UNIVERSITÉ DU QUÉBEC À MONTRÉAL

VITESSE D'ÉCHANGE GAZEUX À L'INTERFACE AIR-EAU:

ÉTUDE MÉTHODOLOGIQUE ET FACTEURS INFLUENTS

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AVANT-PROPOS

Ce mémoire de maîtrise est réparti en quatre sections : une introduction comportant une revue de la littérature, deux chapitres sous forme d'article ainsi qu'une conclusion générale. Les articles sont rédigés en anglais, dans l'objectif d'être publiés. Le chapitre I sera publié dans la revue *Limnology and Oceanography* et le chapitre II sera soumis à *Environmental Science and Technology*. Bien que les articles comportent des co-auteurs, ma contribution à ceux-ci demeure quasi-complète, partant de l'élaboration des concepts, de l'échantillonnage, l'analyse des données jusqu'à la rédaction. Ce document sera suivi d'une conclusion et d'une liste des références utilisées.

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LISTE DES SYMBOLES

μg	microgramme (10^{-6}g)
Pg	petagramme (10^{15}g)
α	constante de Kolmogorov
ε	taux de dissipation de l'énergie cinétique turbulente
ω	nombre d'onde
$S_{(\omega)}$	spectre de densité du nombre d'onde
V	vitesse du courant moyen
D	coefficient de diffusion
ν	viscosité cinématique
Sc	nombre de Schmidt
f_{CO2}	flux de dioxide de carbone
k	vitesse d'échange gazeux
k_{CO2}	vitesse d'échange du dioxide de carbone
k_{600}	vitesse d'échange gazeux standardisée au nombre de Schmidt 600
Kh	constante de Henry
C	carbone
CO_2	dioxide de carbone
pCO_2	pression partielle de dioxide de carbone
SF_6	hexafluorure de souffre

RÉSUMÉ

Une portion importante du cycle du carbone se situe au niveau des échanges gazeux entre l'eau et l'atmosphère. L'importance de ces flux est accentuée par l'enjeu des changements climatiques et de la gestion des gaz à effet de serre. Il reste cependant plusieurs aspects de ce processus qui sont mal compris et plusieurs biais persistent dans la méthodologie. Dans le but d'améliorer les techniques d'échantillonnage, la possibilité d'utiliser la turbulence pour prédire la vitesse d'échange gazeux (k) a été explorée et l'hypothèse que la chambre flottante engendre de la turbulence artificielle a aussi été testée. De plus, dans le but d'unifier les diverses relations entre le vent et k, plusieurs variables facilement mesurables combinées à la vitesse du vent ont été testés. Les données de cette étude ont été échantillonnées d'une part dans le réservoir hydroélectrique d'Eastmain-1 et d'autres parts dans 11 lacs en Estrie, Québec. La vitesse d'échange gazeux à été mesuré *in situ* à l'aide d'une chambre flottante. Plusieurs variables météorologiques dont la turbulence de l'eau ainsi que quelques variables limnologiques ont aussi été mesurés. Un modèle robuste a été élaboré en utilisant la turbulence de l'eau à l'intérieur de la surface d'échantillonnage de la chambre pour expliquer k. Il a aussi été démontré la chambre flottante surestime k et cela est due à la turbulence à l'intérieur de la surface d'échantillonnage créée par celle-ci. Le rapport de surestimation peut atteinte dix fois la valeur réelle et ensuite diminue plus la turbulence naturelle du système augmente. Finalement, il a été montré que l'ajout de l'aire du système aux vitesses de vents dans une régression multiple améliore grandement la prédiction de k dans une variété de systèmes aquatiques différents. En apportant de meilleurs outils de mesure et d'estimation des vitesses d'échanges gazeux, cette étude permettra d'améliorer la précision des estimations des émissions de gaz à effet de serre provenant des milieux aquatiques terrestres.

Mots clés : échanges gazeux, dioxyde de carbone, interface air-eau, turbulence, chambre flottante

INTRODUCTION ET ÉTAT DES CONNAISSANCES

Dans le processus de compréhension du cycle global du carbone, une portion encore mal comprise et rarement considérée se situe au niveau des eaux intérieures. En plus de s'être révélés plus abondants (Downing *et al.,* 2006), les lacs, rivières, ruisseaux, réservoirs et étangs se sont avérées actifs plutôt que passifs dans la transformation du carbone (Cole *et al.*, 2007; Tranvik *et al.*, 2009). En effet, au lieu d'agir comme de simples canaux amenant le carbone terrestre jusqu'aux océans, les eaux intérieures sont des acteurs importants à considérer pour niveler l'équilibre du cycle global du carbone. Une proportion importante du carbone passant par les eaux intérieures est émise dans l'atmosphère et sédimentée. Selon Cole *et al.,* (2007), des 1,9 Pg de carbone (C) provenant des terres, seulement 0,9 Pg se rend aux océans. Ainsi, 0,23 Pg de C est sédimenté et 0,75 Pg sont émis dans l'atmosphère sous forme de CO_2. Cette dimension est accentuée par l'importance des émissions de gaz à effets de serre sur les changements climatique lorsque les émissions de CO_2 par les eaux continentales (0,75 Pg C) sont comparées au carbone capté par les océans (entre 1 et 2 Pg C) (IPCC, 2007).

Le dioxyde de carbone, un important gaz à effet de serre, est souvent émis par les plans d'eau, surtout par les rivières et les lacs oligo et mésotrophiques, mais aussi les régions oligotrophiques des océans (Duarte et Prairie, 2005). Dans ces systèmes, la matière organique, provenant à la fois de la production primaire, mais aussi des terres environnantes, est métabolisée en CO_2. Si ce phénomène prédomine la photosynthèse, le système aquatique est alors hétérotrophe et une accumulation de CO_2 se produit et la surface du plan d'eau devient par conséquent sursaturée en CO_2. La majorité des lacs du monde sont sursaturés en pCO_2 à leur surface (Cole *et al.,* 1994). Enfin, un déséquilibre est créé avec l'atmosphère et un dégazage se produit.

Échange gazeux à l'interface air-eau

Les échanges gazeux par diffusion entre l'eau et l'atmosphère peuvent être modélisés selon la première loi de Fick, où le flux d'échange est proportionnel au gradient de pressions partielles à l'interface. Premièrement, le flux est dirigé dans le sens du gradient de pression partielle du gaz, de la plus grande pression partielle vers la plus faible. Ensuite, la vitesse des échanges est décrit par la vitesse d'échange gazeux, *k,* par la relation suivante :

$$f_X = k \times Kh(\Delta pX) \tag{1}$$

où le flux (*f*) d'un gaz (*X*) représente la quantité émise par unité de surface, par unité de temps, la constante de Henry (*Kh*) permet de convertir la pression partielle du gaz en concentration en fonction de la température et de la salinité de l'eau et le coefficient *k*, est la vitesse d'échange gazeux, aussi appelé coefficient de vélocité piston. Ce dernier correspond à l'épaisseur de la couche d'eau dans laquelle la pression partielle d'un gaz sera équilibrée avec l'air pendant un certain intervalle de temps. La magnitude de la vitesse d'échange gazeux est une fonction de la thermodynamique et de l'hydrodynamique de l'eau agissant à l'interface. Le processus thermodynamique est représenté par le nombre de Schmidt:

$$Sc = \frac{\upsilon}{D} \tag{2}$$

qui est la viscosité cinématique (υ) de l'eau, influencée par la température et la salinité de l'eau, divisé par le coefficient de diffusion spécifique du gaz en question (Wanninkhof, 1992). La vitesse d'échange gazeux (*k*) est donc proportionnelle à Sc^{-n} où *n* est en fonction de la rugosité de la surface. Une étude en laboratoire à montré que *k* est proportionnel à $Sc^{-2/3}$ à vents faibles et à $Sc^{-1/2}$ à vents élevés (Jähne, Heinz et Dietrich, 1987). Par exemple, pour le CO_2, la vitesse d'échange gazeux est souvent utilisé sous forme de k_{600} qui est standardisé au nombre de Schmidt 600 correspondant à une température de 20°C en eaux douces. De cette manière, le k_{600} sera donc uniquement proportionnel à l'hydrodynamique de l'eau, plus particulièrement, la turbulence à l'interface air-eau (MacIntyre, Wanninkhof et Chanton, 1995).

Turbulence

Dans le cas d'un gaz légèrement soluble comme l'O_2 et le CO_2, le mouvement de l'eau sera le principal responsable de la vitesse d'échange gazeux à l'interface air-eau (MacIntyre, Wanninkhof et Chanton, 1995). La turbulence de surface dans un lac ou un réservoir se manifeste à plusieurs échelles, passant des remous microscopiques dans les premiers centimètres de la surface jusqu'au mélange entier de la colonne d'eau. Bien que tous ces types de turbulence soient reliés entre elles, nous nous arrêterons qu'à la petite échelle, celle de Kolmogorov. À cette échelle, les échanges gazeux peuvent être expliqués par le comportement des petits remous directement à l'interface avec l'air. Ce phénomène a été démontré théoriquement par le modèle de *«Small-Eddy»* (Eq. 3) qui décrit l'augmentation des échanges gazeux diffusif en renouvelant constamment le contenu de matière à la surface par les caractéristiques visqueux des remous (Lamont et Scott, 1970). Ce modèle est tiré de la théorie de renouvellement de surface (Dankwerts, 1951) :

$$k \propto (\varepsilon \upsilon)^{1/4} Sc^{-n} , \tag{3}$$

où ε est le taux de dissipation d'énergie cinétique turbulente, ν est la viscosité cinématique de l'eau, *Sc* est le nombre de Schmidt et *k* est la vitesse d'échange gazeux. Cette façon particulière de représenter la turbulence décrit l'état d'énergie de l'eau où les remous se transforment en plus petits remous pour finalement se dissiper complètement au travers de la viscosité. Tokoro *et al.*, (2008) ont démontré que le modèle *«Small-Eddy»* peut être paramétrisé dans des conditions de turbulence et de vitesse d'échanges gazeux élevées en milieux côtiers et océaniques. D'autres études l'ont aussi démontré en estuaire marin (Zappa *et al.*, 2007) et en bassins expérimentales (Zappa *et al.*, 2009). Cependant, les paramètres évoqués par ces études ne s'accordent pas, sauf pour l'étude en bassin et en estuaire. Plusieurs facteurs peuvent induire la turbulence à la surface de l'eau comme le vent, le déferlement des vagues mais aussi le mélange causé par les différences de température (MacIntyre, Wanninkhof et Chanton, 1995).

Influence du vent

Le vent transfert son énergie au plan d'eau, ce qui induit de la turbulence et des courants (Kalff, 2002). De ce fait, la vitesse d'échange gazeux est souvent mise en relation avec la vitesse du vent (Cole et Caraco, 1998; Crusius et Wanninkhof, 2003; Frost et Upstill-Goddard, 2002; Wanninkhof, 1992; Wanninkhof et McGillis, 1999; Zappa *et al.*, 2007). Cependant, les courbes ainsi que la nature des relations entre le vent et la vitesse d'échange gazeux sont souvent discordantes entre les différents travaux. Quelques études ont reliés la vitesse du vent et k linéairement (Borges *et al.*, 2004; Guérin *et al.*, 2007; Kremer, Reischauer et D'Avanzo, 2003) mais aussi par des relations exponentielles (Frost et Upstill-Goddard, 2002; Guérin *et al.*, 2007; Kremer, Reischauer et D'Avanzo, 2003). D'autres ont trouvé une relation de puissance (Cole et Caraco, 1998), cubique (Wanninkhof et McGillis, 1999) et même bilinéaire (Crusius et Wanninkhof, 2003). Dans le cas des relations non linéaire, à faibles vents, d'autres facteurs peuvent entrer en jeu comme la présence de surfactant (Wanninkhof et McGillis, 1999) et de la convection (Crusius et Wanninkhof, 2003), tandis qu'à vents élevés, les échanges peuvent être accéléré lorsque les vagues se forment et se brisent entraînant de l'air avec elles (Wanninkhof et McGillis, 1999). Pour tenter d'expliquer la variabilité entre les différentes relations linéaire de k avec la vitesse du vent, Guérin *et al.*, (2007) ainsi que Borges *et al.*,

(2004) ont corrélés les pentes des fonctions linéaires de k_{600} sur la vitesse du vent avec l'aire des plans d'eau provenant de différentes études. Ceci donne un indice sur l'effet que la course du vent (*«fetch»*), c'est-à-dire la distance sur laquelle le vent souffle, pourrait avoir sur les échanges gazeux. Quelques auteurs ont ainsi considéré la course du vent directement en laboratoire (Zappa *et al.*, 2004) ou indirectement avec la direction du vent (Frost et Upstill-Goddard, 2002) mais sans avoir trouvé de lien concluant.

Convection pénétrative

En présence de vents faibles, Crusius et Wanninkhof (2003) suggère que des évènements de convection peuvent affecter les échanges gazeux. Ces mouvements induits par la convection sont causés par l'augmentation de la densité de l'eau à l'interface due au refroidissement ou à l'évaporation de l'eau (MacIntyre, Wanninkhof et Chanton, 1995). Ce phénomène se manifeste à petite échelle, localisé à seulement quelques centimètres de la surface. Par exemple, une étude en laboratoire a montré que l'eau refroidi à l'interface coule en amenant avec elle de l'oxygène, ce qui augmente les échange entre l'eau et l'air (Schladow *et al.*, 2002). Aussi, le mélange par convection peut s'effectuer sur la quasi-totalité de la couche d'eau sur une échelle de temps plus grande. Une étude portant sur un lac tropical évoque l'effet de refroidissement qui contribue grandement au mélange de la colonne d'eau, particulièrement la nuit (Crill *et al.*, 1988).

Couche de matière organique accumulée à la surface

Wanninkhof *et al.*, (1999) suggèrent qu'à faible vent, la présence de surfactant contenu dans un biofilm à la surface de l'eau ralentirait la vitesse d'échange gazeux. Ces surfactants modifient les propriétés physique de l'eau à l'interface avec l'air et en réduisent les échanges gazeux (Botte et Mansutti, 2005; McKenna et McGillis, 2004).

En milieu océanique, l'activité phytoplanctonique est la principale source de surfactant et la quantité de ces surfactants dépend de la composition en espèce du phytoplancton et de leurs âges (Zutic *et al.,* 1981). En océan toujours, la concentration de matière organiques totale dans les premiers centimètres de la surface de l'eau a aussi été perçu comme facteur de ralentissement des échanges gazeux (Calleja *et al.*, 2009). En laboratoire, une réduction des taux d'évasion d'oxygène de 5 à 50% a été observé en présence de matière organique généré par le phytoplancton marin comparé à de l'eau propre (Frew *et al.*, 1990). Ce phénomène est par conséquent susceptible de se produire en eaux douces, où les concentrations de matières organiques et la production sont souvent élevées.

Autres facteurs physiques

D'autres facteurs peuvent affecter la turbulence à la surface et ainsi influencer les échanges gazeux avec l'atmosphère. Le déferlement des petites vagues aurait beaucoup d'impact sur les transferts des gaz, surtout à des vitesses de vent élevées (Zappa *et al.*, 2004). Une étude menée en laboratoire montre que la proportion de la surface où le déferlement de petites vagues a lieu est positivement corrélé avec la vitesse d'échange gazeux (Zappa *et al.*, 2004). La pluie peut aussi affecter la surface de l'eau causant une augmentation de la vitesse d'échanges gazeux. Une étude récente dans un bassin expérimentale a montrée clairement la turbulence engendré à la surface par la pluie et son lien avec la grosseur des gouttes (Zappa *et al.*, 2009). Ensuite, des expérimentations en laboratoire ont aussi montré que la pluie peut avoir un effet sur les échanges gazeux (Ho *et al.*, 1997) et cet effet peut être aussi remarqué si on la combine à la vitesse du vent (Ho *et al.*, 2007). En milieux naturels, quelques études ont pu aussi observés un effet direct sur les échanges gazeux (Cole et Caraco, 1998; Guérin *et al.*, 2007).

Méthodes de mesure

Plusieurs méthodes sont utilisées pour mesurer les flux de gaz et par conséquent la vitesse de ces échanges en utilisant l'équation (1) réarrangée. Ces méthodes diffèrent dans le degré d'intégration temporelle et spatiale des flux.

