UNIVERSITÉ DU QUÉBEC À MONTRÉAL

ASSESSING THE CONTRIBUTION OF CHEMICAL ENHANCEMENT TO CO_2 EXCHANGE ACROSS THE AIR-WATER INTERFACE IN EUTROPHIC LAKES OF QUEBEC

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ESTIMER L'INFLUENCE DU TAUX D'ACCÉLÉRATION CHIMIQUE SUR LES ÉCHANGES DE CO_2 À L'INTERFACE AIR-EAU DANS LES LACS EUTROPHIQUES DU QUÉBEC

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RÉSUMÉ GÉNÉRAL

Contrairement aux gaz non réactifs comme le méthane (CH_4) et l'oxyde nitreux (N_2O), les flux diffusifs de dioxyde de carbone (CO_2) à travers l'interface air-eau sont influencés par la réaction chimique du CO_2 avec les ions hydroxyles (OH^-), surtout à pH élevé. Dans les lacs eutrophes où le pH est relativement élevé, l'accélération chimique est considérée comme un facteur de contrôle potentiellement influant sur les flux de CO_2. À date, plusieurs études utilisent le modèle de Hoover et Berkshire (1969) (H&B) pour estimer les taux d'accélération chimique (α) afin d'obtenir des estimés précis de flux de CO_2. Cependant, le modèle a rarement été testé dans des conditions réelles sur le terrain. Pour aborder cette question, nous avons quantifié la contribution de l'accélération chimique aux flux de CO_2 entre l'air et l'eau en comparant des mesures de vitesses d'échange gazeux du CO_2 ($k_{600\text{-}CO2}$) et du CH_4 ($k_{600\text{-}CH4}$) dans 21 lacs du Québec durant l'été 2015 et 2016. De plus, nous avons examiné les divergences entre les taux de α mesurés versus prédits basé sur les calculs de H&B pour vérifier l'applicabilité de ce modèle. Dans la majorité des lacs, il n'y avait pas de différence systématique entre le $k_{600\text{-}CO2}$ et le $k_{600\text{-}CH4}$ (en moyenne 2.1 and 2.2 m d^{-1} respectivement), ce qui suggère que l'accélération chimique du CO_2 ne contribue pas significativement aux flux air-eau de CO_2 pour une large gamme de valeurs de k_{600}. De plus, les valeurs de α observées étaient considérablement plus faibles que celles prédites par H&B (jusqu'à 7.4 fois plus faibles), ce qui indique que le modèle de H&B peut surestimer considérablement l'accélération chimique du CO_2, particulièrement dans les lacs aux eaux hautement alcalines. Des raisons possibles de cette différence entre les valeurs de α mesurées versus prédites sont : 1) des prémisses erronées dans le modèle de H&B, 2) une accélération de la vitesse d'échange gazeux du gaz de référence (le CH_4), et 3) une divergence entre les conditions expérimentales dans lesquelles le modèle H&B a été développé et les conditions sur le terrain. Nos résultats suggèrent aussi que les échanges gazeux sont potentiellement mieux décrits par un mécanisme de renouvellement de surface plutôt que par une couche limite stagnante. On s'attend à ce que ces résultats améliorent l'estimation des échanges gazeux dans les systèmes eutrophes, et ailles des conséquences importantes sur les budgets de carbone régionaux.

Mots clés : Échanges gazeux air-eau, Dioxyde de carbone, Accélération chimique, Lacs eutrophes, Vitesse d'échange gazeux, hydratation.

GENERAL SUMMARY

In contrast with chemically non-reactive gases such as methane (CH_4) and nitrous oxide (N_2O), diffusive carbon dioxide (CO_2) exchange across the air-water interface can be enhanced by chemical reactions of CO_2 with hydroxyl ions (OH^-), especially at high pH. In eutrophic lakes where pH is relatively high, chemical enhancement is believed to be an important factor in driving CO_2 fluxes. So far, in many studies, the theoretical model of Hoover and Berkshire (1969) (H&B) was widely used to estimate chemical enhancement rates (α) for accurate estimates of CO_2 flux. However, there is very few tests of the model in field conditions. To address this issue, we quantified the actual contributions of chemical enhancement to air-water CO_2 fluxes by comparing measured gas exchange velocities derived from CO_2 ($k_{600\text{-}CO2}$) and from CH_4 ($k_{600\text{-}CH4}$) in 21 lakes of Quebec during the summer of 2015 and 2016. In addition, we examined any discrepancies that might exist between the observed α and that predicted from the H&B calculation to verify the general applicability of the model. In most lakes, there was no systematic difference between $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$ (on average 2.1 and 2.2 m d^{-1}, respectively), suggesting that chemical enhancement of CO_2 is not a significant contributor to air-water CO_2 flux over a wide range of k_{600} values. In addition, observed α were considerably lower than H&B α (up to 7.4 times), indicating that the H&B model can overestimate chemical enhancement of CO_2, particularly in high alkalinity waters. Likely reasons for the discrepancy between observed and calculated values of α are: 1) some inappropriate assumptions of the H&B model, 2) enhanced gas exchange velocities of reference gas (CH_4), and 3) divergence between the experimental conditions in which the H&B model has been developed and actual field conditions. Our results also suggest that gas exchange may be more appropriately described as a surface renewal mechanism rather than a stagnant boundary layer. We expect these results can improve the estimation of gas exchange in eutrophic systems, and have important consequences for the assessment of regional carbon budgets.

Key words: Air-water gas exchange, Carbon dioxide, Chemical enhancement, Eutrophic lakes, Gas exchange velocity, hydration.

INTRODUCTION

Quantifying accurate greenhouse gas (GHG) fluxes between the Earth's surface and the atmosphere has been considered essential for planning for a sustainable future under global climate changes. Although inland waters occupy a small fraction (about 3%) of the Earth's surface (Downing et al., 2006), their contributions to the GHG fluxes, especially to important biogenic gases such as carbon dioxide (Battin et al., 2009; J. J. Cole et al., 2007) and methane (Bastviken et al., 2011; Rasilo et al., 2014), are comparable to those of terrestrial and ocean ecosystems. Current studies estimate that a significant amounts of carbon (1.4 to 2.1 Pg C y^{-1}) is released to the atmosphere through gas exchange, and a part of the atmospheric carbon pool (0.1 to 0.3 Pg C y^{-1}) is photosynthetically fixed in inland waters (Raymond et al., 2013; Regnier et al., 2013; Tranvik et al., 2009). These numbers are in the same order of magnitude of carbon sinks in terrestrial and ocean ecosystems (1.8 to 3.1 Pg C y^{-1} and 2.3 to 2.6 Pg C y^{-1}, respectively) (Le Quéré et al., 2016; Regnier et al., 2013), and therefore inland waters are increasingly assumed to be critical components of carbon exchange with the atmosphere.

Diffusive gas exchange at the air-water interface occurs in all aquatic systems from small streams to the pelagic ocean (MacIntyre et al., 1995). Thus, a precise knowledge of gas exchange processes, which are regulated by physical, chemical and biological factors (D L Bade, 2009; Smith, 1985), is necessary for properly assessing carbon budgets at either regional or global scales (Donelan & Wanninkhof, 2002; Y. T. Prairie, 2008). In the case of important biogenic gases such as CO_2 and CH_4, chemical considerations of gas exchange are closely linked to gas concentration gradients across the air-water interface, which are in part controlled by solubility of the gases and biological processes that produce or consume them (D L Bade, 2009; Smith, 1985). Also, physical aspects of gas exchange are dependent upon both near-surface turbulence in water (Jonathan J. Cole & Caraco, 1998; Vachon et al., 2010) and molecular diffusion of the gases (Donelan & Wanninkhof, 2002; Jähne et al., 1987), and the rates of gas exchange driven by these physical processes can be expressed as the gas exchange velocity (*k*) from Fick's law of diffusion. While gas concentration gradients can be easily obtained from precise measurements of actual gas partial pressures on either side of the air-water interface (*Cole and Prairie, 2009*), assessing physical processes is more complex, and *k* is relatively difficult to measure. So far, several mechanistic theories are available to describe the physical gas exchange processes. The two most common theories are the boundary layer model (Lewis & Whitman, 1924) and the surface renewal model (Danckwerts, 1951). Although these two ultimately yield the same mathematical formulation (Eq. 1), their basic assumptions are quite different. For the boundary layer model, it is assumed that the interfaces at the water surfaces consist of thin boundary layers (sub-millimeter in thickness) through which molecular diffusion takes place (Figure 1.7a). On the other hand, the surface renewal model describes the surface water as being influenced by turbulent eddies that bring water from underneath, and hence this water interface layers are periodically renewed (Figure 1.7b). Based on these theories, most approaches to estimating *k* use empirical relationships with physical parameters such as wind speed (Jonathan J. Cole & Caraco, 1998), wind and ecosystem size (Vachon & Prairie, 2013), and buoyancy flux models (MacIntyre et al., 2010; Tedford et al., 2014), which influence turbulence near the air-water interface.

0.1 Problem statement

The majority of global lakes are supersaturated in dissolved CO_2 and CH_4, as a result of high respiration rates and significant external inputs of organic carbon from adjacent terrestrial ecosystems along with soil and groundwater, resulting in efflux of these gases to the atmosphere (Ask et al., 2012; Bastviken et al., 2011; Jonathan J. Cole et al., 1994; Duarte & Prairie, 2005; Sobek et al., 2005). In these cases, the empirical parameters for estimating *k* that are mentioned above have been shown to work reasonably well and are often sufficient to provide accurate estimates. However, in eutrophic lakes, although the role of lake metabolism in lake CO_2 dynamics can vary widely (Bogard & Giorgio, 2016), CO_2 undersaturation is prevalent especially during the summer growing season due to primary production subsidized by nutrient enrichments (Balmer & Downing, 2011; Del Giorgio et al., 1999). Consequent CO_2 uptake by phytoplankton results in high pH values, and these lakes often absorb atmospheric CO_2 (Balmer & Downing, 2011; Pacheco et al., 2014). In these cases, physical regulation of non-reactive gases such as CH_4 remains unchanged and the parameters for estimating k can be also used to obtain the rates of flux. On the other hand, more complex physical and chemical processes are responsible for CO_2 regulation. Under high-pH conditions, diffusive CO_2 exchange can be enhanced by chemical reactions of CO_2 with hydroxyl ions (Emerson, 1975; Hoover & Berkshire, 1969). Since *Bolin* (1960) first described chemical enhancement of CO_2, several experimental and theoretical model studies (Emerson, 1975; Hoover & Berkshire, 1969; Kuss & Schneider, 2004; Smith, 1985) have been performed to confirm the magnitude of chemical enhancement (expressed as a chemical enhancement factor, α). However, most measurements of chemically enhanced diffusion were conducted with tank experiments in laboratories, and only a few measurements came from actual field samplings. So far, in many studies of gas exchange, α has been calculated mostly using the theoretical model described by Hoover and Berkshire (1969) nearly half a century ago. It is because their model only requires the input of wind speed, temperature and pH of surface water and hence is easily applicable. However, several field studies showed poor agreement between the observed α and the model predictions (e.g. *Wanninkhof and Knox, 1996; Bade and Cole, 2006*). This implies the tank experiments are probably a poor approximation of what is happening in real lake systems. Furthermore, none of them statistically demonstrated the discrepancies, and the actual chemical enhancement rates are still poorly tested.

