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LAKE-ATMOSPHERE GREENHOUSE GAS EXCHANGE IN RELATION TO ATMOSPHERIC FORCING AND LAKE BIO-GEOCHEMISTRY

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Academic dissertation

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There is another important continuum in life besides the one discussed in this thesis: family, friends and colleagues. We have optimal conditions for creative work when these relations are in balance. From work and colleagues we get the input (net carbon uptake), which is then processed with the support of the family (lake biota), and once in a while extreme events shake the whole mess (friends), and the result is the output of this system (see also Fig. 1). For these reasons, the people to thank are too numerous with impacts too wide to discuss here. I feel obliged to specifically thank Anne Ojala for the continuous support and for introducing me to the wonderful people in Timo's group, and Timo Vesala for the outstanding working environment he has created. For all the people not mentioned here by name, I will show my gratitude by supporting you in your own continuum of life in the role that I currently play, whether it be from carbon source to plankton to the mightiest wind.

Lake-atmosphere greenhouse gas exchange in relation to atmospheric forcing and lake biogeochemistry

Jouni Juhana Heiskanen

University of Helsinki, 2015

Abstract

Greenhouse gas (GHG) emissions from lakes result from processes between the watershed, lake characteristics and the atmosphere. The organic matter loading from the watershed both provides carbon for the lake biota and in major part defines water clarity, which, in addition to wind and heat flux, is essential in thermocline formation. Thermal stratification suppresses the wind-induced momentum input to the surface water preventing effective mixing of gases throughout the water column. The lake biota process the organic matter, producing carbon dioxide (CO_2) in oxic surface water and also methane (CH_4) if the near-bottom water becomes anoxic, and thus influence the chemical properties of the water column. Finally, air-water GHG exchange occurs over a thin layer at the water surface.

Lakes are typically supersaturated with CO_2 and CH_4 in relation to average atmospheric mixing ratios causing fluxes of these gases to the atmosphere. Even though lakes cover only 2 % of the world's land surface, it has been estimated that lakes release about 10 % of the carbon fixed annually by the terrestrial ecosystems back to the atmosphere. A critical parameter in the gas exchange estimates is the gas transfer velocity (*k*), which is governed by turbulence. The implementation of direct flux measurement using the eddy covariance (EC) technique allows the detailed measurements needed to estimate *k*. However, on lakes, the EC method is a novel subject and as of yet, there has been no published estimates of the error related to these measurements nor fully established set of accepted procedures.

The aim of this thesis was to assess the current global CO_2 evasion estimates from lakes to the atmosphere by comparing parameterizations for *k* and the significance of wind and heat flux to the gas transfer in small lakes. To improve future predictions of gas evasion from lakes, we focused on the changes in water clarity and how they affect water column physics and processes in the air-water interface. We used the EC method for the high precision data needed, and therefore also aimed to improve the EC methodology on lakes.

The air-water gas transfer was related to both wind and heat loss during times of seasonal stratification, but only to wind during autumn overturn, and the mean value for *k* of CO_2 was 6.0 cm h^{-1} in Lake Kuivajärvi. When wind-induced thermocline tilting and resulting spatial variability in surface water CO_2 concentrations was accounted for, *k* derived from the measurements dropped to 5.2 cm h^{-1}. This was still over twice the estimate (2.2 cm h^{-1}) calculated with a widely used model for *k* in lakes suggesting that the global estimates of gas evasion from lakes might be underestimations. Unsolved question is that how important factor the thermocline tilting is in other lakes in defining spatial variability? Our results showed that *k* for CH_4 was higher than for CO_2, a result which has been reported in some other studies, but as of yet, no solid explanation has been found.

Water clarity was a significant parameter defining the thermal stratification of the lake: a change from clear to dark water would lead to shorter stratification period and lower water column temperatures in small lakes and therefore have significant impact on the lake-atmosphere exchange processes. Important question is how changes is climate will affect lake water clarity e.g. via precipitation and runoff related DOC loading.

We concluded that the EC method produces reliable results even in a small lake after rigorous data processing. After these procedures, about half of the CO_2 and turbulent heat flux data were of good quality with relative random errors of 10 % and 26 % for heat and CO_2 fluxes, respectively.

When measuring GHG fluxes accurately from lakes, methods that integrate over time and space are a necessity. These will provide more detailed knowledge on the complex processes that contribute to the gas transfer, from large scale physical phenomena such as thermocline tilting to small scale such as near-surface turbulence. Since most of the world's lakes are small and in northern latitudes, our studies have wide implications even to the global level. Better understanding of the lake biogeochemistry will allow us to make more accurate estimates of GHG evasion from lakes in different regions as well as predictions of how the climate change will affect the lake-atmosphere GHG fluxes.

Keywords: lake-atmosphere interactions, greenhouse gas flux, heat flux, water clarity, stratification, gas transfer

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List of publications

This thesis consists of an introductory review, followed by four (4) research articles. In the introductory part, these articles are cited according to their roman numerals. The papers are reproduced with the permission of the journals concerned.

I. Heiskanen, J.J., Mammarella, I., Haapanala, S., Pumpanen, J., Vesala, T., MacIntyre, S. and Ojala, A. 2014. Effects of cooling and internal wave motions on gas transfer coefficients in a boreal lake. *Tellus Ser. B-Chem. Phys. Meteorol.*, 66, 22827.

II. Heiskanen, J.J., Mammarella, I., Ojala, A., Stepanenko, V., Erkkilä, K.-M., Miettinen, H., Sandström, H., Eugster, W., Leppäranta, M., Järvinen, H., Vesala, T. and Nordbo, A. Sensitivity of lake-atmosphere heat and momentum fluxes to water clarity. In review in *Journal of Geophysical Research - Atmospheres*.

III. Rantakari, M., Heiskanen, J. J., Mammarella, I., Tulonen, T., Linnaluoma, J., Kankaala, P. and Ojala, A. Different gas exchange coefficients for CO2 and CH4: Evidence of chemical enhancement in regulating gas exchange in circumneutral boreal lakes. In review in *Environmental Science & Technology*.

IV. Mammarella, I. Nordbo, A., Rannik, Ü., Haapanala, S., Levula, J., Laakso, H., Ojala, A., Peltola, O., Heiskanen, J.J., Pumpanen, J. and Vesala, T. Carbon dioxide and energy fluxes over a small boreal lake in Southern Finland. In review in *Journal of Geophysical Research - Biogeosciences*.

1. Introduction

The two most radiatively active carbon trace gases in lakes are carbon dioxide (CO_2) and methane (CH_4), and lakes are typically supersaturated with these gases in regards to the globally averaged atmospheric mixing ratio, resulting in greenhouse gas (GHG) fluxes to the atmosphere (Kling et al., 1992; Cole et al., 1994; Bastviken et al., 2004, **I, III**). Lakes are disproportionately active sites in carbon cycling relative to their surface area (Cole et al., 2007) and with more accurate estimates of their numbers and surface area (Downing et al., 2006), emissions have been found to be significant relative to terrestrial sources and sinks.

Even though lakes cover only 2 % of the land surface (Lehner and Döll, 2004), it has been estimated that they release about 10 % of the carbon fixed annually by the terrestrial ecosystems back to the atmosphere, since the global estimate for the terrestrial (excluding inland waters) uptake of CO_2 is 3.0 ± 0.9 Pg C yr^{-1} (Le Quéré et al., 2009), and the global evasion rate from lakes and reservoirs is now estimated at 0.32 Pg C yr^{-1} (see Raymond et al., 2013). In terms of carbon budget, CH_4 is a minor factor, but when weighted by its global warming potential (GWP), it has been estimated that globally CH_4 emissions from all inland waters are very significant, 0.65 Pg C yr^{-1} when expressed as CO_2 equivalents (Bastviken et al., 2011).

