

Carbon dioxide and methane exchange between a boreal pristine lake and the atmosphere

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CONTENTS

ABSTRACT

LIST OF ORIGINAL PUBLICATIONS AND AUTHOR'S CONTRIBUTIONS

ABBREVIATIONS

| | |
|--|----|
| 1. INTRODUCTION | 9 |
| 2. MATERIAL AND METHODS | 12 |
| 2.1 Study site | 12 |
| 2.2 Gas concentration measurements | 14 |
| 2.2.1 CH ₄ concentration | 14 |
| 2.2.2 CO ₂ concentration | 14 |
| 2.2.3 Continuous CO ₂ concentration measurements | 14 |
| 2.3 CH ₄ flux measurements | 15 |
| 2.3.1 Chamber measurements | 15 |
| 2.3.2 Boundary-layer diffusion (BLD) | 15 |
| 2.4 CO ₂ flux measurements | 15 |
| 2.4.1 Eddy covariance technique | 15 |
| 2.4.2 Boundary-layer method (BLM) | 16 |
| 2.5 Methanotrophy | 17 |
| 2.6 Free-water approach for determination of primary production and community respiration | 17 |
| 2.7 Additional measurements | 18 |
| 3. RESULTS | 18 |
| 3.1 Stratification of the lake | 18 |
| 3.2 CH ₄ dynamics and flux to the atmosphere | 20 |
| 3.3 CO ₂ dynamics and exchange between the lake and the atmosphere | 22 |
| 3.4 Free-water approach for determination of primary production and community respiration | 27 |
| 4. DISCUSSION | 28 |
| 4.1 CH ₄ concentration and flux | 28 |
| 4.2 CO ₂ concentration and flux | 29 |
| 4.3 CO ₂ exchange between the Lake Valkea-Kotinen and the atmosphere, obtained with different methods | 31 |
| 4.4 Free water approach | 33 |
| 4.5 Regional relevance | 34 |
| 5. CONCLUSIONS | 34 |
| 6. ACKNOWLEDGEMENTS | 36 |
| 7. REFERENCES | 36 |

ABSTRACT

Lakes serve as sites for terrestrially fixed carbon to be remineralized and transferred back to the atmosphere. Their role in regional carbon cycling is especially important in the Boreal Zone, where lakes can cover up to 20% of the land area. Boreal lakes are often characterized by the presence of a brown water colour, which implies high levels of dissolved organic carbon from the surrounding terrestrial ecosystem, but the load of inorganic carbon from the catchment is largely unknown. Organic carbon is transformed to methane (CH₄) and carbon dioxide (CO₂) in biological processes that result in lake water gas concentrations that increase above atmospheric equilibrium, thus making boreal lakes as sources of these important greenhouse gases. However, flux estimates are often based on sporadic sampling and modelling and actual flux measurements are scarce. Thus, the detailed temporal flux dynamics of greenhouse gases are still largely unknown.

One aim here was to reveal the natural dynamics of CH₄ and CO₂ concentrations and fluxes in a small boreal lake. The other aim was to test the applicability of a measuring technique for CO₂ flux, i.e. the eddy covariance (EC) technique, and a computational method for estimation of primary production and community respiration, both commonly used in terrestrial research, in this lake. Continuous surface water CO₂ concentration measurements, also needed in free-water applications to estimate primary production and community respiration, were used over two open water periods in a study of CO₂ concentration dynamics. Traditional methods were also used to measure gas concentration and fluxes. The study lake, Valkea-Kotinen, is a small, humic, headwater lake within an old-growth forest catchment with no local anthropogenic disturbance and thus possible changes in gas dynamics reflect the natural variability in lake ecosystems.

CH₄ accumulated under the ice and in the hypolimnion during summer stratification. The surface water CH₄ concentration was always above atmospheric equilibrium and thus the lake was a continuous source of CH₄ to the atmosphere. However, the annual CH₄ fluxes were small, i.e. 0.11 mol m⁻² yr⁻¹, and the timing of fluxes differed from that of other published estimates. The highest fluxes are usually measured in spring after ice melt but in Lake Valkea-Kotinen CH₄ was effectively oxidised in spring and highest effluxes occurred in autumn after summer stratification period.

