermediate DOC concentration, around 8 mg-L^{-1}, and could be lower in clearer and more humic lakes. However, MeHg bioaccumulation in extremely clear lakes with extremely low DOC concentrations (< 0.8 mg-C-L^{-1}) could be under the influence of other mechanisms than DOC, and deserve further investigation. We found that low DOC lakes (<8 mg-C-L^{-1}) could be more at risk of increases in zooplankton MeHg bioaccumulation as lakes become more enriched with DOC from climate change effects. Low DOC lakes,

with low bioaccumulation rates, could experience increases in Hg loading, and microbial methylation rates may be stimulated by an increase in DOC, resulting in higher MeHg concentration in the zooplankton community. The opposite could be observed in the intermediate DOC concentration lakes (~8 mg-C-L^{-1}), such that these lakes experience a decrease in MeHg bioaccumulation factor with an increase in aqueous DOC due to formation of Hg-DOC complexes that decrease availability of Hg for methylation. An increase in DOC could be followed by a decrease in pH (de Wit et al., 2012; Braaten et al., 2014), which could increase the relative abundance of non-daphniids cladoceran functional groups, such as *Bosmina sp.* and *Holopedium gibberum*, and increase MeHg tissue content in the cladoceran taxa. Another potential problem is that SRB can be SO_4^{2-}-limited (Capone & Kiene, 1988), and enhanced weathering in the Arctic following warming could also liberate SO_4^{2-} into aquatic systems and increase microbial methylation rate (Gilmour et al., 1992). Increases in lake SO_4^{2-} concentration could affect MeHg concentration in the whole zooplankton community as demonstrated in this study. Therefore, further research is required to understand the influence of other abiotic factors in addition to DOC, such as pH and SO_4^{2-}, in determining MeHg bioaccumulation in zooplankton across northern lakes that encompass a broader range of spatial environmental variation.

Taxon-specific collections of live zooplankton is time-consuming, but should be considered for interpreting MeHg bioaccumulation in aquatic food webs. This is because the use of Bulk zooplankton MeHg samples resulted in an underestimation of the DOC threshold concentration (see Table C1), as well as underestimating the individual contributions from both the Cladocera and the Copepoda to the MeHg available to fish and other higher-level consumers. Differences in dietary preference between copepods and cladocerans can lead to differences in trophic level between the two taxa causing Copepoda to occypy a slightly higher trohic level than Cladocera. In our study, this resulted in a higher BAF in Copepoda than in Cladocera, which was

contrary to our initial hypothesis. These results suggest that community composition and functional feeding group play an important role in determining MeHg concentration in the crustacean zooplankton community.

Chételat et al. (2018) proposed the use of a ratio of aqueous MeHg concentration to DOC concentration as a potential indicator of Arctic lake sensitivity to MeHg bioaccumulation. We found no relationship between zooplankton BAF or MeHg tissue concentration and the ratio proposed by Chételat et al. (2018). However, in Chételat et al. (2018), both aqueous MeHg and DOC concentration were correlated with the MeHg concentration of their studied aquatic invertebrate (chironomid larvaeand zooplankton), which was not the case in our study. This suggests that the use of the ratio of aqueous MeHg concentration to DOC concentration may not be appropriate for all lakes, especially in lakes where aqueous MeHg concentration does not predict organismal MeHg tissue concentration.

The Arctic is rapidly warming compared to temperate regions as a result of climate change (Olsen et al., 2011; Vincent et al., 2011; Vincent et al., 2013). This is especially evident in northwestern Arctic regions of North America, where rates of warming are twice as rapid compared to eastern and central Arctic regions (Prowse et al., 2009). As a result of rising temperatures, thawing permafrost is predicted to become an important source of Hg for freshwater Arctic aquatic ecosystems (Macdonald et al., 2005). It is believed that up to $1{,}656 \pm 962$ Gg of Hg are presently contained in permafrost in the Northern Hemisphere, which represents nearly twice the amount found in all other mercury compartments combined (Schuster et al., 2018). This is particularly unsettling if we consider model projections of a $30-99\,\%$ decrease in northern permafrost area by 2100 with current anthropogenic greenhouse gases rates (Koven et al., 2013). In an assessment on mercury in Canada, our biggest knowledge gap is how climate change will impact Hg methylation and cycling in

Canada (Government of Canada, 2017). This emphasizes the importance of our study in understanding the factors, both abiotic and biotic, that modulate MeHg concentration and bioaccumulation in the crustacean zooplankton which are a key trophic link in aquatic food webs.

1.5.5 Conclusion

Zooplankton MeHg bioaccumulation followed a unimodal response along a DOC gradient that peaked at a threshold of 8 mg-C-L^{-1} in Western Arctic lakes. DOC was a strong predictor of copepod MeHg tissue content. Lakewater SO_4^{2-} concentration affected MeHg tissue content of the whole zooplankton community. Higher MeHg in cladocerans was influenced by lower pH in non-daphnid cladocerans such as high-capacity filters such as Holopedium. Further research is needed to confirm if these abiotic variables influenced zooplankton MeHg bioaccumulation and MeHg tissue content via ecological processes in specific taxa, or if they influenced MeHg in zooplankton groups by increasing or decreasing MeHg bioavailability in the surrounding environment.

Acknowledgements

S. Guernon was supported by scholarships from Fonds de recherche du Québec en nature et technologie (FRQNT), the W. Garfield Weston Foundation, the UQAM Faculty of Science, and the NSERC Create ÉcoLac training program, as well as by a grant from the Northern Scientific Training Program (NSTP). The research was funded by the Arctic Land Conservation Cooperative (PI: Christian Zimmerman and HKS, as well as by individual NSERC Discovery NSERC Northern Supplement and Canadian Foundation for Innovation (CFI) grants, to both AMD and HKS.

CONCLUSION

Le sujet d'étude abordé dans ce mémoire est important, car l'Arctique couvre une grande proportion du Canada et bien qu'elle soit vulnérable aux changements climatiques et à la contamination par le Hg, il existe encore beaucoup de lacunes dans nos connaissances concernant ce contaminant dans cet écosystème vulnérable (Government of Canada, 2017). La Figure 2.1 regroupe les concentrations en MeHg dans le zooplancton de l'Arctique de 11 études (incluant ce mémoire). Hormis notre étude, aucune étude n'a activement séparé les groupes taxonomiques. Des données pour les copépodes sont disponibles pour l'île Cornwallis, mais uniquement parce que la communauté zooplanctonique était composée de 98 à 100 % soit du Calanoide *Limnocalanus macrurus* (n=8) ou du Cyplopoide *Cyclops scutifer* (n=1). De plus, à l'exception des études européennes, toutes les recherches (n=8) se sont concentrées sur l'Arctique de l'Est à l'exception des résultats présentés dans ce mémoire. En 2017, le département d'*Environnement et Changement Climatique Canada* précisait dans un rapport sur l'évaluation de l'état du Hg au Canada que la plus grosse lacune dans nos connaissances concernait l'impact qu'auraient les changements climatiques sur la méthylation et le cycle du Hg au Canada. Ce rapport soulignait également l'insuffisance de nos connaissances quant à l'impact de la température, de l'acidité et des matières organiques sur la production et la bioaccumulation du MeHg dans les systèmes aquatiques d'eau douce de l'Arctique (Government of Canada, 2017). Le but principal de cette recherche était d'approfondir notre compréhension du cycle du Hg en Arctique, plus particulièrement dans l'Arctique de l'Ouest, et de déterminer ce qui promeut la bioaccumulation du Hg à la base de la chaîne alimentaire.