La méthode de traceur délibérée (hexafluorure de soufre, SF_6)

Une méthode fréquemment utilisée pour estimer les échanges gazeux avec l'atmosphère est par mesure d'évasion du SF_6 (Cole et Caraco, 1998; Crusius et Wanninkhof, 2003; Upstill-Goddard *et al.*, 1990). Cette méthode utilise un traceur gazeux qui est inactif biologiquement comme le SF_6. Ainsi, en sachant la quantité de gaz (SF_6) ajouté au système, il suffit de suivre cette quantité dans le temps et ensuite, le taux d'évasion du gaz peut être calculé par bilan de masse. Cette méthode permet d'obtenir des données de vitesse d'échange gazeux sur une échelle spatiale allant d'un petit lac (environ 0,15 km^2) à un très grand (environ 450 km^2) et une échelle de temps allant d'une journée à quelques semaines, dépendamment de l'épaisseur de la couche d'eau qui est mélangée et du taux de transfert des gaz (Cole et Caraco, 1998; Wanninkhof, 1991; Wanninkhof, Ledwell et Crusius, 1991). L'hexafluorure de soufre a l'avantage d'être stable à long terme dans l'eau, se détecte à des niveaux très bas et est facile à analyser. Bien que cette méthode permette d'obtenir des vitesses d'échanges gazeux spécifiques au milieu, elle comporte quelques désavantages. Même si le SF_6 est inactif biologiquement, il est possible qu'il s'évade autrement que par diffusion vers l'atmosphère. En effet, le SF_6 est plus soluble dans certains gaz que dans l'eau et peut donc s'échapper lors d'évènement d'ébullition de méthane. Aussi, il peut y avoir un effet de dilution par les eaux entrantes de même que des pertes par les eaux sortantes (Cole et Caraco, 1998; Matthews, St. Louis et Hesslein, 2003). Enfin, la méthode par évasion du SF_6 nécessite de calculer des moyennes sur une échelle temporelle qui est longue comparativement à la variabilité météorologique (Frost et Upstill-Goddard, 2002).

Approche par « eddy covariance »

Une autre manière de mesurer les échanges gazeux est par la méthode *« eddy covariance »*. C'est un système automatisé qui mesure la pression partielle de CO_2 dans l'air en même temps que la turbulence de l'air en trois dimensions. Le principe est simple, lorsque les vecteurs de vitesse du vent allant vers le haut sont couplés avec une concentration plus élevée en CO_2 que celle couplée avec les vecteurs de vent qui descendent, le signal provient donc d'une source de CO_2. Cette méthode permet de couvrir un large territoire avec une échelle temporelle relativement courte (1/2 heure) et est souvent utilisée en systèmes forestiers (Rannik *et al.*, 2004) et en océans (Kondo et Tsukamoto, 2007). Elle nécessite par contre une installation et une instrumentation complexe. Ces instruments ont aussi des limites sensorielles, il est alors conseillé d'utiliser cette technique en absence de vent trop faible ou de différences de pression partielle trop petite (McGillis, 2001). Aussi, les mesures de flux peuvent être contaminées par des signaux provenant des milieux terrestres environnants (Eugster *et al.*, 2003).

Chambres flottantes ou chambres statiques

Cependant, pour avoir une mesure de flux ponctuelle et localisée, en plus d'être peu coûteuse et facile à transporter, seule la méthode de la chambre flottante est appropriée. Cette méthode a été utilisée premièrement pour mesurer le taux de réaération de l'eau en oxygène (Belanger et Korzun, 1991; Copeland et Duffer, 1964; Doyle, 1978). Ensuite, elle a été adaptée pour mesurer le métabolisme en suivant les flux de dioxyde de carbone à la surface du plan d'eau (Frankignoulle, 1988). En mesurant le taux d'accumulation d'un gaz comme le dioxyde de carbone dans une chambre fermée pendant un laps de temps donné, il est possible d'avoir une mesure de flux. Ensuite, avec les données de pressions partielles du gaz dans l'eau et dans l'atmosphère en plus de la température de part et d'autre, il est possible de calculer la vitesse d'échange gazeux (*k*) en manipulant l'équation 1. Généralement, un déploiement de la chambr sur la surface du plan d'eau pendant dix minutes est suffisant pour avoir un taux d'accumulation avec un coefficient de détermination (r^2) souvent supérieur à 0,95.

Il y a cependant des problèmes d'exactitude dans les mesures de flux avec cette méthode. Étant donné que la chambre flottante perturbe l'interface air-eau, il se peut que les flux mesurés ne soient pas exacts. Bien que quelques auteurs suggèrent que cette méthode mesure les flux sans trop de biais (Guérin *et al.*, 2007; Repo *et al.*, 2007; Soumis, Canuel et Lucotte, 2008; Tokoro *et al.*, 2008), d'autres ont constatés que la vitesse d'échange gazeux mesurée par chambre flottante est généralement plus élevée comparée à d'autres méthodes (Duchemin, Lucotte et Canuel, 1999; Eugster *et al.*, 2003; Kremer, Reischauer et D'Avanzo, 2003; Matthews, St. Louis et Hesslein, 2003). Lors d'une étude portée sur les émissions de gaz à effet de serre des réservoirs hydroélectriques, Duchemin *et al.,* (1999) conclurent que les émissions mesurées avec la méthode de la chambre flottante sont plus élevées que celles calculées par les méthodes empiriques établis avec la vitesse du vent (voir description plus bas). Cette différence est d'autant plus marquante pour les stations en eaux peu profondes. Matthews *et al.,* (2003) montrent aussi des résultats de flux estimés par chambres flottantes plus élevés que les techniques de SF_6 et par relations empiriques basées sur la vitesse du vent. Récemment, Repo *et al.,* (2007), ont aussi comparé ces deux méthodes et ont remarqués quelques différences, bien que les deux méthodes aient suggéré des flux saisonniers plutôt semblables. Lorsque comparée avec la méthode *« eddy covariance »*, la chambre flottante semble aussi surestimer les flux de CO_2 (Eugster *et al.*, 2003). Pour faire suite à ces considérations, voici les causes probables des biais causés par la chambre flottante.

Premièrement, la chambre flottante perturbe l'interface air-eau, ce qui affecte les mesures de flux (Kremer, Reischauer et D'Avanzo, 2003; Lambert et Fréchette, 2005). La chambre se déplace constamment sur l'eau, même soumise à des vents faibles, et induit de la turbulence artificielle à l'intérieur de l'aire d'échantillonnage. Une chambre flottante dont les rebords sont au même niveau que la surface de l'eau semble surestimer les flux de 3 à 5 fois plus élevés qu'une chambre flottante donc les rebords pénètrent dans l'eau (Matthews, St. Louis et Hesslein, 2003). Ensuite, la création d'un micro-environnement par la chambre empêche le vent et la pluie d'affecter l'interface air-eau (Duchemin, Lucotte et Canuel, 1999; Matthews, St. Louis et Hesslein, 2003). La réduction de la turbulence de l'air à l'intérieur de la chambre réduit les échanges gazeux, excepté peut-être lorsque que la surface de l'eau est très calme, donc très peu de flux (Matthews, St. Louis et Hesslein, 2003). En ajoutant un petit ventilateur à l'intérieur des chambres d'expérimentation, (Kremer, Reischauer et D'Avanzo, 2003) ont montré qu'à vents de moins de 4 m s^{-1}, les flux mesurés avec les chambres sans ventilateurs sont 12% plus bas que ceux mesurés avec les chambres avec ventilateurs. Sans avoir de solutions précises pour obtenir des estimations de qualité avec la chambre flottante, plusieurs recommandations ont été proposées dans la littérature afin de minimiser la surestimation des flux. Selon Guérin *et al.,* (2007), les mesures de flux doivent être prises à partir d'un bateau à la dérive pour suivre la masse d'eau sous la chambre. Cette méthode limiterait l'effet de la turbulence induite par la chambre. Ensuite, quelques auteurs considèrent qu'une chambre flottante ayant des rebords qui pénètrent dans l'eau surestime moins qu'une chambre avec des rebords au même niveau que l'eau (Guérin *et al.*, 2007; Matthews, St. Louis et Hesslein, 2003).

Estimation en utilisant des modèles empiriques

Une autre méthode largement utilisée pour estimer la vitesse d'échanges gazeux consiste à employer une des relations empiriques disponible dans la littérature. Bien que la plupart de ces relations sont basées sur la vitesse du vent à 10 mètres en milieu océanique (Wanninkhof, 1992) ou en milieu lacustre (Cole et Caraco, 1998), quelques unes emploie plutôt la turbulence à la surface de l'eau (Tokoro *et al.*, 2008; Zappa *et al.*, 2007).

Hypothèses et objectifs

En révisant tous les facteurs qui influencent la vitesse d'échange gazeux, nous pouvons remarquer que la plupart sont directement ou indirectement liés à la turbulence près de l'interface air-eau. Si les échanges gazeux à l'interface air-eau sont en effet un processus diffusif, nous émettons donc comme premier hypothèse que la turbulence près de la surface peut être utilisée directement pour prédire la vitesse d'échange gazeux. Nous avons aussi vu plus haut que la méthode de la chambre flottante est susceptible de surestimer les mesures de flux en engendrant de la turbulence artificielle à l'intérieur de l'aire d'échantillonnage. Nous proposons ici que si c'est le cas, cette turbulence peut être mesurée et comparée à la turbulence présente en absence de chambre flottante. Notre hypothèse est que la turbulence mesurée directement sous l'aire d'échantillonnage de la chambre flottante sera plus élevée qu'en absence de celle-ci. Finalement, nous avons aussi vu qu'il existe beaucoup de différences entre les diverses relations entre la vitesse du vent et la vitesse d'échange gazeux. Nous proposons ici comme dernière hypothèse que ces différences sont due majoritairement aux diverses caractéristiques des systèmes étudiés mais aussi aux quelques biais méthodologiques qui persistent encore dans ce domaine.

Les objectifs de cette étude sont (1) d'établir un modèle basé sur la turbulence à la surface pour prédire la vitesse d'échanges gazeux, (2) de vérifier si la chambre flottante induit de la turbulence artificielle à l'intérieur de l'aire d'échantillonnage et finalement (3) de tenter d'expliquer les différences qui persistent entre les relations de la vitesse du vent avec la vitesse d'échange gazeux dans différents systèmes.

CHAPITRE I: The relationship between near-surface turbulence and gas transfer velocity in freshwater systems and implications for floating chamber measurements of gas exchange

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1.2 Abstract

We performed a series of gas exchange measurements in 12 diverse aquatic systems to develop the direct relationship between near-surface turbulence and gas transfer velocity. The relationship was log-linear, explained 78% of the variation in instantaneous gas transfer velocities, and was valid over a range of turbulent energy dissipation rate spanning about two orders of magnitude. Unlike wind-based relationships, our model is applicable to systems ranging in size from less than 1 km^2 to over 600 km^2. Gas fluxes measured with our specific model of floating chambers can be grossly overestimated (up to 1000%), particularly in low turbulence conditions. In high turbulence regimes, flux overestimation decreases to within 50%. Direct measurements of turbulent energy dissipation rate provide reliable estimation of the associated gas transfer velocity even at short temporal and spatial scales.

1.3 Introduction

Gas exchange at the air-water interface is central to any attempt at establishing a credible carbon budget, whether at a local, regional, or even global scale. While this is particularly obvious for marine systems, inland waters have recently been shown to have a larger-than-expected role in this regard (Cole *et al.*, 2007). However, the physical processes modulating gas exchange with the atmosphere are complex and currently modeled only with great uncertainty (Frost et Upstill-Goddard, 2002; Zappa *et al.*, 2007). Consequently, accurate carbon emission estimations are difficult to achieve. For non-reactive gases, gas exchange can be adequately modeled as a Fickian diffusive process and is therefore driven by two -variables: the difference in gas partial pressure between the air and the water and the gas transfer velocity (k). For gases of low solubility in water such as O_2 or CO_2, dissipation via the mass boundary layer will be the main transfer such that:

$$F = k \times Kh\,(pX_{\text{water}} - pX_{\text{air}}), \tag{1.1}$$

where F is the flux of a slightly soluble gas X across the air-water interface, k is the gas transfer velocity at a given temperature, Kh is the Henry's coefficient (corrected for salinity and temperature) and pX_{water} and pX_{air} are the gas partial pressures in water and air, respectively.

Since both the atmospheric and aqueous CO_2 partial pressure can now be easily measured in the field (Cole et Prairie, 2009), the main challenge in applying Eq. 1.1 is to estimate accurately the gas transfer velocity k. All processes affecting the mass boundary layer condition will mediate gas transfer velocity. It is known that for poorly soluble gas like CO_2 and O_2, water side near-surface turbulence is the main driver of gas transfer velocities across the air-water interface (MacIntyre, Wanninkhof et Chanton, 1995). The coupling between turbulence and gas transfer velocity was originally derived from surface renewal theory (Dankwerts, 1951). By constantly renewing the surface mass content with small-eddies, turbulence thus enhances the rate of diffusive gas exchange. More specifically, the gas transfer velocity k was shown to be directly related to near-surface turbulence from the characteristics of viscous eddies (Lamont et Scott, 1970) as

$$k \propto (\varepsilon \upsilon)^{1/4} Sc^{-n} , \tag{1.2}$$

where ε is the turbulent kinetic energy (TKE) dissipation rate, υ is the kinematic viscosity of water, Sc is the Schmidt number and k is the gas transfer velocity. Depending on the surface contamination, n will vary from 1/2 to 2/3. Because ε varies with depth, this relationship holds only if ε is measured at the interface of interest, i.e., near the surface. This theoretical relationship has been recently examined in natural systems (Tokoro *et al.*, 2008; Zappa *et al.*, 2007) and was found to hold generally.

The relationship between turbulence and gas exchange is also the basis for the many empirical functions relating k to wind speed, where wind speed is used as an integrative proxy for turbulence (Wanninkhof, 1992; Wanninkhof et McGillis, 1999). However, the existence of a unique and universal wind-k relationship for all systems is highly questionable given that for any wind speed, its effect on gas exchange is unlikely to be the same in the ocean and, for example, in a small kettle lake. Moreover, many studies have shown that other factors will affect k, like wind fetch (Borges *et al.*, 2004; Frost et Upstill-Goddard, 2002; Guérin *et al.*, 2007), tidal currents (Borges *et al.*, 2004; Zappa *et al.*, 2007), rainfall (Ho *et al.*, 1997; Ho *et al.*, 2007), micro-scale breaking waves (Zappa *et al.*, 2004), thermal convection (Eugster *et al.*, 2003; Schladow *et al.*, 2002), organic matter or suspended matter (Abril *et al.*, 2009; Calleja *et al.*, 2009), and surfactants (Frew *et al.*, 1990; McKenna et McGillis, 2004).

Establishing a reliable relationship between turbulence and k assumes that both variables can be measured accurately and precisely. While there is consensus that modern instruments such as acoustic Doppler velocimeters can measure turbulence precisely even at micro-scales, methods to measure k are numerous and more diverse although they basically all rely on inverting Eq. 1.1 to isolate k and measuring the other variables in the field, namely the gas partial pressure gradient and the flux. In practice, what varies among methods is the degree of time and space integration in the measured fluxes and this can often lead to different results. At one extreme, gas tracer experiments that typically use sulfur hexafluoride (SF_6), provide the widest spatial (a few km^2) and temporal (days to weeks) integration. However, they are cumbersome to repeat in multisystem studies or over different time periods. They are often inadequate if the purpose of the study is to examine the effects of other environmental characteristics (such as rain or surfactant concentration) which themselves vary on shorter scales than that of the integration scale over which the gas tracer experiment takes place. An alternative approach consists in continuously measuring gas fluxes using the eddy covariance technique over a footprint area of typically a few hundred m^2, depending on the height of the tower. While this approach is highly promising, it remains currently expensive, technically difficult, and again impractical for the study of several systems. At the other extreme, highly localized (less than 0.5 m^2) and nearly instantaneous CO_2 fluxes can be measured directly with floating chambers (FC) (Frankignoulle, 1988). This technique is simple, inexpensive, and highly portable. However, FC-derived fluxes are problematic as well. Some authors have shown that fluxes measured by floating chambers are higher than that obtained from SF_6 additions, from the often-used wind-k parameterization and from 'eddy covariance' method (Eugster *et al.*, 2003; Kremer, Reischauer et D'Avanzo, 2003; Matthews, St. Louis et Hesslein, 2003). Other authors have shown that FC measurements yield values consistent with other methods (Guérin *et al.*, 2007; Repo *et al.*, 2007; Soumis, Canuel et Lucotte, 2008).

There are several reasons why FC may be overestimating true fluxes. First, the floating chamber causes mass boundary layer perturbations and will thus affect the flux measurement (Kremer, Reischauer et D'Avanzo, 2003; Lambert et Fréchette, 2005). Second, by disturbing the air-water interface, the floating chamber generates artificial turbulence inside the sampling area. The chamber moves slightly but constantly on the surface water, even under very weak winds, and the chamber's walls induce artificial turbulence. Matthews *et al.*, (2003) suggest that floating chambers with edges (or skirt) at the same level as the water surface tend to overestimate fluxes up to 3 to 5 fold as compared to chambers with longer edges that enter the water.