0.2 Review of the current scientific knowledge

0.2.1 Gas exchange at the air-water interface

In lake systems, pathways that mediate gas flux with the atmosphere involve diffusive gas exchange at the air-water interface, bubble ebullition from lake sediment, and transport through aquatic plants (Figure 0.1) (Bastviken et al., 2004; MacIntyre et al., 1995). The main pathway of CO_2 exchange differs from that of CH_4 because of their different solubility in water (mole fraction solubility of 7.07×10^{-5}, 2.81×10^{-5} at 20 °C, respectively). While molecular diffusion is the main mode of CO_2 exchange with the atmosphere, bubbles of methane are easily formed in the water column (Delsontro et al., 2010; Walter et al., 2007), and recent studies have shown the potential importance of microbubble-mediated gas exchange in CH_4 flux (McGinnis et al., 2015; Y. T. Prairie & del Giorgio, 2013). However, significant amounts of CH_4 that reaches upper layer of the water column is emitted through molecular diffusion to the atmosphere (Bastviken et al., 2011; Rasilo et al., 2014; Raymond et al., 2013), and therefore, diffusive gas exchange has been generally considered as a key pathway of carbon flux at the air-water interface. Diffusive flux of CO_2 and CH_4 can be adequately described from a Fickian diffusive process as follows:

$$Flux = k_x \times Kh(px_{water} - px_{air})$$

where x is the particular gas, k is the gas exchange velocity, Kh is the Henry's coefficient for correcting temperature and salinity of water, and px_{water} and px_{air} are the gas partial pressure in the water surface and air, respectively. Each gas species can have different diffusion coefficients depending on water temperature, and it can ultimately influence k. Thus, for empirical comparison of different gases, k can be normalized to a k_{600}, which is the Schmidt number of CO_2 at 20 °C in freshwater (Jähne et al., 1987; Wanninkhof, 1992). The *k* of a particular gas, *x* (k_x) at a Schmidt number of 600 (k_{600}) can be described as follows:

$$k_{600} = k_x \left(\frac{600}{Sc_x}\right)^{-n}$$

Where Sc_x is the Schmidt number of a particular gas, *x*, at a given temperature, and *n* is the dimensionless Schmidt exponent to represent the water surface condition. In lakes system, *n* can be determined depending on wind speed ($n = 2/3$ for smooth surface conditions when a normalized-wind speed at a reference height of 10 m, U_{10}, is less than 3.7 m/s, or $n = 1/2$ for rough surface conditions when U_{10} is more than 3.7 m/s) (Jähne et al., 1987).

On average, the recent global atmospheric CO_2 is estimated at 402 ppm and that CH_4 is 1.8 ppm (*Dlugokencky and Tans*, 2016). While these values are relatively constant, the dissolved concentrations of the gases in water surface can vary dramatically depending on lake types such as the depth or area of lakes, and trophic status (Balmer & Downing, 2011; Duarte & Prairie, 2005; Juutinen et al., 2009). The range of lake pCO_2 was between 17 and 65,250 µatm (mean 1,287 µatm) in the global data set of *Sobek et al.* (2005). Also, surface water pCH_4 varied from 6 to 3,612 µatm (mean 191 µatm) in the large summer-data set of *Rasilo et al.* (2014). Consequently, water pCO_2 and pCH_4 regulate the magnitude of flux of the gases, together with gas exchange velocity.

In lake systems, *k* can be directly calculated using several techniques including inert gas tracers such as sulfur hexafluoride (SF_6) (Jonathan J. Cole & Caraco, 1998), eddy covariance (Baldocchi, 2003), or floating chambers (Vachon et al., 2010). In addition, *k* can be determined from a reliable relationship with near-surface turbulence. As measurement techniques continue to be developed, turbulence can be directly obtained with modern instruments such as Acoustic doppler velocimeters (ADV) (Vachon et al., 2010). If such measurements cannot be performed, *k* can be also estimated from other physical characteristics that correlate with turbulence. For example, recent studies have presented several empirical models to estimate *k* with parameters related to turbulence such as wind speed (Jonathan J. Cole & Caraco, 1998; Crusius & Wanninkhof, 2003; Vachon et al., 2010), wind shear and convection (Read et al., 2012), wind and ecosystem size (Vachon & Prairie, 2013), and wind shear and cooling (J. J. Heiskanen et al., 2014). However, under low wind conditions, factors other than wind can also regulate *k*. For example, *k* can be affected by buoyancy flux under low wind conditions overnight (MacIntyre et al., 2010). Also, during long periods of low wind in Amazonian lakes, enhanced *k* resulting from latent heat and sensible heat was reported by *Polsenaere et al.* (2013).

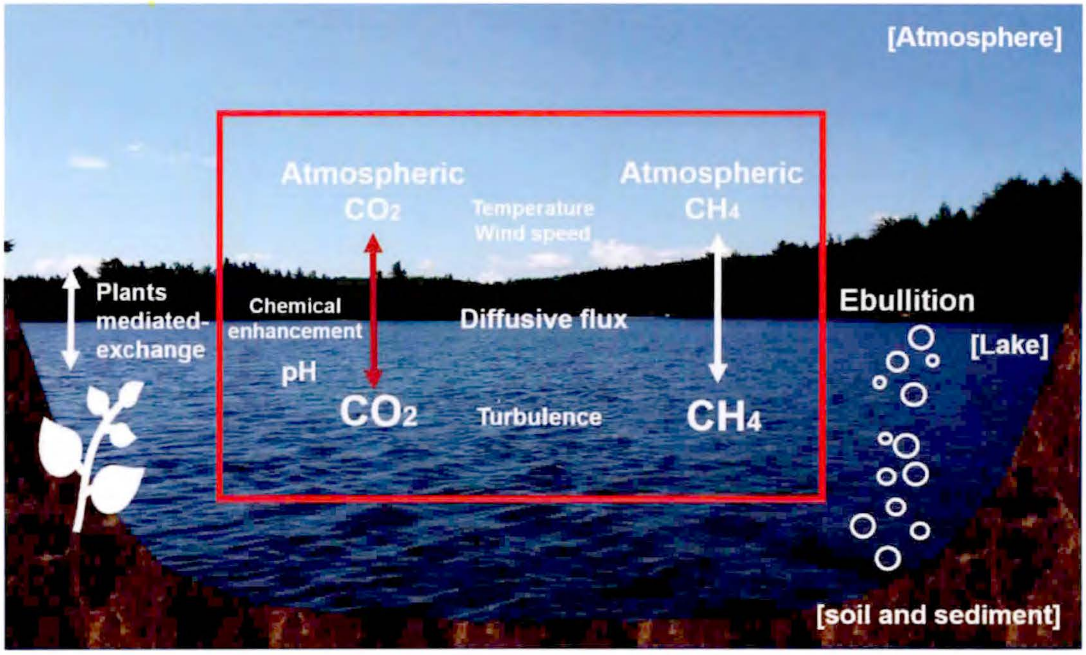

Figure 0.1. Main pathways that mediate CO_2 and CH_4 flux with the atmosphere in lake system

In lake systems, pathways that mediate gas flux with the atmosphere involve diffusive gas exchange at the air-water interface, bubble ebullition from lake sediment, and transport through aquatic plants.

0.2.2 Lake eutrophication and CO_2 flux

Photosynthesis and elevated pH – Dissolved inorganic carbon (DIC) system in lakes consists of aqueous CO_2 (dissolved free CO_2 and the carbonic acid, H_2CO_3), the bicarbonate ion (HCO_3^-) and the carbonate ion (CO_3^{2-}), which are all in approximate equilibrium. The relative proportions of each component can be an important regulator of water pH (J J Cole & Prairie, 2009). For example, aqueous CO_2 is present in large quantities at a pH less than 6.3, HCO_3^- is the predominant species between pH 6.3 to 10.3, and the relative proportion of CO_3^{2-} is large at a pH more than 10.3 (*Stumm and Morgan*, 1996). In lakes, biological processes such as photosynthesis and respiration by phytoplankton can be related to the extensive range of the water pH by consuming or supplying CO_2 as follows:

$$CO_2 + H_2O \leftrightarrow (CH_2O) + O_2$$

Above pH 6.3 where bicarbonate is the dominant species, HCO_3^- is also available for photosynthesis, and the reaction becomes as follows:

$$HCO_3^- + H^+ \leftrightarrow (CH_2O) + O_2$$

The conversion of aqueous CO_2 to particulate organic matter by photosynthesis can raise water pH, and thus eutrophic systems where extreme photosynthesis exists can be often higher in pH (Darren L. Bade & Cole, 2006; Talling, 2010).

Eutrophication and CO_2 influx – As eutrophication increases, inland waters in temperate region tend to have less pCO_2 because of nutrient (phosphorus and nitrogen) driven high primary productivity (Balmer & Downing, 2011; Crawford et al., 2016; Grasset et al., 2016). Thus, the eutrophic systems can emit less CO_2, and often become net sinks for CO_2 (Pacheco et al., 2014). *Balmer and Downing* (2011) showed that pCO_2 values in a large number of eutrophic lakes were significantly lower than those from global data set of *Sobek et al.* (2005), which were taken in oligotrophic to mesotrophic lakes (Figure 0.2a). Also, they obtained negative CO_2 emission rates in most of their sampling sites during the summer, indicating the possibility that eutrophic lakes often act as net atmospheric CO_2 sinks (Figure 0.2b).

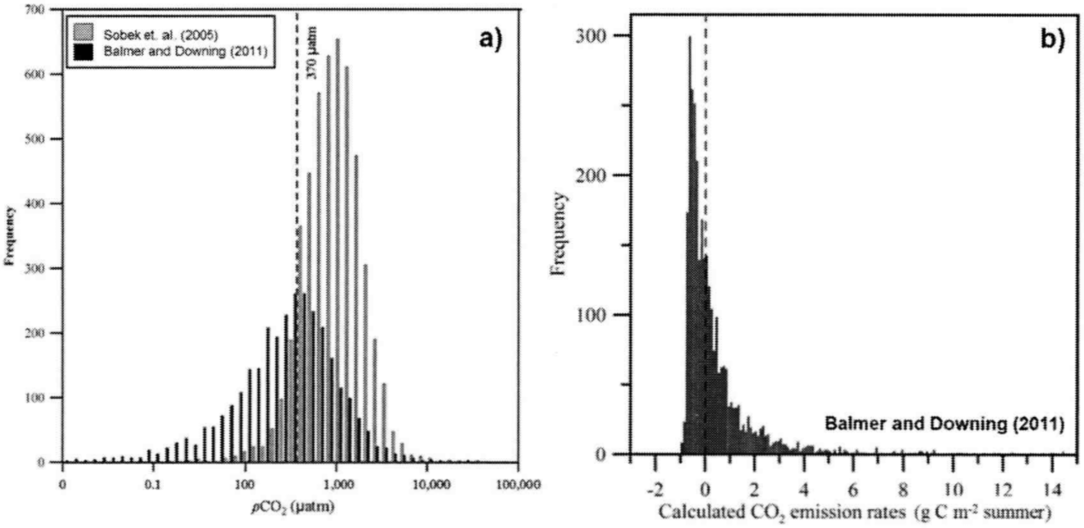

Figure 0.2 Surface water pCO_2 dynamics in lake systems

Results of Balmer and Downing (2011). (a) Frequency distribution of estimated pCO_2 values. The pCO_2 values of dark grey (n = 3,049) were collected in agriculturally eutrophic lakes by Balmer and Downing (2011), and that of light grey (n = 4,902) were taken from the world lakes dataset of Sobek et al. (2005). (b) Calculated carbon emission rate in the eutrophic lakes (n=131) during summer. The dashed line represents atmospheric equilibrium, and the median is -0.1 indicating net atmospheric CO_2 uptake.