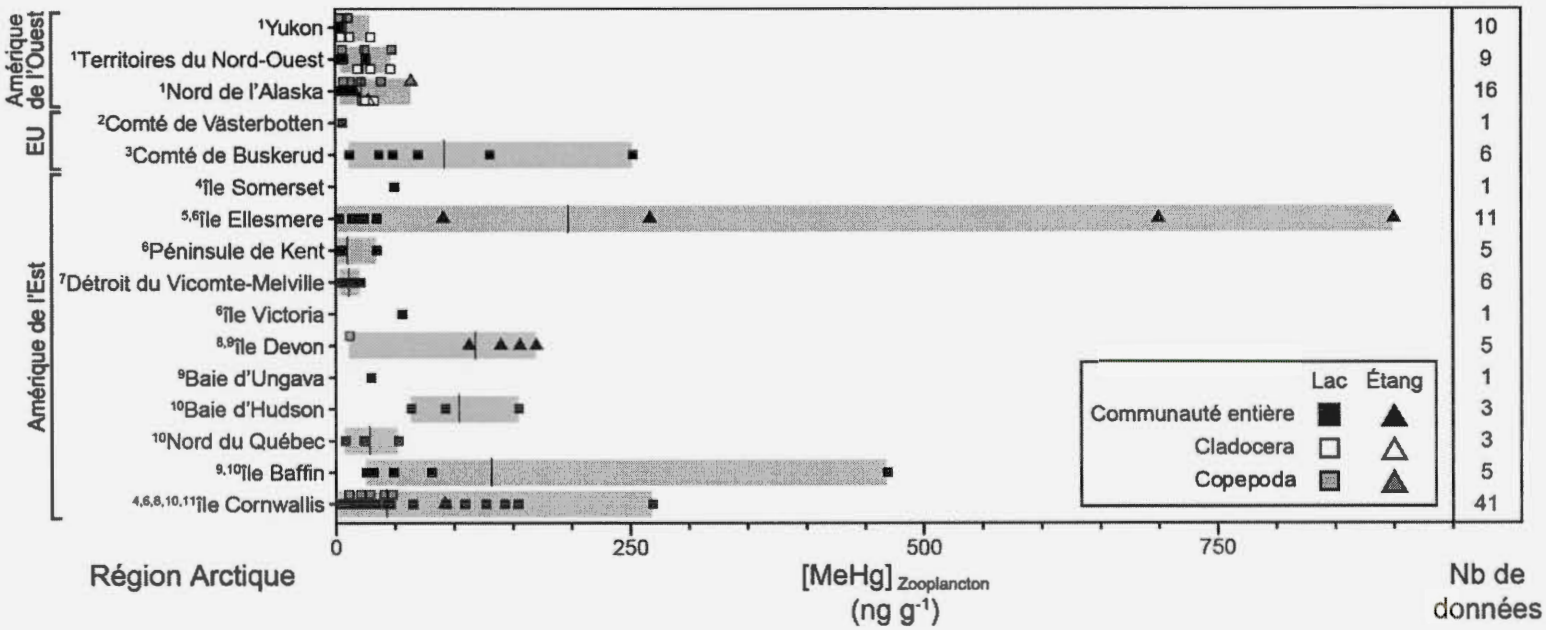


Figure 2.1. Concentration en MeHg (ng-g^{-1}) chez le zooplancton selon les différentes régions arctiques du globe. L'Arctique de l'Ouest est défini comme étant l'Alaska, le Yukon, et les Territoires du Nord-Ouest, et l'Arctique de l'Est comme étant le Québec et le Nunavut. L'île Victoria a été classifiée dans l'Arctique de l'Est puisque le lac échantillonné se situait au Nunavut. EU représente l'Europe; le Comté de Västerbotten ce situe en Suède et le Comté de Buskerud en Norvège. Les étangs ont été définis comme ayant une superficie <0,5 km^2 et ayant une profondeur <3 m. Les données proviennent de [1]cette étude, [2]Wu et al. (2019a), [3]Poste et al. (2019), [4]Chételat & Amyot (2009), [5]Lehnherr et al. (2012), [6]Gantner et al. (2010), [7]Swanson & Kidd (2010), [8]Chételat et al. (2012), [9]van der Velden et al. (2013), [10]Chételat et al. (2018) et [11]Lescord et al. (2015). Les barres grises représentent les concentrations maximales et minimales et les lignes noires représentent les concentrations moyennes de MeHg.

2.1 Sujets Traités et Objectifs

Cette recherche était axée sur le zooplancton crustacé jouant un rôle clé dans les chaînes alimentaires en occupant un niveau trophique intermédiaire reliant les niveaux basaux comme le phytoplancton et les niveaux supérieurs tels que les poissons planctivores (Todorova et al., 2015). Étant donné qu'il est généralement accepté que le COD influence de plusieurs façons le cycle du Hg (Ullrich et al., 2001), cette étude se penche sur cette composante environnementale. Plus particulièrement, cette recherche se concentre sur l'effet que le COD pouvait avoir sur la bioaccumulation du MeHg chez le zooplancton. Outre son pouvoir de modifier la composition de la communauté (Roiha et al., 2012), le COD est un joueur important dans le cycle du Hg dû à sa capacité à former des complexes de solidité variable avec le Hg (Ullrich et al., 2001; AMAP, 2011; Tsui & Finlay, 2011). Cette recherche se base sur les résultats de l'étude menée par French et al. (2014) sur la relation entre le COD et la bioamplification du MeHg chez les amphipodes de l'Arctique. French et al. (2014) ainsi que d'autres chercheurs (Driscoll et al., 1994; Gorski et al., 2008; Tsui & Finlay, 2011; Chiasson-Gould et al., 2014; Chaves-Ulloa et al., 2016; Braaten et al., 2018) ont observé qu'il existait une relation unimodale entre la bioaccumulation du MeHg de certains organismes et la concentration aqueuse en COD. À faible concentration de COD, la bioaccumulation du MeHg est en général augmentée jusqu'à l'atteinte d'une concentration seuil en COD (situé entre 5 et 8 mg-C-L^{-1}), après quoi la bioaccumulation du MeHg se voit être diminuée (French et al., 2014). Avant l'atteinte de la concentration seuil, le COD promeut la méthylation du Hg en augmentant l'apport en Hg au lac et en stimulant l'activité microbienne responsable de la dégradation de la matière organique et de la méthylation du Hg (Porcal et al., 2009). Lorsque la concentration en COD dépasse ~8 mg-C-L^{-1} les complexes formés entre le COD et le Hg deviennent plus difficile à briser ce qui diminue l'accessibilité du Hg à la faune bactérienne (French et al., 2014). Cette perte de biodisponibilité est

due à l'association du Hg avec des molécules de COD plus grosses et moins labiles tel que l'acide humique (Barkay et al., 1997; Tsui & Finlay, 2011; French et al., 2014). Au contraire, à faible concentration les complexes de COD—Hg sont formés de molécules d'acide fulvique qui sont plus petites et plus facilement dégradables par la faune microbienne (French et al., 2014). Cette perte de biodisponibilité à haute concentration de COD explique la diminution de la bioaccumulation du MeHg dans la faune, car même si le Hg est présent en plus grande quantité dans l'eau, il est emprisonné dans les molécules de COD et est moins facilement assimilé par la faune aquatique (French et al., 2014).

Outre le COD, il existe aussi des facteurs biologiques pouvant affecter la quantité de MeHg retrouvée dans la communauté zooplanctonique. Parmi ceux-ci, cette étude s'intéresse à l'effet de la composition de la communauté zooplanctonique. Certains taxa ou espèces seraient plus sensibles à la bioaccumulation du Hg et, lorsque retrouvés en grande abondance dans la communauté, ces taxa et/ou espèces peuvent affecter la concentration totale de MeHg dans la communauté (Pickhardt et al., 2005; Chételat & Amyot, 2009; Long et al., 2018). La disparité dans le niveau de sensibilité associée à la bioaccumulation du Hg entre les cladocères et les copépodes, deux taxa composant la majorité des communautés zooplanctoniques, est principalement reliée à l'utilisation de stratégies alimentaires différentes (Bertilsson et al., 2003; Riisgård, 2015; Todorova et al., 2015). Les copépodes se nourrissent activement sur de plus grandes proies comme des cellules algales et/ou de petits zooplanctons alors que les cladocères sont des filtreurs efficaces se nourrissant de petites cellules comme des bactéries, des algues et des détritus particulaires dans la colonne d'eau (Bertilsson et al., 2003; Karlsson et al., 2003; Riisgård, 2015). En étant directement en contact avec les complexes de COD—Hg, les bactéries peuvent devenir rapidement très concentrées en Hg et être une source importante de MeHg pour les cladocères (AMAP, 2011).

2.2 Résultats Saillants et Implications

En accord avec des recherches ultérieures, cette étude a démontré l'Existence d'une relation unimodale entre la concentration en COD et la bioaccumulation du MeHg de la communauté zooplanctonique entière ainsi que pour les deux taxa testés. Les résultats de cette recherche ont indiqué que la bioaccumulation chez le zooplancton était maximale lorsque la concentration en COD était de 8.01 mg-C-L^{-1}, une concentration associée aux lacs de l'Alaska. Ces résultats concordent avec d'autres études qui ont trouvé des résultats similaires quant aux concentrations seuils (Driscoll et al., 1994; French et al., 2014). Toutefois, il a été impossible de quantifier de façon fiable le facteur de bioaccumulation des lacs ayant des concentrations aqueuses en COD très faible (c.-à-d. le Lac Kathleen (0.31 mg-C-L^{-1}) et le Lac Kluane M (0.77 mg-C-L^{-1})). De plus amples recherches sont donc nécessaires afin d'évaluer adéquatement l'impact qu'aura le COD sur la bioaccumulation du MeHg chez le zooplancton des lacs arctiques de faibles concentrations en COD.

En plus de moduler la bioaccumulation du MeHg chez le zooplancton, le COD peut influencer la concentration en MeHg retrouvé chez les copépodes, sans toutefois influencer la concentration en MeHg des cladocères et de la communauté entière. Ceci suggère que certains taxa, comme les copépodes, seront plus sensibles à un apport en COD dans l'environnement que d'autres. Dans le cadre de cette étude, la concentration en MeHg de la communauté entière était mieux expliquée par la concentration de sulfate dans l'eau. La faune bactérienne joue un rôle important dans la méthylation du Hg et la limitation en substrat peut diminuer la quantité de MeHg qui sera créé dans le milieu (Capone & Kiene, 1988; Gilmour & Henry, 1991). Trois principaux types de bactéries sont associés à la méthylation du Hg, l'un d'entre eux étant les bactéries sulfato-réductrices (Gilmour et al., 1992; AMAP, 2011). Le sulfate peut être transporté en même temps que les complexes de COD—Hg suite à l'érosion

des bassins versants (Gilmour et al., 1992). Cet apport supplémentaire en sulfate pourrait augmenter le taux de méthylation en Hg dans les lacs limité par cet ion (Gilmour et al., 1992). Toutefois, cette augmentation sera éventuellement limitée par l'accumulation de sous-produit (résultat de l'activité des bactéries sulfato-réductrices) qui formera aussi des complexes avec le Hg et réduira sa biodisponibilité (Gorski et al., 2006). Ceci expliquerait la relation négative observée entre la concentration de MeHg dans la communauté entière et l'augmentation de la concentration en sulfate. La concentration en MeHg des cladocères n'était pas influencée par la concentration en COD ou en sulfate, mais bien par le pH dans l'eau. Une augmentation de l'acidité (c.-à-d. une diminution du pH) dans l'eau augmenterait la solubilité du MeHg dans la colonne d'eau et se soldera en une augmentation de la biodisponibilité du MeHg (Davis et al., 1985; Miskimmin et al., 1992; Hintelmann et al., 1995; Ullrich et al., 2001; Jardim et al., 2010). Un pH acide favoriserait aussi la libération de MeHg des sédiments vers la colonne d'eau (Miller & Akagi, 1979; Ullrich et al., 2001) et certaine espèce de cladocère vont s'alimenter directement à la l'interface eau-sédiments (Rautio & Vincent, 2006). Il ne faut toutefois pas exclure la possibilité que ces trois variables environnementales agissent sur la biodisponibilité du MeHg en général et non sur la concentration en MeHg des taxa spécifiquement. L'échantillonnage de plus de lacs et plus d'analyses seraient nécessaires pour déterminer la spécificité de l'effet du sulfate, du pH et du COD sur la concentration en MeHg de la communauté entière, des cladocères et des copépodes respectivement. Il est aussi possible de conclure que l'effet de la concentration en sulfate et en COD sur la concentration en MeHg de la communauté entière et des copépodes respectivement étaient uniquement dus à des processus physico-chimiques. En effet, le sulfate et le COD n'ont pas influencé la concentration en MeHg du zooplancton par l'intermédiaire d'une modification de la composition de la communauté. Au contraire, les communautés de cladocères dominés par des Daphniidae étaient associées aux lacs moins acides dans lesquels la concentration en MeHg des cladocères était moins élevée. À l'opposé des résultats trouvés par Chételat & Amyot (2009) et Pickhardt et