Whether one is fundamentally interested in elucidating the factors driving variations in k or whether one is concerned with measuring k with minimum bias, the relationship between in situ turbulence and gas exchange is the nexus. The aim of this study was thus to explore and quantify the direct link between k and near-surface small scale turbulence in a series of fresh-water systems of different characteristics, both natural and man-made. We then hypothesised that if gas transfer velocities are driven mainly by near-surface turbulence, in situ turbulence could be used to estimate the gas transfer velocity directly. Also, as secondary objective, we assessed the commonly-held view that floating chambers tend to overestimate gas fluxes because of the artificially created turbulence within the sampling area. Our ultimate goal is to develop methods of estimating in situ the local gas transfer velocity either without floating chambers or by providing appropriate correction factors that minimize chamber-induced biases.

1.4 Methods

1.4.1 Study Areas

Samples were taken from two different regions of Quebec. First, as part of a larger project evaluating the net effect of reservoir impoundment on the carbon balance of the landscape relative to the undisturbed conditions, we collected samples from the Eastmain-1 hydroelectric reservoir (602 km^2) located near James's Bay, Québec, Canada (52°7' N, 75°58' W). The sampling campaigns (one in late July and second in early September of 2008) were planned to have a large variability in weather conditions, particularly wind speed. Second, to have a wider range of system types, eleven lakes located in Eastern Township region, Québec, Canada (45°20' N, 72°5' W) were also sampled (n = 23) during August of 2008 and chosen to cover a wide variability in size (lakes surface areas spanning from 0.2 to 11.7 km^2 and average depths ranging from 0.8 to 17.7 m) and biological productivity. For the Eastmain-1 reservoir (ER) samples (n = 98), sites were chosen near an Eddy Covariance tower placed on a small island. For Eastern Township lakes (ETL), samples were taken at the deepest point of lakes.

1.4.2 k_{600} calculations and associated measurements

This method consists of an enclosed chamber (surface area: 0.1 m^2) fitted with floats set over water and in which the rate of CO_2 accumulation is measured. The compartment was made of a plastic storage bin covered with aluminum paper to minimize temperature modulation inside the chamber over the short time (10 minutes) required to obtain good results. Floating devices were placed on the sides to ensure a constant volume of 23 L when deployed and letting 6 cm of the wall extensions penetrate the water column. The enclosed chamber was connected to an infra-red gas analyser (PPSystem, EGM-4) via tygon tubing (inner diameter (i.d.) 3.175 mm) in a closed recirculating loop with an inline moisture trap (drierite) located just before the gas analyzer. The IRGA calibration was checked before each sampling campaign with a standard analyzed gas (CO_2 at 618±12 μatm) and shown to be within the stated accuracy range (less than 1% of the span concentration). Detection limit of the gas analyzer is less than 5 μatm which is much below the lowest CO_2 partial pressure (pCO_2) sampled in this study. The chamber was flushed with ambient air prior to each measurement.

The partial pressures of CO_2 were recorded every minute for 10 minutes and the rate of accumulation was computed by linear regression. Although 95% of the chamber measurements had linear increases with $R^2 > 0.95$, flux measurements were rejected when R^2 was less than 0.90. For purposes of calculating gas transfer velocity, surface water pCO_2 was determined by pumping water from a depth of about 10 cm with a peristaltic pump through a gas equilibrator (membrane contactor MiniModule) itself coupled to an infra-red gas analyser (IRGA) in a closed recirculating loop (Cole et Prairie, 2009). Laboratory tests indicated a half-equilibration time of about 4-5 seconds. Nevertheless, we always waited one minute to allow full equilibration and therefore did not require correction. Floating chamber measurements were made in blocks of four measurement series, taking water pCO_2 and temperature at the beginning and at the end of each block and at the same position where the floating chambers were deployed.

With the resulting measured fluxes (FCO_2), surface water pCO_2 and atmosphere pCO_2, k_{CO_2} was calculated by inverting Eq. 1.1 as:

$$k_{\mathrm{CO}_2} = \frac{F_{\mathrm{CO}_2}}{Kh(p\mathrm{CO}_{2\mathrm{water}} - p\mathrm{CO}_{2\mathrm{air}})}, \quad (1.3)$$

which were then standardized to a Schmidt number of 600 using:

$$k_{600} = k_{\mathrm{CO_2}} \left(\frac{600}{Sc_{\mathrm{CO_2}}}\right)^{-n}, \tag{1.4}$$

where $Sc_{\mathrm{CO_2}}$ is the CO_2 Schmidt number for a given temperature (Kremer, Reischauer et D'Avanzo, 2003; Wanninkhof, 1992). We used n= 2/3 for wind speed < 3.7 m s^{-1} and n= ½ for wind speed > 3.7 m s^{-1} (Guérin *et al.*, 2007).

1.4.3 Turbulent kinetic energy dissipation rate

Of the many possible metrics of turbulence, turbulent kinetic energy dissipation rate (ε) was chosen because of its particular suitability on the Lagrangian reference frame that was used in this study. Turbulent kinetic energy dissipation rates were calculated using the inertial range method from three dimensional (3D) water velocity time series. When the surface water is isotropic and the turbulence is fully developed, eddies break up into smaller eddies to dissipate completely. This phenomenon can be seen on a density spectrum of the fluctuating current velocities according to Kolmogorov's law:

$$P_{(k)} = \alpha \varepsilon^{2/3} \kappa^{-5/3}, \tag{1.5}$$

where $P_{(k)}$ is the wavenumber spectrum of the fluctuating current velocities, α is Kolmogorov's empirical constant (0.52 according to Zappa *et al.*, (2003)) and κ is the wavenumber. We can assume Taylor's hypothesis of frozen turbulence if the turbulent motions are 'slow' (i.e., a long dynamical time) relative to the time required to convect them passed the probe. Because our turbulence measurements followed a Lagrangian reference frame relative to the mean flow, we used the mean wave orbital velocity as the advective velocity (V). Kitaigorodskii *et al.*, (1983) suggested the criterion $(u/V)^3 < 1$ to assess the adequacy of the frozen turbulence hypothesis, where u is the RMS of fluctuating velocities. In all our cases, this criterion was on average less than 0.015 ranging from 0.002 to 0.2. Thus, we derived the wavenumber spectra from the frequency spectra of the currents velocities time series by $\kappa=2\pi f/V$ where f is the frequency and V is the advective velocity, the mean wave orbital velocity.

To measure currents velocity fluctuations, we used an Acoustic Doppler Velocimeter (ADV; Sontek 10 MHz) at 25 Hz during 10 minutes for each sample. The quality of the time series were first tested by checking if the signal-to-noise ratio were over 15db and if correlation between studs were over 70%. Data rejected according to these criteria were replaced by the mean velocity. In addition, data which were different by over 3 times the standard error were also replaced by the mean velocity. Power spectra were then produced from the time series using the *pwelch* function (MATLAB 7.1). Because turbulence is considered three dimensional isotropic, either vertical or horizontal velocities could be used for spectral analysis. In this study, horizontal currents velocities were selected because they showed the greatest consistency. The range of frequency used for calculation of ε were between 3 and 6 Hz to avoid the interference generated by unwanted distortion such as that produced by the wave-induced movements of the ADV at lower frequencies (Lumley et Terray, 1983). As the integration of the power spectra over the entire range of frequencies necessarily represents the variance of the associated velocity measurements (from which an RMS value can be obtained), we calculated the mean wave orbital velocity (V) by integrating the power spectrum of vertical velocities over the region associated with the wave motion (i.e., the hump, between 0.8 and 2.5 Hz). Our V values varied between 0.04 and 0.63 m s^{-1}.

1.4.4 Evaluating the floating chamber method

To evaluate the claim that the FC method tends to overestimate gas fluxes because of artificially enhanced turbulence created by the chamber movements, we duplicated our flux and turbulence measurements under two different configurations. In all cases, the ADV was placed in the water horizontally with a Lagrangian floating structure at a constant sampling depth of 10 cm. In one configuration, the floating structure was positioned such that the ADV would measure directly underneath the center of the floating chamber (Fig. 1.1). In the second configuration, the ADV was positioned sideways to measure turbulence about 25 cm outside the perimeter of the chamber. The samples were thus separated in two sets, inside floating chamber measurements and free water, slightly outside the chamber (ε_{in} and ε_{fw}, respectively). Our working hypothesis is that the relationship between k_{600} and ε_{in} should represent the true relationship between turbulence and gas transfer velocity, even if they are both artificially inflated. Moreover, if FCs do create artificially turbulent regimes, then the data from the k_{600} vs. ε_{fw} should fall above the line of best fit of the k_{600}- ε_{in} relationship because the ε_{fw} would not be compromised by FC-induced turbulence. Thus, the extent of the departure between the k_{600}-ε relationships under the two measurement configurations describes the degree of overestimation induced by floating chambers and can therefore be used as a general correction factor.

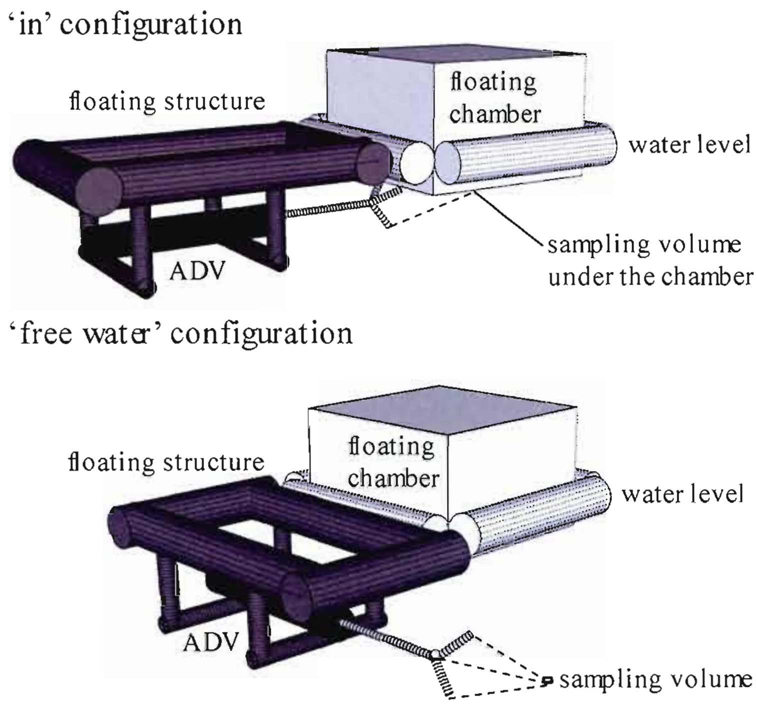

Figure 1.1. Sampling setup for measuring near-surface turbulence with the ADV inside the floating chamber (i.e., 'in' configuration, ε_{in}), directly below the sampling area and the free water turbulence measurement setup (i.e., 'free water' configuration, ε_{fw}). Turbulence sampling was always at 10 cm depth.

1.4.5 Meteorological data

Wind speed measurements were taken on site before and after each FCs using a hand-held anemometer (Kestrel 4000, accuracy 3% of reading, response time of 1 second and operational range of 0.3-40 m s^{-1}) at one meter above the water surface. The two measures during one minute were then averaged to produce a representative wind speed associated with each FC measurement. We extrapolated the wind speed data to wind speed at 10 meters (U_{10}) according to the logarithmic wind profile relationship of Crusius and Wanninkhof (2003):

$$U_{10} = U_z\left[1 + \frac{(C_{d10})^{1/2}}{\kappa}\ln\left(\frac{10}{z}\right)\right], \quad (1.6)$$

where z is the measured wind speed height, C_{d10} is the drag coefficient at 10 meters height (0.0013, (Stauffer, 1980)) and κ is the Von Karman constant (0.41). We also used the handheld anemometer the measure air temperature (±0.5°C). Wave height was coarsely estimated using a graduated stick.

1.5 Results

1.5.1 Wind speed and other meteorological parameters

Table 1 summarizes the data from the different campaigns in the Eastmain-1 reservoir (ER) and Eastern Township lakes (ETL) in August 2008. Reservoir meteorological variables showed a wider range than ETL. Mean wind speed at 10 meters high (U_{10}) at the ER site was 3.8 ± 1.7 m s^{-1} (mean ± SE, n = 98) ranging from 0.0 to 8.8 m s^{-1}, slightly lower than the mean of 4.0 ± 1.3 m s^{-1} (mean ± SE, n = 23) ranging from 1.9 to 6.6 m s^{-1} for Eastern Township sites. The average wind speed standard deviation between the before and after FC measurements was 0.5 m s^{-1}

(n=118). The reliability of the handheld wind speed measurements was assessed when our sampling sites were in close proximity to an eddy covariance tower equipped with a sonic anemometer and those were found to agree well. Mean air temperatures were 15.5 ± 3.9°C (mean ± SE, n = 98, range: 7.4 – 28.0°C) and 19.5 ± 2.8°C (mean ± SE, n = 23, range: 13.9 - 23.3°C) in the ER and ETL sites, respectively.

Table I. General Dataset of the main variables measured on field*. They are separated in three sampling campaigns: in July 2008 on the Eastmain-1 reservoir (ER), in August 2008 on several lakes in Eastern Township (ETL) area and in September 2008 on Eastmain-1 reservoir again.

Site	Eastmain-1 Reservoir	Eastern Township Lakes	Eastmain-1 Reservoir
Sampling Period	July 2008	August 2008	September 2008
fCO_2 (mmol m^{-2} d^{-2})	92.7 ± 46.0 (41)	61.2 ± 62.2 (23)	166.7 ± 66.1 (57)
ΔpCO_2 (μatm)	529 ± 122 (41)	429 ± 477 (23)	895 ± 59 (57)
k_{600} (cm h^{-1})	17.7 ± 6.2 (41)	15.8 ± 4.8 (23)	19.5 ± 7.0 (57)
U_{10} (m s^{-1})	3.3 ± 0.9 (41)	4.0 ± 1.3 (23)	4.2 ± 2.0 (57)
Wave height (m)	0.10 ± 0.08 (37)	0.05 ± 0.04 (17)	0.17 ± 0.13 (57)
Air temp. (°C)	17.8 ± 2.8 (41)	19.5 ± 2.8 (23)	13.8 ± 3.7 (57)
Water temp. (°C)	18.7 ± 0.6 (41)	21.0 ± 0.8 (23)	16.4 ± 0.8 (57)
ε_{in} (m^2 s^{-3})	$1.1\times10^{-4} \pm 6.7\times10^{-5}$ (21)	$1.1\times10^{-4} \pm 9.6\times10^{-5}$ (8)	$1.7\times10^{-4} \pm 1.3\times10^{-4}$ (28)
ε_{fw} (m^2 s^{-3})	$3.1\times10^{-5} \pm 1.8\times10^{-5}$ (20)	$2.2\times10^{-5} \pm 1.5\times10^{-5}$ (15)	$3.5\times10^{-5} \pm 1.4\times10^{-5}$ (29)

* mean ± SE and n in brackets, fCO_2 is the CO_2 flux across air-water interface, ΔpCO_2 is the CO_2 partial pressure difference between water and atmosphere, k_{600} is the gas transfer velocity for Schmidt number of 600, U_{10} is the wind speed at 10 meters high, Air temp. is the ambient air temperature, water temp. is the surface water temperature, ε_{in} is the turbulent kinetic energy dissipation rate measured inside the FC sampling area, and ε_{fw} is the turbulent kinetic energy dissipation rate measured in free water near the FC.

1.5.2 Gas transfer velocities (k_{600})

We estimated the precision of our gas transfer velocities data from first-order error propagation formulas based on the uncertainties of the water pCO_2 measurements and of the slope of the time accumulation rate of CO_2 inside the chamber. Beginning and end pCO_2 measurements were always within 5% of variation of each other. For the ER sites, 90% of the data had coefficient of variations (CV) less than 15%. For Eastern Township lakes, 75% of the dataset had a variation coefficient of less than 20%. In both cases, most (about 80-85%) of the uncertainty in k_{600} values obtained were due to variations in the partial pressure differential while the remainder due to uncertainty in the CO_2 accumulation rate. The slightly greater variation in our k_{600} values obtained from the ETL sites are likely attributable to the generally lower fluxes observed and the corresponding higher relative error of the regression slopes of CO_2 accumulation in the chambers. The average value of gas transfer velocities (k_{600}) on the ER site was 18.8 ± 6.7 cm h^{-1} (mean ± SE, n = 98, range: 3.7 to 31.7 cm h^{-1}) and 15.8 ± 4.8 cm h^{-1} (mean ± SE, n = 23) ranging from 8.4 to 26.5 cm h^{-1} for lakes (Table 1). The sampling conditions considered by Kremer *et al.*, (2003) to be suitable for floating chamber measurements were always met in our study: wind conditions speed was below 8 m s^{-1} and wave height never high enough to break the seal between the chamber and water surface (average wave height was 0.13 ± 0.11 m). Similarly, although whitecaps were not quantified, their rare occurrence and low magnitude would not have influenced our chamber measurements particularly in view that we never found inconstancies in the linearity of gas accumulation rate within the floating chambers. We thus contend that our floating chamber was used within the limits suggested by Kremer *et al.*, (2003).

