UNIVERSITÉ DU QUÉBEC À MONTRÉAL

CONTRIBUTION ET RÉGULATION DE L'ÉBULLITION SUR LES ÉMISSIONS TOTALES DE MÉTHANE PAR LES SYSTÈMES AQUATIQUES TEMPÉRÉS ET BORÉAUX DU QUÉBEC

MÉMOIRE

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AVANT-PROPOS

Ce mémoire portant sur les émissions de méthane par les écosystèmes aquatiques du Québec est séparé en trois sections; une introduction générale, un chapitre sous forme d'article scientifique et une brève conclusion. L'introduction permet de faire un survol des connaissances scientifiques pertinentes à la compréhension de mon sujet et présente également la problématique reliée à mon projet. De plus, on y expose les objectifs généraux ainsi que les hypothèses de ce projet de recherche. Par la suite, on retrouve le corps du projet sous forme d'un article scientifique qui porte sur la dépendance à la température de l'ébullition. Cet article est écrit en anglais dans le but de le publier dans la revue scientifique Ecosystems. Une brève conclusion permet ensuite de placer ce projet d'étude dans un contexte plus large et de faire la lumière sur sa contribution aux savoirs scientifiques actuels.

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C	Carbone
CH_4	Méthane
Chl *a*	Chlorophylle *a*
CO_2	Dioxide de carbone
DOC	Carbone organique dissous
GES	Gaz à effet de serre
H_2	Dihydrogène
ppb	Partie par milliard
ppm	Partie par million
Tg	Téragramme
TN	Azote total
TP	Phosphore total

RÉSUMÉ

Dans les écosystèmes aquatiques, l'ébullition peut représenter une importante composante des émissions totales de méthane (CH_4). Toutefois, en raison de sa nature épisodique et hétérogène, ce processus a rarement été quantifié de façon simultanée avec les flux diffusifs de CH_4. De plus, la régulation de l'ébullition ainsi que sa contribution aux émissions totales demeurent encore grandement méconnues. L'objectif de cette étude est donc de mesurer la contribution de l'ébullition aux émissions totales de CH_4 dans les systèmes aquatiques du Québec et de déterminer quels sont les facteurs qui régulent l'ébullition. Nous avons mesuré l'ébullition (avec des entonnoirs de plastique) et la diffusion (avec une chambre flottante) sur 10 étangs au Saguenay en 2011 et 3 lacs situés dans les Laurentides en 2012 durant l'ensemble de la période sans glace. Dans les environnements peu profonds, l'ébullition contribue de 20 à plus de 90% des émissions totales de CH_4, et ce processus est plus important dans les étangs que pour la zone littorale des lacs. De plus, la température des sédiments a une grande influence sur les flux de CH_4, bien que l'ébullition soit considérablement plus sensible à la température que la diffusion. La dépendance à la température des émissions de CH_4 est aussi étroitement associée à la productivité du système. En conséquence, la contribution de l'ébullition est plus importante dans les endroits chauds et peu profonds tels que les étangs et la zone littorale des lacs productifs. Ces résultats suggèrent donc que l'eutrophisation ainsi qu'un réchauffement régional pourraient augmenter grandement les émissions de gaz à effet de serre, et ce principalement par ébullition.

Mots clés : Ébullition, méthane (CH_4), gaz à effet de serre (GES), écosystèmes aquatiques, changements climatiques

INTRODUCTION

0.1 Le méthane atmosphérique (CH_4)

Le méthane (CH_4) est le deuxième plus important gaz à effet de serre (GES) après le dioxyde de carbone (CO_2). Bien qu'il soit en faible concentration dans l'atmosphère, il a un potentiel de réchauffement climatique 25 fois plus puissant que le CO_2 sur un intervalle de 100 ans (Denman *et al.*, 2007 ; Forster *et al.*, 2007). Depuis l'ère industrielle, les concentrations atmosphériques en CH_4 ont connu une forte augmentation d'environ 150%, passant de 715 ppb à 1774 ppb (Cunnold *et al.*, 2002 ; Dlugokencky *et al.*, 1994). Il est très probable que cette augmentation ait été principalement causée par les activités anthropiques comme l'agriculture et l'utilisation des combustibles fossiles (Solomon *et al.*, 2007). Bien que cette augmentation ait ralenti depuis le début des années 1990 et que les émissions totales de CH_4, anthropiques et naturelles, semblent présentement être constantes aux alentours de 500-600 Tg CH_4/an (Dlugokencky *et al.*, 2003), des études récentes ont démontré que depuis 2007, la concentration en CH_4 atmosphérique serait encore en augmentation et atteint maintenant les 1779 ppb (Dlugokencky *et al.*, 2011 ; Kirschke *et al.*, 2013 ; Rigby *et al.*, 2008).

La majeure partie du CH_4 émis vers l'atmosphère est reliée aux activités anthropiques, représentant plus de 60% des sources totales de CH_4, soit près de 375 Tg CH_4/an (Solomon *et al.*, 2007 ; Wuebbles et Hayhoe, 2002). Le reste du CH_4, émis par des sources naturelles, provient en grande partie des zones humides, représentant à elles seules plus de 20% des émissions totales de CH_4, soit environ 100-230 Tg CH_4/an, (Matthews et Fung, 1987 ; Wuebbles et Hayhoe, 2002). En plus des zones humides, il est maintenant admis que les écosystèmes d'eau douce, c.-à-d. lacs, rivières et réservoirs, jouent eux aussi un rôle important dans le bilan de GES (Bastviken *et al.*, 2011 ; Cole *et al.*, 2007). Ces milieux émettraient annuellement environ 103 Tg CH_4, dont les lacs contribueraient à eux seuls entre 8-18 Tg CH_4/an (Bastviken *et al.*, 2004). Toutefois, bien que les sources de CH_4 aient été bien identifiées, leur contribution relative au budget total de CH_4 demeure encore grandement incertaine (Kirschke *et al.*, 2013 ; Ortiz-Llorente et Alvarez-Cobelas, 2012).

De plus, la répartition des plans d'eau à l'échelle mondiale est grandement hétérogène et se concentre principalement dans l'hémisphère nord, entre les latitudes 50-70°N (Downing *et al.*, 2006 ; Gorham, 1991 ; Matthews et Fung, 1987). L'abondance de plans d'eau en milieu boréal et tempéré fait de ces biomes des lieux de choix pour étudier davantage le rôle des écosystèmes aquatiques dans le bilan global de CH_4. Ces systèmes aquatiques pourraient donc représenter un véritable enjeu pour le climat puisqu'il est maintenant admis qu'ils répondront fortement aux changements climatiques (Flato et Boer, 2001 ; Friedlingstein et Prentice, 2010 ; Gedney, Cox et Huntingford, 2004 ; Tranvik *et al.*, 2009). Toutefois, l'impact de ces changements sur le cycle du CH_4 aquatique reste incertain (Kirschke *et al.*, 2013). Il devient donc essentiel de bien comprendre les processus sous-jacents au cycle du CH_4, soit la production, la consommation et le transport du CH_4 vers l'atmosphère, pour prévoir dans quelle mesure les changements environnementaux engendrés par le réchauffement de la température affecteront les émissions de CH_4.

0.2 La production de CH_4 dans les écosystèmes aquatiques

Plusieurs processus liés à la production de CH_4 dans les milieux aquatiques sont potentiellement sensibles aux changements environnementaux. Dans les écosystèmes aquatiques, le CH_4 est principalement produit lors de la décomposition de la matière organique par l'intermédiaire d'archaea méthanogènes (Borrel *et al.*, 2011 ; Conrad, 2009 ; Kiene, 1991). Ce groupe d'archées est omniprésent dans les environnements anaérobiques tels que les sédiments des milieux aquatiques et l'hypolimnion anoxique des lacs productifs. À eux seuls, les microorganismes méthanogènes seraient responsables de 10-50% de l'ensemble de la minéralisation du carbone dans les lacs (Bastviken *et al.*, 2008). Les deux principaux mécanismes pour la production de CH_4 sont la réduction du CO_2 et la fermentation de l'acétate (Peters et Conrad, 1996 ; Vasander et Kettunen, 2006 ; Zehnder, 1978). Ce dernier mécanisme représente à lui seul environ 70% de tout le CH_4 produit dans les écosystèmes aquatiques. Les taux de production du CH_4 sont toutefois contrôlés par un ensemble de facteurs qui varient selon la localisation et les caractéristiques du milieu (Borrel *et al.*, 2011).

Deux facteurs clés, potentiellement reliés à l'activité humaine, sont à la base de la méthanogenèse. D'abord, étant donné que les bactéries méthanogènes sont strictement anaérobiques, la principale contrainte à la méthanogenèse est la présence d'oxygène. La production de CH_4 est complétement inhibée par des concentrations en oxygène au-dessus de 10 ppm (Borrel *et al.*, 2011 ; Garcia, Patel et Ollivier, 2000 ; Huttunen *et al.*, 2006). La méthanogenèse est également fortement contrôlée par l'apport de substrat pour la décomposition. Des études en laboratoire ont démontré qu'une addition directe (acétate, H_2) ou indirecte de substrats (glucose, éthanol) augmente fortement la production de CH_4 (Boon et Mitchell, 1995 ; Valentine, Holland et Schimel, 1994). La méthanogenèse peut donc être stimulée par l'augmentation du niveau trophique d'un plan d'eau qui amène des apports de carbone organique frais aux sédiments (Casper *et al.*, 2000 ; Coles et Yavitt, 2002 ; Valentine, Holland et Schimel, 1994 ; Whiting et Chanton, 1993). L'eutrophisation d'un plan d'eau par l'enrichissement en nutriments et la diminution de l'oxygène entraine donc des conditions favorables à la production de CH_4.