CO₂ also accumulated under the ice and the hypolimnetic CO₂ concentration increased steadily during stratification period. The surface water CO₂ concentration was highest in spring and in autumn, whereas during the stable stratification it was sometimes under atmospheric equilibrium. It showed diel, daily and seasonal variation; the diel cycle was clearly driven by light and thus reflected the metabolism of the lacustrine ecosystem. However, the diel cycle was sometimes blurred by injection of hypolimnetic water rich in CO₂ and the surface water CO₂ concentration was thus controlled by stratification dynamics. The highest CO₂ fluxes were measured in spring, autumn and during those hypolimnetic injections causing bursts of CO₂ comparable with the spring and autumn fluxes. The annual fluxes averaged 77 (±11 SD) g C m⁻² yr⁻¹. In estimating the importance of the lake in recycling terrestrial carbon, the flux was normalized to the catchment area and this normalized flux was compared with net ecosystem production estimates of -50 to 200 g C m⁻² yr⁻¹ from unmanaged forests in corresponding temperature and precipitation

regimes in the literature. Within this range the flux of Lake Valkea-Kotinen yielded from the increase in source of the surrounding forest by 20% to decrease in sink by 5%.

The free water approach gave primary production and community respiration estimates of 5- and 16-fold, respectively, compared with traditional bottle incubations during a 5-day testing period in autumn. The results are in parallel with findings in the literature. Both methods adopted from the terrestrial community also proved useful in lake studies. A large percentage of the EC data was rejected, due to the unfulfilled prerequisites of the method. However, the amount of data accepted remained large compared with what would be feasible with traditional methods. Use of the EC method revealed underestimation of the widely used gas exchange model and suggests simultaneous measurements of actual turbulence at the water surface with comparison of the different gas flux methods to revise the parameterization of the gas transfer velocity used in the models.

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications:

- I Kankaala P., **Huotari J.**, Peltomaa E., Saloranta T. & Ojala A. 2006. Methanotrophic activity in relation to methane efflux and total heterotrophic bacterial production in a stratified, humic, boreal lake. *Limnology and Oceanography* 51: 1195-1204.
- II Vesala T., **Huotari J.**, Rannik Ü., Suni T., Smolander S., Sogachev A., Launiainen S. & Ojala A. 2006. Eddy covariance measurements of carbon exchange and latent and sensible heat fluxes over a boreal lake for a full open-water period. *Journal of Geophysical Research* 111, D11101, doi: 10.1029/2005JD006365.
- III **Huotari J.**, Ojala A., Peltomaa E., Pumpanen J., Hari P. & Vesala T. 2009. Temporal variations in surface water CO₂ concentration in a boreal humic lake based on high-frequency measurements. *Boreal Environment Research* 14 (suppl A): 48-60.
- IV Hari P., Pumpanen J., **Huotari J.**, Kolari P., Grace J., Vesala T. & Ojala A. 2008. High-frequency measurements of productivity of planktonic algae using rugged nondispersive infrared carbon dioxide probes. *Limnology and Oceanography: Methods* 6: 347-354.
- V **Huotari J.**, Ojala A., Peltomaa E., Nordbo A., Launiainen S., Pumpanen J., Rasilo T., Hari P. & Vesala T. 2010. Boreal lakes as important emitters of terrestrially fixed carbon. *Manuscript*

The thesis also includes unpublished results.

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The publications are referred to in the text by their roman numerals.

Author's contribution

- I JH participated in sampling of the gas data and in flux measurements, prepared Figures 1 and 3 and commented on the manuscript written by PK.
- II JH set up and maintained the EC measurements and was responsible for processing the lake gas concentration, modelling the CO₂ flux and recording

the auxiliary meteorological data. JH participated in processing and analysing the EC data. JH commented on the manuscript written jointly by all writers.

- III The study was planned jointly by JH, AO and JP. JH set up the instrumentation of the continuous CO₂ measurements together with JP and was responsible for maintenance. JH was responsible for processing and analysing the data and he wrote the first version of the manuscript with contribution from AO.
- IV PH and JP set up the instrumentation of the continuous CO₂ measurements and JH was responsible for maintenance, measurements of the meteorological data, calculation of the flux modelled and preparation of the figures. JH commented on the manuscript.
- V JH set up the EC measurements and was responsible for maintenance, with some contributions from EP. The EC data was processed by AN and SL. Data analysis and interpretation of the data were done by JH together with AO. JH wrote the first version of the manuscript.