Most of the world's lakes are in the boreal zone (50-75°N), and small lakes are orders of magnitude more abundant than large lakes (Lehner and Döll, 2004; Downing et al., 2006). In Finland > 95 % of the 190 000 lakes have an area < 1 km^2 and in total can cover locally up to 20% of the land area (Raatikainen and Kuusisto, 1990), and thus play an especially important role in regional carbon cycling.

1.1. Land-lake-atmosphere continuum

Lake, surrounding landscape and the atmosphere form a continuum where each component interacts with each other (Fig. 1). Catchment area governs some of the fundamental properties of the lake: water balance, inflow of carbon and nutrients, and water clarity. Lake morphometry defines the area of littoral and pelagic zone and thus have essential effects on carbon and nutrient cycling within the lake (Wetzel, 2001). The ratio of catchment area to lake area (CA:LA) can be used to roughly estimate the importance of the catchment area to the lake in general.

Incoming solar radiation is absorbed in the water column resulting in thermal stratification – a process where water clarity has a key role as it governs the rate of light extinction (**II**). Wind-caused momentum flux to the lake then modifies the thermal stratification so that typically distinct regions of different properties are formed along the water column: mixing layer on the top (epilimnion), near-bottom layer (hypolimnion) where the waters are relatively stagnant and then a thermocline between these two layers, where there is a strong temperature and thus density gradient separating epilimnion and hypolimnion from each other (Wetzel, 2001). All these factors form a complex system producing the conditions to which the lake biota must adjust.

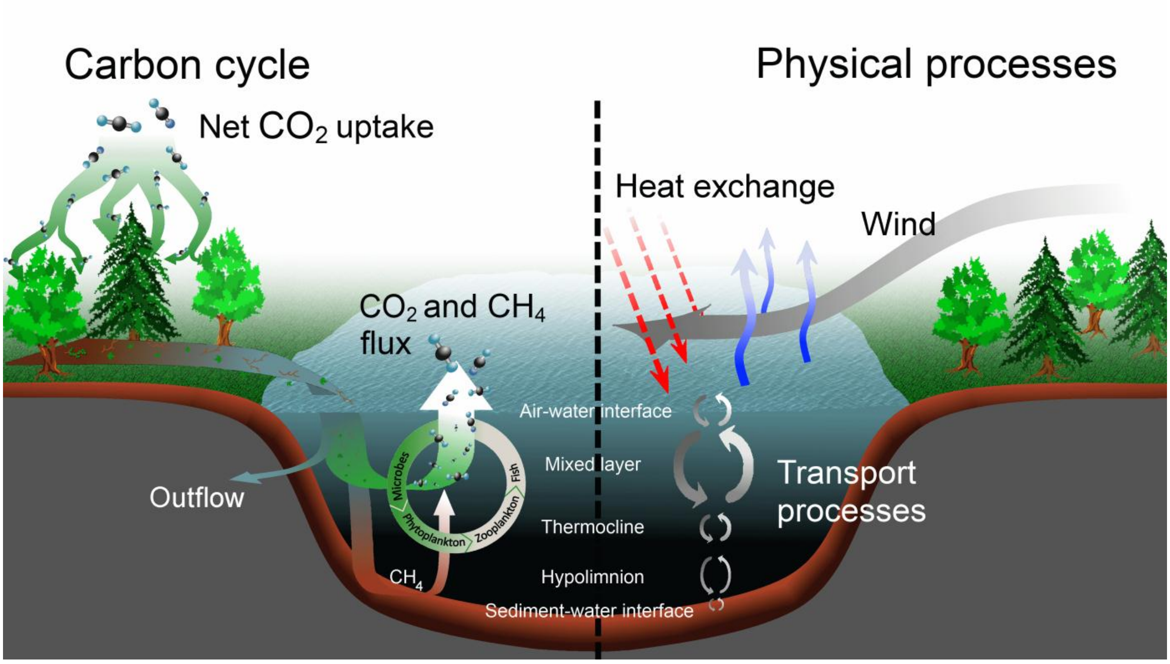

Figure 1. Left side: carbon cycle (storage changes omitted) in atmosphere-forest-lake continuum. The net CO_2 uptake of plants is accumulated as biomass. Dead plant matter and dissolved organic matter (DOM) are transported laterally via rivers and streams to a lake, where some of the matter is further processed by the lake biota. Resulting CO_2 and CH_4 are vertically transported to the air-water interface, where, in case of supersaturation, outgassing occurs. Some of the carbon exits the lake via riverine outflow. Right side: atmospheric forcing over a lake and molecular as well as turbulent transport between the different water layers. During summer, heat gain (red downward arrows) increases the water column stratification whereas wind and heat loss (blue upward arrows) feeds the kinetic energy of the water column, causing turbulent mixing of the water and dissolved gases. The external energy input is dissipated deeper in the lake resulting in calm waters and lower turbulent diffusivity.

On the other hand, the lake biota influences the water chemistry via their metabolism, in which they process the available carbon and produce the emitted greenhouse gases (GHG). Small lakes are hotspots of biogeochemical cycling due to many factors, such as high biological activity and high surface water CO_2 and dissolved organic carbon (DOC) concentrations (Cole et al., 2007; Tranvik et al., 2009; Downing, 2010). The carbon cycle is connected to the thermal cycle of lakes (White et al., 2012), and heat flux into a lake system increases CH_4 flux to the atmosphere (Wik et al., 2014), since stronger stratification increases the oxygen depletion in near-bottom waters which through higher sediment temperatures enhances the production rate of CH_4 (Schulz et al., 1997). Besides the connection to surface temperature and heat budgets, water clarity is connected to GHG budgets via the effect of heat flux to gas transfer (**I, IV**).

Lakes actively interact with their environment via lake-atmosphere interactions (**II**). Lakes have lower albedo, lower surface roughness and greater effective heat capacity than surrounding land areas (e.g. Beyrich et al. 2006). These properties affect weather and climate through changes in surface energy budgets at different spatio-temporal scales (Balsamo et al. 2012; Dutra et al. 2010). Advancing our understanding on physical processes controlling turbulent exchange of energy, water vapour, CO_2 and other trace gases over lacustrine systems is crucial in order to improve climate and weather forecast models (**II**).

For sparingly soluble gases, the thin aquatic mass boundary layer forms the bottleneck for gas transfer at air-water interface (Jähne et al., 1987). The surface water CO_2 concentrations (or related parameters) have been measured from many lakes around the world (Sobek et al., 2005), but for the gas transfer velocity across this boundary layer usually simple regression equations or a global average has been used in lack of proper parameterization in lake environments (Cole et al., 2007; Raymond et al., 2013, **I**). It is known that wind is a crucial driver of gas exchange, but also heat loss seems to enhance gas transfer, even in oceanic conditions with unlimited fetch (Rutgersson et al., 2011). Recent studies have demonstrated that on small lakes, which are shielded from wind by the surrounding forested landscape, heat flux can be the dominant driver (Read et al., 2012). With respect to gas transfer, wind and heat flux form complex interrelations, which might further be augmented by chemical reactions, and to parameterize these correctly, both accurate and continuous measurements of related constituents and improved understanding of the associated physical processes are a necessity (**I, III, IV**).