De plus, comme la plupart des réactions métaboliques, la production de CH_4 est fortement contrôlée par la température du milieu (Glissman *et al.*, 2004 ; McKenzie *et al.*, 1998 ; Schulz et Conrad, 1996). La température optimale pour la production de CH_4 se situe généralement entre 30 et 40°C (Zeikus et Winfrey, 1976 ; Zinder, 1993). En milieu boréal et tempéré, la production de CH_4 serait donc limitée par la température de l'eau, qui se situe généralement sous l'optimum de croissance des méthanogènes (Duc, Crill et Bastviken, 2010 ; Nozhevnikova *et al.*, 2007 ; Schulz et Conrad, 1996). L'influence de la température sur la production de CH_4 a été largement admise dans la littérature (Dunfield *et al.*, 1993 ; Inglett *et al.*, 2012 ; Schulz et Conrad, 1996 ; Yavitt, Williams et Wieder, 2000), mais l'ampleur de sa réaction reste mitigée. Par exemple, on reporte pour les zones humides des Q_{10} (c.-à-d., le facteur d'augmentation de la production de CH_4 pour une augmentation de 10°C en température) allant de 1 à 35 (Segers, 1998 ; van Hulzen *et al.*, 1999 ; Whalen, 2005). Une augmentation de la température moyenne globale ainsi que des activités humaines pourrait donc avoir un impact important sur la quantité de CH_4 produit. Toutefois, l'ampleur de ces changements sur les émissions de CH_4 dépendra également de leurs effets sur l'oxydation du CH_4 dans la colonne d'eau et de son transport vers l'atmosphère.

0.3 L'oxydation du CH_4

L'oxydation du CH_4 joue un rôle fondamental dans la régulation des émissions de CH_4. Les bactéries méthanotrophes oxydent entre 30-99% de tout le CH_4 produit annuellement dans les sédiments (Bastviken *et al.*, 2008 ; Kankaala *et al.*, 2006). Les bactéries méthanotrophes dépendent à la fois de la concentration en CH_4 dans la colonne d'eau et de la concentration en oxygène (Dzyuban, 2010 ; Lofton, Whalen et Hershey, 2013 ; Sundh, Bastviken et Tranvik, 2005). Dans les lacs productifs, durant la période estivale de stratification, on retrouve ainsi des taux maximums d'oxydation dans le métalimnion où les concentrations en O_2 et en CH_4 sont les plus élevées (Dzyuban, 2010). L'oxydation du CH_4 est donc étroitement liée à sa production (Duc, Crill et Bastviken, 2010 ; Sundh, Bastviken et Tranvik, 2005); une disponibilité élevée du CH_4 engendrera une augmentation rapide des taux d'oxydation (Bender et Conrad, 1994). Contrairement à la méthanogenèse, l'oxydation du CH_4 est toutefois beaucoup moins influencée par la température (Duc, Crill et Bastviken, 2010 ; Utsumi *et al.*, 1998). Les valeurs de Q_{10} pour l'oxydation sont généralement de 1.8 à 2.9 (Whalen, 2005). Une augmentation de la température favorisera donc directement la production de CH_4 alors que sa consommation sera affectée indirectement par l'augmentation des teneurs en CH_4 dans l'eau. L'augmentation saisonnière du CH_4 peut donc être en partie contrebalancée par l'oxydation.

0.4 Le transport du CH_4 vers l'atmosphère

La proportion du CH_4 qui sera contrebalancée par l'oxydation dépendra de son mode de transport vers l'atmosphère. Le CH_4 produit dans les sédiments est émis vers l'atmosphère par trois processus; transport par les plantes (Kankaala *et al.*, 2005 ; Whiting et Chanton, 1992), diffusion Fickian et non-Fickian (Bastviken *et al.*, 2004 ; Baulch *et al.*, 2011 ; Beaulieu, Shuster et Rebholz, 2012 ; Prairie et del Giorgio, 2013) et ébullition (Bastviken *et al.*, 2004 ; Joyce et Jewell, 2003). Alors que la présence ou l'absence de plantes aquatiques demeure un aspect imprévisible à estimer, la diffusion et l'ébullition représentent quant à eux les principaux mécanismes pour le transport du CH_4 dans les étangs et les lacs peu profonds (Casper *et al.*, 2000 ; Joyce et Jewell, 2003 ; Weyhenmeyer, 1999). Pour ces raisons, nous avons décidé de focaliser cette étude seulement sur ces deux derniers mécanismes.

0.4.1 La diffusion

Une partie du CH_4 accumulée dans les sédiments diffuse lentement dans la colonne d'eau selon les différences de concentrations et la vitesse d'échange à l'interface sédiment-eau. Aussitôt que le CH_4 atteint la zone oxique, une grande proportion est oxydée en CO_2 par les bactéries méthanotrophes (Bastviken, Ejlertsson et Tranvik, 2002 ; Hanson et Hanson, 1996). La petite portion du CH_4 qui échappe à l'oxydation sera ensuite émise vers l'atmosphère par diffusion à l'interface eau-air. Pour les lacs stratifiés, le CH_4 peut s'accumuler dans l'hypolimnion anoxique durant la saison estivale et être rapidement relâché vers l'atmosphère durant les périodes de brassage, comme au printemps et en automne pour les lacs dimictiques tempérés (Michmerhuizen, Striegl et McDonald, 1996). Ces périodes de brassage peuvent représenter entre 22-48% du budget annuel de CH_4 pour la zone pélagique des lacs (Huttunen *et al.*, 2003b). Ces périodes sont considérées comme des moments importants pour le budget de CH_4 puisqu'elles permettent à une grande quantité de CH_4 d'échapper aux bactéries méthanotrophes en étant rapidement émis vers l'atmosphère. En période de brassage, la diffusion peut donc être un mode de transport efficace pour échapper à l'oxydation.

0.4.2 L'ébullition

Une autre façon efficace pour le CH_4 d'échapper aux bactéries méthanotrophes est d'être directement émis des sédiments vers l'atmosphère par ébullition. En raison de la faible solubilité du CH_4 dans l'eau, lorsque les concentrations en CH_4 excèdent la concentration de saturation du CH_4 dans l'eau, le CH_4 reste accumulé dans les sédiments et mène à la formation de bulles. Le principal constituant des bulles de gaz est le CH_4, suivi par le N_2 et le CO_2 (Casper *et al.*, 2000 ; Chanton et Martens, 1988 ; Martinez et Anderson, 2013). La composition exacte en CH_4 est toutefois variable entres les études, allant de 30-100%, mais la plupart se situent aux alentours de 70% de CH_4 (Bartlett *et al.*, 1988 ; Casper *et al.*, 2000 ; Keller et Stallard, 1994 ; Mattson et Likens, 1990 ; Tokida *et al.*, 2007).

Les évènements de bullages sont très variables dans l'espace et le temps (Bastviken *et al.*, 2008 ; DelSontro *et al.*, 2011 ; Ostrovsky, 2003). Ils sont pour la plupart du temps reliés au relâchement de la pression hydrostatique sur les sédiments qui facilite la libération des bulles de CH_4. Ainsi, l'ébullition est souvent le processus dominant dans les environnements peu profonds comme les zones humides (Keller et Stallard, 1994 ; Weyhenmeyer, 1999) et la zone littorale des lacs (Casper *et al.*, 2000 ; Joyce et Jewell, 2003) en raison de la faible pression exercée par la colonne d'eau. La libération des bulles peut aussi être entraînée par plusieurs déclencheurs dont la perturbation physique par les courants internes ou de forts vents (Joyce et Jewell, 2003 ; Keller et Stallard, 1994), les évènements de basse pression atmosphérique, généralement associé à des systèmes de tempêtes (FechnerLevy et Hemond, 1996 ; Mattson et Likens, 1990 ; Varadharajan et Hemond, 2012) ou une baisse du niveau de l'eau ou de la nappe phréatique selon les milieux (Boles *et al.*, 2001 ; Engle et Melack, 2000). Le transport des bulles de CH_4 des sédiments vers l'atmosphère est donc hautement épisodique et hétérogène à l'intérieur d'un même système et entre les sites.

Contrairement à la diffusion, le CH_4 émis par ébullition n'est pas ou très peu consommé dans la colonne d'eau. Seulement une très petite fraction de CH_4 contenue dans les bulles sera oxydée en CO_2 par dissolution lors de son passage dans la colonne d'eau (McGinnis *et al.*, 2006). Les bulles de CH_4 sont donc une préoccupation grandissante pour le budget global de CH_4 en raison de leur haute efficacité à être transportées des sédiments vers l'atmosphère. Toutefois, la variabilité des émissions de CH_4 par ébullition fait de ce mécanisme un processus difficile à mesurer et à quantifier. Les quelques études qui ont mesuré l'ébullition ainsi que sa contribution aux émissions totales de CH_4 obtiennent un large éventail de résultats, allant de 32% à plus de 95% des émissions totales de CH_4 (Tableau 1). Il est donc primordial d'approfondir les connaissances sur ce mode de transport pour mieux prédire les émissions de CH_4 par ébullition et de comprendre comment les changements environnementaux affecteront ces émissions.