ABBREVIATIONS

| | |
|--------------------------|--|
| CH ₄ | methane |
| CO ₂ | carbon dioxide |
| DIC | dissolved inorganic carbon |
| DOC | dissolved organic carbon |
| EC | eddy covariance |
| EU | European Union |
| FID | flame ionization detector |
| GC | gas chromatograph |
| H ₂ O | water |
| ICP IM | International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems |
| IRGA | infrared gas analyser |
| LTER | Long-Term Ecological Research |
| NEE | net ecosystem exchange |
| NEP | net ecosystem production |
| PAR | photosynthetically active radiation |
| <i>p</i> CO ₂ | partial pressure of CO ₂ |

1. INTRODUCTION

Inland waters play an important role in both global and regional carbon cycling (Cole et al. 2007, Battin et al. 2009, Tranvik et al. 2009). Their role is especially pronounced in the Boreal Zone (Kortelainen et al. 2004, Roehm et al. 2009), where lakes can locally cover up to 20% of the land area (Raatikainen & Kuusisto 1990). A distinct feature of the majority of these boreal lakes is in the brown water colour, implying a high load of terrestrial material through lateral transport processes, mainly in the form of dissolved organic carbon (DOC). Mineralization of this allochthonous carbon leads to carbon dioxide (CO_2) supersaturation in lakes (e.g. Jonsson et al. 2003, Sobek et al. 2003, Duarte & Prairie 2005), although some other sources such as weathering and hydrologic input of CO_2 can be locally significant (Striegl & Michmerhuizen 1998, Stets et al. 2009). Nevertheless, the role of lateral transport of dissolved inorganic carbon (DIC) to lakes is largely unknown. Most lakes worldwide are considered to be net heterotrophic and supersaturated with CO_2 (Cole et al. 1994) and act as atmospheric sources of CO_2 . Since boreal forests are a globally important carbon sink (e.g. Schulze et al. 1999), detailed knowledge of the amount of terrestrial carbon processed naturally in adjacent bodies of water and finally emitted back to the atmosphere as CO_2 is needed to define the regional role of boreal landscapes in carbon cycling. Accurate determination of gas exchange between lakes and the atmosphere is also a vital point in lacustrine studies of carbon dynamics.

Due to the high concentrations of coloured humic matter of terrestrial origin, boreal lakes are often steeply stratified with

hypoxic or even anoxic hypolimnia. Under anoxic conditions, methane (CH_4) is the final product of decomposition of organic matter in the absence of alternative electron acceptors (NO_3^- , Fe_3^+ and SO_4^{2-} ; cf. Capone & Kiene 1988). In boreal humic lakes with anoxic hypolimnia, CH_4 concentrations can be more than 1000-fold higher than atmospheric equilibrium (Kortelainen et al. 2000, Huttunen et al. 2002, Kankaala et al. 2005). CH_4 can be biologically oxidized to CO_2 in the presence of oxygen (O_2) in the water column when part of the carbon in CH_4 is incorporated into the cells of methanotrophic microbes (e.g. Hanson & Hanson 1996). Anaerobic oxidation of CH_4 is also possible (e.g. Schink 1997, Raghoebarsing et al. 2006). However, surface waters of boreal lakes usually have CH_4 concentrations higher than atmospheric equilibrium, indicating that a proportion of CH_4 escapes oxidation and is released to the atmosphere, especially during the spring and autumn turnover periods (Michmerhuizen et al. 1996, Riera et al. 1999). In the atmosphere, CH_4 is a greenhouse gas contributing to global radiative forcing and its global warming potential (GWP) is 25-fold higher than CO_2 when the time horizon is 100 years (Solomon et al. 2007).