Direct and continuous flux measurements using the eddy covariance (EC) technique have been routinely implemented to measure e.g. net ecosystem exchange (NEE) and heat and momentum fluxes above terrestrial ecosystems with hundreds of EC sites around the world (Baldocchi, 2008). For ideal locations, these provide relative accurate (systematic error ~10% and random error ~5%) measurements that integrate over the landscape (Baldocchi, 2008), and the methodology has been thoroughly discussed which has produced commonly accepted procedures (Aubinet et al., 2012). Over lakes, the fluxes of gases have traditionally been measured by using spot measurements with flux chambers or they have been estimated from gas transfer models. The implementation of the EC method over lakes is a relatively novel subject as of yet, there are no published estimates of the error related to these measurements nor fully established set of accepted procedures on these non-ideal locations (**IV**).

1.1.1. Lateral transport and water clarity

In the boreal zone with vast stocks of organic carbon and thus humus in the soil, rivers and streams transport dissolved organic matter (DOM) of terrestrial origin to lakes in great quantities. DOC is the major element in DOM, and the carbon loading to lakes is mostly related to precipitation but also to NEE and litter fall of the previous year (Pumpanen et al., 2014). Typically, the highest loading occurs during spring snow meltdown, but strong rain events even in summer can result in increased DOC loading from the catchment area (e.g. Ojala et al., 2011). Majority of this DOM is colored (CDOM), which to a large extend defines the water clarity – the more CDOM the lower the water clarity (Fee et al., 1996; Pace and Cole, 2002; Arst et al., 2008). On the other hand, suspended particles, such as sediment or plankton affect visibility (Fee et al., 1996). Therefore, turbulence which affects the sedimentation rate of suspended particles (Ji, 2008) can affect the water clarity, as well as the yearly succession of plankton species (Jeppesen et al., 1999). Visibility and turbulence affect also zooplankton and fish (Härkönen et al., 2014), but zooplankton can increase visibility via grazing on phytoplankton (Jeppesen et al., 1999).

1.1.2. Water clarity and thermal stratification

Water clarity is essential in thermal stratification since it affects the scattering and absorption of radiation in the water column (Fig. 2). A low-clarity lake acts partly as a shallow lake since solar radiation is absorbed and immediately stored into the top layer. The epilimnion is shallower than in a clear water lake, and the surface temperature is higher in spring and lower in autumn when cool water from the hypolimnion is mixed into the warmer epilimnion (Persson and Jones, 2008, **II**). The increased spring surface temperatures are counteracted by increased heat loss via turbulent fluxes of sensible (*H*) and latent heat (*LE*) in addition to longwave radiative cooling (Persson and Jones, 2008).

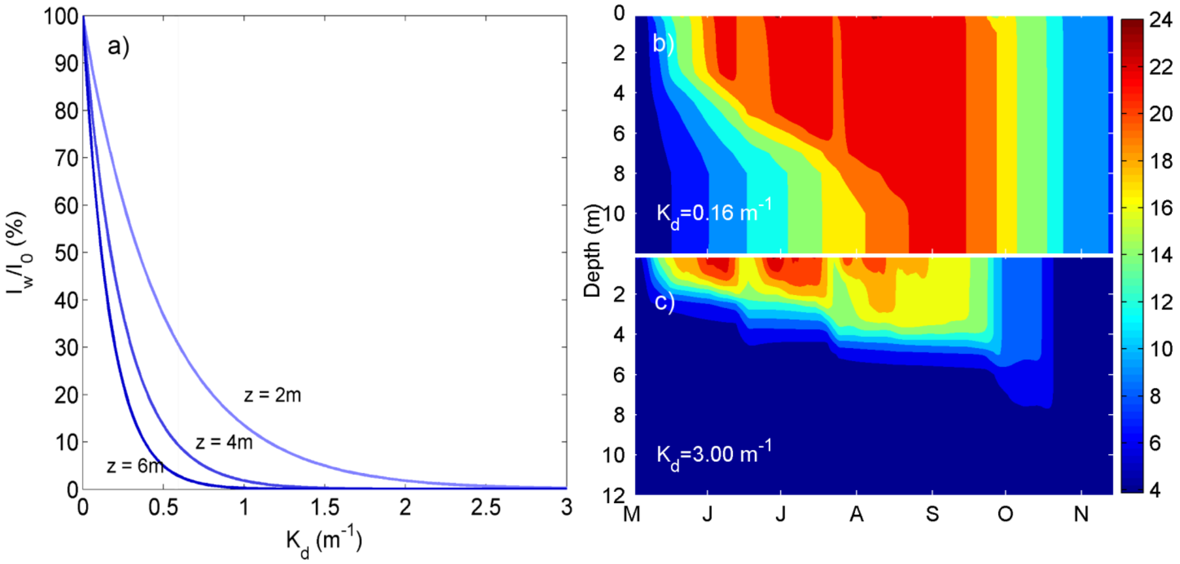

Figure 2. (a) The percentage of incoming shortwave radiation penetrating the thermocline (calculated according to Beer-Lambert law) as a function of light extinction coefficient, K_d (m^{-1}), with different thermocline depths (z, blue lines). (b) The modeled time-depth-temperature data in Lake Kuivajärvi with K_d = 0.16 m^{-1} and (c) with K_d = 3.00 m^{-1}.

Water clarity is expected to influence mixed layer depth of small lakes more than of deep lakes since in small lakes the wind and wave driven turbulent mixing is weaker due to shorter fetch and thus lower wind speed. Some studies show that water clarity affects the mixed layer depth only on small lakes (Fee et al., 1996), whereas others show that even in the biggest lakes water clarity cannot be neglected (Thiery et al., 2014). The sensitivity of mixed layer models to the water clarity was examined in the 1970s (see Niiler and Kraus, 1977). More recently, this problem has been revisited for the sensitivity of lake models to DOC or water clarity, parameterized via the light extinction coefficient, K_d (Perroud and Goyette, 2010; Potes et al., 2012; Read and Rose, 2013). These studies tested the sensitivity of the chosen model to water clarity with two clarity values, but none of these studies had direct flux measurements for validation of simulation results. K_d tells how the shortwave radiative energy is absorbed within the lake water body as a function of depth. This coefficient is an apparent optical property which depends on the properties of lake water and the illumination conditions (e.g. solar zenith angle and cloudiness). K_d is known to vary more between lakes than seasonally within one lake (Arst et al., 2008).

Lakes impact regional weather in lake–abundant areas, and consequently lake subroutines have recently been implemented in numerical weather prediction (NWP) models, leading to improved forecast skills (e.g., Balsamo et al., 2012). Global data on lake coverage and depth are essential for lake subroutines and these data have been created recently (Kourzeneva et al., 2012). However, the importance of in-lake characteristics such as water clarity to lake-atmosphere interactions has not yet been thoroughly investigated (**II**). Since global data on water clarity are not yet available, a global constant value is usually used in the models (Balsamo et al., 2012).