Tableau 0.1 Contribution de l'ébullition (%) aux émissions totales de CH_4 (mmol m^{-2} j^{-1}) pour différents types d'écosystèmes aquatiques où (n) représente le nombre de sites par étude. Tableau adapté de Bastviken et al. (2011)

Type d'écosystème	Latitude	Source	Pays/Région	Type de site	n	Émission (mmol m^{-2} d^{-1})			%
						total	Ébullition	Diffusion	Ébullition
Lacs	>66	Walter et al. (2006)	Sibérie	Thermokarsts	16	4,26 ± 0,39	4,05 ± 1,35	0,22 ± 0,017	95
		Repo et al. (2007)	Sibérie	Lac toundra	1	0.57	0.19	0,38 ± 0,16	33
	>54-66	Bartlett et al. (1992)	Yukon	Lac toundra	44 diffusion 5 ébullition	12.1 ± 4.43	7,0 ± 3,75	5,1 ± 0,68	60
		Huttunen et al. (2003a)	Finlande	Lac dimictique	1	2.74	1.54	1.22	56
				Lac dimictique	1	0.55	0.22	0.32	41
		Repo et al. (2007)	Sibérie	Lac taïga	1	0.82	0.31	0,51 ± 0,54	38
	24-54	Bastviken et al. (2004)	Wisconsin	Lac oligotrophe	11	1.77	0.86	0.58	50
		Casper et al. (2000)	Finlande	Lac hyper-eutrophe	1	12.74	12.4	0.34	96
	<24	Bastviken et al.(2010)	Pantanal	Plaine d'inondation	15	8.8	8	0.8	91
		Smith et al. (2000)	Vénézuéla,	Plaine d'inondation	1	1.45	0.47	0.98	32
		Keller et Stallard (1994)	Panama	Lac tropical	1	74.28 ± 16.92	73,5 ± 16,6	0,78 ± 0,32	98
Étangs	24-54	Weyhenmeyer (1999)	Centre de l'Ontario	Étang de castor	1	2,33 ± 1,9	1,42 ± 1,04	0.91 ± 0.86	65

0.5 Objectifs et hypothèse

En regard des connaissances actuelles sur le cycle du CH_4 et de son importance dans les écosystèmes aquatiques, les systèmes peu profonds et productifs tels que les étangs et les petits lacs, sont des milieux idéaux pour étudier les émissions de CH_4. Bien que la majorité des études s'entendent pour dire que l'ébullition serait majoritaire dans ces systèmes, très peu ont mesuré de façon précise l'ébullition et la diffusion de façon simultanée, et ce, sur une période de plus d'une saison. En raison de ce manque d'information sur l'ébullition, les mécanismes qui expliquent les différences spatiales et saisonnières de la contribution de l'ébullition aux émissions totales de CH_4 restent encore méconnus. Sachant que les changements environnementaux, comme l'eutrophisation et l'augmentation globale de la température, pourraient avoir un impact important sur les émissions de CH_4, il devient aussi une nécessité de comprendre quels sont les facteurs qui régulent les taux d'ébullition.

Dans le but de combler ces lacunes, cette étude vise à quantifier la contribution de l'ébullition dans les systèmes aquatiques et comprendre comment les changements environnementaux futurs pourront affecter ces émissions. Cette étude a donc pour but premier de 1) déterminer et comparer la contribution de l'ébullition sur les émissions totales de CH_4 dans des étangs de la région boréale et lacs de la région tempérée du Québec. De plus, sachant que l'ébullition est un processus variable dans l'espace et le temps, cette étude vise également à 2) déterminer les facteurs qui régulent les différences saisonnières et spatiales de l'ébullition. Dans un dernier temps, ce projet a aussi pour but de 3) développer des outils simples et efficaces pour estimer la contribution de l'ébullition dans les écosystèmes aquatiques. Pour ce faire, nous avons mesuré l'ébullition et la diffusion sur dix étangs de castor de la région du Saguenay et trois lacs situés dans les Laurentides. L'ébullition a été mesurée de façon continue avec des entonnoirs de plastique pour récolter les bulles de CH_4 alors que la diffusion a été mesurée périodiquement à l'aide d'une chambre flottante. L'échantillonnage a été réalisé sur l'ensemble de la période sans glace, soit de juin à octobre 2011 pour les étangs et de mai à novembre 2012 pour les lacs.

Contrairement à la majorité des écosystèmes d'eau douce, les étangs de castor ont la particularité de contenir une très grande quantité de matière organique en décomposition. Ces milieux sont donc très propices à une production de CH_4 élevée puisque les bactéries méthanogènes ne se sont pas ou peu limitées par la quantité de substrats disponibles. De plus, puisque ces étangs sont généralement peu profonds, la température de l'eau y est souvent élevée durant la période estivale, favorisant ainsi la production de CH4 tout en diminuant la solubilité de l'eau. Durant l'été, l'ébullition pourrait donc être le principal mode de transport du CH_4 dans ces systèmes. Pour cette étude, nous testerons les hypothèses suivantes : 1) L'ébullition représentera la majeure partie des émissions totales de CH_4 durant la saison estivale pour les étangs de la région boréale, 2) l'ébullition sera principalement contrôlée par la température des sédiments et 3) les changements environnementaux tels que l'augmentation globale de la température pourraient fortement favoriser les émissions de CH_4 sous forme d'ébullition.

La zone littorale des lacs, milieu peu profond avec des températures élevées en été, est un lieu de choix pour comparer les taux d'ébullition à ceux mesurés dans les étangs. Ces derniers, beaucoup plus productifs que les lacs, devraient avoir des taux d'ébullition beaucoup plus élevés. De plus, dans les lacs, le gradient de température et de profondeur entre la zone littorale à la zone pélagique pourrait conduire à des différences spatiales dans les taux d'ébullition. Nous tenterons donc de tester les hypothèses suivantes : 1) les taux d'ébullition retrouvés dans les lacs seront inférieurs à ceux retrouvés dans les étangs, 2) l'ébullition se produira majoritairement dans la zone peu profonde des lacs et 3) l'ébullition sera principalement contrôlée par la température des sédiments ainsi que par la profondeur de la colonne d'eau.

Par la compréhension des mécanismes qui régulent les émissions de CH_4, la réponse à ces objectifs permettra donc de quantifier adéquatement la contribution de l'ébullition aux émissions totales de CH_4 dans les étangs boréaux et les lacs tempérés du Québec en fournissant des outils simples et efficaces pour prédire l'ébullition. De plus, cette étude nous permettra de mieux comprendre comment les changements environnementaux comme l'eutrophisation et l'augmentation de la température moyenne globale influenceront les émissions de CH_4 sous forme d'ébullition.

CHAPITRE I

THE ECOSYSTEM-LEVEL TEMPERATURE DEPENDENCE OF METHANE EBULLITIVE AND DIFFUSIVE FLUXES IN NORTHERN PONDS AND LAKES

Boutet, L., St-Pierre, A., Prairie T. Y., Del Giorgio A. P.

1.1 Abstract

Ebullition is an important component of total methane (CH_4) emissions from freshwater aquatic ecosystems, but both the regulation of the CH_4 evasion mediated by bubbles in lakes and ponds, and its contribution to total emissions, remain poorly understood. We studied CH_4 ebullitive and diffusive fluxes to the atmosphere from 10 shallow ponds and 3 lakes in Québec, which span a range in morphometry and trophic status, throughout the entire ice-free season of 2011 and 2012. Ebullitive flux from the ponds ranged from 0.07 to 20.1 mmol m^{-2} d^{-1}, corresponding to between 20 and 90% of total (ebullition + diffusion) CH_4 fluxes. In lakes, ebullitive fluxes ranged from 0.01 to 2.0 mmol m^{-2} d^{-1} and comprised between 4 and 10% of the total CH_4 fluxes from the lakes despite being undetectable at water column depths > 3 m. In ponds, CH_4 fluxes were strongly related to sediment temperature, but ebullition had a much stronger dependence than diffusion, with an average ecosystem-level Q_{10} of 43 and 9, respectively. In lakes, the temperature dependence of both diffusive and ebullitive CH_4 fluxes was modulated by lake trophic status (represented as TP concentration): in less productive lakes, organic substrate limitation appears to dampen the influence of temperature on CH_4 fluxes, and results in a lower Q_{10}. Total CH_4 flux (ebullition + diffusion) tended to be higher in shallow environments, such as ponds and the littoral zone of lakes, and also in more productive systems, a pattern driven mostly by higher ebullitive emissions. Our results suggest that aquatic ebullitive CH_4 emissions from northern shallow lentic systems are primarily regulated by the interaction between basin morphometry, nutrient loading and

climate, and constitute the dominant component of the total CH_4 flux at temperatures > 12 °C.

1.2 Introduction

One of the primary uncertainties in the global methane (CH_4) budget is the magnitude and regulation of the main natural sinks and sources (Kirschke *et al.*, 2013). Inland waters (lakes, ponds, rivers and reservoirs) were until recently not considered as significant sources of CH_4 to the atmosphere but this view is rapidly changing. Although the magnitude of this aquatic component remains poorly constrained, recent evidence suggests that aquatic systems may contribute significantly to regional (Campeau *et al.*, 2014 ; Walter, Smith et Chapin, 2007) and even global CH_4 budgets (Bastviken *et al.*, 2004 ; 2011). However, there are still major difficulties in evaluating aquatic CH_4 emissions (Kirschke *et al.*, 2013 ; Ortiz-Llorente et Alvarez-Cobelas, 2012) from these systems. First, the complexity and diversity of continental water networks render the quantification and the up-scaling of CH_4 fluxes to entire regions very challenging. Second, and more importantly, the complexity of the processes underlying aquatic CH_4 emissions makes it hard to identify the main drivers of CH_4 production and in particular what determines the relative importance of the different emission pathways.