CO_2 also accumulates in the hypolimnia of stratified lakes from where, similar to CH_4 , it is released to the atmosphere during turnover periods (e.g. Riera et al. 1999). Hypolimnetic concentrations of CO_2 in small boreal lakes tend to have a rather steady trend to increase over the time of stable stratification, whereas surface waters show more variable concentrations over diel and day-to-day courses (e.g. Sellers et al. 1995, Cole & Caraco 1998, Riera et al. 1999, Hanson et al. 2003). However, the natural variability of surface water CO_2 and

CH₄ of boreal lakes is still somewhat uncertain (Ojala et al. 2011) and even annual flux estimates are often based on sporadic or scanty samples (e.g. Bastviken et al. 2004, Kortelainen et al. 2004).

Estimates of gas exchange between lakes and the atmosphere are commonly based on gas exchange models. In addition to the concentration difference across the air-water interface, turbulence is the major driver of gas exchange (MacIntyre et al. 1995) and thus wind speed, creating turbulence due to wind shear at the interface and, being a rather easy parameter to measure, is most commonly used to describe the gas transfer velocity in models (e.g. Wanninkhof et al. 1985, Cole & Caraco 1998). However, gas transfer is not always dependent on wind speed under low-wind conditions (Ocampo-Torres & Donelan 1994, MacIntyre et al. 1995, Cole & Caraco 1998), indicating that other factors besides wind may control gas transfer. The finding also suggests that in small boreal lakes where low-wind conditions prevail, it may be worthwhile to use other techniques in parallel with the gas exchange models. In addition to gas exchange models, the most commonly used technique in gas flux measurement over lakes is the closed chamber technique (e.g. Duchemin et al. 1999, Riera et al. 1999, Striegl et al. 2001). Both methods have the advantage of being relatively easy and inexpensive. However, they are very labour-intensive when high temporal and spatial coverage is needed and the chambers are prone to some problems, such as possible modification of the flux at the water-air interface (e.g. Belanger & Korzun 1991). Techniques for measuring CO₂ concentration continuously have been developed recently and they help to overcome the problem of temporal

representativeness in gas exchange models (e.g. DeGrandpre et al. 1995, Sellers et al. 1995, Carignan 1998), but uncertainty in gas transfer velocity still remains.

The micrometeorological eddy covariance (EC) technique provides a tool to directly measure ecosystem-scale fluxes continuously without affecting natural gas transfer when the methodological requirements, i.e. the presence of steady-state turbulent flow, are fulfilled. The technique is the most direct way to measure the fluxes between ecosystems and the atmosphere and it is widely used to measure surface fluxes in terrestrial and agricultural sciences (Baldocchi 2003). The technique has also been introduced to lake ecosystem studies of CO₂ exchange (Anderson et al. 1999, Eugster et al. 2003, II, Jonsson et al. 2008), but it has not been used in long-term measurements involving years. Simultaneous EC and continuous surface water CO₂ concentration measurements also provide a promising tool to determine gas transfer velocity and its dependence on environmental variables (Jonsson et al. 2008).

In addition to studies of gas exchange between surface water and the atmosphere, continuous measurements of metabolic gases, i.e. CO₂ and O₂, have been used in attempts to estimate the metabolic processes of lacustrine plankton communities (Cole et al. 2000, Hanson et al. 2003). These free-water measurements avoid the ambiguities of traditional methods for estimating primary production, which are based on O₂, ¹⁴C and bottle incubations (Peterson 1980, Hanson et al. 2003) and allow more frequent, even continuous estimates of metabolic processes. Probes for measurements of dissolved O₂ have been commercially available for decades, whereas CO₂-

measuring systems have been more or less self-made combinations of commercially available gas analysers and researchers' imagination and engineering. Thus, free-water estimates of lake metabolism have usually been based on measurements of O_2 , which has been considered a more reliable and cost-effective method (Cole et al. 2000, Hanson et al. 2003). However, carbon is a better parameter for evaluating production, since it is the initial and the end product of organic metabolism and thus, there is no need for using uncertain photosynthetic or respiratory quotients (Wetzel 2001). With the use of high-frequency measurements, some of the problems inherent in the traditional methodology can be avoided and measurements of metabolic processes in aquatic ecosystems can be brought more in line with continuous, high-frequency EC measurements, which are already commonly used in terrestrial ecology.