1.1.3. Vertical transport of gases within the water column

During overturns the whole water column is mixing and thus the possibly accumulated gases in the hypolimnion reach the surface, leading to high surface water concentrations and gas effluxes. During summer, stratification ensues and the thermocline acts as a strong barrier between the mixing layer and hypolimnion, preventing both the oxidation of hypolimnetic waters and release of accumulated gas from the hypolimnion to the mixing layer (**I**). Consequently, three physical factors dominate the vertical transport of gases: entrainment of CO_2 and CH_4 from the hypolimnion, the turbulent transport of CO_2 and CH_4 in the mixed layer and the exchange of these gases through the air-water interface. All these factors are related to wind forcing and heat flux (**I**).

Entrainment can occur via thermocline tilting and resulting breaking of internal waves or via convection due to heat loss. Thermocline tilting takes place when wind forcing is strong enough to press the surface water masses to one end of the lake or the other. The presence of tilting can be predicted from the Wedderburn number which is a dimensionless ratio of the density stratification to the wind forcing and fetch, $W = \frac{\Delta\rho g h^2}{\rho_0 L u_{*w}^2}$, where $\Delta\rho$ is the water density difference between the epilimnion and the hypolimnion, ρ_0 the mean density of the water column, g the acceleration due to gravity, h the depth of the epilimnion, L the length of the lake and u_{*w} the friction velocity in the surface water. During strong winds, the wind forcing can be high enough to mix hypolimnetic water to the epilimnion (Monismith 1985; MacIntyre et al., 1999; Horn et al., 2001; Boegman et al., 2005, **I**).

When the air is cooler than the lake, the surface water loses heat and becomes heavier than the underlying water masses. This causes convection in the mixed layer, and if the cooling is strong enough, these convective cells can reach the thermocline. When thermocline tilting occurs simultaneously with convection, high concentrations of dissolved gases can reach the surface (Crill et al., 1988; Eugster et al., 2003).

1.1.4. Diffusive gas exchange at air-water interface

The air-water gas exchange is limited by the very thin (<1 mm) top layer of water (Fig. 3), through which the gases must travel by molecular diffusion (Jähne and Haußecker, 1998), and the processes which affect this layer control the gas transfer. The efficiency of this transfer is usually described via the gas transfer velocity, *k*, which is known to be mediated by turbulence (Zappa et al., 2007; MacIntyre et al., 2010; Vachon et al., 2010). The diffusive gas flux, *F*, due to concentration gradient between the surface water and the atmosphere is parameterized as (Cole and Caraco, 1998):

$$F=\alpha k(c_{aq} - c_{eq}), \qquad (1)$$

where α is the chemical enhancement factor, c_{aq} and c_{eq} the concentrations of the given gas in the surface water and when in equilibrium between the air and water, respectively.

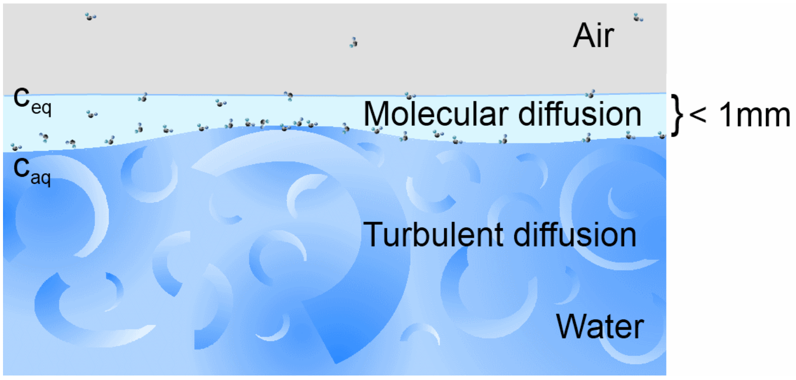

Figure 3. The surface layer of the water column. The gases are transported by turbulent eddies in the mixed layer, and the resulting concentration near the air-water interface is referred as surface water concentration of the given gas, c_{aq}. Between the surface water and the atmosphere there is a thin layer, through which the gases travel by molecular diffusion. At the air-water interface, the gas is in equilibrium concentration, c_{eq}. Also the effect of a more intensive turbulent eddy suppressing the mass boundary layer is depicted in the center of the figure. Note that layers of molecular and turbulent diffusion also exist on the atmosphere side of the interface.

Several mechanisms affect the gas exchange, i.e. factors common to the exchange of all sparingly soluble gases, such as wind and heat loss induced turbulence and wave breaking, as well as gas-specific factors such as chemical enhancement (CO_2) and possibly microbubbles (CH_4) (**I,III, IV**). The relationship between wind speed and *k* has been most intensely studied in oceans and it has been shown that especially at strong winds, wind dominates the gas transfer and that the relation is roughly cubic (Wanninkhof et al., 2009). The most common approach on lakes has been the use of the regression equation proposed by Cole and Caraco (1998):

$$k = 2.07 + 0.215U_{10}^{1.7}, \quad (2)$$

where U_{10} is the wind speed at 10 m height.

The effect of wind speed and heat flux on k can be parameterized as aquatic velocity scales (water friction velocity and penetrative convection velocity, respectively), which can either be used in the models as such or further via their connection to dissipation of turbulent kinetic energy, ε, as is in the surface renewal model (Zappa et al., 2007; MacIntyre et al., 2010):

$$k = c(\varepsilon v)^{0.25}Sc^{-1/2}, \quad (3)$$

where c is a constant, v the kinematic viscosity and Sc the Schmidt number. In **I** and MacIntyre et al. (2010), ε was parameterized via water friction velocity and buoyancy flux. There have also been some attempts to parameterize the suppression of turbulence due to heating-induced stratification (MacIntyre et al., 2010).

CH_4 can be considered as an inert gas, but CO_2 has chemical reactions in water according to pH (**III**). pH governs how much of the CO_2 is in dissolved gaseous form and how much is further hydrated to bicarbonate and carbonic acid (Bolin, 1960). In lakes with high pH and the water unsaturated with CO_2, chemical enhancement should be accounted for, but typically it has small effect on the air-water gas transfer of CO_2 in circumneutral (pH~7) lakes (see Cole and Caraco, 1998, and references therein). In this study, aquatic saturation levels are compared to the ambient atmospheric concentrations unless specified otherwise.

1.2. Eddy covariance technique

In the atmosphere, gases are transported by turbulent eddies. When the horizontal and vertical wind components of the eddies are recorded simultaneously with transported concentrations, such as CO_2, the scalar fluxes, F_s, can be calculated (see e.g. Vesala et al., 2006):

$$F_s = \rho\overline{s'w'}, \quad (4)$$

where ρ is the density of dry air, s' and w' the momentary deviations from the time-averaged (typically 30 min) values of the mixing ratio (of e.g. CO_2) and vertical wind component, respectively. The product of s' and w' is time-averaged (denoted by the overline), and the resulting fluxes are presented as half-hourly values in this study. This is called the eddy covariance (EC) technique. In a similar way, the turbulent heat fluxes and momentum flux can be acquired from the EC measurements (Vesala et al., 2006). Due to the wide size range of turbulent eddies, this requires extensive temporal resolution, i.e. high frequency measurements over long time periods.

The EC technique is widely used for continuous and long-term monitoring of energy and gas exchange between land ecosystems (forest, wetland, arable land, grassland) and atmosphere (Baldocchi, 2003). The implementation of EC method on lakes is a relatively new subject and at the moment there is no network of long term lacustrine EC sites covering different latitude and climatic zones, and lake characteristics. The novelty of this method and the fact that lake EC studies are scarce implies that the methodology is still evolving and there is need to focus on methodological issues (**I,IV**). EC measurements have to undergo laborious processing for evaluating the EC system performance and calculating turbulent fluxes. In addition, data quality control, filtering criteria and flux uncertainty may depend on site characteristics and atmospheric turbulence peculiarities (Vickers et al. 2010; Nordbo et al. 2012). So far, none of the lake studies have reported the random errors associated with the EC fluxes (**IV**).