There are several pathways that may deliver CH_4 from the sites of production to the atmosphere: plant-mediated flux (not discussed here) (Kankaala *et al.*, 2005 ; Noyce *et al.*, 2014 ; Whiting et Chanton, 1992), Fickian and non-Fickian diffusive flux (Bastviken *et al.*, 2004 ; Baulch *et al.*, 2011 ; Beaulieu, Shuster et Rebholz, 2012 ; Prairie et del Giorgio, 2013), and ebullition (Bastviken *et al.*, 2004 ; Walter, Smith et Chapin, 2007). In order to understand the magnitude of aquatic CH_4 emissions, it is necessary to integrate these pathways and understand how their relative contribution varies across aquatic systems and in time. However, there are only a handful of published studies that have measured both diffusion and ebullition at the same time, and those have shown a rather wide range of contribution of ebullition to total CH_4 emissions (30 to 95%) (Casper *et al.*, 2000 ; Repo *et al.*, 2007). This is not entirely surprising given that the environmental factors currently known to control CH_4 ebullition render this pathway extremely episodic and highly spatially heterogeneous (DelSontro *et al.*, 2011 ; Goodrich *et al.*, 2011 ; Varadharajan et Hemond, 2012 ; Wik *et al.*, 2011). Physical parameters such as changes in hydrostatic pressure (due to either climatic barometric fluctuations or change in water level) (Mattson et Likens, 1990 ; Varadharajan et Hemond, 2012 ; Wik *et al.*, 2013) or wind-induced disturbance of the sediments (Joyce et Jewell, 2003) can trigger the release of CH_4 bubbles trapped in the sediment. Furthermore, the morphometry of a water body also plays a role, as ebullition has been shown to be strongly influenced by water column depth so that its contribution to total CH_4 emissions tends to decline steeply with depth (Bastviken *et al.*, 2004 ; DelSontro *et al.*, 2011).

In contrast to the ebullitive pathway, CH_4 diffusing from sediments to an oxic water column can be in large part oxidized to CO_2 by methanotrophic bacteria (Bastviken *et al.*, 2008). CH_4 oxidation rates are coupled to CH_4 production rates (Borrel *et al.*, 2011 ; Duc, Crill et Bastviken, 2010) and, as a result, a large (but variable) fraction of the CH_4 diffusing out of anaerobic sediments of boreal lakes may be oxidized before reaching the water surface, depending on water column depth and other factors (Bastviken, Ejlertsson et Tranvik, 2002 ; Kankaala *et al.*, 2006). At the whole-system scale, it is the relative magnitude and spatial location of each of the pathways what determines the overall efficiency with which the CH_4 produced can be lost and transported to the atmosphere, with direct implications for total CH_4 emissions.

Ultimately, aquatic CH_4 emissions are driven by CH_4 production occurring mostly in anoxic sediments, controlled by redox conditions, organic matter supply and temperature (Peters et Conrad, 1996 ; Valentine, Holland et Schimel, 1994 ; Yavitt, Williams et Wieder, 1997). Cross-system and seasonal changes in primary production (Schulz et Conrad, 1995 ; Waddington, Roulet et Swanson, 1996 ; Whiting et Chanton, 1993) and external carbon (C) loading may strongly influence CH_4 production by stimulating anaerobic conditions and by potentially influencing the supply of organic matter to sites of methanogenesis via dissolved organic matter (DOM) flocculation (von Wachenfeldt *et al.*, 2008). In addition, methanogenic bacteria in anaerobic sediment are highly sensitive to temperature (Schulz et Conrad, 1996 ; Westermann, 1993). There is a wide range of apparent Q_{10} for CH_4 production reported in the literature (between 1 and 35) (Duc, Crill et Bastviken, 2010 ; Inglett *et al.*, 2012 ; Segers, 1998), but a recent meta-analysis of published measurements in pure cultures and sediment slurries reports an overall average Q_{10} for methanogenesis on the order of 4 (Yvon-Durocher *et al.*, 2014). Although functionally linked, the temperature dependence of CH_4 fluxes at the ecosystem level, however, may not mirror that of methanogenesis, since CH_4 fluxes are modulated by multiple biotic and abiotic factors that themselves may be temperature dependent. Furthermore, the proportion of ebullition and diffusion fluxes to total emissions may be affected differently by changes in temperature. Predicted trends in future global mean temperature and the delivery of terrestrial C to aquatic systems, as well as increasing eutrophication of aquatic ecosystems by human activities, should alter CH_4 production. Unfortunately, we still lack the tools to predict how the magnitude and relative contribution of CH_4 ebullition and diffusion may change as a function of climatic and environmental changes; therefore, it is currently not possible to predict how total CH_4 aquatic emissions may be altered by climate change.

In this study, we combined concurrent measurements of CH_4 ebullition and diffusion from ten shallow ponds and three lakes located in temperate and boreal regions of Québec. The objectives were to assess the magnitude and regulation of ebullitive fluxes across these systems. More specifically, we assessed the individual temperature dependence of the ebullitive and diffusive fluxes and their interaction with other environmental factors to identify what shapes their relative contribution of the two pathways to total CH_4 emissions. Finally, we estimate the contribution of CH_4 fluxes to total C (CO_2 + CH_4) emissions from these aquatic systems. The ultimate aim of this study was to develop general simple predictive models to C emissions pathways that apply to both ponds and small lakes. .

1.3 Materials and methods

1.3.1 Study sites

The study was carried out in ten ponds located in the Saguenay region of Québec, Canada (71°25'W, 48°23'N), and on three lakes in the Laurentian region of Québec, Canada (45°59' N 73°59' W). The Saguenay (study area of the ponds) is characterized by mixed boreal forest, composed of spruce, fir, larch and pine. In contrast, the Laurentian (the study area of the lakes) is in a temperate hardwood forest mainly dominated by birch and maple. Ponds and lakes were selected to include a range in morphometry and other environmental characteristics (Table 1). The ponds are all beaver impoundments of various ages, and in general, were shallow (< 1.5 m), small (< 1 ha), and relatively free of aquatic vegetation. However, two of the ten ponds had significant coverage by emergent vegetation. The three lakes studied are typical Canadian Shield lakes, small (between 2 and 18 ha), relatively shallow (2.5 to 4.7 m mean depth) and dimictic. The hypolimnetic waters of all three lakes were hypoxic or anoxic by late summer. By the beginning of November, all lakes were completely mixed and cooled between 4-6°C. Gas measurements and water samples from ponds were collected during three field campaigns (June, July/August, and October, 2011), whereas lakes were sampled monthly from May to November 2012.

Tableau 1.1 Physical and chemical characteristics of the study sites, averaged for the entire ice-free period (May-November).

Sites	Area (m^2)	Mean Depth (m)	TN (mg/L)	DOC (mg/L)	TP (µg/L)	Chl *a* (µg/L)
Pond A	1 600	0.7	0.38	8.9	41.2	6.4
Pond B	3 600	0.8	0.36	11.3	26.6	3.1
Pond C	42 000	0.8	0.36	11.3	25.3	2.8
Pond D	4 800	0.8	0.40	13.4	24.8	5.3
Pond E	12 000	0.9	0.36	11.8	19.1	4.7
Pond F	6 000	0.7	0.61	15.3	48.3	6.3
Pond G	1 200	0.8	0.19	8.3	13.7	0.7
Pond H	7 500	0.6	0.31	9.5	27.9	2.2
Pond J	7 200	0.7	0.28	8.1	21.3	2.6
Pond K	10 000	0.8	0.64	18.2	39.3	4.0
Croche lake	179 000	4.70	0.17	4.07	4.17	1.12
Cromwell lake	110 000	3.50	0.27	5.79	6.89	1.90
Triton lake	17 000	2.50	0.31	5.91	9.69	2.58

1.3.2 Ebullition flux measurements

CH_4 flux by ebullition was measured using bubble traps that were designed and built in house (Fig. 1). The traps consisted of an inverted plastic funnel (63.5 cm of diameter). The neck of the funnel was fitted with a threaded plastic tube, which allowed the attachment of a submerged graduated 1 L glass bottle that was wrapped with aluminum foil to reduce light exposure and warming. The perimeter of the base of the funnel was fitted with a round weight (plastic tube filled with sand), meant to stabilize the system, and the sides of the funnel were attached with 3 strings to a round, cylindrical foam float roughly of the same diameter as the funnel itself, which kept the system afloat at the chosen depth. The bubble traps were deployed such that the base of the funnel was immersed at 0.5 m depth, and the collector bottle right below the surface.

For the ponds, we deployed duplicate bubble traps in proximity to each other, by attaching the surface float ring to sets of two opposing metal rods inserted into the sediments at least 4 m away to avoid disturbance of the local sediments. These were repeatedly sampled over the course of the study period. In lakes, we deployed a transect of five bubble traps attached to each other in a chain from the littoral to the pelagic zone, to cover a range of water column depths (up to 7 meters). In Lac Croche and Lac Cromwell, the traps were deployed in locations that corresponded to 1, 2, 3, 5, and 7 meters in water column depth. Due to its shallowness, we deployed only three traps on Lac Triton, in locations corresponding to approximately 1, 2 and 3 meters water column depth. For both lakes and ponds, the deployment of the traps as well as the subsequent sampling was conducted from a rowboat to avoid disturbance of the sediment surface. At the time of deployment, the sample bottle was filled with in situ water and attached to the neck of the funnel, avoiding any air bubbles.

The pond traps were visited every 3 days to record the volume of gas accumulated in the bottles, and sampled when gas volume exceeded 250 ml. In lakes, bubble accumulation was much slower and required over a month to accumulate comparable amounts. At the time of sampling, the collector bottle was detached and fitted, still underwater, to a stopcock cap with two valves. Upon retrieval of the bottle, a syringe was fitted to each valve, one to withdraw gas, the other filled with nanopure water and used to equilibrate the internal pressure in the bottle. The gas samples were injected into 30-mL glass vials equipped with rubber stoppers (20mm diameter, red bromobutyl), filled with saturated saline solution, and kept inverted until analysis (Campeau et del Giorgio, 2014). In the lab, the gas in the headspace of the vials was injected into a Shimadzu GC-8A Gas chromatograph with FID (flame ionization detector) to determine its CH_4 concentration. Ebullitive flux was calculated from the gas volume accumulation rate, the concentration of CH_4 in the gas, and the base area of the funnel.