1.5.3 Turbulent kinetic energy dissipation rates (ε) and its relationship with gas transfer velocities

Dissipation rates were derived from the adequacy of the -5/3 slope fitting of the Kolmogorov's law on the power spectrum of the horizontal velocities (example shown in Fig. 1.2). The vast majority of the spectra showed a clear hump around 1.3 Hz which represents the relative vertical motion of our measuring system. Some measurements were excluded when the spectrum was visibly not following the expected slope. On this basis, only 10% of the ε values were excluded on the ER dataset but 30% from the ETL. We suggest that the higher exclusion in the ETL region is attributable to the very low turbulence (wind) we often encountered there, making energy dissipation rate more difficult to measure. The overall range in free water TKE dissipation rate (ε_{fw}) spanned nearly two orders of magnitude among our samples and sites and ranged from 5.4×10^{-6} to 7.5×10^{-5} m^2 s^{-3} and from 8.3×10^{-6} to 5.4×10^{-5} m^2 s^{-3} for the ER and ETL sites, respectively. These values are comparable to the upper mixed layer of other lakes (MacIntyre, Wanninkhof et Chanton, 1995) but lower than dissipation rates found under breaking waves conditions (Terray *et al.*, 1996), in estuaries with tidal currents (Zappa *et al.*, 2007) or in turbulent coastal environment (Tokoro *et al.*, 2008). TKE dissipation rate inside the FC (ε_{in}) averaged $1.5 \times 10^{-4} \pm 1.1 \times 10^{-4}$ m^2 s^{-3} (mean ± SE, $n = 49$) at the ER site and $1.1 \times 10^{-4} \pm 9.6 \times 10^{-5}$ m^2 s^{-3} (mean ± SE, $n = 9$) in ET lakes (Table 1).

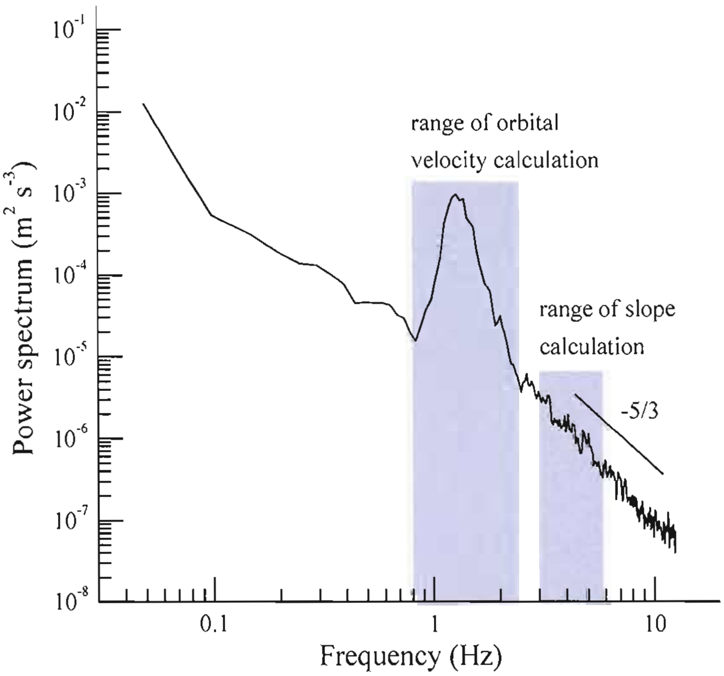

Figure 1.2. Power spectrum of the horizontal current fluctuation measured with ADV. Solid straight line is the -5/3 slope on a log-log scale according to Kolmogorov's law that was used for TKE dissipation rate (ε) calculation. The frequency range used in our calculations was from 3 to 6 Hz. Peak around 1.3 Hz corresponds to the wave motion. Consequently, anything below this range was not use in the calculations.

The relationship between turbulence and gas transfer velocities was first examined using only the measurement pairs with the turbulence measurements taken just 10 cm under the FC (i.e., the 'in' configuration). Figure 1.3 shows the significant relationship between k_{600} and ε_{in}. Least squared linear regression analysis produced the predictive equation ($R^2 = 0.78$, $n = 57$, $p < 0.0001$):

$$k_{600} = 78.22\ (\pm 4.25) + 14.66\ (\pm 1.05) log_{10} \varepsilon_{in} \tag{1.7}$$

where k_{600} is in cm h^{-1} and TKE dissipation rate ε_{in} in $m^2\ s^{-3}$. Note that turbulence measurements are log transformed and the intercept cannot be therefore be interpreted as the k_{600} value at no turbulence. When applying our ε_{in} measurements to the small-eddy model (Eq. 1.2), our data showed a remarkable correspondence with theory (Fig. 1.4). According to this model, the regression slope between the observed and small-eddy modeled k_{600} values must pass through the origin and be linear, with both of these conditions visibly fulfilled. Furthermore, an analysis of covariance (ANCOVA, $p > 0.05$) showed that the parameters of this relationship are not different between lakes and the reservoir, emphasizing the generality of the model for freshwater systems ranging in size from 0.20 to over 600 km^2.

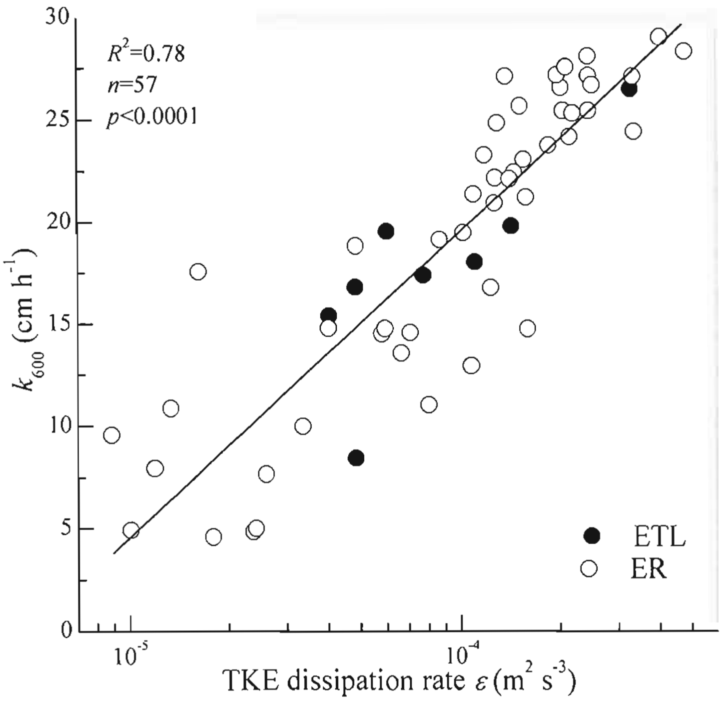

Figure 1.3. Least square linear regression between turbulent kinetic energy dissipation rates inside the FC (ε_{in}) and associated FC's k_{600} for ER and ETL data ($k_{600} = 78.22\ (\pm 4.25) + 14.66\ (\pm 1.05) log_{10}\varepsilon_{in}$, $R^2 = 0.78$, $n = 57$, $p < 0.0001$.

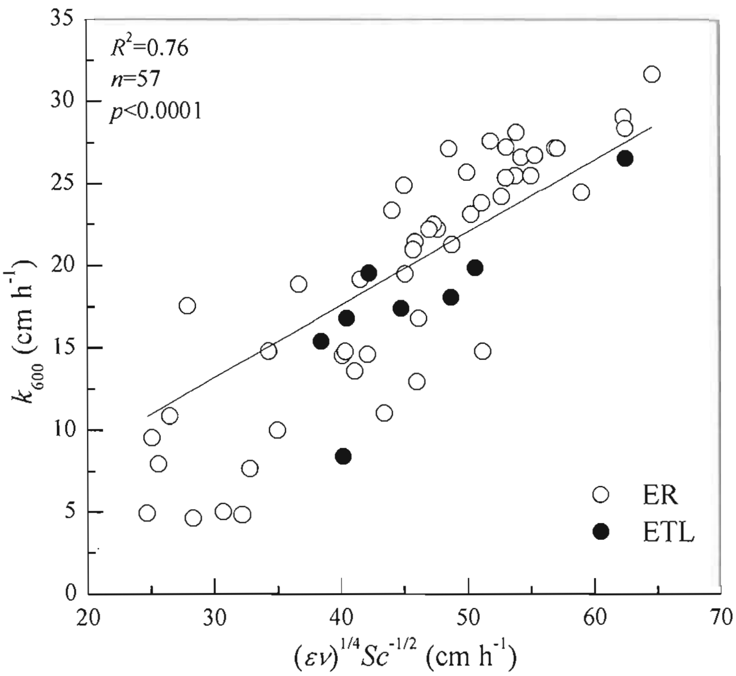

Figure 1.4. Relationship between k_{600} predicted by small-eddy model ($(\varepsilon v)^{1/4}Sc^{-1/2}$) using ε_{in} and measured k_{600} with FC. Solid line represent the linear regression best fit constrained to a 0 intercept ($k_{600} = 0 + 0.43\ (\pm\ 0.012)\ (\varepsilon v)^{1/4}Sc^{-1/2}$, $R^2 = 0.76$, $n = 57$, $p < 0.0001$).

1.5.4 Floating chamber method: biases and corrections

Because a single ADV instrument was available, inside FC and free water turbulence measurements were made sequentially, thus precluding a direct and simultaneous comparison of turbulence in and out of the chamber. Instead, we evaluated the potential bias by comparing the parameters describing the relationship between k_{600} and ε in the two measurement configurations. If floating chambers do not induce bias by modifying turbulence, the two relationships should be the same.

As it was the case for the turbulence data obtained just under the FCs (in configuration, Fig. 1.3), we found a similarly significant relationship between k_{600} and ε_{fw} (Fig. 1.5, R^2 = 0.48, n = 64, $p < 0.0001$) for the data in the 'free water' configuration. However, the position of most of our observations fell above the best fit line obtained earlier (Eq. 1.7 and dashed line in Fig. 1.5) implying that for similar k_{600} values under the two configurations, the turbulence measured under the chamber was higher than the corresponding free water measurements. This strongly demonstrates the contention that FCs overestimate fluxes by turbulence enhancement. A statistical comparison of the least squared regressions of k_{600} vs. ε_{fw} and ε_{in} (R^2 = 0.48, n = 64, $p < 0.0001$ and R^2 = 0.78, n = 57, $p < 0.0001$, respectively) by covariance analysis (ANCOVA) showed that both the slopes and elevations were significantly different (F-test for homogeneity of slopes ($p < 0.0001$) and elevation ($p < 0.0001$). Again, no differences were observed between the reservoir and lake data.

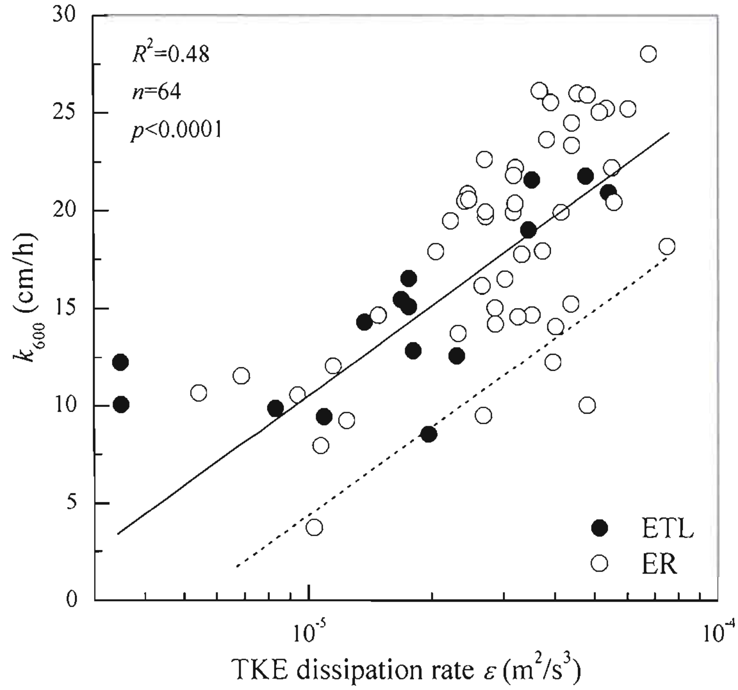

Figure 1.5. Solid line represents the relationship between free water measurements (ε_{fw}) and measured k_{600} with FC (k_{600} = 77.96 (± 7.99) + 13.21 (± 1.74) $\log_{10}\varepsilon_{fw}$, R^2 = 0.48, n = 64, p < 0.0001). The dashed line is the relationship between ε_{in} and k_{600} (Eq. 1.7).

To illustrate the extent to which FCs can overestimate gas fluxes, we constructed an overestimation coefficient as the ratio of the measured k_{600} values in the free water configuration to that predicted from Eq. 1.7. As a further precautionary measure, we excluded data where the predicted k_{600} was outside the range of values observed in the model development (in our case, below a predicted k_{600} of 1.6 cm h^{-1}). A ratio of unity corresponds to an unbiased prediction whereas values above one imply overestimation. As already implied by the divergent slopes in Fig. 1.5, Fig. 1.6 illustrates the highly non-linear behaviour of the overestimation ratio with turbulence. At relatively low turbulence ($< 1.5 \times 10^{-5}$ m^2 s^{-3}, left of 'a' on Fig. 1.6), FCs can easily overestimate true flux by several fold. At intermediate turbulence (between a (1.5×10^{-5} m^2 s^{-3}) and 'b' (4×10^{-5} m^2 s^{-3}) on Fig. 1.6) mean overestimation ratio is 1.58 ± 0.34 (mean ± SE, $n = 34$). At relatively high turbulence ($> 4 \times 10^{-5}$ m^2 s^{-3}, after 'b' on Fig. 1.6), overestimation is, on average, less than 50% (1.41 ± 0.31 (mean ± SE, $n = 17$)). The average overestimation ratio can be described by:

$$\text{Overestimation ratio} = \frac{77.96\ (\pm\ 7.99) + 13.21\ (\pm\ 1.74)\ log_{10}\varepsilon}{78.22\ (\pm\ 4.25) + 14.66\ (\pm\ 1.05)\ log_{10}\varepsilon}. \qquad (1.8)$$

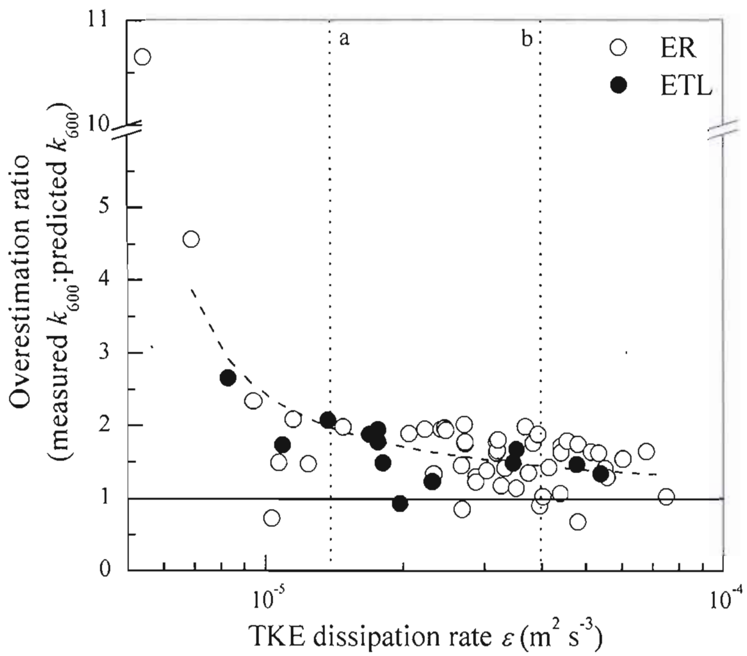

Figure 1.6. Overestimation ratio (measured k_{600}: predicted k_{600}) of the FC in relation with the free water near-surface turbulence measurements (n = 62). Dashed line is the trend of the relationship (Eq. 1.8). Dotted line separations 'a' and 'b' represent first and second threshold, respectively. Left of a section represents situations of high overestimation. Between 'a' and 'b' section has a mean overestimation ratio of 1.58 ± 0.34 (mean ± SE, n = 34). After 'b' section represent situations of low overestimation with a mean of 1.41 ± 0.31 (mean ± SE, n = 17).