al. (2005), cette étude et d'autres (Masson & Tremblay, 2003; Long et al., 2018) démontrent une relation négative entre la présence de *Daphnia* dans la communauté et la concentration en Hg. Au contraire, nous avons trouvé que les lacs dont la communauté entière avait un facteur de bioaccumulation en MeHg plus élevé étaient composés à plus de 85 % de *Bosmina longispina* un petit cladocère filtreur. Thienpont et al. (2015) ont trouvé qu'en période de réchauffement, la communauté de cladocère tendait à changer vers une plus grande abondance d'espèces littorales généralistes comme *Bosmina sp.*. Ainsi, le réchauffement climatique pourrait engendrer un changement dans la communauté zooplanctonique des lacs Arctiques ce qui favoriserait des espèces généralistes comme *Bosmina longispina*. Cela pourrait potentiellement entrainer une augmentation de la concentration en MeHg de la communauté entière. La présence d'*Holopedium gibberum*, un cladocère filtreur efficace, dans les lacs où les cladocères présentaient de plus grandes concentrations en MeHg pourrait aussi expliquer cette disparité entre les résultats obtenus et anticiper. Ainsi, nous pensons que les cladocères seraient, en général, plus sensibles à l'accumulation du MeHg et que cette sensibilité pourrait être dépendante du pH, de l'origine de la matière organique et de la composition de la communauté.

Cette étude souligne l'importance de considérer la concentration en COD, en sulfate ainsi que le pH et dans une certaine mesure la composition de la communauté zooplanctonique dans l'évaluation de la concentration et de la bioaccumulation du MeHg dans les lacs de l'Arctique. Avec l'augmentation de la température prévue reliée aux changements climatiques, la fonte du pergélisol pourrait devenir une source importante de Hg pour les écosystèmes lacustres de l'Arctique (Macdonald et al., 2005). À ce jour, les scientifiques pensent que plus de 1 000 Gg de Hg sont emprisonnés dans le pergélisol (Schuster et al., 2018). Une grande portion de ce Hg sera libérée d'ici 2100 si le dégèle de 30 à 99 % du pergélisol prévu par les modèles se concrétise (Koven et al., 2013). Les lacs plus à risque de cette augmentation en

COD seront les lacs pauvres en COD, qui ont actuellement un taux de bioaccumulation faible. Ces lacs verront leur puits de Hg et l'activité de leur faune microbienne augmentés avec un apport plus important en COD. Le résultat sera une augmentation de la concentration aqueuse en MeHg et possiblement de la concentration et de la bioaccumulation de MeHg dans la communauté zooplanctonique. Le contraire pourra toutefois être observé dans les lacs qui verront leur concentration en COD dépasser la concentration seuil de 8 mg-C-L^{-1}. Les résultats de cette étude démontrent aussi la possibilité que certains taxa serraient plus sensibles que d'autres à certaines variables environnementales. Comprendre la relation entre ces variables environnementales et la composition de la communauté zooplanctonique pourrait aider à mieux comprendre pourquoi certaines communautés sont plus sensibles que d'autres à la bioaccumulation du MeHg.

2.3 Piste de Recherche – Relation entre l'Allochtonie et le MeHg

La composition de la communauté ainsi que la source alimentaire peuvent en plus d'influencer l'accumulation du MeHg aussi agir sur l'allochtonie chez le zooplancton. L'allochtonie se définit comme la portion du contenu corporel en carbone du zooplancton qui est d'origine terrestre (Berggren et al., 2014). L'assimilation du carbone terrestre se produit probablement dans les niveaux trophiques inférieurs de la chaîne trophique où l'activité microbienne dégrade la matière organique dissoute (Jansson et al., 2007). Une augmentation dans la concentration en COD terrestre, plus particulièrement si celle-ci est composée d'une grande quantité d'acide fulvique de faible poids moléculaire, pourrait grandement contribuer à la production bactérienne (Berggren et al., 2010). Dans ces conditions, la biomasse bactérienne peut devenir particulièrement concentrée en carbone organique d'origine terrestre (CO-t) (Guillemette et al., 2016). Ainsi, le rôle de l'allochtonie dans les écosystèmes

aquatiques est étroitement relié à l'abondance, la biomasse et la production bactérienne (Roiha et al., 2012). Inversement, la productivité bactérienne est influencée par la qualité du CO-t et sa quantité affectera la composition de la communauté (Roiha et al., 2012). Ces bactéries, riche en CO-t, peuvent ensuite être consommées par des protistes hétérotrophes ou mixotrophes telles que les ciliés et les flagellés (Martin-Creuzburg et al., 2005). En consommant ces organismes, le zooplancton pourrait assimiler ce carbone d'origine terrestre dans ses propres tissus (Brett et al., 2017) et ainsi rendre cette source de carbone disponible pour les différents zooplanctivores, tels que certains poissons et certains invertébrés (Tanentzap et al., 2014). Outre la quantité de l'allochtonie présente dans leurs proies, les stratégies alimentaires des différentes espèces de zooplanctons peuvent, en plus d'augmenter la bioaccumulation du MeHg, grandement influencer l'allochtonie de la communauté zooplanctonique (Berggren et al., 2014). Par exemple, les copépodes calanoides, qui dépendent normalement de l'abondance du phytoplancton, deviennent plus concentrés en allochtonie lorsque ce dernier est peu abondant et qu'il doit se contenter d'une alimentation bactérienne (Berggren et al., 2014). Les copépodes cyclopoides, quant à eux, sont des zooplanctons prédateurs et omnivores qui dépendront plus du niveau d'allochtonie contenu dans leurs proies (Berggren et al., 2014). La proportion de l'allochtonie retrouvée dans les cladocères dépend de la grosseur des particules dans l'eau et plus particulièrement de ce qu'ils peuvent filtrer (Karlsson et al., 2003). Les cladocères dépendent à la fois de la disponibilité en phytoplancton et de la quantité de matière organique dissoute dans l'environnement (Karlsson et al., 2003) résultant en une composition en carbone interne reflétant celle de leur environnement (Rautio et al., 2011).

Le problème avec l'utilisation de CO-t n'est pas son contenu énergétique en tant que telle, mais plutôt l'accessibilité de ce contenu énergétique et sa composition biochimique (Brett et al., 2017). Il a été démontré que les organismes aquatiques vont

avoir une meilleure croissance s'ils se nourrissent de composé ayant une composition biochimique plus proche de la leur (Brett et al., 2017). Les acides gras nécessaires pour la survie, la croissance et la reproduction des zooplanctons sont des acides gras polyinsaturés ω3 (Brett et al., 2009). Alors que le phytoplancton est reconnu pour synthétiser ces acides gras essentiels, les plantes terrestres synthétisent principalement des acides gras polyinsaturés ω6 et des acides gras saturés que les zooplanctons ne peuvent utiliser directement (Taipale et al., 2014). Il a été démontré que le zooplancton avait une survie, une reproduction et une croissance faibles lorsqu'il s'alimentait exclusivement de matière organique d'origine terrestre (Brett et al., 2009; Taipale et al., 2014). Ainsi, puisque la matière organique d'origine terrestre ne possède pas certains composés essentiels pour la croissance du zooplancton, une grande allochtonie chez les zooplanctons peut diminuer leur potentiel de croissance (Brett et al., 2009). Il a été démontré par Kelly et al. (2014) que la production zooplanctonique des lacs tempérés était négativement corrélée à leur utilisation du carbone d'origine terrestre probablement due à la faible qualité de cette ressource. En Arctique, la température limite le taux de croissance et le métabolisme des poissons et cela favorise en une plus grande concentration de MeHg par g de poisson (Schindler et al., 1995). Étant donné que l'allochtonie a aussi un potentiel limitant sur le taux de croissance du zooplancton, une relation similaire pourrait être observée entre l'allochtonie et la concentration en MeHg du zooplancton crustacé.

Approfondir l'impact que pourrait avoir une plus grande concentration en COD d'origine terrestre dans l'environnement sur l'allochtonie ainsi que sur la concentration en MeHg du zooplancton pourrait aider à mieux prédire l'ampleur de l'effet d'une augmentation de COD dans les lacs de l'Arctique. Comprendre cette relation est d'autant plus important si l'on considère que la concentration en MeHg et l'allochtonie présente dans le zooplancton influenceront directement la concentration en MeHg et la productivité de la faune ichtyenne (Karlsson et al., 2012; Rask et al.,

2014; Karlsson et al., 2015; Brett et al., 2017). Ces deux composantes sont d'un grand intérêt pour l'homme et plus particulièrement pour les communautés du Nord qui dépendent souvent de cette ressource comme moyen de subsistance (Poissant et al., 2008).

APPENDIX A

SUPPLEMENTARY INFORMATION ON METHODS

Table A1. General information about water and zooplankton analyses, including general method employed, instruments used, and location of analysis.