For almost 20 years, to put emissions from lakes into the context of regional carbon budgets, computations have been based either on a conservative value of *k* or one based on wind speed (Cole and Caraco, 1998). Use of EC has led to upward predictions of gas evasion (Jonsson et al., 2008) relative to Cole and Caraco (1998), and some studies indicate that fluxes are enhanced when the lake is heating (McGillis et al., 2004) and others when it is cooling (MacIntyre et al., 2010).

1.3. Aims and research questions

This thesis addresses some of the challenges related to air-water gas exchange parameterizations and measurements with the hypothesis that in-lake physics and water clarity are essential factors in the lake-atmosphere GHG fluxes.

The aim of this thesis was to assess the importance of water clarity to lake-atmosphere interactions, the role of momentum and heat fluxes in lake-atmosphere gas fluxes, to investigate the differences between the gas transfer velocities of CO_2 and CH_4 and to assess the applicability of and provide new insights on the EC methodology on lakes. **The important research questions were**:

i. how important driver is the water clarity for lake-atmosphere interactions and should it be parameterized both in time and space (**II**);
ii. what is the relative importance of wind speed and heat flux to gas flux in small lakes (**I,IV**);
iii. is the spatial variability of gas concentrations in the surface water so large that it should be accounted for when estimating gas transfer velocity from EC measurements (**I**);
iv. does chemical enhancement affect the emissions of CO_2 in circumneutral lakes and can the gas transfer velocity of CO_2 be used to estimate that of CH_4 (**III**);
v. how large is the flux random uncertainty when the EC method is applied on lakes, and what is the energy balance closure in a small lake (**IV**)

2. Material and methods

2.1. Study sites and measurements

2.1.1. Lake Kuivajärvi

The studies which required continuous measurements and EC method were conducted in the same lake (**I,II,IV**). The humic Lake Kuivajärvi (61˚50' N, 24˚17' E) near Hyytiälä (Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR) II), Finland, has been chosen as part of the ICOS (Integrated Carbon Observation System) measuring network since it is a typical small boreal lake and the carbon and energy exchange between the surrounding forest and atmosphere at the site has been intensively studied (e.g. Kolari et al., 2009; Launiainen, 2010). The lake has an area of 0.64 km^2 and the catchment area consists of managed forest. Lake Kuivajärvi is a long and narrow north–south-oriented lake with two distinct basins. The deeper south basin, on which the measurement platform is located, reaches a maximum depth of 13.2 m, and the littoral zone is very narrow with only sparse aquatic vegetation. The measurement platform is placed in Lake Kuivajärvi so that the fetch is longest at the platform when the wind blows from 320° – 350°, approximately 1.8 km, or from 130° – 180°, approximately 0.8 km. From other directions the fetch is only 0.4 km at maximum (**I**). Lake Kuivajärvi is a significant source of CO_2 but only a minor source of CH_4 and nitrous oxide (N_2O) (Miettinen et al., 2014).

The EC measuring system was placed on the platform (Fig. 4), and it provided the turbulent fluxes of momentum, heat, water vapor and CO_2. Auxiliary measurements included radiation components (also above and below water PAR), platform tilting and water temperature and CO_2 profile. Also the light attenuation was measured campaign-wise. Measurements on the lake have been ongoing since 2009, but the data used in **I** were from 2011, in **II** from 2011 and 2013, and in **IV** from 2010-2011. Only open-water periods (usually May-Nov) were used.

Figure 4. Photograph of the measurement platform on Lake Kuivajärvi. Photo courtesy of Juho Aalto.

2.1.2. Lakes Pääjärvi and Ormajärvi

The data collection in **III** was conducted in two different lakes 5 km apart, humic Lake Pääjärvi (area 13.4 km^2 and max. depth 87 m) and Lake Ormajärvi (6.53 km^2 and max. depth 30 m) which is a clear-water lake. Both lakes are in southern Finland and the catchments are similar in respect to land use with some differences in the proportion of peatlands and urban settlements and in soil types. Lake Ormajärvi is more productive and has higher concentrations of phytoplankton and phosphorus than Lake Pääjärvi.

To define the differences in k between CO_2 and CH_4, we used a chamber technique (Kankaala et al. 2006). The samples were taken from the middle of the lake in both lakes. The samples for the concentrations of CO_2 and CH_4 in the surface water (c_{CO2}, c_{CH4}) were taken with a Limnos water sampler from the surface using a headspace extraction technique (Ojala et al., 2011). The samples were analyzed with a gas chromatograph, and from the results the gas transfer velocities were calculated by inverting Eq 1. Both lakes were sampled weekly in 2004.

2.2. Lake models

In **II**, the chosen lake models were the multilayer model LAKE (Stepanenko et al., 2011) and the model FLake, which assumes a parameterized non-dimensional temperature profile (Mironov et al., 2010; Kirillin et al., 2011). The LAKE model treats the water column through multiple layers, and it is thus computationally more expensive than the FLake model, but predicts the water temperature evolution more accurately.

The meteorological forcing variables of the models are air temperature, wind speed, specific humidity, incoming shortwave and longwave radiation and air pressure. LAKE additionally uses wind direction and precipitation, and water inflows and outflows are dynamically adjusted to keep the lake water level nearly constant.

2.3. Gas transfer models

In **I**, we derived a new model, based on boundary layer theory (see the details in **I**):

$$k = \sqrt{(C_1 U)^2 + (C_2 w_*)^2} Sc^{-\frac{1}{2}}, \tag{5}$$

where U is the wind speed. The dimensionless constants C_1 and C_2 were fitted to the data and the penetrative convective velocity, w_*, was estimated according to Imberger (1985). This model accounts both wind speed and heat loss and is independent of the empiricism inherent in applications of the surface renewal model currently relying on similarity scaling from ocean sites for estimates of turbulence (Eugster et al., 2003; MacIntyre et al., 2010; Read et al., 2012).

The calculated k from EC and water surface measurements (by inverting Eq. 1, $k = F/(c_{aq}-c_{eq})$) was compared to the performance of the new model (Eq. 5) and to the results given by Eqs. 2 and 3. All models were fitted to the *in situ* temperature with the Schmidt number correction (Jähne et al., 1987).

3. Results

3.1. Water clarity, thermal stratification and lake-atmosphere interactions

The median value for K_d in Lake Kuivajärvi was 0.59 m^{-1} and it was lowest during spring and autumn overturns, ~0.5 m^{-1}, and highest in midsummer, ~0.7 m^{-1} (Fig. 4 in **II**). DOC concentration was high, > 10 mg l^{-1}, all the time. The data suggest that DOC defined the general level of K_d, whereas the yearly succession of phytoplankton may have been behind the small, but visible intra-annual pattern in K_d.

According to the model runs, the thermocline depth strongly depended on K_d, the difference between the simulations with the clearest (K_d = 0.01) and darkest water (K_d = 3.00) was as high as 4 m before autumn turnover in Lake Kuivajärvi (Fig. 5).