One aim of this thesis was to adopt the measuring techniques (II, V) and computational methods (IV) commonly used in terrestrial research and test their applicability in lake ecosystems, thus narrowing the gap between these disciplines. This enhances the possibility of comprehensive understanding of landscape-level carbon cycling. The CO_2 flux data presented over the five consecutive open-water periods are now the longest time series available for CO_2 exchange between a lake and the atmosphere measured with EC (V). The approach presented here for estimating lake primary production and community respiration is also a step ahead in estimating the metabolic processes of the lake (IV). The study lake is a small pristine body of water that is the uppermost lake of a lake chain surrounded by an unmanaged old-growth forest. Thus, it is a true reference lake under minimal

anthropogenic influence and the information given here can be utilized, e.g. in studies on the effects of climate change on boreal lacustrine ecosystems. The site also serves as a reference for studies of land-use effects on lakes. By investigating a small lake, the focus also deliberately changes from large- and medium-sized lakes to small lakes, which represent the bulk of the global freshwater area (Downing et al. 2006), but have so far been inadequately represented in studies. The other aim was to study the natural dynamics of concentrations and fluxes of CH_4 (I) and CO_2 (II, III, V) in a pristine boreal lake.

The specific objectives of the thesis were:

- determine the natural course of the CH_4 and CO_2 concentrations of a boreal, pristine lake
- determine the CH_4 efflux to the atmosphere as related to the diffusion of CH_4 from the sediment and methanotrophic activity in the water column
- determine the natural course and level of CO_2 efflux of a boreal, pristine lake
- test the applicability of the EC technique in long-term measurements in a lake
- compare the CO_2 fluxes obtained with the widely used gas exchange model and EC
- test the computational methods used in forest ecology to determine aquatic photosynthesis and community respiration from surface water CO_2 concentration data
- estimate the importance of a lake in an undisturbed catchment as a conduit of terrestrial carbon to the atmosphere

The concentration and flux of CH₄ was studied over an entire year from ice-out until the end of spring turnover of the following year (I). The applicability of EC in measuring CO₂ fluxes over the lake was tested (II) and the flux dynamics were further examined over the five consecutive open-water periods (V). The diel, daily and seasonal variations in surface water CO₂ were determined over two consecutive open-water periods and the winter in between (III). The computational methods used in forest ecology were modified and applied to determinations of aquatic photosynthesis and community respiration from surface water CO₂ concentration data (IV).

2. MATERIAL AND METHODS

All the studies were conducted in Lake Valkea-Kotinen during 2002–2007. The focus was on CO₂ (II–V) whereas only one study dealt with the concentration and flux of CH₄ (I). The CH₄ measurements covered one year from ice-out in 2002 until the end of spring turnover in 2003, whereas the CO₂ concentration and fluxes were measured during five consecutive open-water periods in 2003–2007.

2.1 Study site

The study lake (Fig. 1), Lake Valkea-Kotinen (61°14' N, 25°04' E), is situated in nature reserve area in Evo, southern Finland. The area has been protected since 1955 and is the major Finnish site of the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM). The monitoring of water properties was initiated in Lake Valkea-Kotinen in 1989 (Rask et

al. 1998). The site was originally selected because it is representative of its biogeographical province, is primarily forested and is in as natural a state as possible. Moreover, its catchment area is distinct and unambiguous. The area also belongs to the Natura 2000 of the European Union and the Finnish Long-Term Ecological Research (LTER) network. Maps for the location and bathymetry of the lake as well as topography of the area can be found in I and II, respectively.

Lake Valkea-Kotinen is a small headwater lake with a surface area of 0.041 km². The mean and maximum depths are 2.5 m and 6.5 m, respectively. There is no inlet to the lake, whereas it has a small outlet. Due to the humic water and sheltered position of the lake it is thermally stratified and in summer the hypolimnion below 1.5–3 m becomes anoxic (Keskitalo et al. 1998). The euphotic zone is restricted to the shallow surface layer of 1–1.5 m in thickness and during summer stratification the mixing layer equals the euphotic zone in depth or is somewhat shallower. The water is slightly acidic and its buffer capacity low. Hence, most of the inorganic carbon present is in the form of CO₂. Although appearing as a rather typical boreal lake, it has surprisingly high annual primary production that often results in low surface water CO₂ concentration in summer. The mean values over seven consecutive open-water periods (1990–1996) for daily primary production, annual production, daily net production, daily community respiration and chlorophyll *a* concentration are 177 mg C m⁻² d⁻¹, 30.9 g C m⁻² yr⁻¹, 58.4 mg C m⁻² d⁻¹, 191.3 mg C m⁻² d⁻¹ and 21.7 mg m⁻³, respectively (Keskitalo et al. 1998). The basic chemical characteristics of Lake Valkea-Kotinen can be found in Keskitalo et al. (1998) and their