Sample	Laboratory	Parameters	Units	Methods	Instruments
Water	Biogeochemical Analytical Service Laboratory†	Chl-a	$\mu g\ L^{-1}$	Overnight extraction on filter with 95% ethanol	Shimadzu RF-1501 spectrofluorophotometer
		pH	—	Autotitrator	Man-Tech PC-Titrate with conductivity probe
		TN and TP	$\mu g\ L^{-1}$	Flow Injection Analysis	Lachat QuikChem 8500 FIA automated ion analyser
	The Biotron Center for Experimental Climate change Research‡	ABS	—	Absorbance at 254-nm	Aqualog spectrophotometer
		DOC	$mg\ L^{-1}$	Persulfate oxidation	Aurora 1030W
		F.I.		McKnight et al. 2001	Aqualog spectrophotometer
		MeHg	$ng\ L^{-1}$	Cold Vapour Atomic Fluorescence spectrophotometry	Tekran 2700 Automated Sample Analysis System
		SO_4^{2-}	$mg\ L^{-1}$	Ion Chromatography	DIONEX ion chromatograph with an AS14 analytical column
		SUVA	—	Weishaar et al. 2003	UV absorbance at 254 nm, divided by DOC concentration
		Total Hg	$ng\ L^{-1}$	Cold Vapour Atomic Fluorescence - Digestion	Tekran 2600 Automated Sample Analysis System
	Biogeochemistry Lab§	SO_4^{2-}	$mg\ L^{-1}$	Ion Chromatography	DIONEX ion chromatograph with an AS14 analytical column

Table A1 (*continued*)

Sample	Laboratory	Parameters	Units	Methods	Instruments
Zooplankton tissue	Derry Lab[††]	Tissue collection	—	Manually separated with pipettes and tweezers under a dissecting stereo-microscope	Olympus SZ61TR microscope
	Environmental Isotope Laboratory[¶]	$\delta^{13}C$ and $\delta^{15}N$	‰	Continuous flow isotope ratio mass spectrometer	Costech 4010 Elemental Analyzer coupled to a Thermo-Finnigan Delta^{Plus} XL
	The Biotron Center for Experimental Climate change	MeHg	ng g^{-1}	Cold Vapour Atomic Fluorescence spectrophotometry	Tekran 2700 Automated Sample Analysis System
Zooplankton identification	Derry Lab	Taxonomic ID	—	Combination of high-resolution dissecting microscope and inverted microscope	Olympus SZX10 and Olympus CKX41 microscope
		Relative abundance count	Indiv. L^{-1}	Girard & Reid, 1990	—

[†] 2-255 Centennial Centre of Interdisciplinary Science, University of Alberta, Edmonton, Alberta, Canada, T6G 2E1
[‡] 1151 Richmond Street, Biotron Building, Western University, London, Ontario, Canada, N6A 5B7
[§] 200 University Avenue West, Environment 1 Building (EV1 243), University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1
[¶] 263 Phillip Street, Center for Environmental and Information Technology Building (EIT 5019), University of Waterloo, Waterloo, Ontario, Canada, N2L 3W8
[††] 141 Avenue du Président-Kennedy, Pavillon des Sciences Biologiques (SB 2135), Université du Québec à Montréal, Montréal, Québec, Canada, H2X 1Y4

Table A2. Supplementary information relative to lake stratification and what methods were used for zooplankton sampling.

Region	Lake	Depth (m)	Secchi disc (m)	T°		O_2		Community sampling	
				Surface	Bottom	Surface	Bottom	Methods	Depth/Speed/Liter
Yukon	Kluane M	13.5	5.0	10.0	12.0	9.0	10.0	Vertical tow	13.0 m tow
	Kluane B	6.0	2.5	16.6	16.5	9.0	10.0	Horizontal tow	2.0 km h^{-1} * 17 sec
	Kathleen	30.0	13.5	10.5	9.0	9.6	12.2	Vertical tow	18.0 m tow
Alaska	ATQ200	2.56	2.00	11.3	11.2	10.9	10.8	Pump	60 L
	ATQ201	3.00	2.75	10.3	10.7	11.1	9.4	Pump	60 L
	ATQ206	2.96	2.50	10.0	9.8	11.2	11.3	Pump	60 L
	RDC308	4.08	3.10	12.3	10.7	11.5	11.9	Pump	60 L
	RDC309	2.07	2.10	10.9	10.7	11.2	11.1	Pump	60 L
	RDC311	3.05	—	10.4	9.9	11.5	12.3	Pump	60 L
NWT	Big Island	28	—	17.0	13.4	8.5	5.9	Horizontal tow	1.6 km h^{-1} * 40 sec
	Sanguez	18	3.25	15.2	8.9	7.4	0.2	Vertical tow	8.0 m tow
	Ekali	10	2.60	19.1	17.1	7.4	0.3	Vertical tow	9.0 m tow

Table A3. Relative information on each species such as trophic groups and size used to generate a functional trait based dendrogram.

Taxa	Order/Family	Genus	Species	Trophic group	Size (mm)
Copepoda		Nauplii		Immature	
	Calanoida	Copepodite		Immature	
		Eurytemora	*sp.*	Omni-Herbivore[1]	1.3[1]
		Heterocope	*septentrionalis*	Carnivore[2]	3.0, 3.8, 4.0[3]
		Leptodiaptomus	*pribilofensis*	Herbivore[4]	1.0, 1.8[5]
		Leptodiaptomus	*sicilis*	Omnivore[1,6]	1.24[1], 1.07[6]
		Leptodiaptomus	*siciloides*	Herbivore[1]	0.95[1],1.0, 1.1, 1.3[3]
		Senecella	*calanoides*	Omni-Herbivore[1]	1.98[1], 2.65, 2.9, 2.45, 2.55[3]
	Cyclopoida	Copepodite		Immature	
		Acanthocyclops	*robustus x vernalis*	Omnivore[6]	0.72[6],1.2[1],1.14[1,6]
		Cyclops	*scutifer*	Omnivore[1,6,4]	1.5[1], 0.88[6], 1.0, 1.29, 1.4, 1.9[3], 1.0, 1.8[5]
		Eucyclops	*agilis*	Omni-Herbivore[1]	1.1[1], 0.68,0.8,1.5[3]
		Microcyclops	*rubellus*	Carnivore[7]	0.36, 0.424, 0.46[8]
	Poecilostomatoida	*Ergasilus*	*sp.*	Parasitic[9]	
	Harpacticoida	*Harpacticoida*	*sp.*	Omnivore[1]	0.47[1], 0.9[4]
Cladocera	Bosminidae	*Bosmina*	*longirostris*	Herbivore[1,6]	0.33[1], 0.4[6]
		Eubosmina	*longispina*	Herbivore[6]	0.44[6]
	Chydoridae	*Acroperus*	*harpae*	Herbivore[1]	0.95[1]
		Alona	*sp.*	Herbivore[1]	0.32[1]
		Camptocercus	*sp.*	Herbivore[1]	0.78[1]
		Chydorus	*sphaericus*	Herbivore[1,6]	0.29[1],0.46[6,10]
		Graptoleberus	*testudinaria*	Herbivore[11]	0.5, 0.7[3]

Table A3 (*continued*)

Taxa	Order/Family	Genus	Species	Trophic group	Size (mm)
Cladocera	Daphniidae	*Daphnia*	*ambigua*	Herbivore[1,6]	0.88[1,6], 0.75, 0.9, 1.0[3]
		Daphnia	*longiremis*	Herbivore[1]	0.84[1], 0.8, 1.2[3]
		Daphnia	*mandotae*	Herbivore[11]	1.3, 3.0, 1.0[3]
		Daphnia	*middendorffiana*	Herbivore[11]	2.5, 3.00[3], 1.9, 2.7[12]
		Daphnia	*parvula*	Herbivore[1]	1.1[1], 0.75, 1.0, 0.6[3]
		Daphnia	*pulex x pluricaria*	Herbivore[1,6]	1.2, 1.3[1], 1.75[6]
	Dapniidae	*Ceriodaphnia*	*lacustris*	Herbivore[1,6]	0.416[1],0.85[6], 0.8, 0.9[3]
	Holopedidae	*Holopedium*	*gibberum*	Herbivore[1,6]	0.77[1], 1.04[6],0.5, 0.6, 1.5, 2.2[3]
	Leptodoridae	*Leptodora*	*kindti*	Carnivore[1]	3.8[1]
	Macrothricidae	*Macrothrix*	*sp.*	Herbivore[1]	0.55[1]
	Sididae	*Diaphanosoma*	*branchyurum*	Herbivore[1,6]	0.54[1], 0.85[6], 0.4, 0.8, 0.9[3]
		Sida	*crystallina*	Herbivore[1,6]	1.47[1], 2.55[6], 1.5, 2.0, 3.0, 4.0[3]

Omni-Herbivore referes to an omnivorous diet but with a herbivorous preference. Superscript references: [1]Hébert et al. (2016), [2]O'Brien (1988), [3]Edmondson (1959), [4]Kling (1994), [5]Johnson et al. (2007), [6]Barnett et al. (2007), [7]Poelen et al. (2014), [8]Reid (1992), [9]Hudson et al. (2003b), [10]Tümpling & Friedrich (1999), [11]Thorp & Rogers (2014) and [12]Hebert (1995).