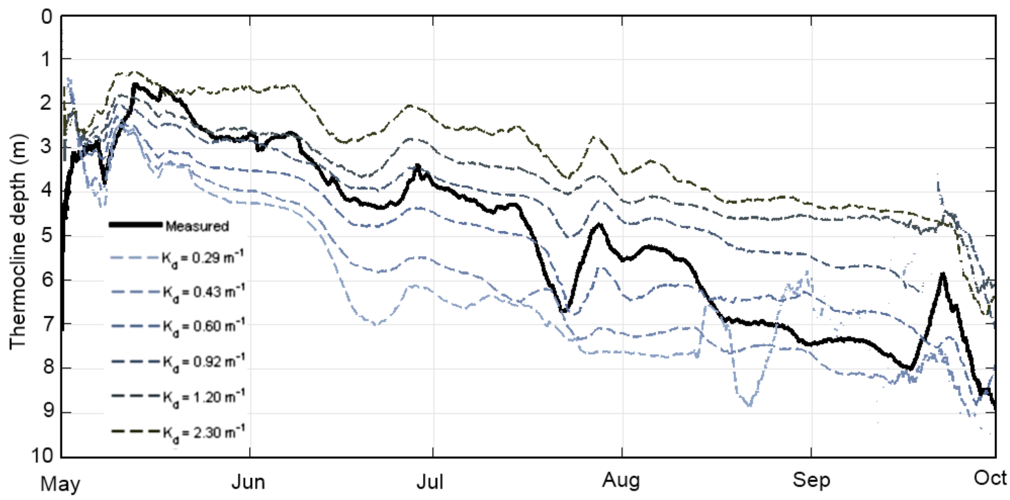

Figure 5. The measured thermocline (Lake Kuivajärvi, K_d = 0.59 m^{-1}) and modeled ones with varying K_d.

Water clarity also had an impact on the atmospheric turbulent fluxes of heat and momentum via its effect on surface water temperature. When the water was too clear (low K_d) in the simulations, surface water temperatures remained low in the spring and were higher in the autumn. Too high K_d had the opposite effect: if K_d was increased by 25%, in the end of the simulations the epilimnion was almost 0.7°C and the surface water around 0.3°C colder. This is reasonable since in both cases (clear or dark water) the same amount of incoming solar radiation is absorbed to the water column, but in the case of dark water more of the incoming radiation is trapped to the epilimnion thus heating it more than in the case of clear water. When K_d was increased by 25%, both turbulent fluxes increased: *H* by 3.4% (FLake) and 1.6% (LAKE) whereas *LE* increased by 4.0% and 2.3%, respectively. Thus, for a dark water lake, higher surface water temperature led to stronger longwave cooling and turbulent fluxes, and the seasonally averaged temperatures of the whole water column remained lower than for a clear water lake.

We also conducted a simulation with 30-minute averaged measured K_d and compared it with a constant K_d. Both produced very similar results. There was no detectable seasonal difference either and turbulent fluxes were not significantly affected.

3.2. The differences between the gas transfer velocities of CO_2 and CH_4

Both Lake Pääjärvi and Lake Ormajärvi were supersaturated with CH_4 and the seasonally averaged gas transfer velocity for CH_4 (k_{CH4}) was equal for the lakes (**III**). The gas transfer velocity of CO_2 (k_{CO2}) was also similar between the lakes when there was excess CO_2 in the water, but during high primary production Lake Ormajärvi was a sink of CO_2 and the gas transfer velocity into the lake was significantly higher than during CO_2 efflux. Moreover, the k_{CH4} values were on average 2.0 times higher than the k_{CO2} (Fig. 6). We expect the effect of chemical enhancement during the chamber incubation and sample extraction to be negligible since the sample volume is small compared to the chamber volume and thus the results to be reliable.

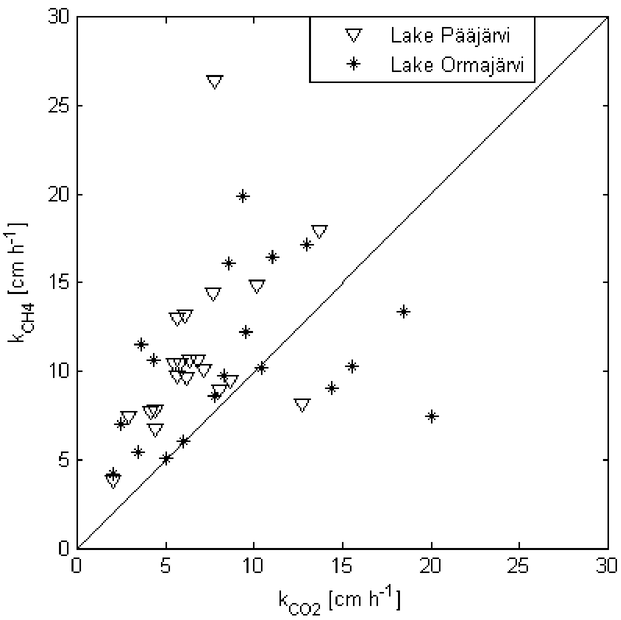

Figure 6. Relationship between k_{CO2} and k_{CH4} for Lake Pääjärvi and Lake Ormajärvi.

In Lake Pääjärvi, the surface-water pH range was 7.2 – 7.6, and in Lake Ormajärvi 7.5 – 8.0. Surface water in Lake Pääjärvi ranged from slight subsaturation of CO_2 (saturation ratio, i.e. surface water gas concentration to equilibrium concentration, of 0.86) to high supersaturation (saturation ratio of 3.7), whereas the saturation ratio varied between 0.64 and 3.3 in Lake Ormajärvi. Both lakes were always supersaturated by CH_4, the saturation ratios being on average 14 and 24 in Lake Pääjärvi and in Lake Ormajärvi, respectively. The amount of CH_4 are high enough in the sediments to form macrobubbles but these are probably dissolved in the water column and not confounding the measurements according to the good fit (r^2>0.9) of the linear regressions to the head-space sampled concentrations. In general, we measured high fluxes of CH_4 when the concentration gradient of CH_4 between the atmosphere and surface water was high, but we did not find a significant relationship between the supersaturation ratio of CH_4 and k_{CH4}, suggesting that high supersaturation did not contribute to high k_{CH4} values.

3.3. Wind, heat flux and gas transfer velocity

The gas transfer velocity of CO_2 was related to both wind and heat loss during seasonal stratification (i.e. summer) in Lake Kuivajärvi, and k_{600} (k after Schmidt number normalization) was relatively high, ~7 cm h^{-1}. In the autumn, when the temperature gradient between the atmosphere and lake decreased and the wind started to be the only driver of gas transfer, k_{600} was on average smaller, ~5 cm h^{-1} (Fig. 7).