1.6 Discussion

1.6.1 Relationship between k_{600} and turbulence

Many authors have pointed out that near surface turbulence is a key factor governing gas exchanges across the air-water interface because it constitutes a direct proxy of the physical state of the mass boundary layer (Tokoro *et al.*, 2008). The gas transfer velocity estimation from turbulence has the advantage of being likely quasi-universal among the different system types, irrespectively of what drives that turbulence. The relationship between near-surface turbulence and gas transfer velocity developed in this study (Fig. 1.3, Eq. 1.7) is promising in both its general applicability and for its precision (R^2 = 0.78). We however suggest that this relationship, itself derived from several systems, is probably generally applicable to other temperate or boreal freshwater systems provided the same turbulence measurement setup is used, in particular the depth at which turbulence is measured (10 cm). It is likely that the exact parameters of the relationship are dependent on the depth of the turbulence measurements (Zappa *et al.*, 2007). We therefore suggest that further tests should be performed under different conditions before it can be widely accepted. For practical purposes, we propose that given the consistency of the k_{600}-ε derived above, gas flux could therefore be estimated more simply by measuring turbulence (and deriving k_{600} from Eq. 1.7) in conjunction with gas partial pressure measurements. This approach would be likely preferable to measuring gas flux directly with a floating chamber, given the biases it introduces (*see* discussion below).

The predictive utility of a single turbulence based model lies not only in its precision but also in its wide application to a variety of systems, from rivers and lakes to reservoir and estuaries (Tokoro *et al.*, 2008; Zappa *et al.*, 2007). This is a major advantage of k_{600} models based on turbulence over those based on a proxy such as wind speed. As pointed out by Borges *et al.,* (2004) and Guérin *et al.,* (2007), there is strong evidence that the parameters of the wind-k_{600} relationship vary systematically with system size, as demonstrated by the linear trend between the slope of wind-k_{600} relationships and the surface area of the system over which they were developed (Guérin *et al.*, 2007). This argument is however well-known in the literature (Upstill-Goddard *et al.*, 1990; Wanninkhof, 1992) and our results support this contention. Using Eq. 1.7 in conjunction with the observed free water turbulence allows us to calculate a corrected k_{600} value for each observation. Fig. 1.7 shows the relationship between corrected k_{600} and wind speed for both the ER and ETL data. Both data sets show relatively poor relationships particularly for Eastern Township lakes which also had a tendency to have lower gas exchange for any given wind speed. System size could thus be a significant issue when estimating k_{600} from wind speed. It is obvious that the longer (in time and distance) the wind is blowing, the more it will transfer its energy to the surface waters. Thus, we submit that when only wind data are available, wind fetch together with wind speed and duration may be better predictors of surface turbulence conditions than wind speed alone. Such models have yet to be developed however and the major advantage of turbulence based models is that they can be used regardless of the size of the system.

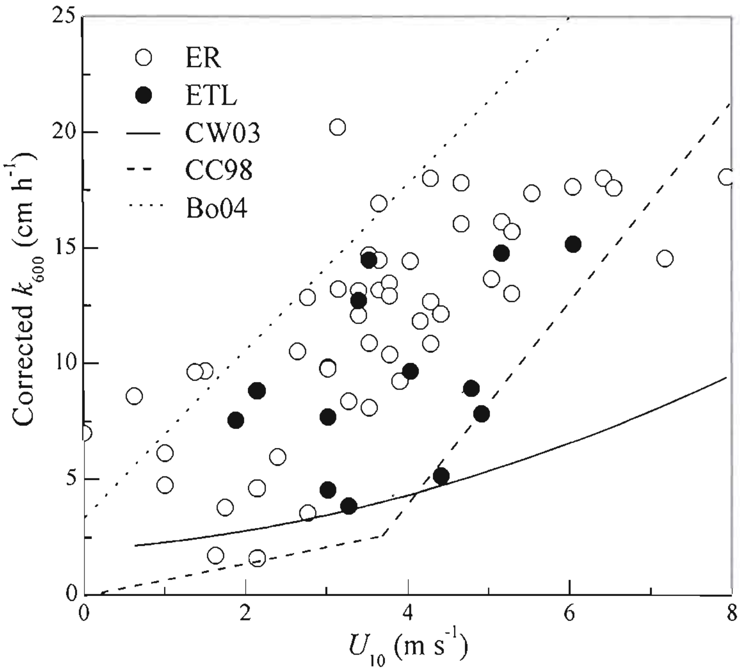

Figure 1.7. Corrected k_{600} data plotted against wind speed at 10 meters (U_{10}). Dashed line represents the Cole et Caraco, (1998) relationship (CC98), dotted line represent Borges *et al.* (2004) relationship (Bo04), and long dash line represents Crusius et Wanninkhof, (2003) relationship (CW03).

Figure 1.7 also compares our corrected k_{600} to wind speed trends with other published relationships. For the same wind speed range, our reservoir data are somewhat lower that those reported from the Scheldt estuary (Borges *et al.*, 2004) also estimated using FCs. However, our lake values were higher than that predicted by Crusius et Wanninkhof, (2003) or from the Cole et Caraco, (1998) relationship, both of which had been developed using SF_6 as a tracer. Differences between FC measurements (our study) and SF_6 (Cole and Caraco 1998; Crusius and Wanninkhof 2003) reside mainly in the temporal and spatial integration scales of the measurements. FC method usually integrates fluxes in an area of about 0.1 m^2 area over less than 30 minutes (in our case, 10 minutes) while the SF_6 addition integrates fluxes at the whole lake scale over periods of a few days. This may in part explain our results being higher than the oft-cited relationship of Cole and Caraco (1998) because our central sampling point was located at the more wind exposed area. However, we also had higher k_{600} values compared to the study from Guérin *et al.*, (2007) who also used FC. Although the observed discrepancy could be related to further methodological biases which were not taken into account in our correction factor (e.g., models of floating chamber and time of deployment), it may also involve other as yet unidentified environmental factors influencing gas exchanges at low wind speed. These may include thermocline depth, fetch, lake depth, and chemical factors such as surfactants. Nevertheless, we contend that turbulence variables have the advantage of taking into account the modulating effects of such factors on the turbulence generated by a given wind speed in itself (Jonsson *et al.*, 2008).

1.6.2 Small-eddy model

Our results are also useful in evaluating the appropriateness of certain theoretical models to field applications. The small-eddy model states that k_{600} should be proportional to the 0.25 power of ε. Figure 1.4 shows the relationship between k_{600} predicted from the small-eddy model based on ε_{in} and the measured k_{600} with FC at the same ε_{in} ($k_{600} = 0 + 0.43\ (\pm\ 0.012)\ (\varepsilon\upsilon)^{1/4}Sc^{-1/2}$, $R^2 = 0.76$, $n = 57$, $p < 0.0001$). Again, we consider this relationship to be valid even if FCs induces artificial turbulence because our turbulence measurements (ε_{in}) were made inside the FC sampling area thus encompassing the turbulence produced by the chamber. Our results as well as other studies demonstrate the universality of the small-eddy model to many types of aquatic systems. Zappa *et al.*, (2007) found a good relationship when combining data from four different systems: rivers to estuaries. Similar results were obtained in a recent study in marine coastal systems, using floating chamber method (Tokoro *et al.*, 2008). However, some difference appears between the slopes of these relationships. By rearranging Eq. 1.2,

$$k_{600} = A(\varepsilon\upsilon)^{1/4}Sc^{-n}, \tag{1.9}$$

the coefficient A represents the slope parameter that explains the difference between relationships. For our study, when separating ER and ETL data, slopes of the least squared regressions with 0 intercepts are similar ($k_{600} = 0.44\ (\pm\ 0.01)\ (\varepsilon\upsilon)^{1/4}Sc^{-1/2}$, $R^2 = 0.78$, $n = 49$, $p < 0.0001$ and $k_{600} = 0.39\ (\pm\ 0.02)\ (\varepsilon\upsilon)^{1/4}Sc^{-1/2}$, $R^2 = 0.66$, $n = 8$, $p < 0.0001$, for ER and ETL respectively). In our case, differences among systems do not affect the applicability of this relationship. However, when comparing our results to other studies (Tokoro *et al.*, 2008; Zappa *et al.*, 2007), some differences remain, even if our slope is similar to that of Zappa *et al.*, (2007) (A = 0.43, A = 0.419, respectively).

A solid predictive model to determine air-water gas exchanges using small-eddy model requires that A be parameterized with precision. Several factors may explain differences in parameter A between our study and that of Zappa *et al.*, (2007) and Tokoro *et al.*, (2008) but we suggest that they are most likely attributable to differences in the acquisition of the turbulence measurements which were not at the same depth. Because turbulence will dissipate vertically and non-linearly from the forcing source, sampling depth will be critical when comparing measured *k* to turbulence modelled *k*.

1.6.3 Bias and corrections for FC measurements

Our FC evaluation agrees with many other studies that fluxes are overestimated when measured by FC methods by perturbing the air-water interface (Kremer, Reischauer et D'Avanzo, 2003; Lambert et Fréchette, 2005; Matthews, St. Louis et Hesslein, 2003). Tokoro *et al.*, (2008) also measured turbulence inside and outside their FC but they did not find major disagreements between the two types of measurements. However, their inside chamber measurements were made from an ADV that was fixed on the sea floor and the near-surface turbulences were extrapolated. FC perturbation is certainly more significant at the first centimetres from the surface and therefore likely undetectable from sea floor probe extrapolated turbulence values.

Our results are showing that, most of the time, overestimation ratio is under 2 (90% of the data are between 0.67 and 2.05). However, the overestimation caused by floating chambers is not constant but depends strongly on the turbulence regime (Fig. 1.6). FC introduces a strong bias in calm, low turbulence waters, where the FC movements on the surface will increase significantly the water movements inside the sampling area relative to the natural water state. At higher turbulence regimes, when wind waves are added, artificially created turbulence caused by movements of FC on surface waters is relatively less important. Figure 1.6 illustrates what we consider two important turbulence thresholds, 'a' and 'b'. At very low turbulence (left of a), FC measurements are at high risk of important flux overestimations. On small lakes like ETL, this water condition is corresponding to wind speed less than 2 to 3 m s^{-1} which is usually frequent. On larger systems like ER, this low turbulence condition is equivalent of wind speed less than 1 to 2 m s^{-1}. At the other end of Fig. 1.6, threshold 'b' represents the point which FC measurements are comparatively much more adequate (overestimation less that 50%). This point corresponds to wind speed of over 6.5 m s^{-1} on small systems like ETL, an infrequent situation. In general, our results imply that using FC on small systems will be most problematic. On reservoirs or very large lakes, the threshold 'b' corresponds to wind speed of over 4 to 6 m s^{-1}. According to our results at Eastmain reservoir, those conditions are more frequent, thus reducing flux exaggerations considerably. Therefore, our mean overestimation on the reservoir is still about 50% which is non negligible. Thus, thresholds in the relationship with wind speed are themselves probably dependent of system size. Consequently, fluxes measured by FC on small lakes (< 2 km^2), which are numerous in Quebec, are probably overestimated by between 2 to 10 fold.

The overall trend of our results on FC overestimations is still coherent with the conclusions of Matthews *et al.*, (2003). Their FC overestimations were much more important in calm water conditions than when waves were present at higher wind speed. However, their hypothesis that this was due to the lack of side walls penetrating the surface is not supported by our data since our chamber had 6 cm walls extending into the water column. Even if FC designs may influence flux measurements by disturbing differently the air-water interface, further experiments are clearly needed to evaluate the real effect of wall extensions. Although our overestimation trend is general, it is important to note the absolute overestimation extent is probably specific to our own particular FC design. Floating chambers of other configuration may overestimate true flux differently. Also, because our model is linear (Fig. 1.3), extremely low turbulence may still contain some biases because we could not observe such low turbulence with floating chambers (hence our exclusion of data outside the observed range). Theoretically, if water completely stops moving (i.e., $\varepsilon \rightarrow 0$), there will still be gas exchanges across air-water interface. We suggest that k_{600} values derived from extremely low turbulence (< 5 × 10-6 m^2 s^{-3}) values should be interpreted with caution. Moreover, while our system enabled us to examine the artificial turbulence generated by the chamber and therefore correct for it, it is still possible that our turbulence measurement system itself generated some additional perturbations (Fig. 1.1).

1.7 Conclusion

When estimating carbon exchanges between water surfaces and the atmosphere, choosing the right k remained a major challenge. By using a dual series of concurrent flux and turbulence measurements, we have shown that near-surface turbulence can be used effectively to derive robust k values and that the theoretical small-eddy model was well supported by our data. We also showed that our floating chamber overestimate gas fluxes by up to 10 fold in calm water conditions but that they are adequate in more turbulent conditions (i.e., less than 50%). These numbers may be specific to our FC design and need further testing. Finally, we propose that turbulence based models are more general and accurate than k-wind relationships, which we contend are largely system-specific.

CHAPTER II: Unifying relationships between wind speed and gas transfer velocity in lakes

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2.1 Acknowledgment

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2.2 Abstract

There are many discrepancies remaining between the different wind speed to gas transfer velocity relationships. These differences can be related to systems characteristics implying that wind-k_{600} relationship could therefore be system-specific. Gas transfer velocities, measured by floating chamber method corrected for artificially-induced turbulence, were related to different meteorological, biochemical and physical variables in a series of freshwater systems in Québec, Canada. Lake size together with wind speed have been found to provide the best predictive model of gas transfer velocity although the addition of fetch length and difference in air-water temperature also showed to affect gas exchange. However, no effects of past wind regime, surface water chlorophyll *a* and dissolved organic carbon and rainfall have been found to have significant effect within wind-k_{600} relationship. The implication of system size in the wind-k_{600} relationship can have a large impact on future predictions of gas exchange on a whole landscape featuring a large heterogeneity of freshwater systems.

2.3 Introduction

Carbon transformations in ecosystems are central to our understanding of biome functioning. In the continental landscape, freshwater systems are often particularly active at processing carbon because of their close connection to the surrounding terrestrial ecosystem (Christensen, 2007; Prairie, 2008; Tranvik *et al.*, 2009). The terrestrial carbon load received by aquatic systems can be either stored in the sediments, emitted to the atmosphere (mainly as carbon dioxide) or flushed through the system, all in non-negligible quantities (Cole *et al.*, 2007). While variable among systems, carbon gas exchange is quantitatively often dominant over sediment accumulation (Tranvik *et al.*, 2009). Better understanding of gas exchanges processes across air-water interface is therefore critical to achieving robust local, regional or even global carbon budgets. However, freshwater systems are highly heterogeneous, physically, chemically and geographically. Quantifying the role played by aquatic ecosystems in the carbon economy of the landscape will require upscaling tools that can integrate the different gas exchange behaviour of these diverse systems. Indeed, the use of a unique model to predict gas exchange across the air-water interface, as is currently done (Algesten *et al.*, 2005; Kortelainen *et al.*, 2006; Teodoru *et al.*, 2009), may be a more precarious exercise than is currently acknowledged.

Diffusive gas exchange between air and water is represented by the variable k, also known as the gas transfer or piston velocity. In freshwater systems, gas transfer velocity is often represented by the variable k_{600} standardized with the Schmidt number 600 which depend on temperature (Wanninkhof, 1992). For slightly soluble gases like CO_2 and O_2, water-side near-surface turbulence is the main driver of gas transfer velocities across the air-water interface (MacIntyre, Wanninkhof et Chanton, 1995). It has been shown theoretically by the small-eddy model (Eq. 2.1), which describes the enhancement of diffusive gas exchange by constant renewal of the surface mass content with viscous eddies characteristics (Lamont et Scott, 1970). This model has been derived from surface renewal theory (Dankwerts, 1951),

$$k \propto (\varepsilon \upsilon)^{1/4} Sc^{-n}\ , \tag{2.1}$$

where ε is the turbulent kinetic energy dissipation rate, υ is the kinematic viscosity of water, Sc^{-n} is the Schmidt number dependant of surface roughness and k is the gas transfer velocity. A turbulence-based model, using ε as the descriptor of turbulent water movements, has been recently shown to be widely applicable in the field (Tokoro *et al.*, 2008; Vachon, Prairie et Cole, 2010; Zappa *et al.*, 2004; Zappa *et al.*, 2009; Zappa *et al.*, 2007). This particular metric of turbulence describes the energy state of water where eddies dissipate into smaller ones to finally disappear completely through viscosity. ε has been shown recently to relate directly to instantaneous k (Vachon, Prairie et Cole, 2010). Turbulence-based k models have the significant advantage of being quasi-universal, equally applicable to aquatic systems of different types, and independently of the particular phenomenon driving the turbulence. However, to be applicable on a whole-lake scale, they also require that turbulence be measured adequately in both space in time, and this limitation constitutes a major challenge with current instrumentation. There thus remains a need to infer turbulence parameters from more easily obtained physical and meteorological variables.