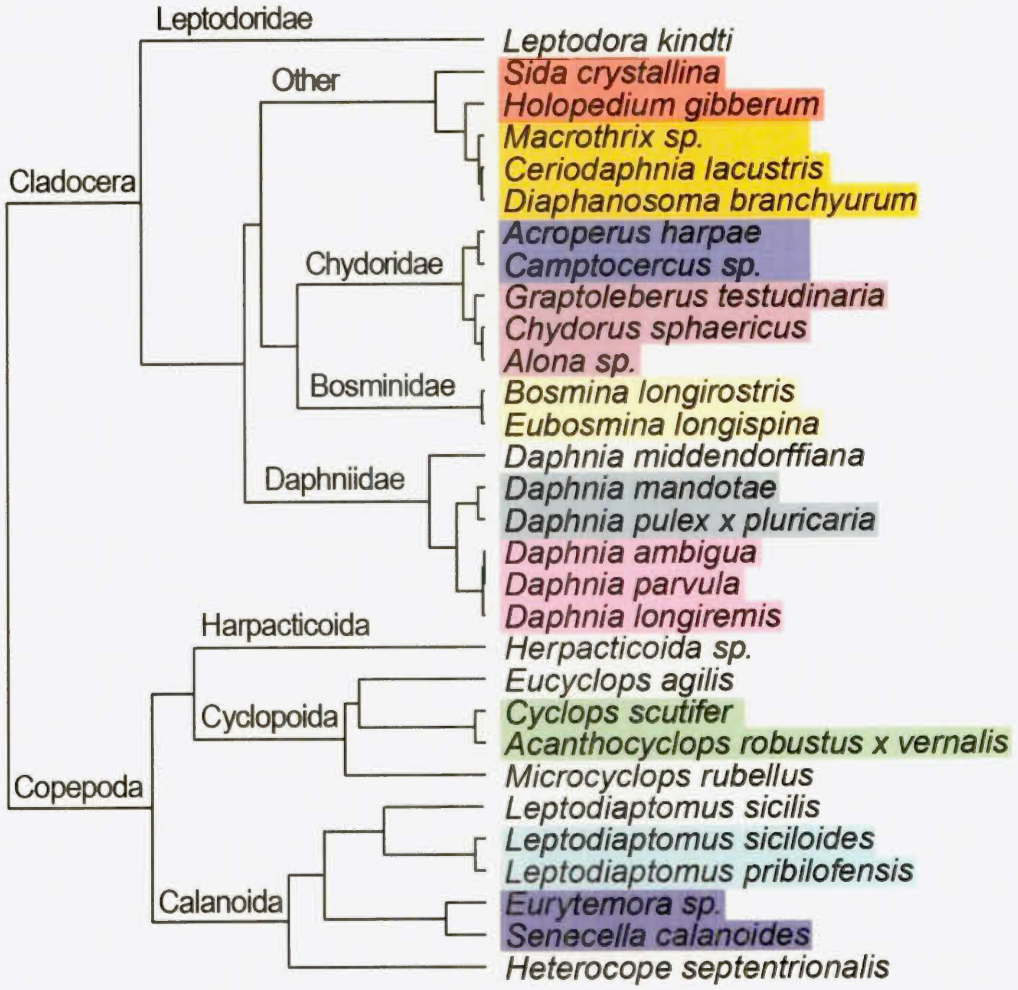


Figure A1. Functional trait dendogram based on species specific trophic group and mean size. Species specific information can be found in Table A3. Species of same color were grouped. Species left blank mean they were not combined with any other species.

APPENDIX B

SUPPLEMENTARY STATISTICAL METHODS

Lake exclusions

Certain lakes were excluded from taxon-specific series of correlation analyses and multiple regression models. Ekali Lake was excluded from all correlation and regression analyses. Visual analyses of Bulk zooplankton results revealed that Ekali Lake had high leverage in all bivariate analyses between MeHg in Bulk zooplankton and environmental covariates; in short, the MeHg concentration in Bulk zooplankton was very high (more than 1.5 x interquartile range ± the median) and qualified as an outlier. Further analyses revealed that the Bulk zooplankton sample from the pelagic zone of Ekali Lake was uniquely and unexpectedly dominated by parasitic copepods. These parasitic copepods occupied a higher trophic position than copepods found in the other lakes, which explained the high MeHg concentration (Figure 1.5). For this reason, we also excluded Ekali Lake from the Copepoda taxon-specific analyses.

Ekali Lake was excluded from Cladocera taxon-specific analyses because the field sampling from this lake represented a mixed sample of inshore and offshore individuals, and thus was not representative of the pelagic community. For the same reason, RDC308 Lake was excluded from the Copepoda taxon-specific analyses, while RDC309 Lake was excluded from both Copepoda and Cladocera taxon-specific analyses. Lakes RDC311 and ATQ201 were excluded from Cladocera and Copepoda analyses, respectively, because of lack of sufficient biomass for isotopic and MeHg tissue analyses. Consequently, correlation and multiple linear regression model analyses were performed with 11 lakes for Bulk zooplankton (n=11), 9 lakes for Cladocera (n=9), and 8 lakes for Copepoda (n=8).

Missing Data

Certain lakes had environmental or MeHg concentrations in water or zooplankton tissue that were below analytical detection limits, and this limited some statistical analyses. SO_4^{2-} was below detection in one lake (ATQ200), and unfiltered concentrations of MeHg in water were below detection limits in Kluane M and in Kathleen Lake. Further, filtered MeHg in water was below detection limits in ATQ200, ATQ201 and Kathleen lakes, bellow the method detection limit for Kluane M, and at the detection limit for ATQ206 (0.006 ng-L^{-1}). There was insufficient tissue to conduct $\delta^{15}N$ analyses in four lakes for Cladocera (RDC311, RDC308, Big Island and Sanguez) and Copepoda (ATQ201. RDC311, RDC309 and RDC308).

Model selection – multiple linear regression

Correlations: For Bulk zooplankton, six environmental variables were correlated with zooplankton MeHg tissue concentration; SO_4^{2-} ($p = 0.0005$; r=-0.8933), Conduc. ($p = 0.0041$; r = -0.7860), CladPerL ($p = 0.0061$; r = 0.7648), SUVA ($p = 0.0128$; r = -0.7181), Chl-a ($p = 0.0857$; r = 0.54093) and TN ($p = 0.1084$; r = 0.5107). Because nutrients influence Chl-a concentration in lakes (Smith, 1982), we chose to include TN in the multiple regression models rather than Chl-a. With five variables, we had 31 possible models to explain zooplankton MeHg tissue concentration in the Bulk zooplankton samples (Table 1.4). For Cladocera, two variables were included in the model selection: pH ($p = 0.0245$, r = -0.7336) and $\delta^{15}N$ ($p = 0.049$, r = 0.8134), for a total of three possible models to explain Cladocera zooplankton MeHg tissue concentration (Table 1.5). For Copepoda, three variables were showing linear relationship with Copepoda MeHg tissue concentration: DOC ($p = 0.0031$, r =

0.8891), Abs. (p = 0.0099, r = 0.8348) and filtered MeHg concentration in the water (FMeHgW) (p = 0.0433, r = 0.8249). However, FMeHgW concentrations were lower then detection limits for ATQ200, Kluane M and Kathleen lakes and at the detection limit for ATQ206 (0.006 ng-L^{-1}) resulting in not having enough data lake to include FMeHgW in the model set. With only DOC and Abs. included in the model set, a total of three possible models were tested to explain Copepoda MeHg (Table 1.6). For each series of taxon -specific models, a null model was included in the model set.

APPENDIX C

SUPPLEMENTARY GRAPHICS AND RESULTS

Table C1. Taxon-specific three-factor Lorentzian model and parameter estimation statistics.

Taxa	Model df	Model error df	*F* value	Model *p*-value	Model parameter	Parameter Estimate	Std. Error	Confidence limits	*T* value	Parameter *p*-value
Bulk	3	7	8.91	**0.009**	a	67.87	16.00	± 37.83	4.24	**0.004**
					b	3.99	2.05	± 4.84	1.95	0.092
					X0	5.44	3.78	± 8.94	1.44	0.194
Cladocera	3	6	13.52	**0.005**	a	151.80	3.17	± 78.74	4.72	**0.003**
					b	4.09	1.22	± 2.99	3.35	**0.015**
					X0	7.39	2.22	± 5.43	3.33	**0.016**
Copepoda	3	7	32.61	**< 0.001**	a	342.90	39.33	± 93.00	8.72	**< 0.001**
					b	1.16	0.41	± 0.96	2.85	**0.025**
					X0	8.05	0.43	± 1.03	18.55	**< 0.001**

Where *a* is the inflection point of the curve on the y-axis, *X0* is the DOC concentration at the inflection point on the x axis (or the DOC threshold concentration (DOC T_c)), and *b* is a measure of the spread of the curve. Limits of confidence intervals were set at 95%. Kathleen lake was excluded from all analysis. Taxa-specific parameters were estimated from each data set and computed in separated models.

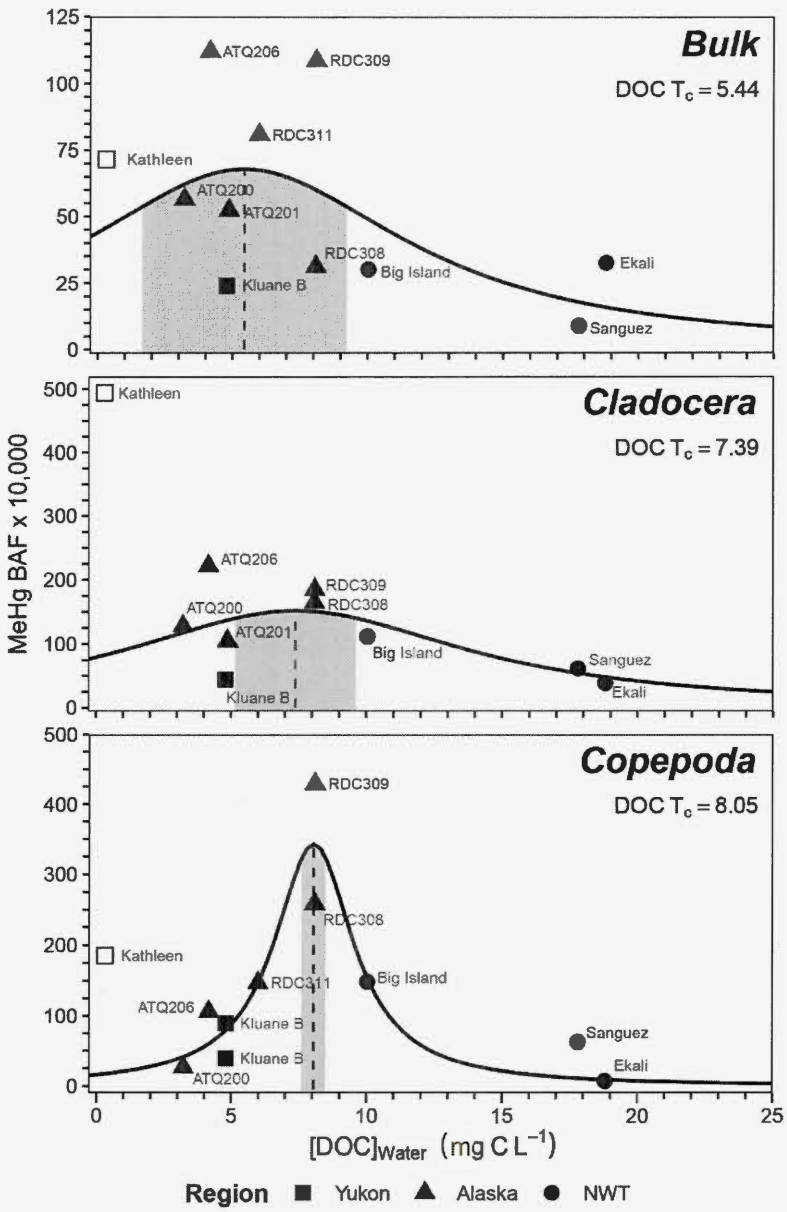


Figure C1. Zooplankton MeHg BAF in relation to a freshwater gradient in DOC concentration among lakes across three regions of the Western Arctic. A three-factor Lorentzian model was used (French et al. 2014) to determine the DOC threshold concentration (DOC Tc; dotted gray line) (mg-C-L^{-1}) for each taxa past which MeHg BAF begins to decline. Shaded region: standard error for DOC Tc. Kathleen Lake is represented by open symbols, and is plotted on graph panels but was excluded from models because of uncertainty in lakewater MeHg concentration related to analytical detection limits. Model parameter statistics are shown in are shown in Table C1.