0.2.3 Chemical enhancement of CO_2

CO_2 hydration and enhanced gas flux – Diffusive gas exchange of CO_2 is different from that of other low-soluble gases because of its chemical characteristics. When CO_2 dissolves in water, it undergoes hydration through two chemical reactions as follows:

(1) $CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$

(2) $CO_2 + OH^- \leftrightarrow HCO_3^-$

The reaction of CO_2 with water to form H_2CO_3, which is a weak acid that dissociates immediately into bicarbonate, is prominent for pH ≤ 8 and does not significantly increase CO_2 diffusion in natural waters. However, the ionic reaction of CO_2 with hydroxyl ion to form HCO_3^- is believed to enhance CO_2 diffusion into the water surface layer several times (D L Bade, 2009; Bolin, 1960). The rate of chemical enhancement (termed chemical enhancement factor) increases with increasing pH and temperature, and is inversely related to the surface turbulence (*MacIntyre et al.*, 1995; *Stumm and Morgan*, 1996). Several experimental and theoretical model studies (Darren L. Bade & Cole, 2006; Emerson, 1975; Hoover & Berkshire, 1969; Kuss & Schneider, 2004; Smith, 1985; Wanninkhof & Knox, 1996) have been conducted to quantify chemical enhancement of CO_2 at either a seawater surface and a freshwater surface. Because of low pH (normal range 7.7 to 8.2) (Taylor & Fenchel, 2011) and strong turbulence of seawater, chemical enhancement of CO_2 is negligible over the ocean (*Smith*, 1985; *Emerson*, 1995; *Wanninkhof and Knox*, 1996) except in equatorial regions where surface water temperature is high under low wind speed ($U_{10} \leq 3 \text{m s}^{-1}$) (*Boutin and Etcheto*, 1995). However, inland waters have a wide variation in water chemistry, and pH of eutrophic lakes can reach up to 11 (Balmer & Downing, 2011; Jeppesen et al., 1998). Particularly, during extreme photosynthesis, surface water often become undersaturated in CO_2, and pH can be relatively elevated. Thus, the influx rates of atmospheric CO_2 are more likely to be intensified by chemical enhancement (*Smith*,1985; *Emerson*, 1995; *Kuss and Schneider*, 2004; *Bade and Cole*, 2006).

However, presently used models for estimating *k* from other physical parameters (e.g. Cole and Caraco, 1998; Read et al., 2012; Vachon and Prairie, 2013; Heiskanen et al., 2014) don't account for chemically enhanced transfer. Consequently, *k* of reactive gases should be necessarily corrected with a theoretical chemical enhancement factor especially at high-pH conditions. For example, chemical enhancement factor can be added into the CO_2 flux equation (Alshboul & Lorke, 2015; Wanninkhof & Knox, 1996) as follows:

$$Flux = \alpha \times k_{CO2} \times Kh(pCO_{2\,water} - pCO_{2\,air})$$

where α is the theoretical chemical enhancement factor, *Kh* is the Henry's constant, and $pCO_{2\,water}$ and $pCO_{2\,air}$ are the partial pressures of CO_2 in water and air, respectively. In this formula, k_{CO2} is the gas exchange velocity of CO_2 estimated from the models of *k* or calculated from k_{600}, which is derived from a flux measurement of a non-reactive gas such as CH_4, N_2O, and Rn (Jähne et al., 1987; Wanninkhof, 1992).

Calculation of Hoover and Berkshire – So far, in many studies, the theoretical model of Hoover and Berkshire (1969) has been often used to estimate the chemical enhancement factor (α) because of its simplicity. The calculation of Hoover and Berkshire can be described as follows (Hoover & Berkshire, 1969; Wanninkhof & Knox, 1996):

$$\text{Expected } \alpha = \frac{T}{\left[(T-1) + \left\{tanh\left[\left(\frac{rT}{D}\right)^{0.5} Z\right] / \left(\frac{rT}{D}\right)^{0.5} Z\right\}\right]}$$

where T is defined as follows:

$$T = 1 + \frac{[\mathrm{H}^+]^2}{K_1 K_2 + K_1[\mathrm{H}^+]}$$

Where $[\mathrm{H}^+]$ is the hydrogen ion activity; $[\mathrm{H}^+] = 10^{-pH}$, K_1 and K_2 are the dissociation constants for the reactions between CO_2 and HCO_3^-, and HCO_3^- and CO_3^{2-}, respectively (Dickson & Millero, 1987). The *r* is a combination of reaction rate and is described as:

$$\mathrm{r} = r_1 + r_2[OH^-]$$

where r_1 and r_2 are the hydration rate constants for CO_2 reacting with H_2O and OH^-, respectively (K. S. Johnson, 1982). The $[OH^-]$ is the hydroxyl ion activity and described as:

$$[OH^-] = \frac{K_w}{[\mathrm{H}^+]}$$

where K_w is the dissociation constant for water determined by the temperature. Also, *D* is the molecular diffusion coefficient for CO_2 (Jähne et al., 1987) and Z is the boundary layer thickness; $Z = D/k_{co2}$ and the k_{co2} is described as:

$$k_{CO2} = \frac{\{2.07 + 0.215 \times \ [\text{wind speed (m/s)}]^{1.7}\}}{3600}$$

In this calculations, Hoover and Berkshire utilized the Lewis and Whitman stagnant boundary layer model (1924). For the stagnant boundary layer model, it is assumed that the water surfaces consist of the boundary layers where CO_2 molecular diffusion takes place. The CO_2 concentration is in non-equilibrium within the boundary layer while the concentration of CO_2 and carbon species are in thermodynamic equilibrium in the turbulent water body. They also assumed that the pH inside the boundary layer would be roughly same as that of the turbulent water body, resulting from fast movement of hydrogen ion and the acid buffering capacity in water. The model predictions of α can lead to a raised gas exchange by up to several-fold depending on pH and temperature in the range of lake waters under low turbulence conditions (Figure 0.3). For example, *Alshboul and Lorke* (2015) obtained α up to fourteen (on average, four) using the theoretical model of Hoover and Berkshire (Figure 0.4). It led to enhanced CO_2 exchange up to fourteenfold beyond what would be expected from wind speed model of *Crusius and Wanninkhof* (2003).

Discrepancies between theoretical and observed α – In addition to theoretically calculated α, it can be directly obtained by comparing the gas exchange velocity of a reactive gas ($k_{600\text{-}enh}$) and that of a non-reactive gas ($k_{600\text{-}non}$) as follows:

$$\alpha = k_{600\text{-}enh} / k_{600\text{-}non}$$

For example, *α* of CO_2 can be determined from the ratio of k_{600} derived from CO_2 flux measurements ($k_{600\text{-}CO2}$) and that of CH_4 ($k_{600\text{-}CH4}$) or N_2O ($k_{600\text{-}N2O}$) (Wanninkhof & Knox, 1996), which is non-reactive gas and have similar diffusion coefficient (1.91×10^{-5}, 1.84×10^{-5}, and 2.57×10^{-5} cm^2/s at 25°C, respectively) (Jähne et al., 1987). Several experimental studies were performed to estimate α from the ratio of *k* using the floating chamber approach in lakes, and to compare them with theoretical α estimated from the model of Hoover and Berkshire. In the study of *Wanninkhof and Knox* (1996), $k_{600\text{-}CO2}$ was much higher than $k_{600\text{-}CH4}$ and $k_{600\text{-}N2O}$ indicating enhanced CO_2 exchanges in four alkaline lakes where salinity was more than 5.2 g L^{-1} and pH ranged from 8.6 to 9.8. In these cases, the observed α was larger than the theoretical prediction. On the other hand, for their freshwater experiments in Sterling Lake (salinity was 0 g L^{-1} and pH was 5) and in the laboratory tank, $k_{600\text{-}CO2}$ was similar to $k_{600\text{-}N2O}$ showing negligible chemical enhancement. In these cases, there were no discrepancies between the observed α and the theoretical *α*. However, it should be noted that the experimental tank was filled with acidified freshwater, and statistical analysis could not be applied due to lack of replication. *Bade and Cole* (2006) also investigated chemical enhancement of CO_2 in Peter Lake where increasing nutrient led to a decrease in total DIC and an increase in pH. During the summer, pH of the lake surface exceeded 9.5, and $k_{600\text{-}CO2}$ were higher than that of $k_{600\text{-}CH4}$ (3.5- to 7.5-fold) indicating significant contributions of chemical enhancement to CO_2 influxes. In most of their cases, the observed *α* was larger than the theoretical prediction (Figure 0.5).

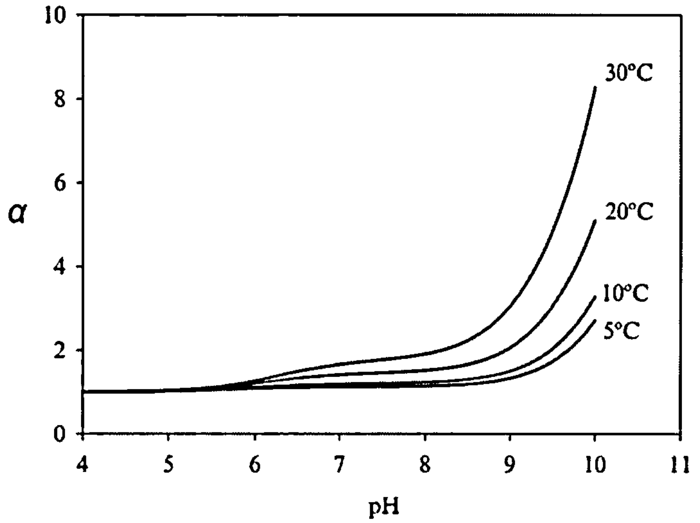

Figure 0. 3 Relationship between theoretical chemical enhancement factor (α) estimated from H&B model and pH for typical temperature

Result of *Bade and Cole* (2006). Relationship between theoretical chemical enhancement factor (α) from the Hoover and Berkshire model (1969) and pH for typical temperature in lakes under low turbulence condition ($k_{600} = 0.43$ m d^{-1}). The predicted chemical enhancement rates are a function of temperature and pH.

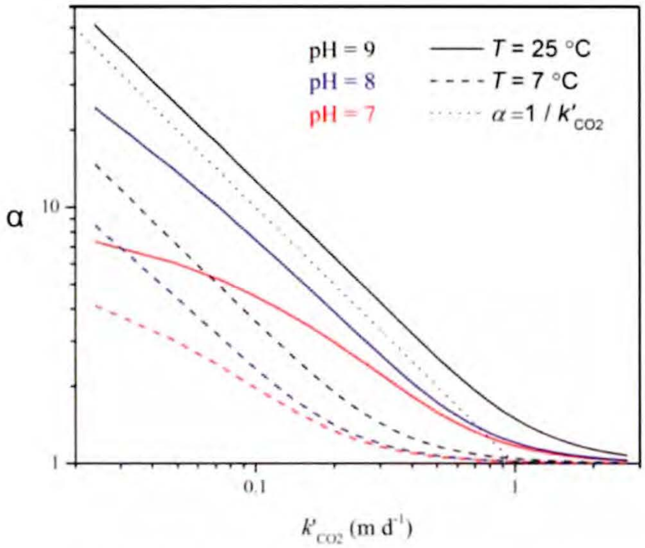

Figure 0. 4 Relationship between theoretical chemical enhancement factor (α) estimated from H&B model and unenhanced gas exchange velocity (k'_{CO2}) for typical pH and temperatures

Result of *Alshboul and Lorke* (2015). Relationship between theoretical chemical enhancement factor (α) from the Hoover and Berkshire model (1969) and unenhanced gas exchange velocity (k'_{CO2}) for three different pH and two different temperatures in reservoirs. The unenhanced gas exchange velocity (k'_{CO2}) was estimated from k_{600}, which is calculated from wind speed model of *Crusius and Wanninkhof* (2003). When pH is 8 and 9, α tends to become conversely related to k'_{CO2} (dotted line).

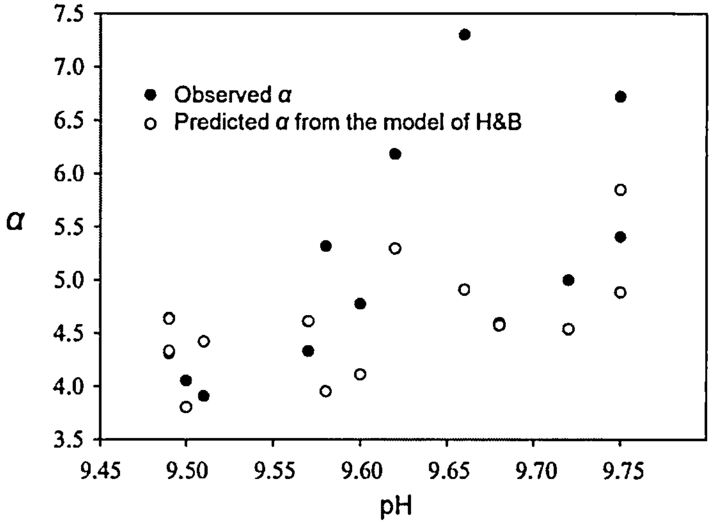

Figure 0. 5 Empirically observed α from chamber measurements and predicted α from H&B model

Result of *Bade and Cole* (2006). Empirically observed α from chamber measurements and predicted α from the model of Hoover and Berkshire (1969) related to pH at low turbulence conditions (on average $k_{600\text{-}CH4} = 0.44$ m d^{-1}).