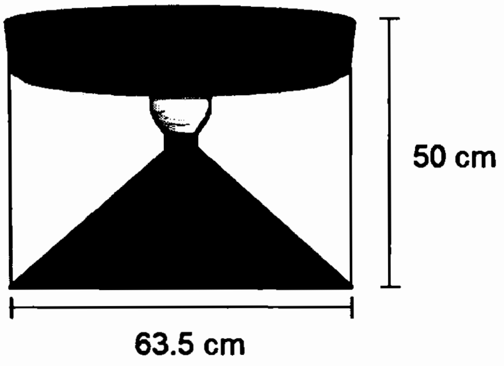

Figure 1.1 Schematic of the bubble traps, consisting in an inverted plastic funnel (63.5 cm diam.) with a threaded neck, where a graduated 1 L glass collector bottle was attached. The perimeter of the base of the funnel was fitted with a round weight to stabilize the system, and the sides of the funnel were attached with 3 cords to a round cylindrical foam float, which kept the system afloat at the chosen depth.

1.3.3 Diffusive flux measurements

The diffusive CO_2 and CH_4 fluxes at the water-air interface were measured using a floating plastic chamber (0.09 m^2 diameter, 16 L total volume) following Campeau and del Giorgio (2014). The chamber was covered with aluminum foil to reduce sun heating and equipped with a valve to equilibrate initial pressure upon deployment, and with an internal thermometer to monitor temperature changes that may affect the exchange rates during the measurements. In the ponds, the chamber was deployed near the shoreline, and in lakes, chamber measurements were made next to each bubble trap by boat. To measure the CO_2 flux, the chamber was connected to an infrared CO_2 analyser (EGM-4, PP-Systems) in a closed re-circulating loop, and CO_2 partial pressure in the chamber space was measured every minute for 10 minutes. To measure the CH_4 flux, gas samples from the chamber space were withdrawn with a syringe through a sampling valve immediately after deployment, and after 10, 20 and 30 minutes. The gas samples for CH_4 were stored and analyzed as described above. We carried out diffusive flux measurements every time we sampled the bubble traps. Diffusive CO_2 and CH_4 fluxes were determined using the following equation:

$$Flux = \frac{(s \times V_{ch})}{(V_m \times A)} \times 1.44 \qquad (1.1)$$

where s is the slope of the rate of gas accumulation in the chamber with time (µatm min^{-1}), V_{ch} is the volume of the chamber (L), V_m is the molar volume of the gas at ambient temperature (L atm mol^{-1}), A is the area of the chamber (m^2), and *1.44* is a unit conversion factor to obtain a flux in mmol gas m^{-2} d^{-1} (1d = 1440 min).

1.3.4 Other measurements

At each sampling, we measured sediment temperature with a digital thermometer (AquaCal ClineFinfer) in the proximity of each bubble trap. In addition, dissolved oxygen (O_2) concentrations, water temperature, pH and conductivity were measured at each site using a multi-parameter probe (YSI 5000). For ponds, water samples were taken near the shoreline at 0.2 m below the surface at the beginning of each field campaign. These samples were used to measure the concentrations of dissolved organic carbon (DOC), chlorophyll *a* (Chl *a*), total phosphorus (TP) and total nitrogen (TN). For lakes, water samples were also taken at 0.2 m below the surface near the trap located at the deepest point of each transect. Chl *a* was determined spectrophotometrically on Whatman GF/F filtered-samples following sonication and pigment extraction with hot (90%) ethanol (Mush, 1980). DOC concentration was measured in 0.45 µm filtered samples using OI 1010 TIC-TOC analyzer following sodium persulfate digestion. TP was measured using the colorimetric molybdenum blue method after persulfate digestion. TN was analysed as nitrate following alkaline persulfate digestion and measured on an Alpkem FlowSolution IV auto-analyzer.

1.3.5 Statistical analyses and calculation of ecosystem-level Q_{10}

We calculated the temperature dependence of CH_4 fluxes as a Q_{10}, which corresponds to the proportional change in the process per 10°C change in sediment temperature. There were no sediment temperature measurements made in the first pond campaign, so we used the relationship between ambient sediment and water column temperature to estimate the missing data. For data sets with multiple observations of rates and temperatures, a constant Q_{10} corresponds to a linear relationship between the logarithm of CH_4 flux rates and sediment temperature (untransformed), the slope (b) of which can be used to estimate a Q_{10} value as

$Q_{10}=10^{10b}$. The Q_{10} of fluxes is not equivalent to a physiological Q_{10}, because fluxes are modulated by multiple biotic and abiotic factors that can themselves be temperature dependent. Because it represents the combined effects of multiple factors, it is more appropriately termed an "ecosystem-level" Q_{10}.

The estimates of CH_4 and CO_2 fluxes were log-transformed to attain normality and homoscedasticity. Simple and multiple regressions were performed with JMP software version 7.0 (SAS Institute, NC, USA).

1.4 Results

1.4.1 General characteristics of the study sites

The ponds sampled varied widely in terms of trophic status, ranging in average Chl *a* concentrations from 0.7 to 6.4 μg L^{-1}, and from 14 to 48 μg L^{-1} in TP. The three lakes sampled were oligo- mesotrophic, ranging in Chl *a* and TP from 1 to 3 μg L^{-1} and from 4 to 10 μg L^{-1}, respectively (Table 1). There was a four-fold range in DOC concentration across all systems, from 4 to 18 mg L^{-1} (Table 1). Overall, ponds had significantly higher ($p < 0.05$) concentrations of nutrients and DOC compared to the three lakes, which are well within the typical range of values found for lakes in the Laurentian region. Our different sampling sites and periods covered sediments temperatures between 6 and 24°C.

1.4.2 Magnitude of CH_4 ebullitive and diffusive fluxes

For ponds, the proportion of CH_4 in the gas sampled from the collector bottle ranged from 11% to 97%, and averaged 59% across all samples. In contrast, the gas collected in lakes ranged from 0.01% to 60%, with an overall lake average of 11%. This major difference in CH_4 concentrations in the bubbles between lakes and ponds may be related to the actual sampling scheme. Because of the marked differences in the time required to collect sufficient gas for the GC analysis between pond and lake traps, the low CH_4 concentration in lake bubbles may be the result of loss due to diffusion and oxidation at the water-air interface in the collector bottle during the long accumulation period. To examine this hypothesis, we deployed a sediment trap at 1 m water column depth in Lac Cromwell, and proceeded to lightly disturb the sediment in the vicinity in order to release sediment bubbles, and the gas that accumulated in the collector bottle was sampled immediately and analyzed for CH_4 as described above. The average proportion of CH_4 in the gas obtained in two samples was 50%, close to the average we had measured in the shorter-term pond deployments, suggesting that long-term deployments may greatly underestimate the amount of CH_4 that was originally in the gas. We subsequently applied this average CH_4 concentration of 50% to all gas samples to calculate ebullitive fluxes in lakes, which results in a potential upper limit for ebullition in these systems. For pond samples, we used the actual measured CH_4 concentrations.

Ebullitive CH_4 fluxes were systematically higher in ponds than in lakes, averaging 6.0 mmol m^{-2} d^{-1} and 0.30 mmol m^{-2} d^{-1}, respectively (Fig. 2). It is important to note that in the case of lakes these ebullitive fluxes apply only to the littoral zone (< 3 m) where bubbling was actually detected; fluxes integrated over the entire surface of the lakes were much lower and are discussed below. Diffusive fluxes were in the same order of magnitude, and averaged 4.2 mmol m^{-2} d^{-1} in ponds, and 2.2 mmol m^{-2} d^{-1} in lakes, and were much more variable in the former (Fig. 2). For comparison, diffusive CO_2 fluxes, measured in the same chambers used for CH_4, averaged 57 and 52 mmol m^{-2} d^{-1} for ponds and lakes, respectively. CO_2 concentrations in bubbles were generally < 1%, and the corresponding CO_2 ebullitive fluxes were negligible, never exceeding 0.25 mmol m^{-2} d^{-1}.

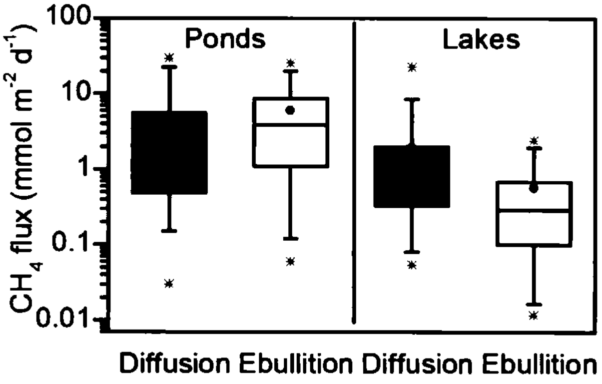

Figure 1.2 CH$_4$ fluxes (in mmol m^{-2} d^{-1}) for ebullition (white) and diffusion (grey) for ponds (left panel) and lakes (right panel). In the case of lakes, ebullition fluxes correspond only to the areas where bubbles were detected, and are not scaled to the entire lake area. The black circles represent average fluxes and the asterisks represent maximum fluxes.

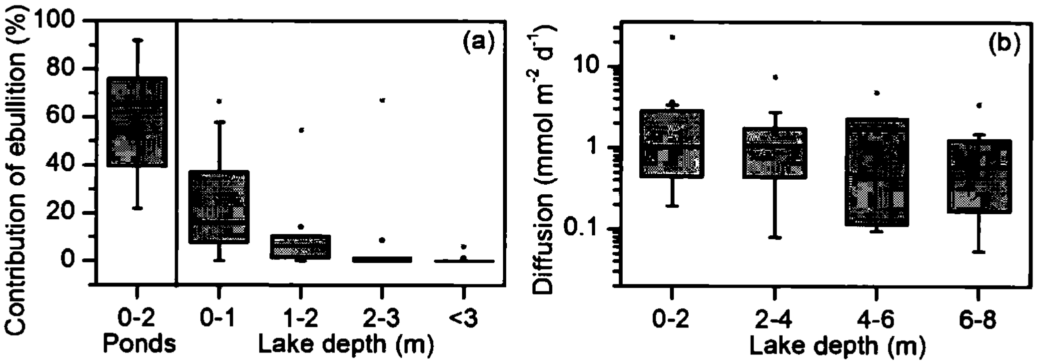

Figure 1.3 a) Relative contribution of ebullition to total CH$_4$ emissions for ponds and lakes at different depths (m). b) Diffusive CH$_4$ fluxes (mmol m^{-2} d^{-1}) measured along a littoral to pelagic transect at different water column depths (m) in lakes. The black circles represent average fluxes and the asterisks represent maximum fluxes.