mean values over seven consecutive open-water periods (1990–1996) are given in Table 1. In terms of nutrients, Lake Valkea-Kotinen can be classified as oligotrophic or mesotrophic, but due to the occasionally high chlorophyll *a* concentrations, the lake appears to be meso-eutrophic (Wetzel

2001). The narrow lake littoral zone has scant growth of water lilies (*Nymphaea* L. spp. and the yellow water-lily *Nuphar lutea* [L.] Sm.) and a dense mat of sphagnum mosses (*Sphagnum* L. spp.).



Figure 1. Lake Valkea-Kotinen and its forested catchment. The red circle illustrates the location of a measuring platform. © Ilpo Hakala.

Table 1. Chemical characteristics of Lake Valke-Kotinen in the epilimnion (0–1 m) and hypolimnion (3–5 m) as mean values calculated over the open-water periods of 1990–1996 (data from Keskitalo et al. 1998). N.D. stands for ‘not determined’.

| | pH | Conductivity $mS m^{-1}$ | Colour $g Pt m^{-3}$ | TN $mg m^{-3}$ | NH_4-N $mg m^{-3}$ | NO_3-N $mg m^{-3}$ | TP $mg m^{-3}$ | Alkalinity $eq m^{-3}$ | DIC $g m^{-3}$ | DOC $g m^{-3}$ |
|-------------|-----|-----------------------------|-------------------------|-------------------|-------------------------|-------------------------|-------------------|---------------------------|-------------------|-------------------|
| Epilimnion | 5.2 | 3.0 | 136.7 | 487.4 | 12.1 | 7.5 | 18.6 | 0.005 | 0.6 | 11.3 |
| Hypolimnion | 5.3 | 3.3 | 161.6 | 640.3 | 137.0 | 12.5 | 22.9 | 0.053 | 5.2 | N.D. |

The catchment area is app. 30 ha in size and is mainly covered by old-growth coniferous forest dominated by 80–150-yr-old Norway spruce (*Picea abies* [L.] H. Karst.), while some birch (*Betula* L. spp.), aspen (*Populus tremula* L.) as well as old Scots pines (*Pinus sylvestris* L.) grow

among the spruce. Upland forest covers 62% and peatlands 25% of the catchment area. The riparian zone is also formed of peaty soil. The annual mean temperature is 3.1 °C, annual mean precipitation is 618 mm and the growing season ($T > 5$ °C) is 112 days long (Mäkelä 1995).

2.2 Gas concentration measurements

2.2.1 CH₄ concentration

The concentration of CH₄ in the water (I) was measured, using the headspace equilibrium technique (McAuliffe 1971). The sampling frequency was once per week, starting right after ice-out in 2002 and continuing until the freeze-over. Samples were taken once per month during the ice-covered time. Duplicate samples of water (30 mL) were taken into 60-mL polypropylene syringes (Terumo Europe N. V., Leuven, Belgium) that were closed with three-way stopcocks (Luer-lock, Codan Ltd, Wokingham, Berkshire, UK). The headspace of the syringes was filled with 30 mL of nitrogen gas (N₂), followed by vigorous shaking of the syringes to equilibrate the sample with the headspace, from which the CH₄ concentration was measured, using gas chromatography (GC) [Hewlett-Packard 5710A (Hewlett-Packard, Palo Alto, CA, USA) and Agilent 6890N (Agilent Technologies Inc., Palo Alto), flame ionization detector (FID)]. The CH₄ concentration in the water was calculated as described in Huttunen et al. (2001). Samples for the different depths were taken with a Limnos (2 L) tube sampler. Temperature and O₂ profiles of the lake were measured twice a week at 0.5 m intervals with an oxygen thermometer (YSI 55; Yellow Springs Instrument Co. Inc., Yellow Springs, OH, USA).