0.3 Objectives and hypothesis

The main goal of this thesis is to improve current understanding of CO_2 chemical enhancement, and better integrate them in air-water CO_2 flux estimates in eutrophic systems. To address this goal, the specific objectives are as follows:

First, we quantify the actual contributions of chemical enhancement to CO_2 fluxes between the air and water. Using a floating chamber approach, we investigate diffusive gas exchange of CO_2 and that of CH_4, which does not react with hydroxyl ions in water. Then, chemical enhancement rates are obtained from the ratio of gas exchange velocities derived from CO_2 and CH_4 fluxes. Field sampling is conducted in 23 lakes of Quebec to estimate chemical enhancement rates under different trophic status, temperature, wind, and pH regimes, which influence chemical reaction of CO_2.

Second, we examine any discrepancies that might exist between the observed α in the field and that predicted from the calculation of Hoover and Berkshire (1969) to verify the general applicability of the model, which is often used for CO_2 chemical enhancement estimates. We expect that eutrophic lakes among the sampling lakes are relatively undersaturated in CO_2 resulting in invasion of CO_2 into the lakes. As pH is elevated, gas exchange velocities of CO_2 are larger than those of CH_4 showing significant contributions of chemical enhancement. Empirical evidence that the rate of CO_2 influx especially in calm conditions is much faster than that of CO_2 efflux was found from the laboratory of Prairie (Y. Prairie, 2015) and Kankaala (J. Heiskanen, 2015). Also, from previous experimental results of *Wanninkhof and Knox* (1996) and *Bade and Cole* (2006), we expect discrepancies between the observed α and that predicted from the theoretical model especially under low-wind conditions ($U_{10} < 3$ m s^{-1}). This phenomenon indicates that we can underestimate or overestimate the actual chemical enhancement and hence obtain incomplete CO_2 flux estimates.

Likely reasons for the discrepancies that might exist between calculated and observed values of α would be as follows:

First, some assumptions in the development of the chemical enhancement model of Hoover and Berkshire may be inappropriate. H&B utilized the stagnant boundary layer model (Lewis & Whitman, 1924). For the stagnant boundary layer model, it is assumed that the CO_2 concentration is in non-equilibrium within the layer while the concentration of CO_2 and carbon species are in thermodynamic equilibrium in the turbulent water body. However, H&B assumed that the pH inside the boundary layer would be constant and roughly same as that of turbulent water body. Contrary to their assumption, if boundary layer is non-existent or the pH of the boundary layer is different that of the turbulent water body resulting from atmospheric CO_2 absorption or CO_2 release to the atmosphere, the actual chemical enhancement that is driven by pH can be different than what we expect from the H&B theory. Therefore, in this study, we also explore the implications of using the surface renewal model (Danckwerts, 1951) as well as the thin boundary layer model to estimate the extent of chemical enhancement.

Second, enhanced gas exchange velocities of reference gas ($k_{600\text{-}CH_4}$) can decrease the observed α values. Recent studies have shown the potential influence of microbubble-mediated CH_4 fluxes (Y. T. Prairie & del Giorgio, 2013; Rosentreter et al., 2016). Microbubble is a non-Fickian diffusive process, and the presence of a microbubble flux can increase the mass transport rates of CH_4. It can lead to partially decrease observed chemical enhancement. However, from the previous studies, microbubbles are generated at the water surface by precipitation, wind induced breaking waves, or CH_4 supersaturation (B. D. Johnson & Cooke, 1981; Y. T. Prairie & del Giorgio, 2013; Uchida et al., 2016). There is little to believe that it is pH driven. Therefore, we estimate contributions of microbubbles by comparing observed $k_{600\text{-}CH_4}$ and that estimated from the models using wind speed (Jonathan J. Cole & Caraco, 1998) and wind-lake system size (Vachon & Prairie, 2013). If the observed $k_{600\text{-}CH_4}$ is higher than what we expect from the physical parameters, we can assume existence of microbubbles and estimate that contributions to higher $k_{600\text{-}CH4}$.

We use the conclusions from these efforts to develop methods for improving the estimation of gas exchange in eutrophic systems.

CHAPITRE I

ASSESSING THE CONTRIBUTION OF CHEMICAL ENHANCEMENT TO CO_2 EXCHANGE ACROSS THE AIR-WATER INTERFACE IN EUTROPHIC LAKES OF QUEBEC

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1.1 ABSTRACT

A detailed knowledge of gas exchange processes across the air-water interface of lakes is necessary for properly assessing carbon budgets at regional and global scales. In contrast with chemically non-reactive gases such as methane (CH_4), nitrous oxide (N_2O) and radon (Rn), diffusive carbon dioxide (CO_2) exchange across the air-water interface can be enhanced by chemical reactions of CO_2 with hydroxyl ions (OH^-), especially at high pH. In eutrophic lakes where pH is relatively high, chemical enhancement is believed to be an important factor in driving CO_2 fluxes. So far, in many studies, the theoretical model of Hoover and Berkshire (1969) (H&B) were widely used to estimate chemical enhancement rates (α) for accurate estimates of CO_2 flux. Although the H&B model was developed based on tank experiments nearly half a century ago, only few field-based measurements were provided to test their theory and the actual extent of chemical enhancement is still poorly tested. To address this issue, first, we quantified the actual contributions of chemical enhancement to air-water CO_2 fluxes by comparing measured gas exchange velocities derived from CO_2 ($k_{600\text{-}CO2}$) and from CH_4 ($k_{600\text{-}CH4}$) in 21 lakes of Quebec during the summer of 2015 and 2016. Second, we examined any discrepancies that might exist between the observed α and that predicted from the H&B calculation to verify the general applicability of the model. In addition, we revisited several assumptions of the H&B model and explored implications of using different gas exchange mechanisms. In most lakes, there was no systematic difference between $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$ (on average 2.1 and 2.2 m d^{-1}, respectively), suggesting that chemical enhancement of CO_2 is not a significant contributor to air-water CO_2 flux over a wide range of k_{600} values. In addition, observed α were considerably lower than H&B α (up to 7.4 times), indicating that the H&B model can overestimate chemical enhancement of CO_2, particularly in high alkalinity waters. Likely reasons for the discrepancy between observed and calculated values of α are: 1) some inappropriate assumptions of the H&B model, 2) enhanced gas exchange velocities of reference gas (CH_4), and 3) divergence between the experimental conditions in which the H&B model has been developed and actual field conditions. Our results also suggest that gas exchange may be more appropriately described as a surface renewal mechanism rather than a stagnant boundary layer. We expect these results can improve the estimation of gas exchange in eutrophic systems, and have important consequences for the assessment of regional carbon budgets.

Key words: Air-water gas exchange, Carbon dioxide, Chemical enhancement, Eutrophic lakes, Gas exchange velocity, hydration.

1.2 INTRODUCTION

Quantifying accurate greenhouse gas (GHG) fluxes between the Earth's surface and the atmosphere has been considered essential for planning for a sustainable future under global climate changes. Lakes are now well known sites of GHG emissions to the atmosphere, especially important biogenic gases such as CO_2 and CH_4, and one of the primary pathways is through diffusive emission (Bastviken et al., 2011; J. J. Cole et al., 2007; Holgerson & Raymond, 2016; Rasilo et al., 2014; Raymond et al., 2013). Diffusive gas exchange is regulated by physical, chemical and biological factors, and the dependency on these factors can be adequately described using the Fick's first law of diffusion as follows:

$$Flux = k_x \times Kh(px_{water} - px_{air}) \qquad \text{Eq.1}$$

where x is the particular gas, k is the gas exchange velocity, Kh is the Henry's coefficient for correcting temperature and salinity of water, and px_{water} and px_{air} are the gas partial pressure in the water surface and air, respectively. Chemical considerations of gas exchange are closely linked to gas concentration gradients across the air-water interface, which are in part controlled by solubility of the gases and biological processes that produce or consume them (D L Bade, 2009; Smith, 1985). Also, physical aspects of gas exchange are dependent upon both near-surface turbulence in water (Jonathan J. Cole & Caraco, 1998; Vachon et al., 2010) and molecular diffusion of the gases (Donelan & Wanninkhof, 2002; Jähne et al., 1987), and the rates of gas exchange driven by these physical processes can be expressed as the gas exchange velocity (k). While gas concentration gradients can be easily obtained from precise measurements of actual gas partial pressures on either side of the air-water interface (*Cole and Prairie, 2009*), assessing physical processes is more complex, and k is relatively difficult to measure. So far, several mechanistic theories are available to describe the physical gas exchange processes. The two most common theories are the boundary layer model (Lewis & Whitman, 1924) and the surface renewal model (Danckwerts, 1951). Although these two ultimately yield the same mathematical formulation (Eq. 1), their basic assumptions are quite different. For the boundary layer model, it is assumed that the interfaces at the water surfaces consist of thin boundary layers (sub-millimeter in thickness) through which molecular diffusion takes place (Figure 1.7a). On the other hand, the surface renewal model describes the surface water as being influenced by turbulent eddies that bring water from underneath, and hence this water interface layers are periodically renewed (Figure 1.7b). Based on these theories, most approaches to estimating k use empirical relationships with physical parameters such as wind speed (Jonathan J. Cole & Caraco, 1998), wind and ecosystem size (Vachon & Prairie, 2013), and buoyancy flux models (MacIntyre et al., 2010; Tedford et al., 2014), which influence turbulence near the air-water interface.

In eutrophic lakes, although the role of lake metabolism in lake CO_2 dynamics can vary widely (Bogard & Giorgio, 2016), CO_2 undersaturation is prevalent especially during the summer due to extreme primary production subsidized by nutrient enrichments (Balmer & Downing, 2011; Del Giorgio et al., 1999). Consequent CO_2 depletion in surface water results in high pH values, and in these cases, more complex physical and chemical processes are responsible for the air-water CO_2 flux regulation than other gases such as CH_4, N_2O, and Rn. Under high-pH conditions, instead of just diffusing, CO_2 can react directly with hydroxyl ions (OH^-) within the water-side surface boundary layer (Bolin, 1960).

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad \text{Eq. 2}$$

This chemical reaction increases the CO_2 gradient between the air and water, and then the absolute value of CO_2 flux is believed to be enhanced beyond the flux derived from diffusion process (Emerson, 1975; Hoover & Berkshire, 1969). Therefore, at high pH, the air-water CO_2 flux can be described with the rate of chemical enhancement (expressed as a chemical enhancement factor, α) as follows:

$$Flux = k_{CO2} \times \alpha \times Kh(pCO_{2_{water}} - pCO_{2_{air}}) \qquad \text{Eq. 3}$$

where k_{CO2} is the gas exchange velocity of CO_2, Kh is the Henry's coefficient for correcting temperature and salinity of water, and $pCO_{2_{water}}$ and $pCO_{2_{air}}$ are the gas partial pressure of CO_2 in the water surface and air, respectively. Since *Bolin* (1960) first described chemical enhancement of CO_2, several experimental and theoretical model studies (e.g., Hoover and Berkshire 1969; Quinn and Otto 1971; Smith 1985; Keller 1994; Emerson 1995) have been performed to estimate α. So far, in many studies, the model of Hoover and Berkshire (H&B, 1969) has been widely used to calculate α because it only requires the input of boundary layer thickness, temperature, and pH of surface water and hence is easily applicable. Since the chemical reaction time is assumed to be proportional to the residence time of CO_2 molecules in the boundary layer, the magnitude of theoretical chemical enhancement is determined by the boundary layer thickness. Also, the pH and temperature of surface water, all of which adjust the equilibrium of three carbon species (CO_2, HCO_3^-, and CO_3^{2-}), are determinants of α in their model. In diverse systems such as saline lakes (Duarte et al., 2008), hardwater lakes (Finlay et al., 2015; Wiik et al., 2018), and eutrophic reservoirs (Alshboul & Lorke, 2015), the theoretical α of H&B led to increases of CO_2 gas exchange by up to fourteenfold. However, although this model was developed based on tank experiments nearly half a century ago, only few field-based data were provided to test their theory and even showed poor agreement between observed α and the model predictions (Darren L. Bade & Cole, 2006; Wanninkhof & Knox, 1996). Furthermore, none of them statistically demonstrated the discrepancies, and the actual extent of chemical enhancement is still poorly tested. To address this issue, first, we quantified the actual contribution of chemical enhancement to the air-water CO_2 flux by taking field-based measurements in a suit of diverse lakes. α was empirically observed from the ratio between the gas exchange velocities estimated from the flux measurements of two different gases. One is CO_2 subject to chemical enhancement, and the other is CH_4 not subject to that. Within the same floating chamber, the fluxes of two gases were measured simultaneously. Second, we examined any discrepancies that might exist between the observed α and the predicted α from the theoretical calculation of Hoover and Berkshire (1969) to verify the general applicability of the model. In addition, we revisited several assumptions of the H&B model and explored implications of using different gas exchange mechanisms.