1.4.3 Contribution of ebullition to total CH_4 flux

The contribution of ebullition to total CH_4 flux (ebullition + diffusion) in ponds ranged from 22% to 92% and averaged 60% (Fig. 3a). In lakes, CH_4 ebullition varied greatly with depth and was essentially confined to water column depths shallower than 3 m. In contrast, diffusion remained relatively constant along the lake depth transects (Fig. 3b), leading to a rapid decrease in the contribution of ebullition to total CH_4 flux with increasing water depth (Fig. 3a). The maximum contribution of ebullition in lakes occurred in the littoral zone between 0 and 1 m, with a potential upper limit of 24%, consistently lower relative to ponds of comparable depths (Fig. 3a).

1.4.4 The temperature dependence of CH_4 fluxes and ecosystem-level Q_{10} values

The strongest predictor of CH_4 fluxes in ponds (filled dots, Fig. 4) was sediment temperature, which explained 61%, 35%, and 62% of the variabillity in ebullition, diffusion, and total CH_4 flux, respectively (Fig. 4). The log-linear relationships presented in Table 2 show that ebullition responded more strongly (i.e. steeper slope) to temperature than did diffusion, implying that the relative contribution of ebullition to total flux increased with sediment temperature (Fig. 5). Solution of these regression equations suggests a sediment temperature threshold of about 12°C, above which ebullition dominantes (>50%) in these shallow systems (dash line in Fig. 5). Above 20°C, ebullition accounts for more than 75% of the total CH_4 emissions.

The strong temperature dependence of CH_4 fluxes corresponds to a high ecosystem-level Q_{10}. Based on the log-linear relationship between flux and temperature, the estimated ecosystem-level Q_{10} for diffusion and ebullition was 9 and 43, respectively (Table 2), and the ecosystem-level Q_{10} for total CH_4 flux was intermediate (Q_{10} = 17) between that of the two pathways (Table 2). In contrast to ponds, there was no significant relationship between ebullitive or diffusive CH_4 fluxes and temperature when data from the three lakes were combined (empty dots, Fig. 4; Table 2).

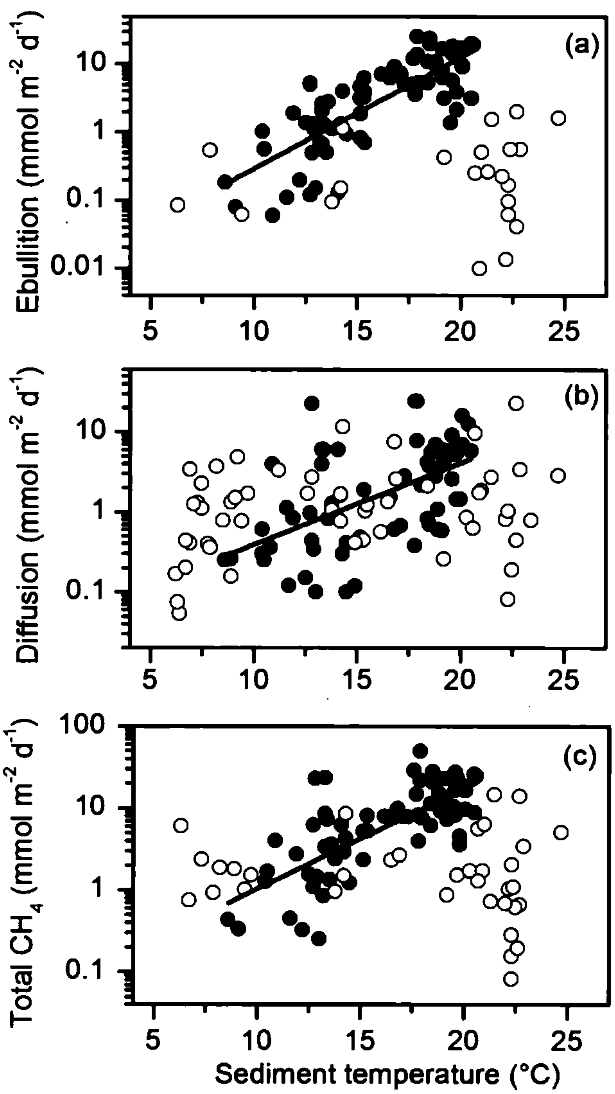

Figure 1.4 Ebullitive fluxes (a), diffusive fluxes (b) and total CH_4 emissions (c) in mmol m^{-2} d^{-1} for ponds (full circles) and lakes (empty circles) as a function of sediment temperature (°C). The solid lines represent the relationships between pond CH_4 fluxes and sediment temperature for ebullition, diffusion and total CH_4 emissions (equations in table 2). Note that total CH_4 emissions are the sum of ebullitive and diffusive fluxes for each site.

Tableau 1.2 Description of relationships (used in figure 4) between CH_4 emissions and sediment temperatures (T_{sed}). Only ecosystem-level Q_{10} derived from significant relationships are shown.

Systems	CH_4 emissions	Equation	n	p	r^2	Ecosystem-level Q_{10}
Ponds	Ebullition	Log_{10} ebullition = -2.17 + 0.16*Tsed	73	<0.001	0.61	9.2
	Diffusion	Log_{10} diffusion = -1.38 + 0.10*Tsed	85	<0.001	0.28	43.1
	Total	log_{10} total CH_4 -1.21 + 0.12*Tsed	68	<0.001	0.54	16.7
Lakes	Ebullition	Log_{10} ebullition = -0.92 + 0.01*Tsed	22	0.633	-0.04	
	Diffusion	Log_{10} diffusion = -0.29+ 0.02*Tsed	53	0.090	0.04	
	Total	Log_{10} total CH_4 = 0.36 - 0.01*Tsed	35	0.462	-0.01	

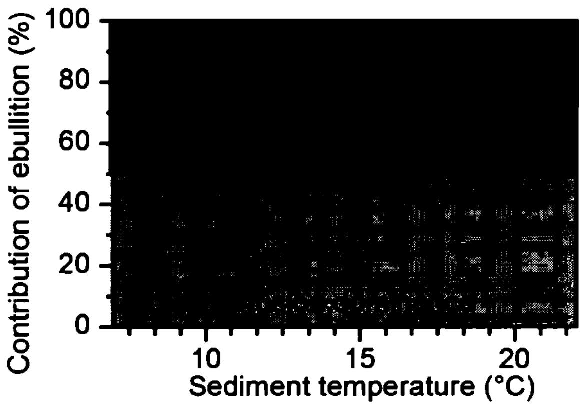

Figure 1.5 Relative contribution of ebullition (%) to total CH_4 emissions in ponds as a function of sediment temperature (°C). Above 12°C fluxes shift from being diffusion-dominated to ebullition-dominated (see main text for explanation).

1.4.5 Interaction between nutrients and temperature

Although the above comparison suggests that lakes and ponds behave fundamentally differently in terms of their respective temperature dependencies, closer inspection reveals that in lakes the temperature dependence of ebullition varied directly as a function of the average TP concentration (Fig. 6a). In particular, the slope of the relationship between ebullitive flux and sediment temperature for the individual lakes increased steeply as a function of the average lake TP concentration (Fig. 6b) and the slope of the overall relationship for ponds from Figure 3a fits with this pattern well (Fig. 6b). The link between temperature and trophic status (as TP) is further supported by the multiple regression models of CH_4 flux where both variables were highly significant, and which explained more than half of the variability in CH_4 ebullition flux across lakes and ponds combined (equation 2). This equation includes data from lake sites where ebullition was measured (sites with water column depth < 3 m). Diffusive and total fluxes from lakes and ponds together were also predicted by this combination of temperature and TP (equation 3 and 4).

$$Log\ Ebullition = -2.96 + 1.21\ Log\ TP + 0.10\ T_{sed} + 0.19\ (\log TP - 1.26)(T_{sed} - 16.49)$$

$$R^2 = 0.54\ n = 89\ (p < 0.001)$$

$$(1.2)$$

$$Log\ Diffusion = -1.32 + 0.40\ Log\ TP + 0.06\ T_{sed} + 0.10\ (logTP - 1.16)(T_{sed} - 15.00)$$

$$R^2 = 0.27\ n = 106\ (p < 0.001$$

$$(1.3)$$

$$Log\ Total\ CH_4 = -2.05 + 1.1\ Log\ TP + 0.07\ T_{sed} + 0.16\ (logTP - 1.22)(T_{sed} - 16.53)$$

$$R^2 = 0.57\ n = 94\ (p < 0.001)$$

$$(1.4)$$

Other environmental variables related to trophic status, such as Chl *a* and TN, were also significant alone and together with temperature, but did not perform as well as TP in terms of predicting CH_4 fluxes. It is interesting to note that the three multiple regression equations all had a significant positive interaction term between TP and temperature, indicating that the effect of temperature on CH_4 emission increases with trophic state. When considering ponds only, Chl *a* was weakly, positively related to both ebullitive (R^2=0.15, p=0.036) and diffusive (R^2=0.15, p=0.021) fluxes, suggesting again that more productive systems tend to have higher CH_4 fluxes.