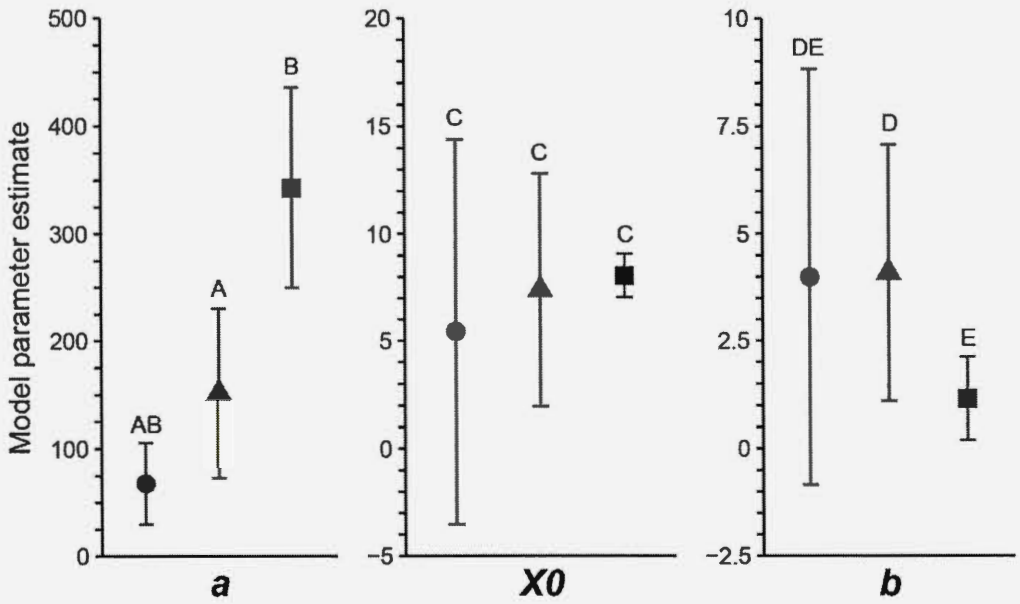


Figure C2. Comparisions among taxon-specific groups of zooplankton of the three factor Lorentzian model parameter estimates and their 95% confidence intervals. The left panel represents taxon-specific estimation for model parameter *a,* the inflection point of the curve on the y-axis. The middle panel represents taxon-specific estimation for model parameter *X0*, the DOC concentration at the inflection point on the x-axis. The right panel represents taxon-specific estimation for model parameter *b*, which is a measure of the spread of the curve. Each taxon-specific group is represented by the following symbols: circle for Bulk zooplankton samples, triangle for Cladocera samples, and a square for Copepoda samples. Significant differences between taxon-specific groups for each model parameter estimate ($P \leq 0.05$) are indicated by different letters, as revealed by likelihood ratio tests.

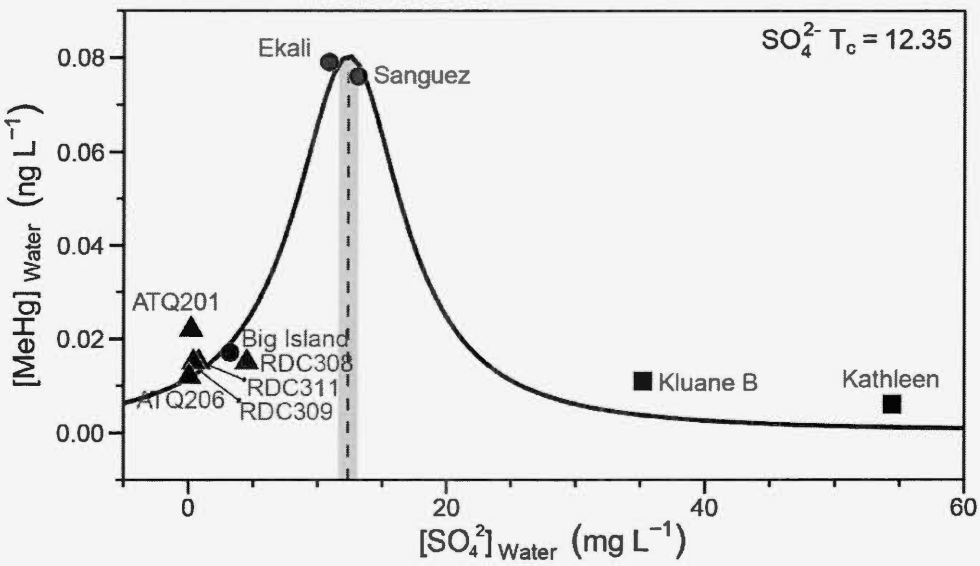


Figure C3. A unimodal relationship between lakewater sulfate (SO_4^{2-}) concentration and unfiltered aqueous MeHg (UFMeHgW). The regions are represented by different symbols, square: Yukon lakes; triangle: Alaska lakes; circle: NWT lakes. Dashed line: SO_4^{2-} threshold concentration (SO_4^{2-} Tc; mg-L^{-1}) past which UFMeHgW starts to decline. Shaded region: SO_4^{2-} Tc standard error. The unimodal relationship was calculated with a three-factor Lorentzian model.

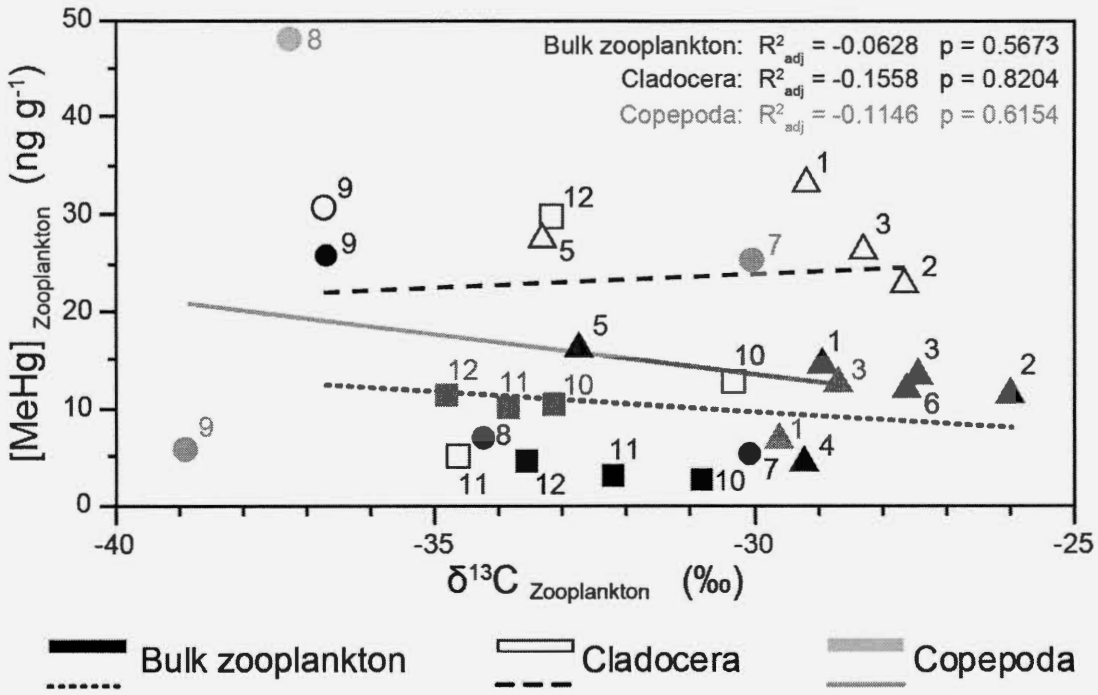


Figure C4. Carbon isotopes ratio ($\delta^{13}C$; ‰) for each taxa in each lake in relation with their specific MeHg tissue concentration (ng-g^{-1}). Regions are represented by different symbols, square: Yukon lakes, triangle: Alaska lakes, and circle: NWT lakes. Lakes are numbered as followed: **1.** ATQ200, **2.** ATQ201, **3.** ATQ206, **4.** RDC308, **5.** RDC309, **6.** RDC311, **7.** Big Island, **8.** Sanguez, **9.** Ekali, **10.** Kluane M, **11.** Kluane B, and **12.** Kathleen. More negative value of $\delta^{13}C$ represent a more pelagic or outshore feeding, while less negative value of $\delta^{13}C$ represent a more benthic or nearshore feeding.