1.3 MATERIALS AND METHODS

1.3.1 Study area and sampling periods

Samples were taken in a total of 21 lakes (area range 0.05 to 1269 km^2). Among them, 16 lakes in Eastern Townships region (~100 km east of Montreal) of Quebec were sampled in 2016. The other 5 lakes were sampled in Laurentide region (~50 km north of Montreal) and Lake Champlain in 2015 by Tonya Delsontro (Université du Québec à Montréal) (Figure 1.1). The lakes were selected to cover a wide range of chemical and physical conditions (i.e. pH, water temperature, wind speed, surface water pCO_2, and trophic gradients) based on the data of *Galvez-Cloutier and Sanchez* (2007) who worked on trophic status evaluation for 154 lakes in Quebec, and on the data of *Prairie et al.* (2002) who collected physical and chemical characteristics in lakes of the Eastern Townships region, in order to test the general applicability of the Hoover and Berkshire model (1969) in lake systems. Samplings were carried out in daytime during the summer to satisfy the conditions of low surface water pCO_2 and high pH in sampled lakes. Also, to remove any effect of precipitation on the gas exchange of two gases, all measurements were performed without rain.

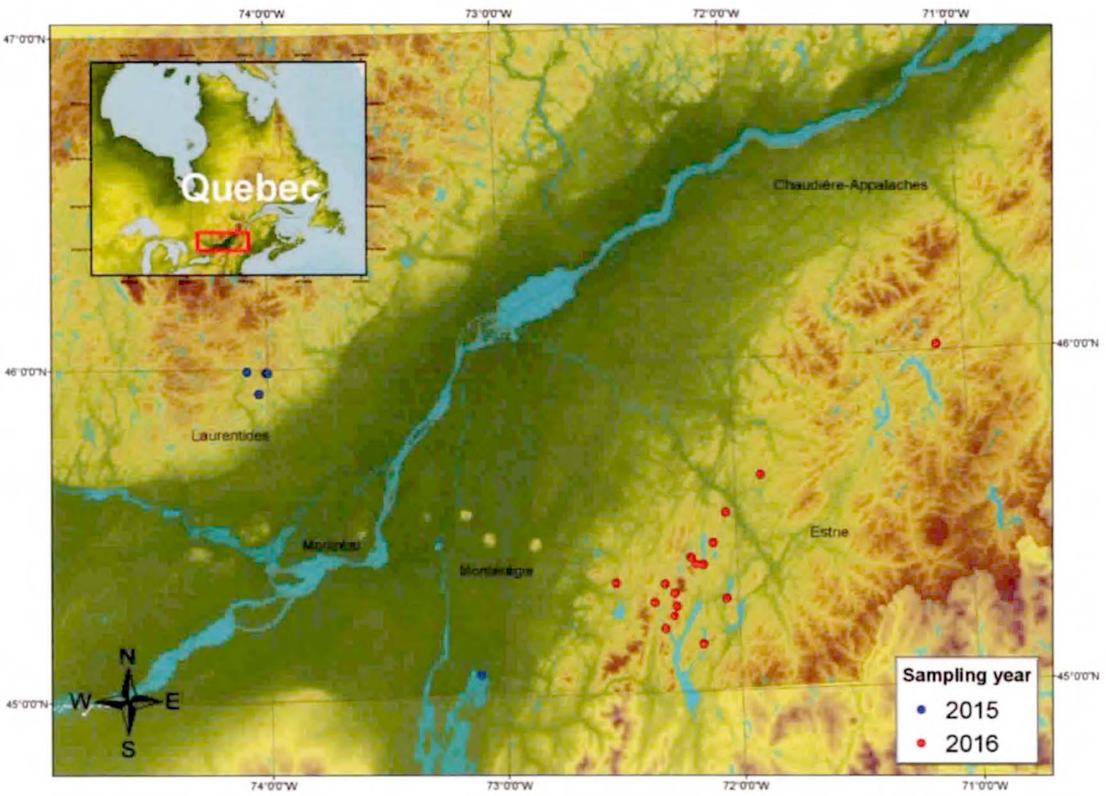

Figure 1. 1 Map of sampled lakes

Map of temperate region of Quebec, showing the distribution of the sampled lakes. The red solid circles represent the locations of the sampled lakes in 2016 (n = 16), and the blue solid circles are those of 2015 (n = 5).

1.3.2 Sample collection and Processing

The way we approached the problem is to compare the gas exchange velocities estimated from two different gases within the same measurement deployment. One is CO_2, subject to chemical enhancement, and the other is the gas, not subject to chemical enhancement, in our case, CH_4. The empirical estimates of chemical enhancement rate (α) are, therefore, derived from the ratio between the gas exchange velocities (k_{600}) of two gases, as follows:

$$\text{Observed } \alpha = k_{600\text{-}CO2} / k_{600\text{-}CH4}$$

To obtain the gas exchange velocities of two different gases, the air-water fluxes and surface water concentration of the gases were directly measured in each site. The fluxes of the two gases measured simultaneously, using a floating-chamber (volume: 15.48 L; area: 0.09 m^2; water penetration: 6 cm) technique. The chamber was connected to the gas analyzer (LGR Ultraportable 915-0011) in an air-tight recirculating loop, and the partial pressure of CO_2 and CH_4 (pCO_2 and p CH_4, respectively) were simultaneously recorded every second for 5 minutes. The gas accumulation rate inside the chamber was computed by linear regression to estimate the gas flux for each sampling occasion. More than 95% of the chamber measurements for both gases had linear increases or decreases with $R^2 > 0.96$, representing little evidence of bubble existence during the chamber measurements and little bias derived from the different measurement methods between two gases. In many studies, pCO_2 and pCH_4 of surface water are commonly measured based on the headspace equilibration technique (K. M. Johnson et al., 1990). However, in cases of pCO_2 undersaturated systems with respect to the headspace gases (i.e. atmosphere), the physical shaking technique for making CO_2 equilibrium can cause negative pCO_2. It is because CO_2 molecules in the headspace can become hydrated with the sample water to form HCO_3^-, and therefore, it can modify the equilibrium between CO_2 and HCO_3^-. pCO_2 is one of critical component to calculate $k_{600\text{-}CO2}$ and the observed α, and most of our study lakes are undersaturated in pCO_2.

Consequently, in our study lakes, the usual headspace method is insufficient to precisely estimate the original water pCO_2. To solve this issue, we took into account the displacement of CO_2 in HCO_3^- by incorporating the alkalinity of the sample water in the pCO_2 calculation. Then, gas exchange velocity (k) of both CO_2 and CH_4 were as follows:

$$k_x = \frac{Flux\ of\ x}{Kh \times (px_{water} - px_{air})}$$

Where x is a particular gas, *Flux* is the gas flux between the air-water interface ($mmol\ m^{-2}\ d^{-1}$), *Kh* is the Henry's coefficient for correcting temperature and salinity of water for each gas, and px_{water} and px_{air} are the gas partial pressure (*ppm*) of each gas in water surface and air, respectively. Then, the calculated k_{CO2} and k_{CH4} were normalized with the Schmidt number of 600 to $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$, respectively.

$$k_{600} = k_x \left(\frac{600}{Sc_x}\right)^{-n}$$

Where Sc_x is the Schmidt number of a particular gas, x, at a given temperature, and n can be determined depending on wind speed. In lake systems, $n = 2/3$ for wind speed <3.7 m/s, or $n = 1/2$ for higher wind speed than 3.7 m/s (Jähne et al., 1987). The floating-chamber (FC) techniques are regularly and easily used to measure gas fluxes, but the empirical data of *Matthews et al.* (2003) and *Vachon et al.* (2010) indicated that chamber deployment could enhance the true flux by perturbing the air-water interface inside the chamber especially in calm and low turbulence condition. To correct chamber-induced overestimation, both $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$ were divided by the overestimation ratio of Vachon et al. (2010) and Prairie and del Giorgio (2013). However, it should be noted that the chamber-induced bias is possibly canceled when α is estimated from the ratio of k_{600} since any perturbation affecting estimates of $k_{600\text{-}CO2}$ should also affect $k_{600\text{-}CH4}$ in the same chamber.

$$Overestimation\, ratio = \frac{54.30 + 10.491 \log_{10} \varepsilon_w}{66.76 + 15.081 \log_{10} \varepsilon_w}$$

where ε_w is the turbulent kinetic energy (TKE) dissipation rate (m^2 s^{-3}) for lake systems, and the base-10 logarithm of ε_w can be expressed as $\log_{10} \varepsilon_w = -5.272 + 0.114U_{10}$ from the empirical data to use the different effect of wind instead of TKE dissipation rate (Y. T. Prairie & del Giorgio, 2013).

In addition, α was theoretically calculated based on the model of Hoover and Berkshire as follows (Hoover & Berkshire, 1969; Wanninkhof & Knox, 1996):

$$\text{Expected } \alpha = \frac{T}{\left[(T-1)+\left\{tanh\left[(\frac{rT}{D})^{0.5}Z\right]/(\frac{rT}{D})^{0.5}Z\right\}\right]} \qquad \text{Eq. 4}$$

where T is defined as follows:

$$T = 1 + \frac{[\mathrm{H}^+]^2}{K_1 K_2 + K_1[\mathrm{H}^+]} \qquad \text{Eq. 5}$$

Where $[\mathrm{H}^+]$ is the hydrogen ion activity; $[\mathrm{H}^+] = 10^{-pH}$, K_1 and K_2 are the dissociation constants for the reactions between CO_2 and HCO_3^-, and HCO_3^- and CO_3^{2-}, respectively (Dickson & Millero, 1987). The r is a combination of reaction rate and described as:

$$\mathrm{r} = r_1 + r_2[OH^-] \qquad \text{Eq. 6}$$

where r_1 and r_2 are the hydration rate constants for CO_2 reacting with H_2O and OH^-, respectively (K. S. Johnson, 1982). The $[OH^-]$ is the hydroxyl ion activity and described as:

$$[OH^-] = \frac{K_w}{[\mathrm{H}^+]} \qquad \text{Eq. 7}$$

where K_w is the dissociation constant for water determined by the temperature. Also, D is the molecular diffusion coefficient for CO_2 (Jähne et al., 1987) and Z is the boundary layer thickness; $Z = D/k_{co2}$ and the k_{co2} is described as:

$$k_{CO2} = \frac{\{2.07+0.215\times[\text{wind speed (m/s)}]^{1.7}\}}{3600} \qquad \text{Eq. 8}$$

Since the chemical reaction time is assumed to be proportional to the residence time of CO_2 molecules in the boundary layer, the magnitude of theoretical chemical enhancement is determined by the boundary layer thickness. In this study, two empirical model (Jonathan J. Cole & Caraco, 1998; Vachon & Prairie, 2013) were used to estimate the boundary layer thickness. The pH and temperature of surface water, all of which are considered as important regulators for chemical enhancement, were measured on each sampling site while the gas exchange velocities were obtained. The pH was measured using a portable pH meter (Metrohm Ltd, pH meter 913) fixed on a polystyrene board, so that the sensor probe would be consistently placed under 1 cm of water surface in order to minimize error in the pH measurements derived from causal effects from different depth.