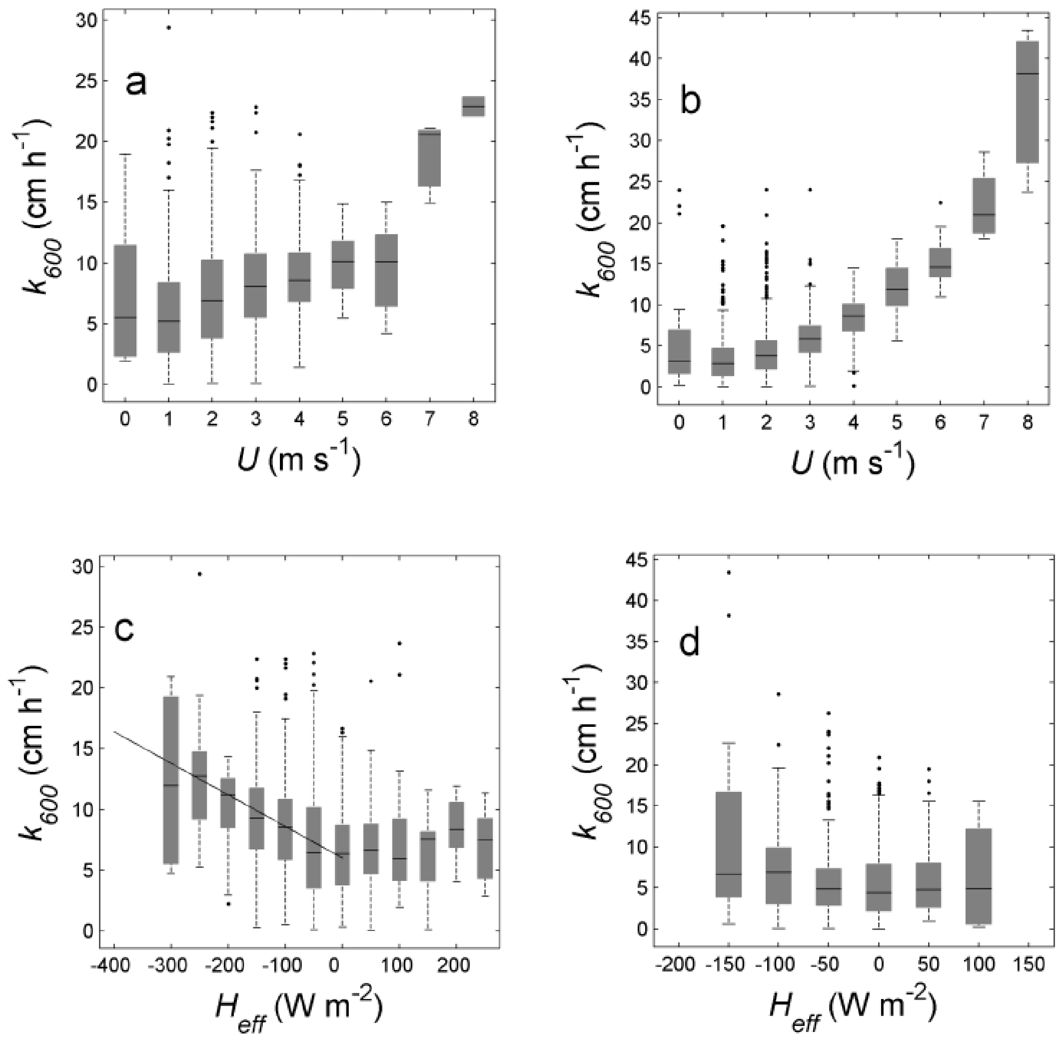

Figure 7. The k_{600} (cm h^{-1}) plotted against wind speed (m s^{-1}) during (a) seasonal stratification and (b) autumn overturn, and against the effective heat flux, H_{eff} (W m^{-2}), during (c)

seasonal stratification and (d) autumn overturn. H_{eff} is the sum of latent and sensible heat flux, net longwave radiation and the portion of the shortwave radiation which is trapped to the mixing layer (Imberger, 1985).The central black line of the box is the median, the edges of the box the 25th and 75th percentiles, the whiskers show the extreme values (±2.7σ) and the black dots are remaining outliers. In (a) and (b), the data was binned by wind speed, every 1 m s^{-1}, and the bins from 0 to 8 contain about 300, 800, 600, 400, 200, 100, 30, 10 and 5 data points, respectively. In (c) and (d), the data were binned by heat flux, every 50 W m^{-2}. The bins from -300 to 250 in (c) contain about 10, 20, 50, 200, 400, 400, 200, 100, 50, 20, 10 and 10 data points, respectively, and the bins from -150 to 100 in (d) contain about 50, 200, 500, 900, 100 and 10 data points, respectively.

We estimated the impact of spatial variability in surface water CO_2 concentration, due to wind-induced thermocline tilting (parameterized via the Wedderburn number), to the k derived from the direct measurements (Fig. 8). For partial upwelling with cooling either during or after the event, convection would mix water with higher CO_2 concentrations into the upper mixed layer. For this purpose, we derived an equation which predicts the depth, z_E, where E denotes for entrainment, from which the CO_2 might reach the surface:

$$z_E = \frac{h_1}{W} + z_{AML} \,, \tag{6}$$

where h_1/W is the maximum thermocline displacement (Monismith 1986; Horn et al. 2001) and z_{AML} the depth of the actively mixing layer (in our study, the depth within the upper water column where the temperature was within 0.25 °C of the surface temperature). When the spatial variability in surface water CO_2 concentrations were accordingly accounted for in the estimates of k from the EC measurements in the CO_2 supersaturated lake, the mean gas transfer velocity was 5.2 cm h^{-1}. This is over 10 % lower than when the spot measurements of surface CO_2 concentrations were used in k estimations (mean k=6.0 cm h^{-1}) and most of the unrealistically high values were dropped to values reasonable at current conditions.

Compared even to the corrected estimate for k, the gas transfer velocity estimated with the widely used equation (mean value 2.2 cm h^{-1}, Cole and Caraco, 1998) highly underestimated the actual k. We also noticed that the stronger the convection the more the fluxes calculated with the equation by Cole and Caraco (1998) deviated from the measured fluxes (Fig. 10 in **IV**).

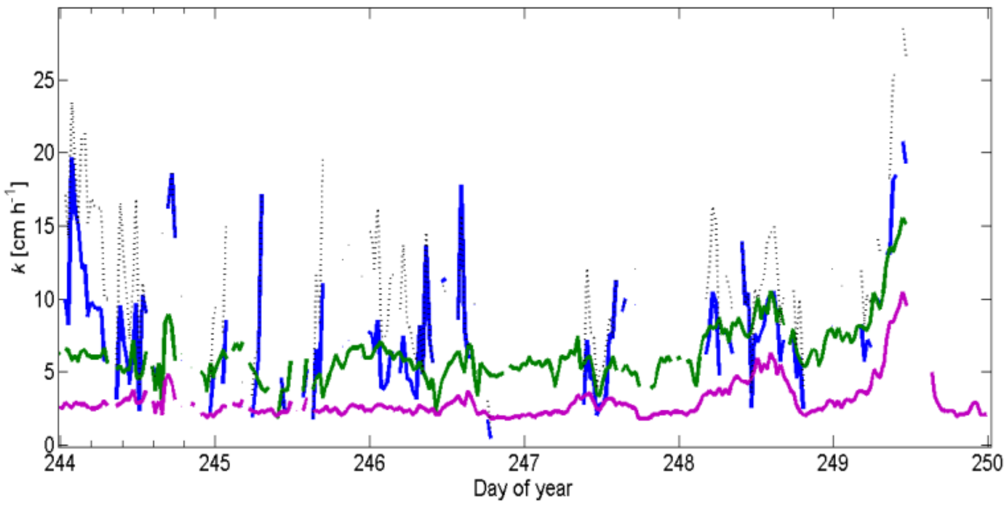

Figure 8. An example period of the *k* derived from measurements (dotted line), spatial-variability-corrected *k* (blue), the *k* used in global estimates (purple, Cole and Caraco, 1998), and the new model for *k* (green, **I**) in Lake Kuivajärvi in 2011. The surface renewal model (Eq. 3) performed very similarly to the new model and therefore is not shown.