Wind forcing is an important factor inducing surface turbulence in lakes (MacIntyre, Wanninkhof et Chanton, 1995). As a result, a number of empirical relationships have been developed relating gas transfer velocity to wind speed as a proxy for near-surface turbulence (Cole et Caraco, 1998; Wanninkhof, 1992; Wanninkhof et McGillis, 1999). The majority of studies requiring estimates of gas flux generally rely on these published relationships and simply derive gas transfer velocity from the easily obtainable local wind speed distribution. However, there are a number of problems associated with this approach. First, the underlying scatter of these relationships is quite large (Cole et Caraco, 1998) and the predictive use of the central trend line is appropriate only if the scatter is random and unbiased with respect to other fluctuating conditions. Second, it also assumes that the scatter is random and unbiased with respect to individual lake or lake types. In other words, it assumes that the cascading effects of wind on turbulence and gas exchange is the same for all lakes, regardless of their size, shape, morphometry and chemistry. This tenet is particularly hard to defend for lakes as it is widely acknowledged that the energy transferred from wind to waves will be greatly different between, for example, a small pond and an inland sea.

Not surprisingly, existing wind-*k* relationships vary in slopes, intercepts, scatter and even curve shapes (Cole et Caraco, 1998; Crusius et Wanninkhof, 2003; Kremer, Reischauer et D'Avanzo, 2003; Wanninkhof et McGillis, 1999). Some authors have suggested that these inconsistencies may be related to systematic differences in the systems used to quantify the relationships such as widely different wind fetch or its corresponding surface area (Borges *et al.*, 2004; Frost et Upstill-Goddard, 2002; Guérin *et al.*, 2007). This hypothesis was strongly supported by the work of Borges *et al.*, (2004) and recently updated by Guérin *et al.*, (2007) who showed a direct link between the slopes of wind-*k* relationships and ecosystem size. Finally, apart from wind speed, a large variety of processes are known to affect the physical state of the top water layer and thus *k*. Those include rainfall characteristics (Cole et Caraco, 1998; Guérin *et al.*, 2007; Ho *et al.*, 1997; Zappa *et al.*, 2009), micro-scale breaking waves (Zappa *et al.* 2004), chemical surfactants (McKenna et McGillis, 2004), tidal currents (Borges *et al.*, 2004; Zappa *et al.*, 2007), and thermal mixing by penetrative convection (Eugster *et al.*, 2003). To date however, these influencing factors have not been widely integrated in general predictive models of gas exchange.

The above considerations suggest that wind-k_{600} relationships are, at best, system-specific. More likely, improving k_{600} predictions will require the simultaneous consideration of the most relevant and variable factors. In this paper, we evaluate the possibility of using simple and easy to obtain variables like lake area (LA), wind fetch, potential for penetrative convection (ΔT) and surface water dissolved organic carbon (DOC) and chlorophyll *a* (chl*a*) content as proxies for surfactants to be used together with wind speed to develop a more complete predictive model of gas transfer velocities in lakes of differing characteristics. Our approach focuses on the necessity of developing simple yet flexible models to improve estimates of gas transfer velocity in lakes of different types and thus of the gas flux they sustain.

2.4 Methods

2.4.1 Study Areas

Samples were taken from two different regions of Quebec, Canada. The majority of the samples came from a hydroelectric Eastmain-1 reservoir (602 km^2) located near James's Bay, Québec, Canada (52°7' N, 75°58' W). The sampling campaigns (one from July 28th to 1st of August and second from September 5th to September 12th 2008) were planned to cover a wide variability in meteorological conditions, particularly wind speed. Sampling sites were chosen near an eddy covariance tower installed on a small island. To have a wider range of system types, we complemented the sampling with 8 lakes located in the vicinity of Montreal. These lakes were chosen to cover a larger range in size and productivity (averaged lake area of 1.36 km^2 ranging from 0.19 to 4.0 km^2 and averaged chl*a* of 5.8 $\mu g\ L^{-1}$ ranging from 0.5 to 20.0 $\mu g\ L^{-1}$). The two regions and system types are thereafter abbreviated as ER for Eastmain-1 reservoir and TL for temperate lakes.

2.4.2 Gas transfer velocity estimations

Gas transfer velocities were estimated using floating chamber methods corrected for chamber-induced flux overestimation as described in Vachon, Prairie et Cole, (2010). Briefly, gas transfer velocities were estimated from the concurrent measurement of gas flux and air-water partial pressure differential. Floating chamber measurements of flux tend to overestimate true flux because of the turbulence they themselves generate; particularly in low turbulence environments (Vachon, Prairie et Cole, 2010). To account for this overestimation, Vachon, Prairie et Cole, (2010) developed correction equations (their Eq. 7) based on in situ turbulence. Our flux measurements were thus made in conjunction with nearby turbulence measurements (about 25 cm away from the perimeter of the chamber) expressed as turbulent kinetic energy dissipation rate, ε . Turbulence measurements were taken with an acoustic Doppler velocimeter (ADV 10 MHz, Sontek) at 0.1 m depth at 25 Hz of sampling rate for 10 minutes. Turbulent kinetic energy dissipation rates (ε) were then calculated using the inertial dissipation method based on Kolmogorov's law using orbitral wave velocity as advective velocity (*see* Vachon, Prairie et Cole, 2000 for details).

2.4.3 Meteorological Data

For the temperate lakes, *in situ* wind speed measurements were obtained on site before and after each FC measurements using a handheld anemometer (Kestrel 4000, accuracy 3%) at one meter above the water surface. Both measures lasted one minute and were averaged to have the mean wind speed associated with the FC measurement. Dominant wind direction was obtained from nearby Environment Canada meteorological stations. We extrapolated the wind speed data to wind speed at 10 meters (U_{10}) according to the logarithmic wind profile relationship of Crusius and Wanninkhof (2003):

$$U_{10} = U_z \left[1 + \frac{(C_{d10})^{1/2}}{\kappa} \ln\left(\frac{10}{z}\right)\right], \tag{2.2}$$

where z is the measured wind speed height, C_{d10} is the drag coefficient at 10 meters height (0.0013, (Stauffer, 1980)) and κ is the Von Karman constant (0.41). At the Eastmain-1 reservoir, an 11 meters high tower located on a small island of the reservoir recorded wind speed and direction as well as rainfall at 30 minute intervals (Marie-Claude Bonneville, Pers. Comm., McGill University). Wind speeds were corrected at 10 meters using Eq. 2.2. No rainfall event happened when sampling were done on TL sites. Wind fetch lengths were estimated using ArcGIS (ESRI) by measuring the distance between the sampling point and the nearest shore in a straight line according to the wind directions. To examine the potential of wind duration effect on gas transfer velocity, average wind speed and fetch lengths were calculated over the 2.5 hours prior to the sampling event resulting in five 30 minutes averaged data using Environment Canada wind data for TL and the flux tower data for ER. Air and water temperature differences (ΔT, air-water) were measured as a proxy for penetrative convection potential. Negative values are thus suggesting a potential effect of thermal mixing by the air temperature that is being lower than water temperature. On the opposite, when values were positive, i.e. no penetrative convection occurring, ΔT values were all set to 0.

2.4.4 Limnological variables

For the northern reservoir, chl*a* ($\mu g\ L^{-1}$) and DOC ($mg\ L^{-1}$) were sampled at 0.5 meter depth as part of a separate field campaigns at nearby sites. For the first and second campaign, we used the averaged chl*a* and DOC data from July 27th and September 9th, respectively. For Eastern Township lakes, chl*a* and DOC samples were taken at 0.5 meter depth at every sampling. Chlorophyll samples were analyzed spectrophotometrically following filtration on Whatman (GF/F) filters and hot ethanol (90%) extraction (Wetzel et Likens, 1991). DOC concentration was measured in 0.2 mm filtered water samples in an OI-1010 Total Carbon Analyzer (OI Analyticals) using wet persulfate oxidation.

2.5 Results

A total of 64 independent measurements were obtained (20 from the temperate lakes and 44 from Eastmain-1 Reservoir). Average results and general characteristics of the sampled systems are summarized in Table II. Mean corrected gas transfer velocities were significantly different between the two regions (t-test, $p<$ 0.05), and spanned a slightly wider range in Eastmain-1 reservoir (from 1.6 to 19.4 cm h^{-1}) than in temperate lakes (from 1.9 to 15.2 cm h^{-1}). However, mean turbulence (ε) value from ER (3.4×10^{-5} m^2s^{-3}) and TL (2.9×10^{-5} m^2s^{-3}) are not statistically different (t-test, $p > 0.05$). ER also showed a slightly wider range in ε values (from 5.4×10^{-6} m^2s^{-3} to 7.5×10^{-5} m^2s^{-3} for ER and from 6.0×10^{-6} m^2s^{-3} to 7.4×10^{-5} m^2s^{-3} for TL). Average wind speeds were not significantly different between the two regions (t-test, $p > 0.05$) but spanned on a wider range on Eastmain-1 reservoir (from 0.8 m s^{-1} to 7.2 m s^{-1}) than in temperate lakes (from 1.8 m s^{-1} to 6.0 m s^{-1}). All samples from the reservoir necessarily have the same surface area value (602 km^2) but spanned a large range of fetch lengths, varying from 0.4 to 7.1 km. For the temperate lakes, their surface area ranged from 0.19 to 4.0 km^2 (average 1 km^2) with fetches varying between 0.1 to 1.1 km.

2.5.1 Relationship between k_{600} and wind speed, system size and fetch

We found a significant relationship between gas transfer velocity (standardized to a Schmidt number of 600) and wind speed at 10 meters ($r^2 = 0.51$, $n = 64$, $p < 0.0001$). However, taking the two region separately, only ER data showed to be significant (ER: $r^2 = 0.69$, $n = 44$, $p < 0.0001$, TL: $r^2 = 0.14$, $n = 20$, $p = 0.10$):

ER: $$k_{600} = 1.87\ (\pm\ 1.13) + 2.52\ (\pm\ 0.26)\ U_{10} \tag{2.3}$$

TL: $$k_{600} = 3.54\ (\pm\ 2.69) + 1.19\ (\pm\ 0.69)\ U_{10} \tag{2.4}$$

where k_{600} is the gas transfer velocity and U_{10} is wind speed at 10 m. We also tested for a potential effect of wind duration on gas exchange by regressing, alone or in combination, our k_{600} values with past wind regime going to 2.5 hours before the k_{600} measurement. However, we found no significant relationships between any past wind regime (wind speed, fetch and wind speed-fetch interaction) and gas transfer velocity ($p > 0.05$).

Table II. Limnological variables (mean [range]): individual sample lake area (LA), fetch length (fetch), wind speed at 10m (U_{10}), turbulent kinetic energy dissipation rate (ε), corrected gas transfer velocity (k_{600}), air-water temperature gradient (ΔT), dissolved organic carbon (DOC), chlorophyll *a* (chl*a*) and precipitation.

	Eastmain-1 reservoir (n = 44)	Temperate Lakes*(n = 20)
LA (km^2)	602	1.0 [0.19-4.0]
fetch (km)	3.9 [0.4-7.2]	0.4 [0.1-1.1]
U_{10} ($m\ s^{-1}$)	4.1 [0.8-7.2]	3.7 [1.8-6.0]
ε ($m^2\ s^{-3}$)	3.4×10^{-5} [5.4×10^{-6}-7.5×10^{-5}]	2.9×10^{-5} [6.0×10^{-6}-7.4×10^{-5}]
k_{600} ($cm\ h^{-1}$)	12.2 [1.6-19.4]	8.0 [1.9-15.2]
ΔT (°c)	-2.6 [-8.1-0.0]	-1.4 [-6.4-0]
DOC ($mg\ L^{-1}$)	6.1 [6.0-6.2]	6.2 [3.7-12.8]
chl*a* ($\mu g\ L^{-1}$)	2.9 [2.8-3.0]	3.8 [0.5-20.0]
Precipitation ($mm\ h^{-1}$)	0.035 [0.0-0.55]	0

*Temperate lakes included Waterloo, Roxton, Parker, Orford, d'Argent, Simonneau, Fraser and Croche.

As a first approach to explore the effect of system size, we extended the work of Guérin *et al.,* 2007 and Borges *et al.,* 2004 with the addition of our data from TL and ER. Their work had shown that the slope of the k_{600}-wind speed relationships varies systematically with system size (surface area). Figure 2.1 shows that our data generally fit this overall tendency very well both in trend and magnitude. Note here that we used non-corrected k_{600} (i.e. no correction for floating chamber bias) to compare to other studies that also used the floating chamber method. To obtain a fuller parameterization of the k_{600}-wind speed relationships for system of different sizes, we developed several empirical models using multiple regression with wind speed, system area and fetch and their interactions as potential independent variables. Figure 2.2 illustrates the predictive power of the best three models to predict gas transfer velocities: Model A uses wind speed alone ($r^2 = 0.51$, $n = 64$, $p < 0.0001$), model B uses both wind speed and wind-fetch interaction ($r^2 = 0.56$, $n = 64$, $p < 0.0001$) while model C uses wind speed and the wind-lake area (log transformed) interaction ($r^2 = 0.67$, $n = 64$, $p < 0.0001$) as independent variables:

Model A: $k_{600} = 1.44\ (\pm 1.25) + 2.37\ (\pm 0.30)\ U_{10}$ (2.5)

Model B: $k_{600} = 1.24\ (\pm 1.20) + 2.09\ (\pm 0.30)\ U_{10} + 0.12\ (\pm 0.05)\ \mathrm{U}_{10}{*}\mathrm{fetch}$ (2.6)

Model C: $k_{600} = 2.48\ (\pm 1.05) + 1.45\ (\pm 0.30)\ U_{10} + 0.35\ (\pm 0.06)\ \mathrm{U}_{10}{*}\log_{10}\mathrm{LA}$ (2.7)

where k_{600} is in cm h^{-1}, U_{10} in m s^{-1}, fetch in km and LA in km^2. All slope parameters in these models are significant ($p<0.05$).

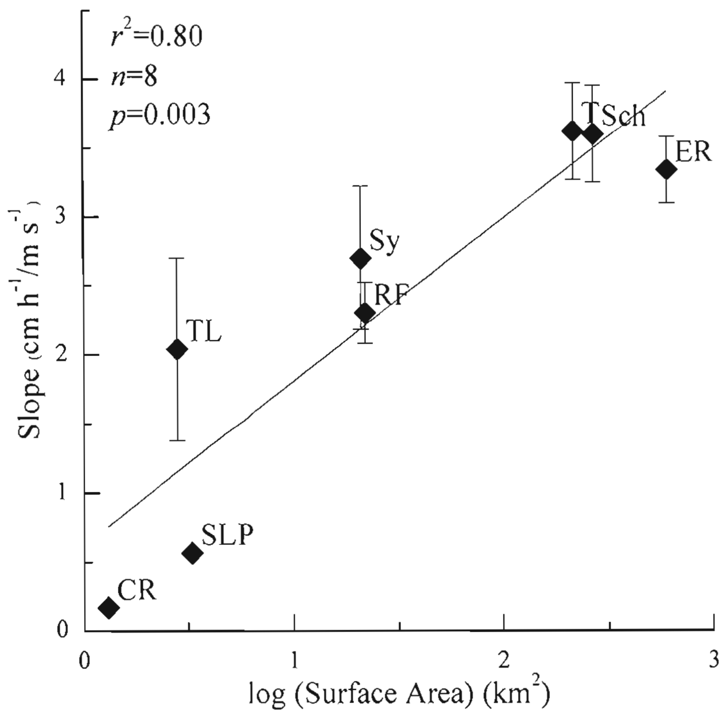

Figure 2.1. Relationship between slope of linear regression functions of k_{600} versus U_{10} of reservoir (ER) and temperate lakes (TL) from this study, Scheldt (Sch), Thames (T) and Randers Fjord (RD) from Borges *et al.*. (2004), Sinnamary Estuary (Sy) from Guérin *et al.*, (2007), Child River (CR) and Sage Lot Pond (SLP) from Kremer *et al.*, (2003).