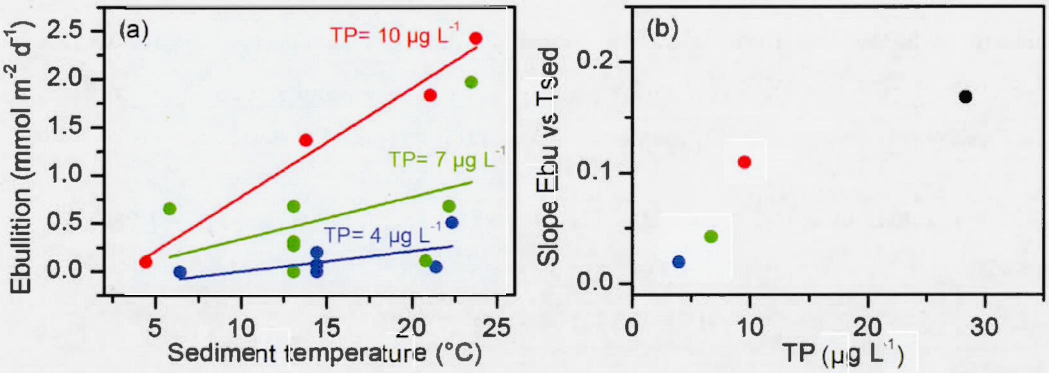

Figure 1.6 a) Relationship between CH_4 ebullition (mmol m^{-2} d^{-1}) and sediment temperature (°C) for the three sampled lakes: Lac Croche (blue), Lac Cromwell (green) and Lac Triton (red). Average total phosphorus concentration for the ice-free season is indicated for each lake in µg L^{-1}. b) Slopes of the relationships in panel A as a function of total phosphorus concentration (µg L^{-1}). Colours for lakes are as in panel A and the black circle is the average value for ponds derived from the relationship in Figure 3a.

1.5 Discussion

1.5.1 CH_4 emissions and the contribution of ebullition

The results of this study confirm that CH_4 emissions by ebullition represent an important pathway for CH_4 transport to the atmosphere in shallow environments (Bastviken *et al.*, 2011 ; Casper *et al.*, 2000). The average diffusive CH_4 emission rates (4.2 mmol m^{-2} d^{-1}) for ponds that we report here is comparable to CH_4 emissions rates measured from other beaver ponds in North America (1.68 to 9.38 mmol m^{-2} d^{-1}) (Ford et Naiman, 1988 ; Roulet *et al.*, 1997 ; Yavitt *et al.*, 1992). For lakes, the average total CH_4 fluxes that we observed (2.6 mmol m^{-2} d^{-1}) are also similar to previously reported estimates from Wisconsin lakes (1.8 mmol m^{-2} d^{-1}) (Bastviken *et al.*, 2004), and for boreal lakes in Finland (2.7 mmol m^{-2} d^{-1}) (Huttunen *et al.*, 2003a). However, all of our results are much lower than the worldwide average for CH_4 emissions from wetlands (80 mmol m^{-2} d^{-1}) and lakes (11 mmol m^{-2} d^{-1}) reported in a recent review by (Ortiz-Llorente et Alvarez-Cobelas, 2012).

In our ponds, ebullition contributed on average 60% of the total CH_4 emissions, a result comparable to the study in a beaver pond in Ontario (65%) (Weyhenmeyer, 1999). Hamilton et al. (1994) reported similar rates of diffusive CH_4 fluxes from shallow wetlands in the Hudson Bay region. However, they found no ebullitive emissions from these systems, highlighting the extreme temporal and spatial heterogeneity of this process, and the potential methodological caveats associated to its measurement, particularly in terms of deployment duration.

Ebullition in our study lakes contributed up to 24% of the total CH_4 emissions in the shallow zones, but this contribution decreased rapidly to essentially zero at depths greater than 3 m. On average, bubble flux decreased by about one order of magnitude with every additional meter in depth. The depth-dependence of ebullition has been previously reported (Bastviken *et al.*, 2004 ; Casper *et al.*, 2000), although the depth at which ebullition ceases varies between ecosystem types and studies. For example, CH_4 bubbling has been observed from greater depths in deep lakes (>10 m) and recently flooded reservoirs (Chandrashekhar, 2013 ; DelSontro *et al.*, 2011), and in both cases may be related to the absolute CH_4 production rate.

Between 70 and 100% of the ebullitive fluxes occurred at depths < 2m in our study lakes, and the zones that had measurable bubble fluxes represented between 34 to 79% of the total surface area. The decrease in bubbling rates with depth may be the result of lower production rates due to colder temperatures combined with a lower proportion of CH_4 bubbles escaping the sediments with increasing hydrostatic pressure, and significant bubble dissolution of those that do escape (Delsontro *et al.*, 2010). Integrated over the entire lake surface, however, CH_4 bubble emissions accounted for only 4 to 10% of the total CH_4 emissions, significantly lower than that reported in the meta-analysis by Bastivken et al. (2011) (38 to 96%). Regardless of the exact maximum depth of bubble occurrence, the importance of ebullition to CH_4 emissions at the whole ecosystem level is critically dependent on lake bathymetry, and more specifically on the fraction of the lake surface area occupied by the shallow littoral zone.

1.5.2 Ecosystem-level temperature dependence of CH_4 fluxes in ponds

The effect of temperature on methanogenesis is surprisingly poorly constrained but the recent meta-analysis (Yvon-Durocher *et al.*, 2014) suggests that the Q_{10} associated with the physiology of methanogenesis converges to a value near 4. Although this physiological Q_{10} is an important parameter, it is only one of the factors influencing total CH_4 fluxes. In addition, release and transport processes, as well as transformation in transit, further modulate the temperature dependence of CH_4 emission in what we term "ecosystem-level" Q_{10} for CH_4 fluxes. Indeed, time lags between production and release from the sediments, concurrent changes in methanogenic bacterial biomass, in the supply of organic substrate, in the spatial extent of anoxic sites suitable for CH_4 production, and in the solubility of CH_4 with temperature, among other factors, all interact to yield apparent Q_{10} values for CH_4 fluxes at the air-water interface that are much higher and also more variable than that of methanogenesis. This may explain the extremely wide range in apparent Q_{10} for aquatic CH_4 fluxes that has been reported in the literature (1 to over 35, (Duc, Crill et Bastviken, 2010 ; Segers, 1998 ; Whalen, 2005). Our results demonstrate that such synergistic interactions must occur in these natural systems and that ecosystem processes, such as emission fluxes, may have a much different temperature sensitive than the intrinsic physiological rates of methanogenic bacteria. In addition, our ecosystem-level Q_{10} values are very different according to the particular emission pathway through which CH_4 is evaded to the atmosphere. The average Q_{10} values for CH_4 fluxes in ponds were 43 and 9 for ebullition and diffusion, respectively. Interestingly, Wik et al. (2014) recently also reported a high Q_{10} value of 17 for lake CH_4 ebullition.

Together, these findings suggest that "ecosystem-level" Q_{10} estimates represent an emergent property that integrates, in a multiplicative way, the temperature dependencies of a number of biotic and abiotic processes. For example, if a 10°C rise in sediment temperature were to induce an increased cellular rate of CH_4 production by a factor of 4 (Yvon-Durocher *et al.*, 2014) but that the biomass of methanogens would double in that same interval, the resulting compounded Q_{10} should be 8, or even higher if other processes affected by temperature, for example, CH_4 solubility, also impact CH_4 production and delivery to the atmosphere. In our view, this emergent Q_{10} property is nearly unpredictable without an integrated ecosystem approach to CH_4 emission calculations. Provided that the other interacting factors react to temperature changes in a reasonably stable and general pattern, which our results suggest they do, we also argue that such ecosystem-level Q_{10} values are more relevant than physiologic Q_{10} when modelling the likely CH_4 response of these northern systems to temperature changes. In aquatic systems experiencing less temporal variation in temperature, it is possible that physiological Q_{10} more tightly couples production to emissions. Regardless of the exact synergistic mechanisms involved, the ebullitive pathway appears to be highly sensitive to temperature (as also reported by Wik et al., 2014) much more so than diffusive fluxes, with the ensuing total flux having a composite Q_{10} value of about 17. Expressed in terms of activation energy (E_A) (Dunfield *et al.*, 1993), diffusive, ebullitive, and total CH_4 fluxes have E_A values corresponding to 154, 261, and 195 kJ mol^{-1}, respectively.

The higher temperature-sensitivity of ebullition compared to diffusion in ponds implies that the absolute amount and relative contribution of ebullition will increase with temperature and this may have important implications on how the magnitude of these natural greenhouse gas (GHG) emissions from shallow lentic systems may vary under different warming scenarios. It has been hypothesized that CH_4 emissions from wetlands and freshwater ecosystems will increase with ongoing environmental changes, particularly in northern latitudes (Bohn *et al.*, 2007 ; Gedney, Cox et Huntingford, 2004), and the high ecosystem-level temperature dependence we report here supports these predictions.

To illustrate these potential changes, we estimated the temperature dependence of total GHG emissions for an average shallow pond in our region, as the sum of the average CO_2 fluxes observed (since these did not vary with temperature), and CH_4 fluxes (diffusion+ebullition) derived from the relationships in Figure 4 expressed as CO_2 equivalents. Figure 7 shows that at low temperatures (<12°C), GHG emissions occur mostly in the form of CO_2 but that the CH_4 contribution increases rapidly with temperature, and 18°C is a threshold temperature above which CH_4 dominates over CO_2. Above 20°C, CH_4 bubbles are largely responsible for the increase in GHG emissions. Assuming that the anticipated increasing air temperature is reflected in the water and sediment temperatures of shallow ponds - which is the case in our systems where these strongly covary (data not shown) - a modest increase of 2°C would induce a 75% increase in relative to current CH_4 emissions.