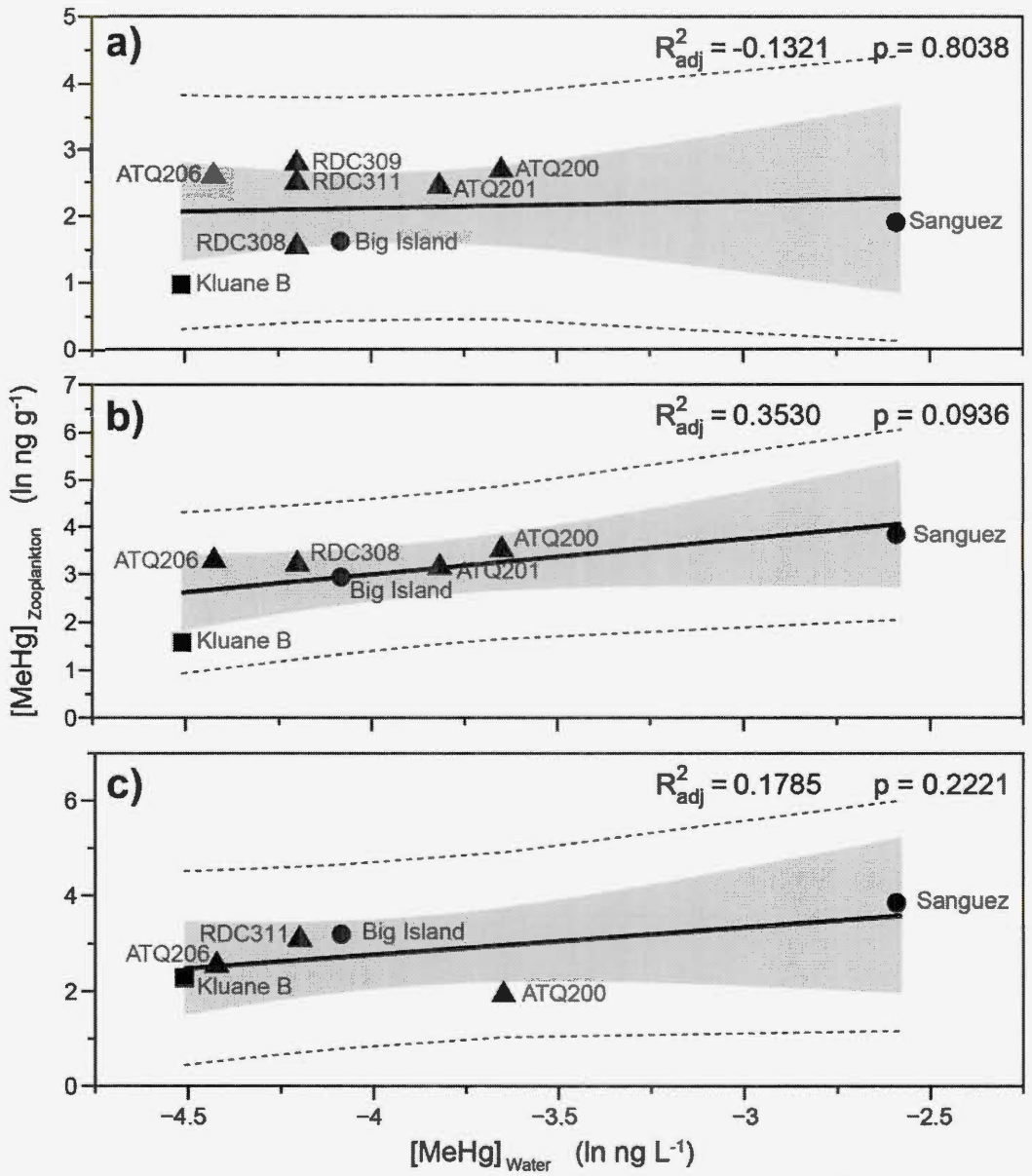


Figure C5. Linear regression models for relationships between a) Bulk zooplankton, b) Cladocera and c) Copepoda MeHg tissue concentration and aqueous unfiltered MeHg. Shaded areas: 95% confidence intervals, dotted line: prediction intervals. Regions are represented by different symbols, square: Yukon lakes, triangle: Alaska lakes, and circle: NWT lakes. Ekali, Kluane M and Kathleen were excluded from all taxa. RDC309 was excluded from both Cladocera and Copepoda, RDC311 was exclude only from Cladocera and RDC308 and ATQ201 were exclude from Copepoda. Statistics are presented in Table 1.3.

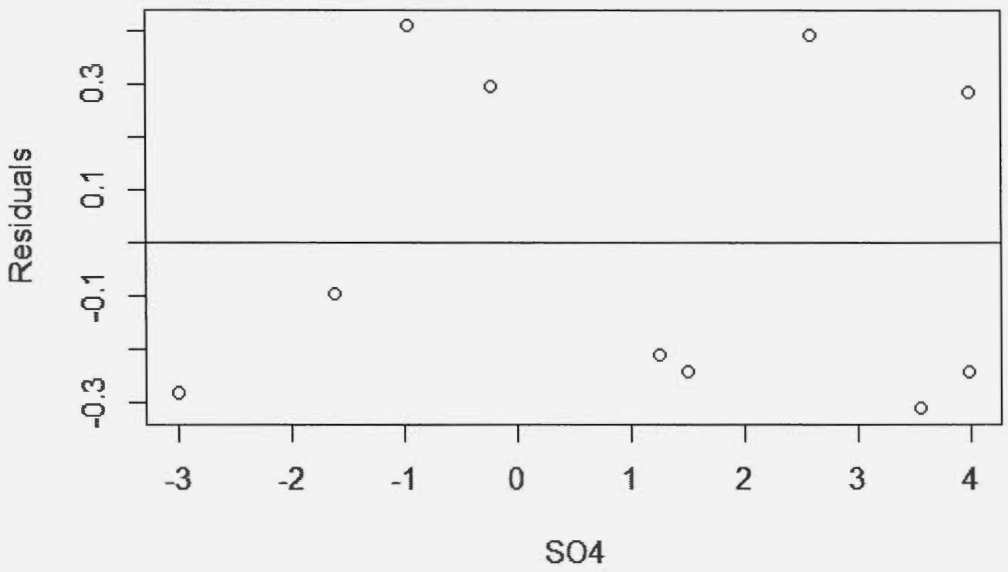
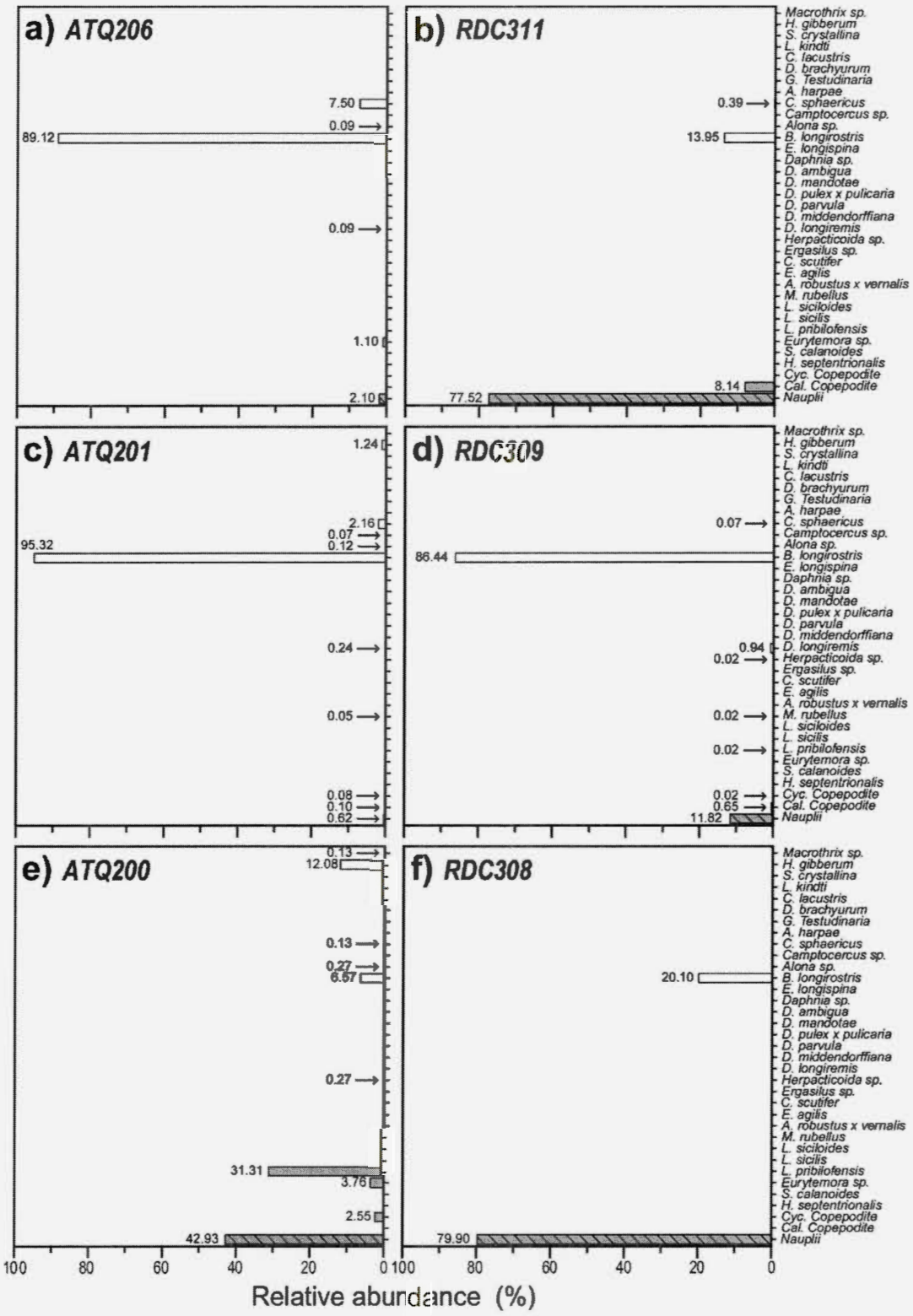


Figure C6. Residuals plots for model looking at how Bulk zooplankton MeHg concentration is related to sulfate (SO_4^{2-}). Both Bulk zooplankton MeHg concentration and SO_4^{2-} were *ln* transformed.


a) ATQ206
7.50
0.09
89.12
0.09
1.10
2.10
b) RDC311
0.39
13.95
8.14
77.52
c) ATQ201
1.24
2.16
0.07
0.12
95.32
0.24
0.05
0.08
0.10
0.62
d) RDC309
0.07
86.44
0.94
0.02
0.02
0.02
0.02
0.65
11.82
e) ATQ200
0.13
12.08
0.13
0.27
6.57
0.27
31.31
3.76
2.55
42.93
f) RDC308
20.10
79.90
Macrothrix sp.
H. gibberum
S. crystallina
L. kindti
C. lacustris
D. brachyurum
G. Testudinaria
A. harpae
C. sphaericus
Camptocercus sp.
Alona sp.
B. longirostris
E. longispina
Daphnia sp.
D. ambigua
D. mandotae
D. pulex x pulicaria
D. parvula
D. middendorffiana
D. longiremis
Herpacticoida sp.
Ergasilus sp.
C. scutifer
E. agilis
A. robustus x vernalis
M. rubellus
L. siciloides
L. sicilis
L. pribilofensis
Eurytemora sp.
S. calanoides
H. septentrionalis
Cyc. Copepodite
Cal. Copepodite
Nauplii
100
80
60
40
20
0
Relative abundance (%)