3.4. Quality control and error estimates of EC fluxes

Due to the low measurement height (1.7 m) the footprint was small – average source area contributing to 80% of the flux ranged from 100 m in slightly unstable conditions up to about 300 m in near-neutral conditions (Fig. 1 in **IV**) – which ensured that the fluxes were measured from the lake as opposed to the surrounding vegetation. The atmosphere was never strongly stably stratified over Lake Kuivajärvi, which would have extended the footprint. In late afternoon, when *H* was smallest, the atmosphere was typically near-neutrally stratified and when upward *H* peaked during night, the atmosphere was unstably stratified.

Due to strict quality criteria (according to stationarity, skewness and curtosis, flux steady test, wind direction), the overall data coverage for CO_2 and fluxes of *H* and *LE* during the selected period was 37%, 63% and 53%, respectively (**IV**). The relative random errors associated to CO_2 fluxes (average value equal to 26%) were larger than those for *H* and *LE* (10% and 11%, respectively).

The energy balance closure (*EBC*) ranged from 70% to 99% depending on the season, the averaged values being 83% and 79% for 2010 and 2011, respectively (**IV**).

4. Discussion and conclusions

Since thermocline depth depended strongly on K_d, it has implications to greenhouse gas emissions from lakes: in small lakes with large catchment areas, changes in the external loading of CDOM will result in different K_d, which will alter the vertical mixing of GHGs and thus GHG fluxes. Moreover, the radiation penetration through the epilimnion increases exponentially the clearer the lake is and therefore even small changes in water clarity in the region of $K_d < 0.5$ will have significant impact on the lake stratification behavior (Fig. 10 in **II**).

In Lake Kuivajärvi, the use of 30-minute averaged measured K_d in the FLake model did not improve the simulations as opposed to constant (i.e. seasonal average) K_d and thus it seems adequate to consider only the variability of K_d between different lakes. Both the LAKE and FLake models were very sensitive to K_d if simulations were performed with a too low value (overly clear water) and the sensitivity to overly high K_d was negligible. For these reasons, in regions of relatively clear lakes, e.g. at high altitudes, NWP will benefit most from a global mapping of K_d, and at least for humic lakes, time-independent global mapping of K_d could be recommended. Such a global map could be created using satellite remote sensing, as was done for Lake Taihu (Wang et al., 2011) and Alqueva reservoir (Potes et al., 2012).

The gas transfer velocity of CH_4 was continuously higher than that of CO_2 at the times of CO_2 efflux in Lake Pääjärvi and Lake Ormajärvi. In theory, $k_{CO2} \geq k_{CH4}$ since the molecular diffusion coefficient values are almost the same for both gases and CH_4 is inert whereas CO_2 transfer can further be enhanced by chemical reactions (Ojala et al., 2011). We found no evidence of macrobubbles in the chamber data and therefore our findings were similar to those e.g. by McGinnis et al. (2014) and Prairie and del Giorgio (2013), who observed higher k_{600} values for CH_4 than for CO_2 and suggested that the presence of semistable CH_4 microbubbles was the reason behind the higher evasion rates of CH_4. However, our research did not provide any definite evidence on the existence of microbubbles. Laboratory experiments and derived models for microbubble-enhanced gas transfer could prove useful when estimating the role of microbubbles in gas transfer under natural conditions.

The observation of high k_{CO2} when Lake Ormajärvi was a sink of CO_2 might be explained by chemical enhancement of the CO_2 transfer. On the other hand, the same chemical reactions may have confounded the analysis of surface water CO_2 concentrations from the headspace sampling. Both explanations suggest that the chemical enhancement might be significant also in circumneutral lakes (**III**). Before the differences between k_{CH4} and k_{CO2} are explained, it is recommended not to use one to estimate the other.

During the stratified period, k for CO_2 did not depend on wind speed until winds reached approximately 6 m s^{-1} (Fig. 7a). The median k values of different bins according to wind speed were 6 – 9 cm h^{-1} at wind speed < 6 m s^{-1}. These results are similar to observations of McGillis et al. (2004) in an oceanic study, and even though surface water cooling probably enhances the gas transfer and thus weakens the correlation between wind speed and k at low wind speeds, the spatial variability of CO_2 concentrations in the EC footprint might also have caused some discrepancy. Since k was ca. 7 cm h^{-1} in average during late summer when heat losses were significant and ca. 5 cm h^{-1} in average during autumn when heat losses were small, it seems that in Lake Kuivajärvi, which is long and narrow and the wind is channeled along the lake, wind is more significant parameter in the gas transfer than heat flux.

Accurate estimates of k require the consideration of lake physics. Our study (**I**) indicates that Wedderburn numbers drop to values low enough that thermocline tilting and non-linear wave formation probably occur in small boreal lakes during fall cooling. Consequently, internal wave induced motions as well as convection from cooling deliver GHGs as well as other dissolved substances to the upper mixed layer. Importantly, the resulting higher CO_2 flux is captured by EC technique where the flux, and inherently the spatial variability of CO_2 concentrations, from large areas is recorded. When we considered the spatial variability when k was derived from EC measurements in Lake Kuivajärvi, the mean k was reduced over 10 % and many of the very high k (> 15 cm h^{-1}) decreased to values estimated with models which were independent from measured concentrations. Thus, the EC technique, in contrast to chamber measurements, unless distributed over a lake surface, provides more accurate estimates of fluxes.

Since the relative random errors in EC method associated with CO_2 fluxes (on average 26%) were larger than those of H (10%) and LE (11%), we suggest that the main reason for higher CO_2 flux random uncertainty is the larger spatial variability in CO_2 surface water partial pressure than in surface temperature. In addition to variation of entrainment rates in different areas, e.g. lateral transport can result in spatial variability of scalar quantities (e.g. CO_2, nitrogen and phosphorus concentrations), which in turn can lead to spatial variability in lake biota. Previously, most studies have been focused on temporal aspects, but also spatial aspects should be considered in the future.

The energy balance closure was relatively precise and close to those reported from other sites (Nordbo et al., 2011; Liu et al., 2012). This indicates that although the proportion of accepted EC data was quite low, it was of good quality. The amount of accepted data was also comparable with earlier studies reporting EC measurements over lakes (Vesala et al., 2006; Jonsson et al., 2008; Nordbo et al., 2011).

The lake-landscape-atmosphere continuum should be regarded as a whole when the role of lakes in global carbon cycle is assessed and also for estimations how lakes are affected by and how they affect the climate change. When considering gas fluxes, lake characteristics (water clarity and pH), and atmospheric forcing should be coupled to physics within the water column. These would provide improved estimates of the GHG exchange between lakes and the atmosphere and allow both upscaling and predictions of the emissions in the future.

5. Author's contribution to the publications

I. Heiskanen designed the study together with the supervisors, processed and analyzed most of the data, wrote the first version of the manuscript and finalized it on the basis of the comments by co-authors.

II. Heiskanen was together with A. Nordbo responsible for the data processing and analysis, and was responsible for the manuscript preparation.

III. Heiskanen was responsible for the topics related to gas transfer physics and together with M. Rantakari responsible for the related data analysis, and actively participated in writing the article.

IV. Heiskanen was for the most part responsible for the instrument maintenance and data quality assurance related to aquatic measurements, took part in data analysis in regards to water column physics and gas transfer, and actively participated in manuscript preparation.

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