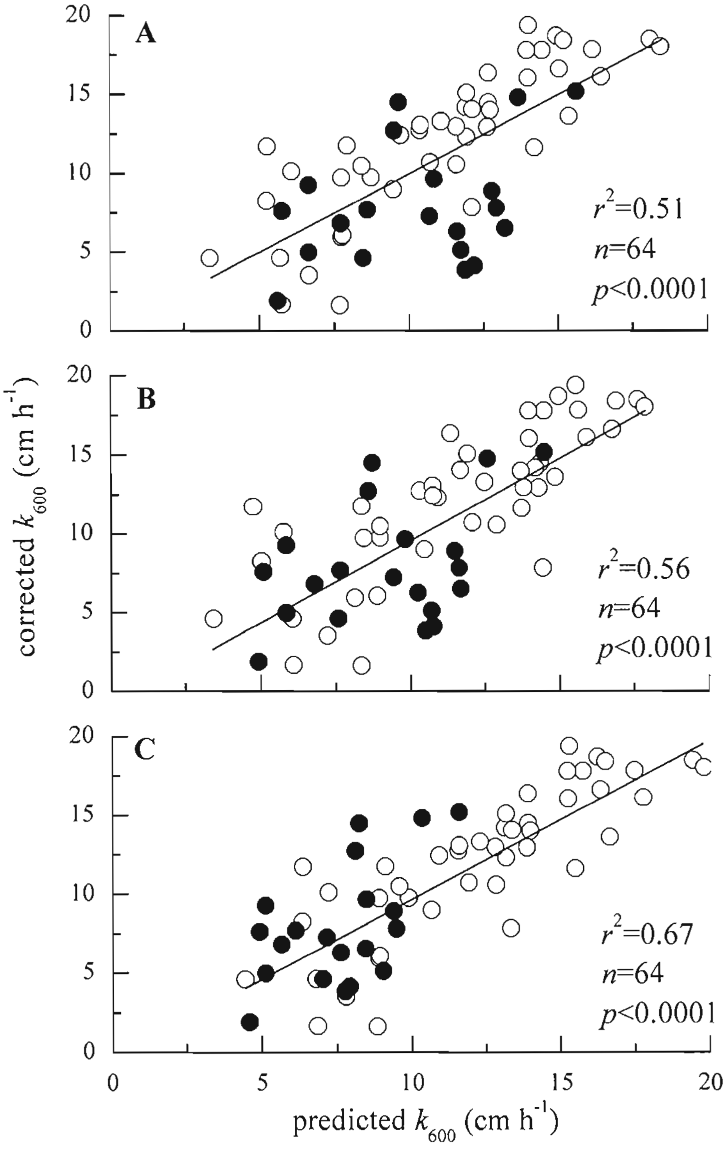

Figure 2.2. Corrected k_{600} in relationship with predicted k_{600} from different variables; (A) is using U_{10} (m s^{-1}) only (k_{600} = 1.44 (±1.25) + 2.37 (±0.30) U_{10}, r^2 = 0.51, n = 64, p < 0.0001), (B) is U_{10} (m s^{-1}) and fetch (km) (k_{600} = 1.24 (±1.20) + 2.09 U_{10} + 0.12 U_{10}*fetch, r^2 = 0.56, n = 64, p < 0.0001) and (C) is U_{10} (m s^{-1}) and lake area (km^2) (k_{600} = 2.48 (±1.05) + 1.45 (±0.30) U_{10} + 0.34 (±0.06) U_{10}*log$_{10}$LA, r^2 = 0.67, n = 64, p < 0.0001). Black dots are TL data and white dots are ER data.

2.5.2 Effect of chemical and physical variables

Our systems covered wide gradients in trophic status and DOC concentrations. The most productive lake had an average of 20.0 μg L^{-1} chl*a* and the less productive had less than 0.5 μg L^{-1} chl*a* with an average of 3.2 ± 3.5 μg L^{-1} for the combined dataset (n = 64). The mean DOC was 6.1 ± 1.9 mg L^{-1} (mean ± SD) ranging from 3.7 to 12.8 mg L^{-1} (n = 64). We examined the potential influence of these variables by testing their statistical significance in a multiple regression setting together with wind speed as independent variables. In a stepwise variables selection, no variables were selected in addition to wind speed to explain gas transfer velocities in all the systems. We also did the same exercise restricting our dataset to observations with low wind speed regime only (U_{10} < 3.7 m s^{-1}) and we found no significant variables in addition to U_{10}.

Similarly, we tested the effects of penetrative convection using multiple regression with the air-water temperature difference (ΔT) as a potential additional independent variable. The mean ΔT for all sites was -2.5 ± 2.2 °c (mean ± SD) ranging from -8.1 to 0 °c (n = 56). We found a significant effect of ΔT on the wind speed to gas transfer velocity relationships ($r^2 = 0.54$, $n = 64$, $p < 0.0001$):

$$k_{600} = 1.67\ (\pm 1.22) + 2.06\ (\pm 0.32)\ U_{10} - 0.46\ (\pm 0.21)\ \Delta T \qquad (2.8)$$

where k_{600} is in cm h^{-1}, U_{10} in m s^{-1} and ΔT is in Celsius. All parameters in this models were significant (p<0.05) except for intercept (p>0.05) indicating that k_{600} is very close to zero in the absence of wind and air-water thermal gradient.

2.6 Discussion

2.6.1 Relationship between k_{600} and wind speed, system size and fetch

Our wind-k_{600} data are within the variability range of some published relationships (Fig. 2.3). Most of our k_{600} measurements are therefore higher than the power function developed by Cole et Caraco, (1998) and the bilinear trend of Crusius et Wanninkhof, (2003) but still lower than the relationship developed by Borges *et al.*, (2004). Some of these discrepancies may be methodological and related to the differential time and space integration afforded by different techniques: from high localized and nearly instantaneous *k* values obtained from floating chamber deployments (Borges *et al.*, 2004; Guérin *et al.*, 2007) to gas tracer experiments (e.g. Sulphur Hexafluoride [SF_6]) which integrate fluctuations of *k* over the entire lake, and over a period of few days (Cole et Caraco, 1998; Upstill-Goddard *et al.*, 1990; Wanninkhof, 1991). While the overall relationship between corrected gas transfer velocities and wind speed was highly significant (Eq. 2.5), it exhibited a substantial scatter particularly at moderate wind speed where k_{600} values spanned a range of nearly 10 cm h^{-1}. However, when we examined the wind-k_{600} relationships of the two regions separately, different patterns emerged. As we found a much tighter wind-k_{600} relationship with the ER data than for the temperate lakes, it quickly suggests that gas exchange is not solely dependent on wind speed when several systems are considered and instead supports the notion of system-specific wind-k_{600} curves. However, our analysis demonstrates that most of the inter-lake differences can be attributed to system size, creating a family of k_{600}-wind curves for different system sizes. Indeed, our results, illustrated by the extension of Guerin's work (Fig. 2.1) and our empirical model (Eq. 2.7), suggests that system size acts as the main modulator of the effect of wind speed on gas exchange, in line with the conclusions of Borges *et al.*, (2004) and Guérin *et al.*, (2007). Figure 2.4 illustrates the interaction of wind speed and lake area on gas exchange. Clearly, the difference in gas exchange for lake of different sizes can be substantial, particularly at high wind speeds. For example, under no wind condition, gas exchange is the same in small and large lakes. However, even for a moderate wind speed of 4 m s^{-1}, gas transfer velocity for a 0.1 km^2 lake would increase by about two fold for a 1000 km^2 lake.

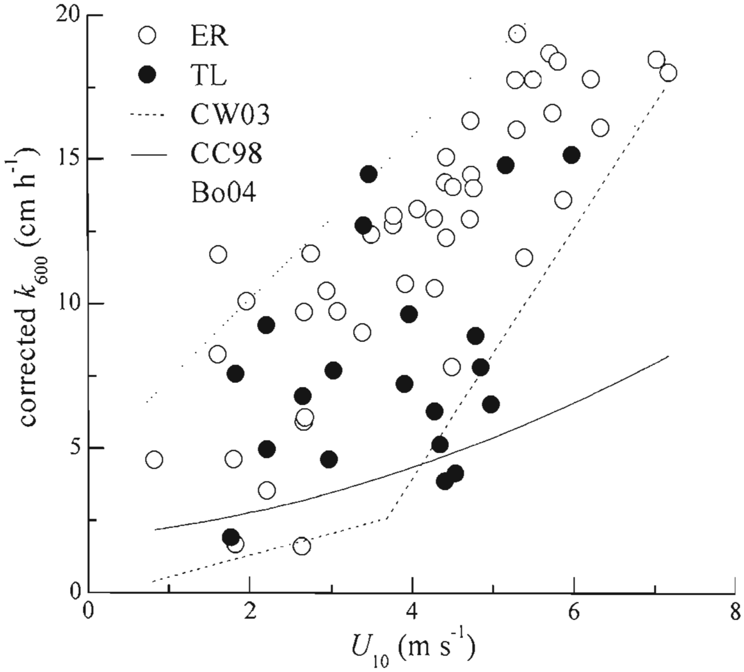

Figure 2.3. Relationship between corrected gas transfer velocities and wind speed at 10 m showing the comparison between Eastmain-1 reservoir (ER) (k_{600} = 1.87 (± 1.13) + 2.52 (± 0.26) U_{10}, $r^2 = 0.69$, $n = 44$, $p < 0.0001$) and temperate lakes (TL) (k_{600} = 3.54 (± 2.69) + 1.19 (± 0.69) U_{10}, $r^2 = 0.14$, $n = 20$, $p = 0.10$) data with other relationships from other studies: Borges *et al.*, (2004) linear relationship (Bo04), Cole et Caraco, (1998) power relationship (CC98) and Crusius et Wanninkhof, (2003) bilinear relationship (CW03).

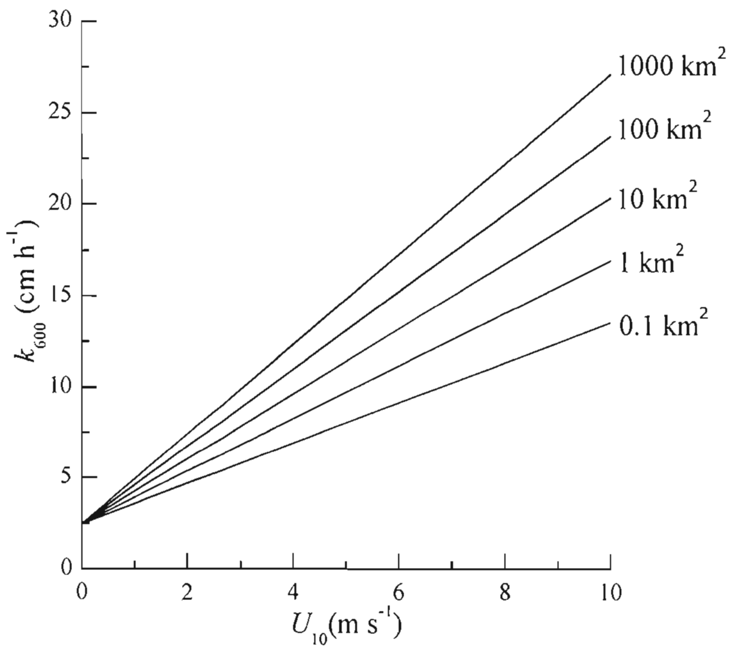

Figure 2.4. Using Eq. 2.7 from figure 2.2C, five relationships of wind speed at 10 m height U_{10} (m s^{-1}) and gas transfer velocity k_{600} (cm h^{-1}) representing lake area of 0.1, 1, 10, 100 and 1000 km^2.

Although significant in conjunction with wind speed (Eq. 2.6), we were surprised that fetch length did not add any significant predictive power over lake size alone given that, depending on the shape of the lake, fetch is generally thought a better proxy of the energy that can be transferred from wind to waves. We suggest that because wind direction dictates fetches differently according to an individual lake's shape, a general measure of system size such as lake area provides a more integrative index of past fetch lengths that were due to wind direction variations. That is, if past fetches are different than instantaneous fetch, it is possible that lake area acts as a better proxy for effective fetch and therefore performs as a better predictor of instantaneous k_{600}.

The intercept estimated (2.5 cm h^{-1}) in our best model (Eq. 2.7) is nearly identical and not significantly different from that obtained by Cole et Caraco, (1998) and corresponds to the gas exchange velocity due to factors other than wind. Here, the lack of a unique LA term (not as an interaction with U_{10}) in the multiple regression (Eq. 2.7) implies that the family of k_{600}-wind lines for different system sizes all converge to a common value at no wind. Our results strongly confirm that lake area has a determining effect on wind-k_{600} relationships that that a unique model for all lakes is untenable.

2.6.2 Effect of chemical and physical variables

We explored the potential significance of chlorophyll *a* and DOC concentrations as proxies for surfactants that can modulate the exchange of gases at the air-water interface. However, none of the variables considered explained statistically significant portions of the wind-k_{600} relationship. So far, only marine and laboratory experiments have found some effect of surfactant (Frew *et al.*, 1990; McKenna et McGillis, 2004) or organic matter (Calleja *et al.*, 2009) on gas exchanges. We were surprised by our results particularly in view that surface chl*a* and DOC span a much larger range of variation in lakes than in the ocean. In the case of DOC, this may reflect that, for a large portion of our data (the Eastmain-1 Reservoir data), DOC only varies very narrowly. This was not the case for the temperate lakes. Clearly, either DOC and chlorophyll *a* are not good measures of surfactant concentrations or their effect on modulating gas exchange or masked by the much larger influence of wind and system size.

Although the inclusion of ΔT did not improve our ability to predict k_{600} above that possible from wind and system size, Eq. 2.8 is informative as the magnitude of influence penetrative convection can play in modulating gas exchange. According to Eq. 2.8, a thermal gradient of just 1 °C is enough to create sufficient turbulence to increase gas exchange under no wind condition by more than 25%. Such as situation is often observed at night and suggests that gas fluxes estimated from wind alone may be severely biased downwards. Admittedly, this effect may be confounded by the lake size effect because we found that, in our data, the largest air-water thermal gradients (ΔT) were found in the smaller lakes (r = -0.30). Disentangling these two effects will require more detailed studies on a few well-monitored systems.

2.6.3 Implication at landscape level

Knowing that the effect that wind imparts on gas exchange is not constant over lakes of different sizes and because landscapes harbour a wide spectrum of lake sizes (Downing *et al.*, 2006), our findings may have important implications on the amount of gas flux emanating from the aquatic system of landscapes or regions. To examine this potential bias, we used our Eq. 2.7 in conjunction with the empirical model of Roehm *et al.,* (2009) linking pCO_2 to lake area as well as a coarse description of the lake size distribution in the same region (76% between 0.01 and 0.1 km^2, 23% between 0.1 and 1 km^2 and 1% between 1 and 10 km^2; Prairie, unpublished data). Assuming a constant average wind speed of 3 m s^{-1}, our calculations show diffusive CO_2 fluxes would be much higher than previously estimated and that using the general wind-*k* relationship of Cole et Caraco, (1998) would have resulted in a 40% underestimation of the aquatic flux from this landscape. This exercise clearly shows the potential impact of the lake size dependence on gas exchange when constructing regional estimates of gas flux. This bias would be further exacerbated in region less dominated by very small lakes.

2.7 Conclusion

Our results showed that lake area greatly influences the effect exerted by winds of a given speed on gas exchange. Our model combining both variables provide a simple yet reliable of means of predicting of gas transfer velocity in a suite of lakes of different sizes when individual measurements are not possible. Accounting for the lake size dependence is important to achieving reasonable flux estimates at the whole landscape level.

CONCLUSION

Lorsque vient le temps d'estimer les échanges gazeux entre l'eau et l'atmosphère, le choix de la vitesse d'échange gazeux demeure un défi majeur. Malgré plusieurs études tentant d'identifier les multiples acteurs impliqués dans le processus des échanges gazeux à la surface d'un plan d'eau, beaucoup d'incertitudes demeurent dans la méthodologie utilisée et dans la magnitude de l'influence de chacun des facteurs considérant l'hétérogénéité des écosystèmes aquatiques. Dans cette étude, il a été montré que la vitesse d'échange gazeux est directement reliée à la turbulence de surface et ce, dans une série de systèmes aquatiques différents. De plus, il a été confirmé que la méthode de la chambre flottante surestime les échanges gazeux due à la turbulence artificielle qu'elle engendre à l'intérieur son aire d'échantillonnage. Cette surestimation, pouvant atteindre jusqu'à dix fois la valeur réelle, diminue en fonction de la turbulence naturelle du système. Toutefois, bien que la turbulence de surface soit directement reliée à la vitesse d'échange gazeux, ce modèle n'est vrai que pour des valeurs locales et instantanées. Dans le but d'estimer la valeur de k à l'échelle du paysage, d'autres outils sont donc nécessaire. La vitesse du vent semble bien expliquer la vitesse d'échange gazeux à plus grande échelle mais les relations diffèrent selon les caractéristiques des milieux et des techniques utilisées. Nous avons vu que le vent, combiné à la course du vent ou *«fetch»*, améliore le pouvoir prédictif des échange gazeux d'une série de systèmes aquatiques. Cependant, en utilisant l'aire du système, toujours combiné à la vitesse du vent, la relation s'améliore d'autant plus. Considérant cela, il sera donc possible d'estimer les vitesses d'échanges gazeux d'une variété de lacs en n'utilisant que les vitesses de vents jumelé aux aires des systèmes étudiés. Ici, l'utilisation de variables facilement mesurable donne donc accès à des modèles fiables de prédictions des échanges gazeux qui peuvent s'appliqué à un paysage entier.