1.3.3 Statistical analyses

All statistical analyses were performed using JMP software version 12.0 (SAS Institute, Inc.). Variables with non-normal distribution were log transformed to attain assumptions of normality. Linear regression and Pearson's correlations were used to describe the relationships between $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$, and H&B α and the observed α. A paired t-test was applied to test for differences between H&B α and the observed α. We also assessed the differences in pH and observed α among the CO_2 in-gassing and out-gassing sites using nonparametric analyses of variances (Wilcoxon test).

1.4 RESULTS

1.4.1 Chemical and physical characteristics of sampled lakes

The 21 different lakes covered a broad range of pH, wind speeds, and water temperatures, all of which are considered as important determinants for estimates of chemical enhancement in the H&B model. Across the sampled lakes, pH ranged from 6.5 to 9.3 (mean = 7.9, median = 8.2, and interquartile range = 7.0 to 8.4; Figure 1.2a), wind speed (U_{10}) ranged from 0.1 to 7.7 m s^{-1} (mean = 2.8, median = 2.7, and interquartile range = 1.4 to 3.3 m s^{-1}; Figure 1.2b), and water temperature ranged from 19.4 to 28.8 °C (mean = 23.2, median = 23.1, and interquartile range = 20.5 to 25.3 °C; Figure 1.2c). Total phosphorus values of the lakes were also variable, ranging from 3 to 179 μg L^{-1} (mean = 29, median = 14, and interquartile range = 9 to 20 μg L^{-1}; Figure 1.2d), showing a wide range of trophic status from oligotrophic to hypereutrophic lakes. Total phosphorus was significantly correlated with surface water pH ($R^2 = 0.32$, $p = 0.0004$).

1.4.2 CO_2 undersaturation and CH_4 supersaturation

We obtained 60 measurements pairs of CO_2 and CH_4 fluxes and corresponding partial pressures from the sampled lakes over two summer field campaigns. Surface water pCO_2 ranged from 66 to 2132 ppm (mean = 632, median = 273, and interquartile range = 175 to 967 ppm; Figure 1.2e), with the air-water CO_2 fluxes ranging from -189 to 226 mmol m^2 d^{-1} (mean = 4, median = -8, and interquartile range = -22 to 30 mmol m^2 d^{-1}; Figure 1.2f). Surface water pCO_2 was significantly correlated with surface water pH ($R^2 = 0.84$, $p < 0.0001$). 58% of surface water samples were undersaturated in CO_2 relative to the atmosphere (which was assumed to be around 402 ppm), and these lakes, therefore, acted as net sinks of atmospheric CO_2. Unsurprisingly, the pH values of CO_2 in-gassing sites were significantly greater than those of CO_2 out-gassing sites (Wilcoxon test, $p < 0.0001$; Figure 1.3a). In contrast, all of our sampled lakes were highly supersaturated in CH_4 relative to the atmosphere (which was assumed to be around 1.9 ppm), and the degree of supersaturation averaged 304-fold (ranged from 21 to 1939-fold).

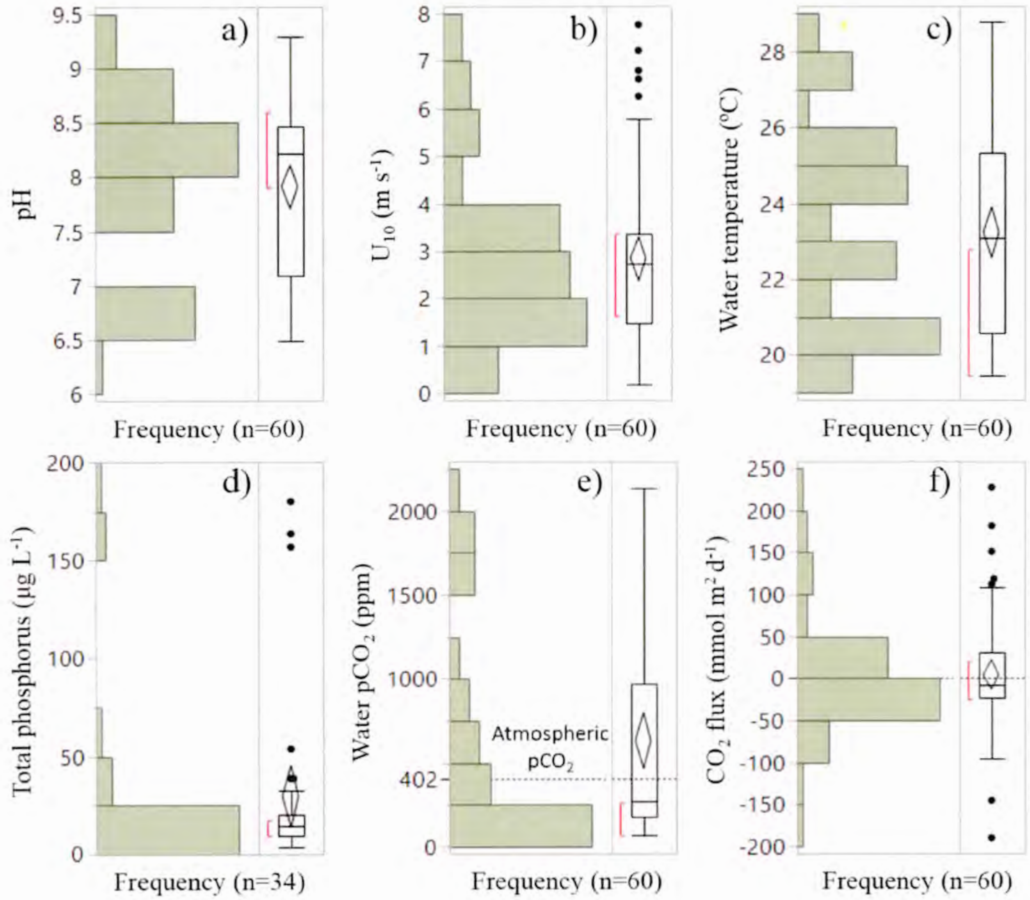

Figure 1. 2 Chemical and physical conditions of sampled lakes

Figure 1.2 illustrates the data distribution of chemical and physical conditions of sampled lakes; a) surface water pH, b) wind speed (normalized to a reference height of 10 m, U_{10}), c) surface water temperature, d) Total phosphorus, e) Surface water pCO_2 (the dashed line represents the average values of atmospheric pCO_2), and f) CO_2 flux across the air-water interface. On the right part of these graphs, diamonds represent mean values, red lines are for median, and square boxes are for interquartile range of each parameter.

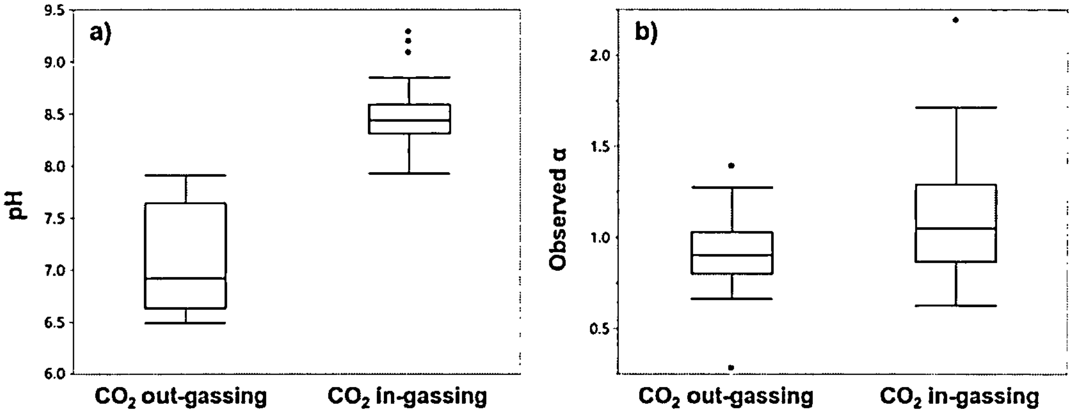

Figure 1. 3 pH and observed *α* associated with CO_2 out-gassing and in-gassing

a) The pH values of CO_2 in-gassing sites were significantly greater than those of CO_2 out-gassing sites (Wilcoxon test, $p < 0.0001$), and b) The empirically observed α values of CO_2 in-gassing sites were slightly higher than those of CO_2 out-gassing sites (Wilcoxon test, $p = 0.0201$). However, the observed α values of CO_2 in-gassing sites were not significantly different from 1.0 (One sample t-test, $p > 0.0529$).

1.4.3 Relationship between k_{600} derived from two different gases

In the combined dataset, k_{600} values derived from CO_2 ($k_{600\text{-}CO2}$) and CH_4 ($k_{600\text{-}CH4}$) measurements varied from 0.2 to 14.9 m d^{-1} (mean = 2.1, median = 1.1, and interquartile range = 0.6 to 1.9 m d^{-1}) and from 0.2 to 17.2 m d^{-1} (mean = 2.2, median = 1.0, and interquartile range = 0.6 to 1.7 m d^{-1}), respectively. Exceptionally high values of k_{600} of both gases (more than 10 m d^{-1}) were obtained only from the large L. Champlain (1269 km^2) at high wind conditions ($U_{10} > 3.7$ m s^{-1}). In all other sampled lakes $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$ were less than 4.1 and 4.2 m d^{-1} (average 1.9 and 1.8 m d^{-1}, respectively). $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$ values were, as expected, very tightly correlated with each other (Figure 1.4; $R^2 = 0.91$, $p < 0.0001$) and there was no evidence of systematic bias in the estimation of k_{600} from the two different gases (slope and intercept are not significantly different from 1 and 0, respectively) and the discrepancies between the two were largely the result of measurement uncertainty (Figure 1.4). This suggests that high k_{600} values for CO_2 were indicative of highly turbulent conditions and not chemical enhancement (Figure 1.4).

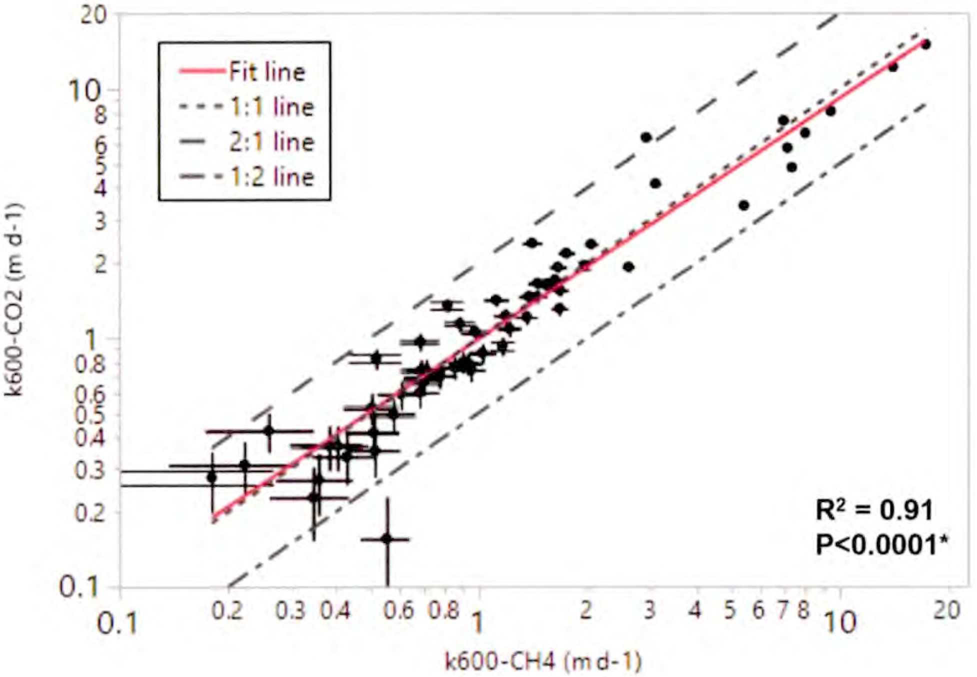

Figure 1. 4 The relationship between the gas exchange velocity (k_{600}) estimated from carbon dioxide (y axis) and methane (x axis)

Red line represents regression fit, dotted line is the 1 to 1 line, dashed line is the 2 to 1 line, and dashed-dotted line is the 1:2 line. The error bars represent the standard deviation of k using the Taylor's expansion for the standard deviation of a ratio. Figure 1.4 illustrates $k_{600\text{-}CO2}$ and $k_{600\text{-}CH4}$ were very tightly correlated with each other (R^2 = 0.91, $p < 0.0001$).