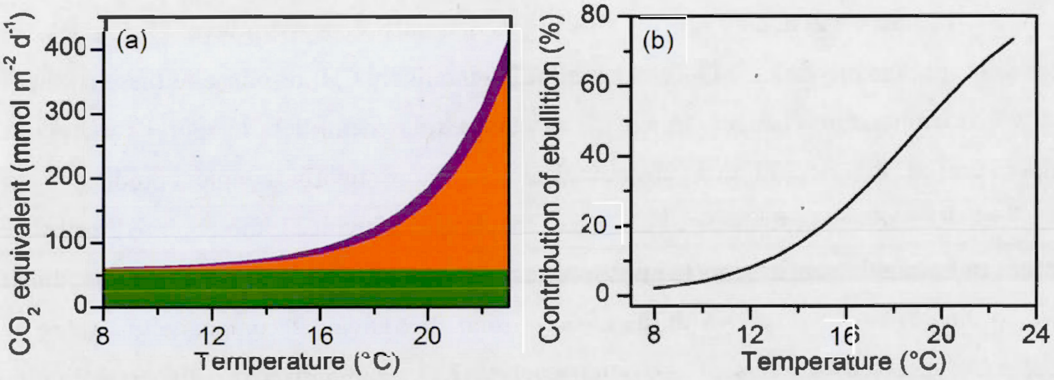

Figure 1.7 a) CO_2 fluxes (green), CH_4 ebullition (orange) and CH_4 diffusive fluxes (purple), all expressed as CO_2 equivalents (in mmol m^{-2} d^{-1}) as a function of temperature (°C) for an average pond in our region. Since the relationship between CO_2 flux and (water) temperature is not significant, we used the overall average CO_2 flux for ponds (57 mmol m^{-2} d^{-1}). For the two CH_4 fluxes we used the relationships shown in Figs 3a and b. b) Contribution of ebullition (%) to total greenhouse gas emissions (expressed as CO_2 equivalents) as a function of water temperature.

1.5.3 Interaction between nutrients and temperature

Relative to ponds, lake CH_4 fluxes differ in terms of their sensitivity to temperature, as can be seen in Figure 4. CH_4 fluxes are ultimately linked to rates of methanogenesis in both lakes and ponds, and there is no *a priori* reason to think that the basic physiological temperature dependence of this process is different across systems (Duc, Crill et Bastviken, 2010 ; Lofton, Whalen et Hershey, 2013 ; Schulz et Conrad, 1996 ; Segers, 1998). The absence of a significant relationship between total surface CH_4 fluxes and temperature in lakes thus suggests that other factors intervene to either limit CH_4 production independent of temperature, or to decouple production and emission. In terms of the latter, CH_4 oxidation in the water column plays a major role in modulating the relationship between CH_4 production and emission, and its influence is likely to be stronger in lakes, which have deeper and generally oxic water columns, relative to shallow ponds (Bastviken, Ejlertsson et Tranvik, 2002 ; Juutinen *et al.*, 2009). In terms of the former, differences in organic substrate supply may be the limiting factor for some systems and thus obscure a temperature-dependence of CH_4 fluxes as it is the production that is already reduced. In our study, CH_4 fluxes were strongly related to system productivity, as reflected in the highly significant phosphorus term in the multiple regression models (eq. 2, 3 and 4). The link between CH_4 emissions and system productivity has already been shown for lakes (Huttunen *et al.*, 2003a ; Juutinen *et al.*, 2003 ; Juutinen *et al.*, 2009) and also for wetlands (Bellisario *et al.*, 1999 ; Waddington, Roulet et Swanson, 1996 ; Whiting et Chanton, 1993), and is probably related to both the supply of organic substrate fuelling methanogenesis, and also to the development of anoxic conditions that allow the process to proceed.

Perhaps more importantly from an environmental change point of view, we found a highly significant, positive interaction term between TP and temperature, which would suggest that the temperature dependence of CH_4 fluxes actually increases with TP, and therefore, with the overall system productivity. This suggests that methanogenesis may be strongly substrate-limited in these oligotrophic lakes relative to the much more productive ponds, such that the physiological temperature dependence is either highly suppressed, or not expressed at all in lakes. As system productivity and the supply of organic matter increase, substrate limitation is alleviated, allowing the CH_4 production to be increasingly temperature regulated, as graphically shown in Figure 6b. Here we show that using both a proxy for system productivity (TP) and temperature allows to reconcile these apparently divergent patterns in fluxes and in the apparent responses to temperature, and to effectively predict CH_4 fluxes across diverse shallow systems.

The coefficient for this temperature and TP interaction term in the multiple regression model was highest for ebullition, but was nevertheless highly significant for diffusive fluxes, and consequently for the resulting total CH_4 fluxes. We further explored the consequences of this interaction term on the ecosystem Q_{10} of both the ebullitive and diffusive fluxes by calculating the fluxes at different temperatures for a range of TP concentrations, using equations 2 (for ebullition) and 3 (for diffusion). Figure 8 shows the resulting relationships between the apparent ecosystem-level Q_{10} of CH_4 fluxes as a function of TP concentration. For both ebullition and diffusion, Q_{10} tends to increase with system TP concentration, linearly in the case of diffusion (dashed line, Fig. 8), but non-linearly in the case of ebullition (solid line, Fig. 8). Our results thus suggest that not only are ebullitive fluxes on average more temperature dependent than diffusive fluxes for any given system, but in addition the temperature dependence of ebullition may be disproportionately enhanced by ecosystem productivity relative to diffusion, which in turn leads to an increase in total CH_4 emission.

While there clearly must be an upper limit of this nutrient enrichment effect on the temperature dependence of CH_4 emissions, and therefore the relationships shown in Fig. 8 must necessarily plateau, these observations still have consequences for future GHG emissions from aquatic ecosystems that are facing multiple simultaneous environmental changes, including both climate warming (Bonan, 2008 ; Denman *et al.*, 2007 ; Flato et Boer, 2001) and overall greater nutrient and organic C loading (Evans, Monteith et Cooper, 2005 ; Roulet et Moore, 2006 ; Tilman *et al.*, 2001). Our results suggest that the influence of these environmental changes on aquatic CH_4 fluxes is not simply additive, but rather that there are compounded non-linear positive interactions between regional eutrophication and climate trends that may greatly amplify the role of aquatic systems as natural sources of CH_4 in these water-rich landscapes.

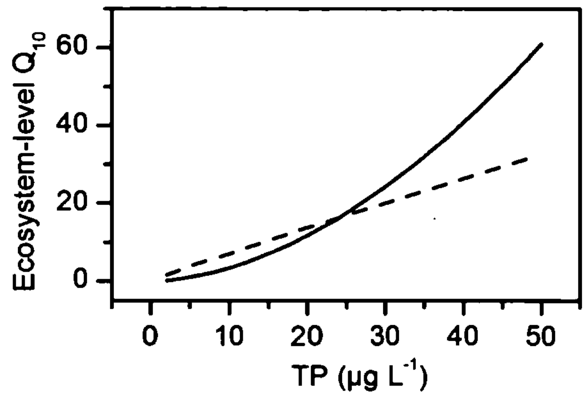

Figure 1.8 Ecosystem-level Q_{10} of ebullition (full line) and diffusive fluxes (dashed line) as a function of total phosphorus concentration (µg L^{-1}) for ponds and the shallow portions (< 3 m) of lakes. This relationship is derived from multiple regressions between ebullition and diffusive fluxes as a function of sediment temperature and TP, as described in the text.

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CONCLUSION

Bien que plusieurs études démontrent que l'ébullition peut représenter une importante composante des émissions totales de CH_4 pour les systèmes aquatiques, la régulation de l'ébullition ainsi que sa contribution aux émissions totales de CH_4 demeurent grandement méconnues. Il devient ainsi nécessaire de connaître les facteurs qui régulent l'ébullition afin de quantifier ce processus de façon efficace et de prédire sa réponse face aux futurs changements environnementaux. En mesurant l'ébullition et la diffusion de façon simultanée sur une longue période ainsi qu'en intégrant plusieurs variables limnologiques susceptibles d'influencer ces processus, cette étude a donc permis de combler plusieurs lacunes présentes dans la littérature.

Les résultats de cette étude montrent que l'ébullition est un processus important pour le transport du CH_4 dans les milieux aquatiques peu profonds, mais hautement hétérogène entre les systèmes. Dans les étangs, l'ébullition représente en moyenne 60% des émissions totales de CH_4 alors que l'ébullition ne représente que 24% des émissions totales pour la zone littorale des lacs et décroît fortement avec l'augmentation de la profondeur de la colonne d'eau. De plus, les flux de CH_4 pour chacun de ces systèmes réagissent différemment à une augmentation de la température. Dans les étangs, les flux de CH_4 sont fortement contrôlés par la température des sédiments, avec des flux par ébullition beaucoup plus sensibles à la température que la diffusion. À l'inverse, pour les lacs, on ne retrouve aucune relation entre le flux de CH_4 et la température. Toutefois, lorsque l'on combine les étangs et les lacs, les flux de CH_4 deviennent positivement reliés au statut trophique (exprimé par la concentration en TP) ainsi qu'à la température. La combinaison de ces deux variables permet donc de fournir un outil simple et efficace pour prédire les émissions de CH_4 pour ces deux systèmes qui pourtant, semblaient extrêmement disparates en termes de magnitude des émissions de GES et de leur réponse à la température. En plus de cette combinaison, nous avons également trouvé une interaction positive entre le TP et la température suggérant que la dépendance à la température des flux de CH_4 augmente avec la productivité d'un système, et ce, de façon plus prononcée pour l'ébullition.

Nos résultats montrent donc que l'ébullition est non seulement plus sensible à la température que la diffusion, mais également que la dépendance à la température de l'ébullition augmente de façon disproportionnée avec l'enrichissement en nutriments d'un système comparée à la diffusion. Ces résultats ont pour conséquence de favoriser une augmentation des émissions totales de CH_4 principalement par ébullition. De plus, ces observations pourraient avoir une incidence majeure sur les futures émissions de GES par les écosystèmes aquatiques boréaux et tempérés susceptibles de répondre fortement aux changements environnementaux comme le réchauffement climatique ainsi qu'un enrichissement global en nutriments.

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