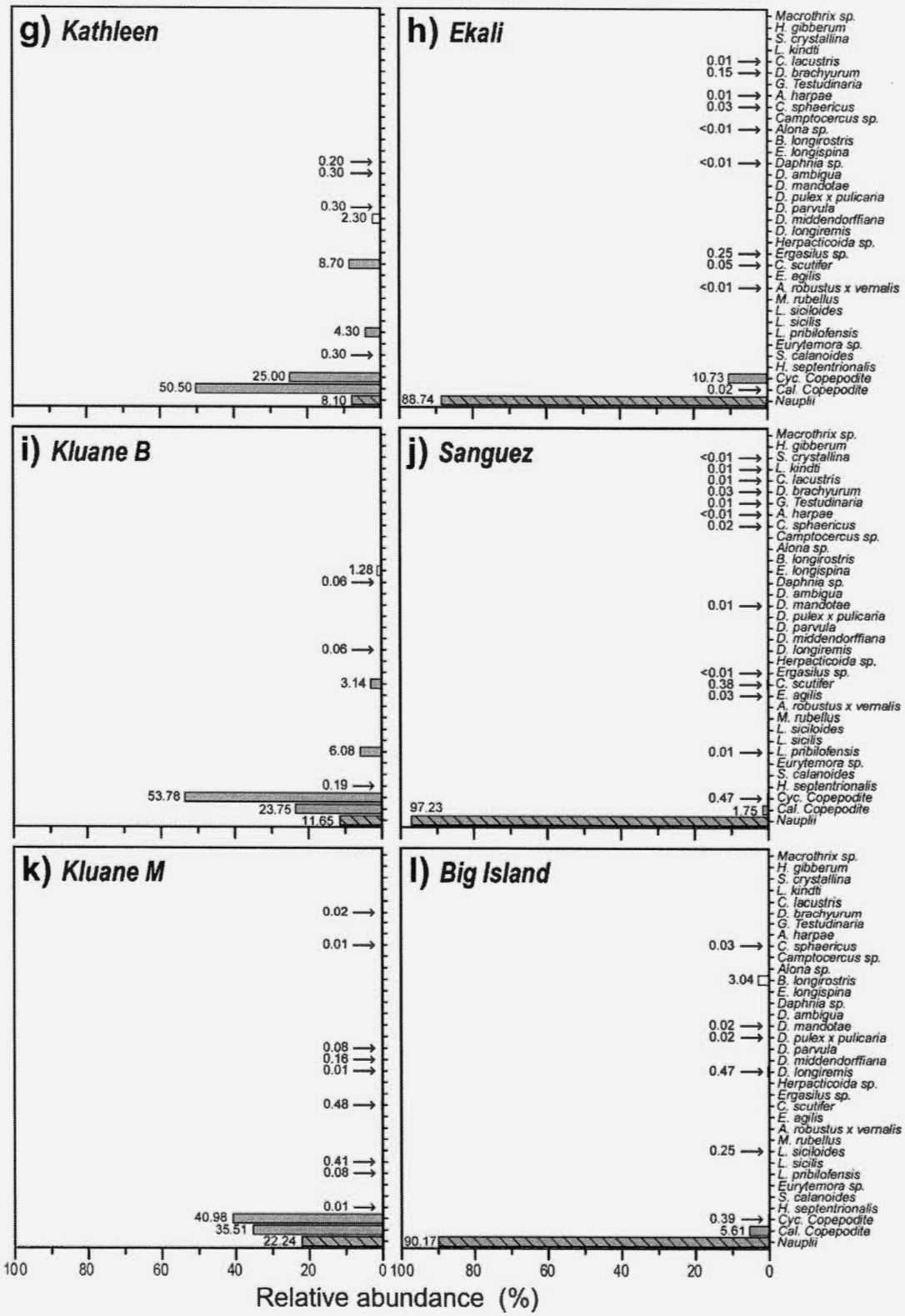

g) Kathleen
0.20
0.30
0.30
2.30
8.70
4.30
0.30
25.00
50.50
8.10
h) Ekali
0.01
0.15
0.01
0.03
<0.01
<0.01
0.25
0.05
<0.01
10.73
0.02
88.74
i) Kluane B
1.28
0.06
0.06
3.14
6.08
0.19
53.78
23.75
11.65
j) Sanguez
<0.01
0.01
0.01
0.03
0.01
<0.01
0.02
0.01
<0.01
0.38
0.03
0.01
0.47
97.23
1.75
k) Kluane M
0.02
0.01
0.08
0.16
0.01
0.48
0.41
0.08
0.01
40.98
35.51
22.24
l) Big Island
0.03
3.04
0.02
0.02
0.47
0.25
0.39
5.61
90.17
Macrothrix sp.
H. gibberum
S. crystallina
L. kindti
C. lacustris
D. brachyurum
G. Testudinaria
A. harpae
C. sphaericus
Camptocercus sp.
Alona sp.
B. longirostris
E. longispina
Daphnia sp.
D. ambigua
D. mandotae
D. pulex x pulicaria
D. parvula
D. middendorffiana
D. longiremis
Herpacticoida sp.
Ergasilus sp.
C. scutifer
E. agilis
A. robustus x vernalis
M. rubellus
L. siciloides
L. sicilis
L. pribilofensis
Eurytemora sp.
S. calanoides
H. septentrionalis
Cyc. Copepodite
Cal. Copepodite
Nauplii
100
80
60
40
20
0
Relative abundance (%)

Figure C7. Relative abundance of zooplankton species in the crustacean zooplankton community for each lake in Alaska (a to f), Yukon (g, i and k), and Northwest Territories (h, j and l). Copepoda species are presented in gray, while cladoceran species are presented in white. Dashed region represent nauplii, the larval stage of Copepoda. Copepodites, the immature stage of Copepoda, are separated in calanoide (Cal. Copepodite) and cyclopoid (Cyc. Copepodite). Arrow represent species that were present in the community, but in too small percentage to be represented visually on the graph. Number above bars or arrows represent the exact percentage accupied by this species/group in the community for each lake.

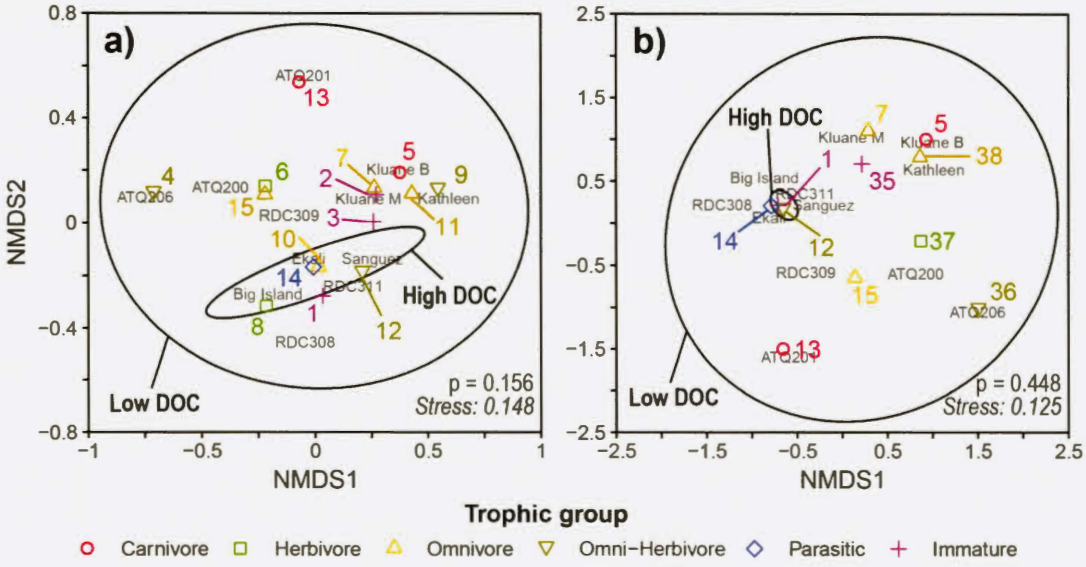


Figure C8. NMDS biplots of Copepoda community composition among lakes across three western Arctic regions according to taxonomic species abundance (left panels: a) and functional group abundance (right panels: b). The distribution of species and functional groups in copepods communities was determined by aqueous DOC concentration (low: from 0 to 9.49 mg-C-L^{-1}; high: 9.50 to 19 mg-C-L^{-1}). Species ordination positions are represented by numbers: ***Juvenile copepod stages:*** **1.** Nauplii, **2.** Copepedite calanoida, **3.** Copepedite cyclopoida; ***Calanoid copepods:*** **4.** *Eurytemora sp.*, **5.** *Heterocope septentrionalis*, **6.** *Leptodiaptomus pribilofensis,* **7.** *Leptodiaptomus sicilis*, **8.** *Leptodiaptomus siciloides,* **9.** *Senecella calanoides*; ***Cyclopoid copepods: 10.*** *Acanthocyclops robustus/vernalis,* **11.** *Cyclops scutifer*, **12.** *Eucyclops agilis*, **13.** *Microcyclops rubellus*; ***Other copepods:*** **14.** *Ergasilus sp.*, and **15.** *Herpacticoida sp.*. Numbers over 34 represent species groups that were clustered according to ***functional traits:*** Order, trophic feeding group, and mean body length (see Table A3 and Figure A1): **35.** *2* and *3*, **36.** *4* and *9*, **37.** *6* and *8*, and **38.** *10* and *11*. Trophic groups are represented by shape; circles for carnivore, square for herbivores, triangles for omnivore, upside down triangle for omnivore with herbivory preferences, diamond for parasitic and cross for immature.

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