1.4.4 Discrepancies between observed α and H&B α

While the α values estimated from the H&B model varied between 1.0 and 11.7 (mean = 2.1, median = 1.5, and interquartile range = 1.0 to 2.3), those empirically observed by comparing k_{600} derived from two different gases only ranged from 0.3 to 2.2 (mean = 1.0, median = 1.0, and interquartile range = 0.8 to 1.1). The observed α values of CO_2 in-gassing sites were slightly higher than those of CO_2 out-gassing sites (Wilcoxon test, $p = 0.0201$; Figure 1.3b), in agreement with the previous study of Emerson (1995) and Keller (1994). It is because the pH of CO_2 out-gassing waters is much lower than that of CO_2 in-gassing waters (Figure 1.3a), and the back-reaction of HCO_3^- to CO_2 (dehydration of CO_2) is less efficient than the reaction of CO_2 to from HCO_3^- (hydration of CO_2) (Keller, 1994). However, the observed α values of CO_2 in-gassing sites were uniformly low (mean = 1.1, median = 1.0, and interquartile range = 0.9 to 1.3) and not significantly different from 1.0 (One sample t-test, $p > 0.0529$), indicating little to no chemical enhancement across the sampled lakes. Although we found a significant relationship between observed α and H&B α (Figure 1.5; $R^2 = 0.16$, $p < 0.0014$), the observed α was considerably lower than H&B α in more than 88% of the cases (paired t-test, $p < 0.0001$). Expressed as a ratio (H&B α : observed α), the difference ranged from 0.6 to 7.4-fold (mean = 2.1, median = 1.7, and interquartile range = 1.3 to 2.3-fold). The observed α values less than 1 were largely the result of measurement uncertainty (mean = 1.0, median = 1.0, and interquartile range = 0.8 to 1.1). Figure 1.6 implies that H&B α, as expected, increased with increasing surface water pH. However, observed α values were independent of the pH, and especially at higher pH (from 8.3 to 9.3) where chemical enhancement should be most prevalent, the observed α values were consistently close to 1, showing negligible chemical enhancement. Within the high pH range, the H&B model overestimated actual chemical enhancement rates by 1.3 to 7.4-fold (mean = 2.8, median = 2.3, and interquartile range = 1.7 to 3.6-fold).

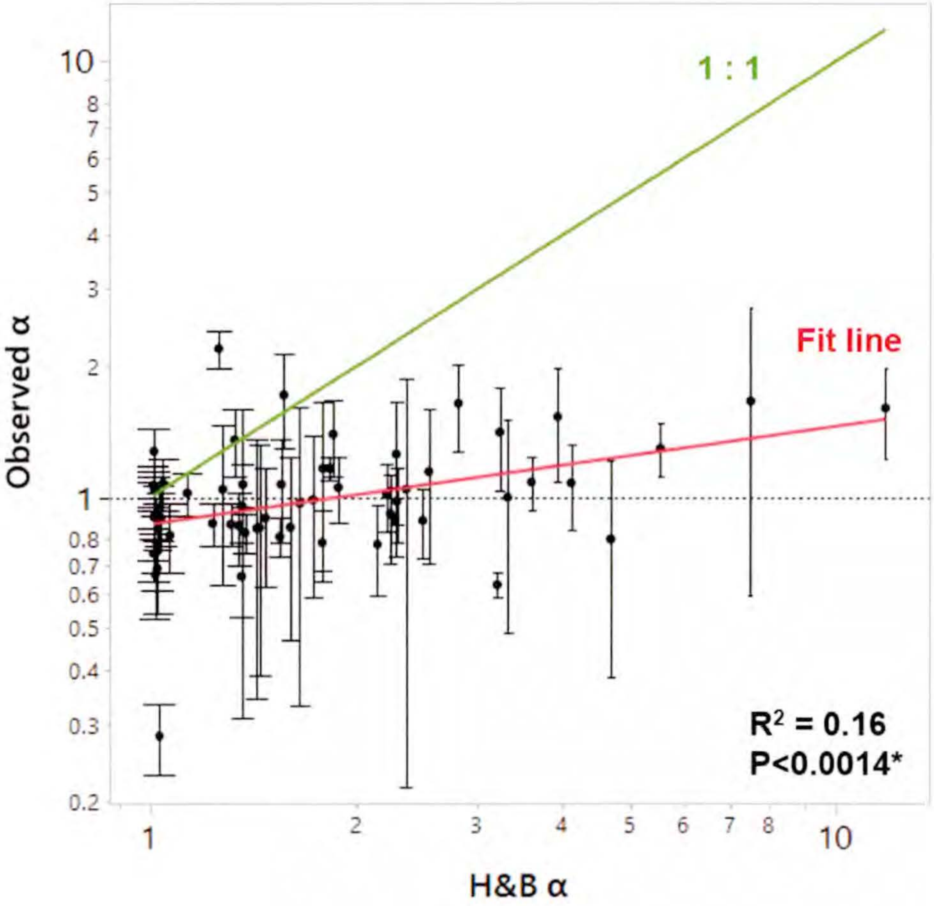

Figure 1. 5 The relationship between empirically observed chemical enhancement (observed α, y axis) and that estimated from the Hoover and Berkshire model (H&B α, x axis)

Red line represents regression fit, and dashed line represents 1 to 1 line. Observed α and H&B α were very correlated with each other ($R^2 = 0.16$, $p < 0.0014$). Figure 1.5 illustrates the observed α was considerably lower than that H&B α in more than 88% of the cases (paired t-test, $p < 0.0001$).

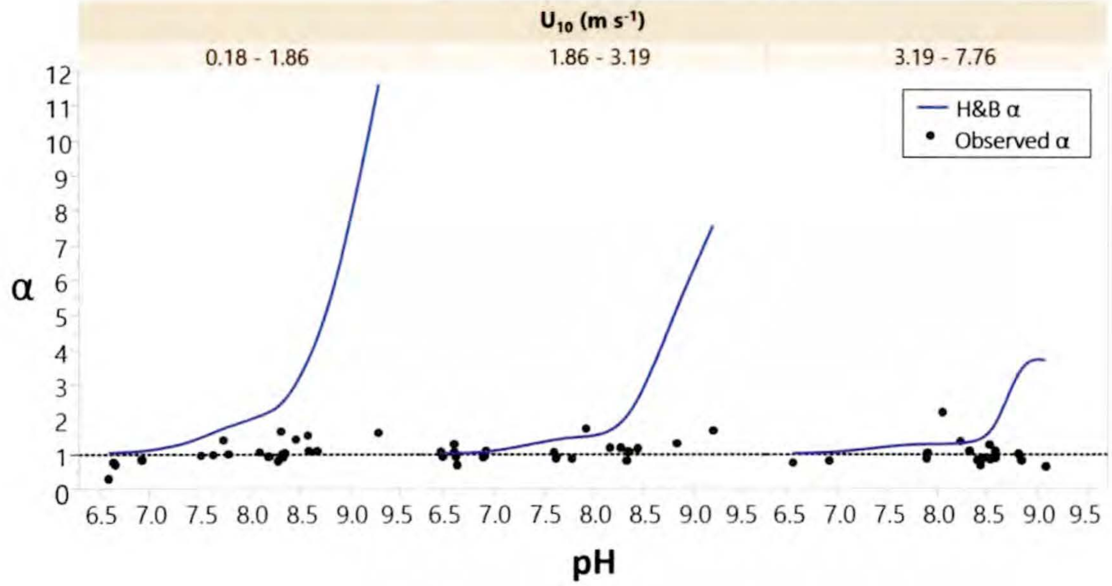

Figure 1. 6 The relationship between the chemical enhancement factors (α) and surface water pH

Blue line represents the chemical enhancement factors estimated from H&B model, and dots represent those empirically observed from chamber measurements. While H&B α increased with increasing surface water pH, observed α values were close to 1 (dashed line), even at higher pH (from 8.3 to 9.3) where chemical enhancement should be higher.

1.5 DISCUSSION

The results of this study clearly indicate that chemical enhancement mechanism is not particularly relevant (observed α close to 1) even under high pH conditions such as those encountered in eutrophic lakes. The intense CO_2 depletion in eutrophic systems among our sampled lakes led to increases in surface water pH (Figure 1.3a) and therefore in the theoretical chemical enhancement rates expected from the H&B model. It seems to reflect the importance of chemical enhancement as a driver of air-water CO_2 flux in such eutrophic systems. However, surprisingly, our data do not support this paradigm and instead suggest that the chemical mechanism theory is not applicable in actual field systems. In this study, we only used the H&B model to calculate theoretical α for comparison with our empirically observed α because it is a simplest model and thus most widely used (Alshboul & Lorke, 2015; Duarte et al., 2008; Finlay et al., 2015; Wiik et al., 2018). However, the same result is expected given other existing but more complex models (e.g., Bolin 1960; Quinn and Otto 1971; Smith 1985; Keller 1994; Emerson 1995) give very similar results to those of the H&B model (*Keller*, 1994; *DeGrandpre and McGillis*, 1995; *Wanninkhof and Knox*, 1996).

There are a number of hypotheses to explain the discrepancies between the observed and H&B chemical enhancement while others can be ruled out. For example, our approach of using the two different gases (CO_2 and CH_4) measured simultaneously at high frequency (1 Hz) in the same chamber deployments, should eliminate methodological concerns over chamber effects or different methods to measure the two gases, which might have affected previous studies (Darren L. Bade & Cole, 2006; Wanninkhof & Knox, 1996). Alternatively, H&B model makes a number of assumptions that may not be generally appropriate to many field situations. First and foremost, the H&B model is based on equilibrium reactions occurring within a thin boundary layer (TBL) and therefore depends on the existence of a stable thin boundary layer. Diffusive gas exchange at the air-water interface is often conceived as molecular diffusion occurring within a stagnant TBL bounded by a turbulent water body underneath and a turbulent atmosphere at the surface. This model can be mathematically expressed as Fick's first law (Eq. 1) in which k_{600} is modulated by wind-derived surface turbulence (Jonathan J. Cole & Caraco, 1998; Vachon & Prairie, 2013). As a conceptual model however, it is more exact to view different gas exchange velocities as the result of changes in the thickness of the TBL induced by wind. For k_{600} values typical of calm conditions (0.5 m d^{-1}), the implied thickness of the TBL is about 720 μm but is reduced to 160 μm in a mid-size lake experiencing moderate winds (U_{10} of 6-7 m s^{-1}) (Smith, 1985; Cole and Caraco, 1998; Crusius and Wanninkhof, 2003). Whether such thin boundary layer can remain stable is speculative given that other conceptual models of gas exchange can yield the same mathematical formulation (Eq. 1) without requiring the existence of a TBL. In particular, the surface renewal model first described by Danckwerts (1951) and further explored by many others (*Schwarzenbach et al.,* 1993; *Zappa et al.,* 2007; *Jessup et al.,* 2009; *Vachon et al.,* 2010; *Dugan et al.,* 2016) depicts gas exchange at the interface as eddies of various small sizes randomly reaching the interface equilibrate with the atmosphere and are replaced by deeper water within a time interval (Donelan & Wanninkhof, 2002) (Figure 1.7b). If such model is a more realistic description of the gas exchange process in lakes, then the applicability of the H&B model of chemical enhancement largely vanishes.