Les nombreux processus impliqués dans les échanges gazeux entre l'eau et l'atmosphère restent encore mal compris. L'hétérogénéité des systèmes aquatiques terrestres ainsi que les incertitudes concernant les techniques de mesures ajoutent un défi de taille dans le but de cette compréhension. Considérant que les environnements aquatiques sont en perpétuel changement, due à la création de réservoirs ou au réchauffement climatique par exemple, la compréhension et l'accès à des techniques de mesures précises des échanges gazeux demeurent primordial pour bien maîtriser leurs impacts sur le bilan global du carbone. Ces processus prennent de l'importance face aux importants défis que les changements climatiques apportent à l'humanité.

Abril, G., M.-V. Commarieu, A. Sottolichio, P. Bretel and F. Guérin. 2009. «Turbidity limits gas exchange in a large macrotidal estuary». *Estuarine, Coastal and Shelf Science*, vol. 83, no p. 342-348.

Algesten, G., S. Sobek, A.-K. Bergström, A. Jonsson, L. J. Tranvik and M. Jansson. 2005. «Contribution of sediment respiration to summer CO2 emission from low productive boreal and subarctic lakes». *Microbial ecology*, vol. 50, no 4, p. 529-535.

Belanger, T. V. and E. A. Korzun. 1991. «Critique of floating-dome technique for estimating reaeration rates». *Journal of Environmental Engineering*, vol. 117, no 1, p. 144-150.

Borges, A. V., B. Delille, L.-S. Schiettecatte, F. Gazeau, G. Abril and M. Frankignoulle. 2004. «Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt, and Thames)». *Limnology and oceanography*, vol. 49, no 5, p. 1630-1641.

Botte, V. and D. Mansutti. 2005. «Numerical modelling of the Marangoni effects induced by plankton-generated surfactants». *Journal of Marine Systems*, vol. 57, no 1-2, p. 55-69.

Calleja, M. L., C. M. Duarte, Y. T. Prairie, S. Agustì and G. J. Herndl. 2009. «Evidence for surface organic matter modulation of air-sea CO_2 gas exchange». *Biogeosciences*, vol. 6, no p. 1105-1114.

Christensen, T. R. 2007. «A catchment-scale carbon and greenhouse gas budget of a subarctic landscape». *Philosophical transactions - Royal Society. Mathematical, Physical and engineering sciences*, vol. 365, no 1856, p. 1643-1656.

Cole, J. J. and F. C. Caraco. 1998. «Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF_6». *Limnology and oceanography*, vol. 43, no 4, p. 647-656.

Cole, J. J., N. F. Caraco, G. W. Kling and T. K. Kratz. 1994. «Carbon dioxide supersaturation in the surface waters of lakes». *Science*, vol. 265, no 5178, p. 1568-1570.

Cole, J. J. and Y. T. Prairie. 2009. «Dissolved CO_2». In *Encyclopedia of Inland Waters*, G. E. Likens (éd.), p. 30-34. Oxford: Elsevier.

Cole, J. J., Y. T. Prairie, N. F. Caraco, W. H. McDowell, L. J. Tranvik, R. G. Striegl, C. M. Duarte, P. Kortelainen, J. A. Downing, J. J. Middleburg and J. Melack. 2007. «Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget». *Ecosystems*, vol. 10, no 1, p. 171-184.

Copeland, B. J. and W. R. Duffer. 1964. «Use of a clear plastic dome to measure gaseous diffusion rates in natural waters». *Limnology and oceanography*, vol. 9, no 4, p. 494-499.

Crill, P. M., K. B. Bartlett, J. O. Wilson, D. I. Sebacher, R. C. Harriss, J. M. Melack, S. MacIntyre, L. Lesack and L. Smith-Morrill. 1988. «Tropospheric methane from an Amazonian floodplain lake». *Journal of geophysical research*, vol. 93, no D2, p. 1564-1570.

Crusius, J. and R. Wanninkhof. 2003. «Gas transfer velocities measured at low wind speed over a lake». *Limnology and oceanography*, vol. 48, no 3, p. 1010-1017.

Dankwerts, P. V. 1951. «Significance of liquid-film coefficients in gas adsorption». *Industrial and Engineering Chemistry*, vol. 43, no 6, p. 1460-1467.

Downing, J. A., Y. T. Prairie, J. J. Cole, C. M. Duarte, L. J. Tranvik, R. G. Striegl, W. H. McDowell, P. Kortelainen, N. F. Caraco, J. Melack and J. J. Middleburg. 2006. «The global abundance and size distribution of lakes, ponds, and impoundments». *Limnology and oceanography*, vol. 51, no 5, p. 2388-2397.

Doyle, W. S. 1978. «Preliminary evaluation of the floating dome method of measuring reaeration rates». *Jour. Research U.S. Geol. Survey*, vol. 6, no 4, p. 547-552.

Duarte, C. M. and Y. T. Prairie. 2005. «Prevalence of heterotrophy and atmospheric CO_2 emissions from aquatic ecosystems». *Ecosystems*, vol. 8, no 7, p. 862-870.

Duchemin, E., M. Lucotte and R. Canuel. 1999. «Comparison of static chamber and thin boundary layer equation methods for measuring greenhouse gas emissions from large water bodies». *Environmental Science &Technology*, vol. 33, no 2, p. 350-357.

Eugster, W., G. Kling, T. Jonas, J. P. McFadden, A. Wüest, S. Macintyre and F. S. Chapin III. 2003. «CO_2 exchange between air and water in an Arctic Alaskan and midlatitude Swiss lake: Importance of convective mixing». *Journal of geophysical research*, vol. 108, no p. 4362.

Frankignoulle, M. 1988. «Field measurements of air-sea CO_2 exchange». *Limnology and oceanography*, vol. 33, no 3, p. 313-322.

Frew, N. M., J. C. Goldman, M. R. Dennett and A. S. Johnson. 1990. «Impact of phytoplankton-generated surfactants on air-sea gas exchange». *Journal of geophysical research*, vol. 95, no C3, p. 3337-3352.

Frost, T. and R. C. Upstill-Goddard. 2002. «Meteorological controls of gas exchange at a small English lake». *Limnology and oceanography*, vol. 47, no 4, p. 1165-1174.

Guérin, F. F., G. Abril, D. Serça, C. Delon, S. Richard, R. Delmas, A. Tremblay and L. Varfalvy. 2007. «Gas transfer velocities of CO_2 and CH_4 in a tropical reservoir and its river downstream». *Journal of Marine Systems*, vol. 66, no 1-4, p. 161-172.

Ho, D. T., L. F. Bliven, R. Wanninkhof and P. Schlosser. 1997. «The effect of rain on air-water gas exchange». *Tellus*, vol. 49, no 2, p. 149-158.

Ho, D. T., F. Veron, E. Harrison, L. F. Bliven, N. Scott and W. R. McGillis. 2007. «The combined effect of rain and wind on air-water gas exchange: A feasibility study». *Journal of Marine Systems*, vol. 66, no 1-4, p. 150-160.

IPCC. 2007. «Climate Change 2007 : The Physical Science Basis». *Cambridge University PressNew York, NY, USA.*

Jähne, B., G. Heinz and W. Dietrich. 1987. «Measurement of the diffusion coefficients of sparingly soluble gases in water». *Journal of geophysical research*, vol. 92, no C10, p. 10,767-710,776.

Jonsson, A., J. Aberg, A. Lindroth and M. Jansson. 2008. «Gas transfer rate and CO_2 flux between an unproductive lake and the atmosphere in northern Sweden». *Journal of geophysical research*, vol. 113, no 4, G04006.

Kalff, J. (éd.). 2002. *Limnology - Inland Water Ecosystems*. Upper Saddle River, NJ.

Kitaigorodskii, S. A., M. A. Donelan, J. L. Lumley and E. A. Terray. 1983. «Wave-turbulence interactions in the upper ocean. Part II: Statistical characteristics of wave and turbulent components of the random velocity field in the marine surface layer». *Journal of oceanography*, vol. 13, no p. 1988-1999.

Kondo, F. and O. Tsukamoto. 2007. «Air-sea CO_2 flux by eddy covariance technique in the equatorial Indian Ocean». *Journal of oceanography*, vol. 63, no 3, p. 449-456.

Kortelainen, P., M. Rantakari, J. T. Huttunen, T. Mattsson, J. Alm, S. Juutinen, T. Larmola, J. Silvola and P. J. Martikainen. 2006. «Sediment respiration and lake trophic state are important predictors of large CO2 evasion from small boreal lakes». *Global change biology*, vol. 12, no 8, p. 1554-1567.

Kremer, J. N., A. Reischauer and C. D'Avanzo. 2003. «Estuary-specific variation in the air-water gas exchange coefficient for oxygen». *Estuaries*, vol. 26, no 4A, p. 829-836.

Kremer, J. N., A. Reischauer and C. D'Avanzo. 2003. «Technical note: Conditions for using the floating chamber method to estimate air-water gas exchange». *Estuaries*, vol. 26, no 4A, p. 985-990.

Lambert, M. and J.-L. Fréchette. 2005. «Analytical techniques for measuring fluxes of CO_2 and CH_4 from hydroelectric reservoirs and natural water bodies». In *Greenhouse gas emissions – Fluxes and processes: Hydroelectric reservoirs and natural environments*, A. Tremblay, L. Varfalvy, C. Roehm and M. Garneau (éd.), Berlin: Springer Press.

Lamont, J. C. and D. S. Scott. 1970. «Eddy cell model of mass transfer into the surface of a turbulent liquid». *AIChE journal*, vol. 16, no 4, p. 513-519.

Lumley, J. L. and E. A. Terray. 1983. «Kinematics of turbulence convected by a random wave field». *Journal of physical oceanography*, vol. 13, no p. 2000-2007.

MacIntyre, S., R. Wanninkhof and J. P. Chanton. 1995. «Trace gas exchange across the air-water interface in freshwater and coastal marine environments». In *Biogenic trace gases: Measuring emissions from soil and water*, P. A. Matson and R. C. Harriss (éd.), p. 52-97. Blackwell.

Matthews, C. J. D., V. L. St. Louis and R. H. Hesslein. 2003. «Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces». vol. 37, no 4, p. 772-780.

McGillis, W. R. 2001. «Carbon dioxide flux techniques performed during GasEx-98». *Marine chemistry*, vol. 75, no 4, p. 267-280.

McKenna, S. P. and W. R. McGillis. 2004. «The role of free-surface turbulence and surfactants in air-water gas transfer». *International journal of heat and mass transfer*, vol. 47, no 3, p. 539-553.

Prairie, Y. T. 2008. «Carbocentric limnology: Looking back, looking forward». *Canadian Journal of Fisheries and Aquatic Sciences*, vol. 65, no 3, p. 543-548.

Rannik, U., P. Keronen, P. Hari and T. Vesala. 2004. «Estimation of forest-atmosphere CO_2 exchange by eddy covariance and profile techniques». *Agricultural and forest meteorology*, vol. 126, no 1-2, p. 141-155.

Repo, M. E., J. T. Huttunen, A. V. Naumov, A. V. Chichulin, E. D. Lapshina, W. Bleuten and P. J. Martikainen. 2007. «Release of CO_2 and CH_4 from small wetland lakes in western Siberia». *Tellus*, vol. 59, no 5, p. 788-796.

Schladow, S. G., M. Lee, B. E. Hürzeler and P. B. Kelly. 2002. «Oxygen transfer across the air-water interface by natural convection in lakes». *Limnology and oceanography*, vol. 47, no 5, p. 1394-1404.

Soumis, N., R. Canuel and M. Lucotte. 2008. «Evaluation of two current approaches for the measurement of carbon dioxide diffusive fluxes from lentic ecosystems». *Environmental science & technology*, vol. 42, no 8, p. 2964-2969.

Stauffer, R. E. 1980. «Wind power time series above a temperate lake». *Limnology and oceanography*, vol. 25, no 3 , 1980, p. 513-528.

Teodoru, C. R., P. A. del Giorgio, Y. T. Prairie and M. Camire. 2009. «Patterns in pCO2 in boreal streams and rivers of northern Quebec, Canada». *Global Biogeochemical Cycles*, vol. 23, no GB2012.

Terray, E. A., M. A. Donelan, Y. C. Agrawal, W. M. Drennan, K. K. Kahma, A. J. Williams III, P. A. Hwang and S. A. Kitaigorodskii. 1996. «Estimates of kinetics energy dissipation under breaking waves». *Journal of physical oceanography*, vol. 26, p. 792-807.

Tokoro, T., H. Kayanne, A. Watanabe, K. Nadaoka, H. Tamura, K. Nozaki, K. Kato and A. Negishi. 2008. «High gas-transfer velocity in coastal regions with high energy-dissipation rates». *Journal of geophysical research*, vol. 113, no 11, C11006.

Tranvik, L. J., J. A. Downing, J. B. Cotner, S. A. Loiselle, R. G. Striegl, T. J. Ballatore, P. Dillon, K. Finlay, K. Fortino, L. B. Knoll, P. L. Kortelainen, T. Kuster, S. Larsen, I. Laurion, D. M. Leech, S. L. McCallister, D. M. McKnight, J. M. Melack, E. Overholt, J. A. Porter, Y. T. Prairie, W. H. Renwick, F. Roland, B. S. Sherman, D. W. Schindler, S. Sobek, A. Tremblay, M. J. Vanni, A. M. Verschoor, E. von Wachenfeldt and G. A. Weyhenmeyer. 2009. «Lakes and reservoirs as regulators of carbon cycling and climate». *Limnology and oceanography*, vol. 54, no 6, part 2, p. 2298-2314.

Upstill-Goddard, R. C., A. J. Watson, P. S. Liss and M. I. Liddicoat. 1990. «Gas transfer velocities in lakes measured with SF_6». *Tellus*, vol. 42b, no p. 364-377.

Vachon, D., Y. T. Prairie and J. J. Cole. 2010. «The relationship between near-surface turbulence and gas transfer velocity in freshwater systems and its implications for floating chamber measurements of gas exchange». *Limnology and oceanography*, vol. 55, no 4, p. 1723-1732.

Wanninkhof, R. 1992. «Relationship between wind speed and gas exchange over the ocean». *Journal of geophysical research*, vol. 97, no C5, p. 7373-7382.

Wanninkhof, R., J. Ledwell and J. Crusius. 1991. «Gas transfer velocities on lakes measured with sulfur hexafluoride». In *Air-Water Mass Transfer*, S. C. Wilhelms and J. S. Gulliver (éd.), p. 441-458. New York, N.Y.: American Society of Civil Engineers.

Wanninkhof, R. and W. R. McGillis. 1999. «A cubic relationship between air-sea CO_2 exchange and wind speed». *Geophysical research letters*, vol. 26, no 13, p. 1889-1892.

Wetzel, R. G., and G. E. Likens (Éds.). 2000. *Limnological Analyses*. Third Edition. Springer-Verlag, New York, Inc. 429 pp.

Zappa, C. J., W. E. Asher, A. T. Jessup, J. Klinke and S. R. Long. 2004. «Microbreaking and the enhancement of air-water transfer velocity». *Journal of geophysical research*, vol. 109, no 8, p. C08S16.

Zappa, C. J., D. T. Ho, W. R. McGillis, M. L. Banner, J. W. H. Dacey, L. F. Bliven, B. Ma and J. Nystuen. 2009. «Rain-induced turbulence and air-sea gas transfer». *Journal of geophysical research*, vol. 114, no 7, C07009.

Zappa, C. J., W. R. McGillis, P. A. Raymond, J. B. Edson, E. J. Hintsa, H. J. Zemmelink, J. W. H. Dacey and D. T. Ho. 2007. «Environmental turbulent mixing controls on air-water gas exchange in marine and aquatic systems». *Geophysical research letters*, vol. 34, no 10, L10601.

Zutic, V., B. Cosovic, E. Marcenko, N. Bihari and F. Krsinic. 1981. «Surfactant production by marine phytoplankton». *Marine chemistry*, vol. 10, no 6, p. 505.