A second, related assumption of the H&B model is that the pH within a boundary layer is constant and equal to that of the turbulent water body because of the mobilities of ionic species (Bolin, 1960; Hoover & Berkshire, 1969). The equations developed by H&B are therefore appropriate for estimating chemical enhancement rates only if this assumption is generally valid in our sampled systems. The basic idea for the stagnant boundary layer model is that, three carbon species (CO_2, HCO_3^-, and CO_3^{2-}) are in non-equilibrium and readjust their equilibrium within the boundary layer, while those species are in thermodynamic equilibrium in the turbulent water body (Lewis & Whitman, 1924). If the pH is indeed maintained within the boundary layer, there would be a transfer of CO_2 that is not strictly diffusive but instead resulting from the direct hydration with OH- directly to HCO_3^- by displacing the equilibrium (Figure 1.7a). However, Quinn and Otto (1971) pointed out that a pH gradient would be required to maintain electroneutrality in the TBL and this would yield an equilibrium displacement and therefore chemical enhancement that is less important than predicted by the H&B model. Although we could not examine empirically the existence of pH gradient at the interface because of the size of our pH sensor, this hypothesis is also compatible with our results.

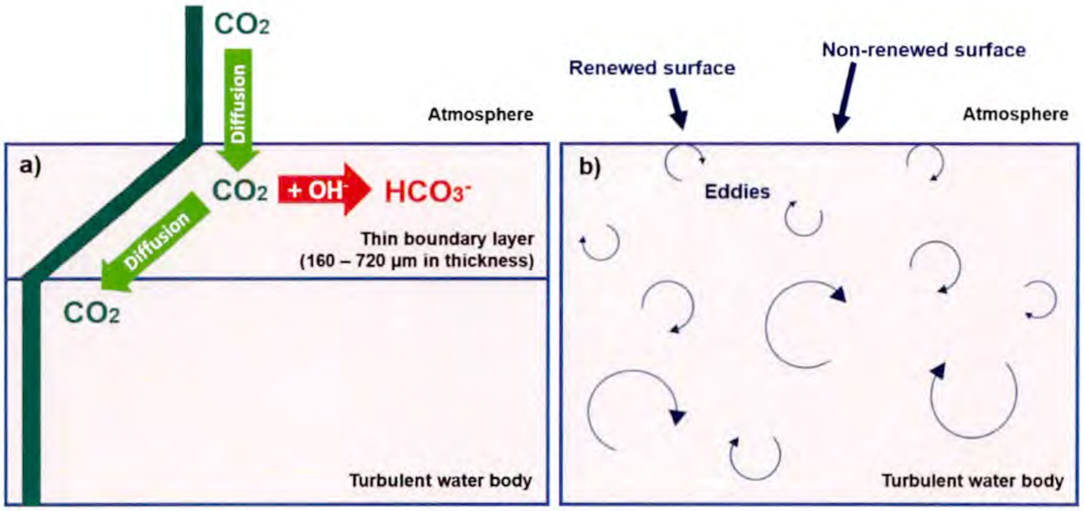

Figure 1. 7 Two different gas exchange models; a) Thin boundary layer model and b) Surface renewal model

A third hypothesis to consider in evaluating the adequacy of the H&B model is whether our reference gas (CH_4) is appropriate as a tracer of a strictly Fickian diffusive process. Recent studies have suggested the existence of CH_4 microbubbles in as diverse systems as boreal lakes and reservoirs (Y. T. Prairie & del Giorgio, 2013), oligotrophic temperate lakes (McGinnis et al., 2015), and mangrove dominated estuaries (Rosentreter et al., 2016). The presence of CH_4 microbubbles would enhance CH_4 flux through a non-Fickian diffusive process and would therefore increase the apparent $k_{600\text{-}CH4}$, thereby possibly confounding our empirical estimates of chemical enhancement. Microbubbles are created at the water surface layer by precipitation, breaking waves derived from strong wind ($U_{10} > 10$ m s^{-1}), or through spontaneous bubble seeding because of high CH_4 supersaturation (Mulhearn, 1981; Y. T. Prairie & del Giorgio, 2013; Vagle et al., 2010). For microbubbles to potentially obscure a chemical enhancement effect would require that they form in the same conditions favouring chemical enhancement, namely high pH and low turbulence. To our knowledge, there is no evidence that microbubble formation is facilitated at high pH. Similarly, all our chamber measurements were performed without rain, and a rare maximum U_{10} of our dataset of 7.7 m s^{-1}. Nevertheless, to explore this potential caveat further, we examined whether our observed $k_{600\text{-}CH4}$ are higher than expected based on the wind-based models of Cole and Caraco (1998) and Vachon and Prairie (2013). At high wind speed ($U_{10} > 3.7$ m s^{-1}), our $k_{600\text{-}CH4}$ values were larger than those predicted from the wind based models, indicating that there could be microbubble-mediated CH_4 flux (Figure 1.8a). However, those observations were not expected to exhibit chemical enhancement (lower pH and thinner TBL). More importantly, at low wind speed ($U_{10} < 3.7$ m s^{-1}) where the boundary layer thickness is larger and chemical enhancement is thus putatively more important according to the H&B model, our $k_{600\text{-}CH4}$ values were entirely consistent with the wind based models (Wilcoxon test, $p = 0.6007$; Figure 1.8a and 1.8b). This result suggests that there is little evidence of microbubble-mediated CH_4 flux in our sampled lakes at low wind speed. We thus conclude that the use of CH_4

as the reference gas is unlikely responsible for the discrepancies between our data and the H&B model.

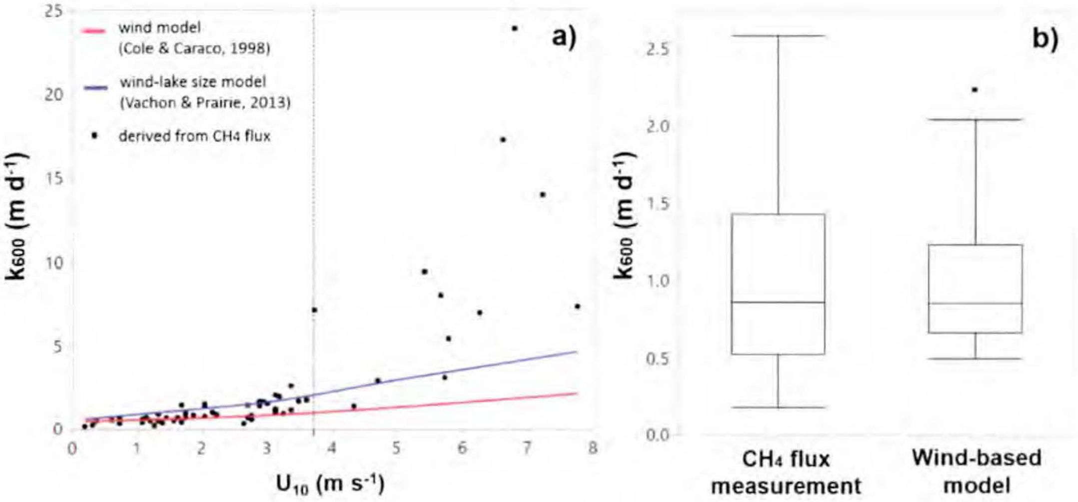

Figure 1. 8 Little evidence of microbubble-effect on $k_{600\text{-}CH_4}$

a) To investigate whether our methane-derived k_{600} (black dots) was affected by microbubbles, we examined how they compared with the k_{600} predicted from the wind (red line) (Jonathan J. Cole & Caraco, 1998) and the wind-lake size relationship (blue line) (Vachon & Prairie, 2013).

b) At low wind speed ($U_{10} < 3.7$ m s^{-1}) where the boundary layer thickness is large and chemical enhancement is thus believed to be important, our $k_{600\text{-}CH_4}$ values were entirely consistent with the wind based models (Wilcoxon test, $p = 0.6007$). These results indicate that there is little evidence of microbubble-mediated CH_4 flux in our sampled lakes at low wind speed.

H&B model and our results could also be attributed to vastly divergent experimental conditions. The H&B model was developed and tested in laboratory tank experiments with distilled water, clearly far from the environmental conditions found in our study lakes. Given that chemical enhancement is the result of the direct hydration of CO_2 with hydroxyl ions to form HCO_3^-, we speculate that the alkalinity of the system (HCO_3^- being the main alkalinity species in our lakes) takes also part in the equilibrium reaction involved in the chemical enhancement. In contrast to distilled water which contains negligible alkalinity, our sampled lakes instead had high alkalinities, ranging from 483 to 1800 μeq L^{-1} (mean = 914, median = 811, and interquartile range = 676 to 1035 μeq L^{-1}). We suggest that H&B model may overestimate α in high alkalinity waters. As evidence, the discrepancy between observed α and H&B α increased with increasing total alkalinity, showing that H&B model overestimate α, especially when the alkalinity value was more than 700 μeq L^{-1} (Figure 1.9). This hypothesis may also explain the results of Bade and Cole (2006) which were more consistent with the H&B model but obtained from a lake with very low alkalinity (less than 140 μeq L^{-1}), further questioning the generality of the H&B model.

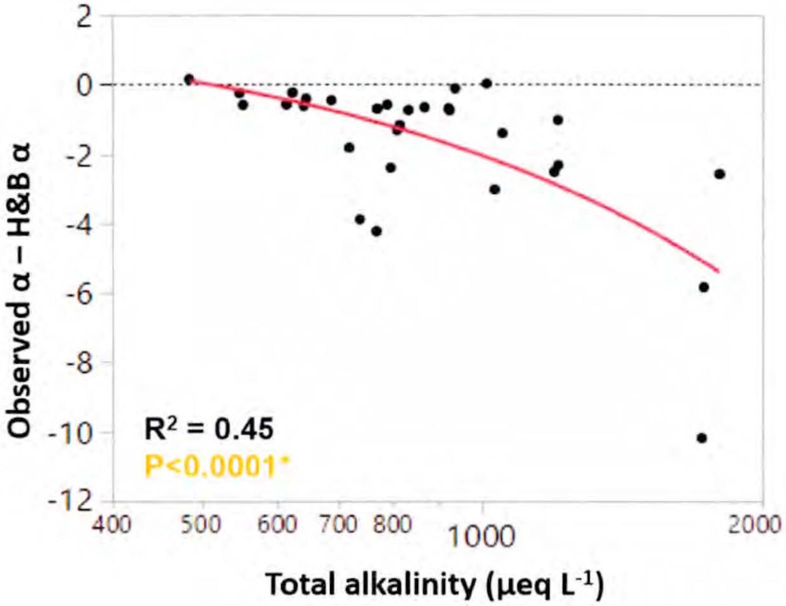

Figure 1. 9 The significant relationship between the total alkalinity of our sampled lakes and the differences between observed α and H&B α

Red line represents regression fit. If the H&B model fits well, dots should be close to the dashed line. Under the very high alkalinity conditions (more than 700 μeq L^{-1}), the observed alpha was much lower than predicted one, indicating that the H&B model is not appropriate in high alkalinity conditions.

1.6 CONCLUSION

In many previous studies, the chemical enhancement of CO_2 exchange described by the theoretical model of Hoover and Berkshire (H&B, 1969) has been widely used to estimate the CO_2 fluxes in aquatic systems. However, the results of a field-based measurements of chemical enhancement factor α suggest instead that the actual contribution of chemical enhancement to CO_2 flux is very small (close to 1), showing large deviations from the H&B α. Our results indicate that the H&B model can overestimate α widely, particularly in high alkalinity waters. Also, we suggest that the discrepancies with our observed α are likely the result of the partially inappropriate assumptions underlying the H&B model, in particular in the depiction of the gas exchange process across the air-water interface. We suggest that the surface renewal model rather than the stagnant boundary layer assumption (required in the H&B model) is more consistent with our empirical results. We expect these results will improve the estimation of gas exchange in eutrophic systems, and have important consequences for the assessment of carbon budgets.

1.7 ACKNOLEDGMENTS

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