2.2.2 CO₂ concentration

The concentration of CO₂ in the water (II, III, V) was calculated from the DIC, pH and temperature according to Butler (1982). For DIC analyses the samples were

taken in duplicate 25-mL glass stoppered bottles that were allowed to overflow to at least three times their own volume to ensure that no air bubbles were left inside. The bottles were taken to the laboratory in a darkened icebox and the DIC was measured within 3 hours by lowering the pH of the sample with strong acid and measuring the CO₂ released with an infrared (IR) gas analyser (URAS 3G; Hartmann & Braun AG, Frankfurt am Mein, Germany). The samples for pH were measured in the laboratory (Orion Research SA 720 pH/ISE; Orion Research Inc., Beverly, MA, USA). Samples for the different depths were taken with a Limnos 2-L tube sampler. Temperature and O₂ profiles of the lake were measured twice per week at 0.5 m intervals with an oxygen thermometer (YSI 55; Yellow Springs). The equilibrium concentration with the atmosphere (C_{eq}) was calculated, using the air CO₂ concentration and the temperature-adjusted Henry's law constant.

2.2.3 Continuous CO₂ concentration measurements

Continuous CO₂ measurements (III, IV) were conducted at depths of 0.1, 0.5 and 1.5 m with a measuring system in which the continuous airstream was circulated by a diaphragm pump in a closed loop that consisted of gas-impermeable tubing, CO₂ analyser (CARBOCAP® GMP343, Vaisala Oyj, Helsinki, Finland), semipermeable tubing and the pump. The pumps and CO₂ analysers were placed on the same raft with the EC equipment (see below) in a temperature-controlled box, whereas the semipermeable tubing was placed in the water at the measuring depth. The semipermeable tubing, CO₂ analyser and the pump were connected with gas-

impermeable tubing. The gas concentrations of the continuous airstream within the loop equilibrated with that in the water around the semipermeable tubing. Thus, the CO₂ concentration of the water could be continuously measured in the gaseous phase with a CO₂ analyser. The concentration of CO₂ in the water (C ; $\mu\text{mol L}^{-1}$) could then be determined, using the dependence of solubility of CO₂ as a function of temperature with the appropriate Henry's law constant (K_H ; mol (L atm)^{-1}):

$$(1) \quad C = x_{\text{CO}_2} P K_H,$$

where x_{CO_2} is the CO₂ concentration (= probe output, parts per million) and P is the pressure (atm).

2.3 CH₄ flux measurements

2.3.1 Chamber measurements

The CH₄ efflux from the water surface to the atmosphere was measured weekly during the open-water period, using the static chamber technique (I). Air samples were transferred from three floating chambers (volume 5.8 L, height 0.125 m) into 60-mL polypropylene syringes through a tube mounted on the top of the chambers at 5-min intervals for 30 min. The headspace of the chambers was mixed by pumping air in and out of the syringe several times before closing the sample inside the syringe. The air temperature in the chambers during the incubation was measured. The concentration of CH₄ was measured by GC. CH₄ efflux was calculated as a linear increase ($P < 0.05$) in CH₄ over time according to the Ideal Gas Law.

2.3.2 Boundary-layer diffusion (BLD)

Another estimate of CH₄ efflux (I) was calculated with the boundary-layer diffusion (BLD) equations presented by Kling et al. (1992) and Phelps et al. (1998):

$$(2) \quad F_{\text{CH}_4} = \frac{D_b}{z_b} (C_{\text{sur}} - C_{\text{eq}}),$$

where z_b is the thickness of the aqueous boundary layer, C_{sur} the concentration of CH₄ at 0–30-cm depths and C_{eq} the concentration of CH₄ in equilibrium with the air. The values of C_{eq} were calculated with Henry's law constants for surface temperatures (Lide & Fredikse 1995), assuming a stable atmospheric CH₄ concentration of 1.745 ppm (Houghton et al. 2001). The diffusion coefficient (D_b , $\text{cm}^2 \text{s}^{-1}$) and boundary-layer thickness (z_b , μm) were calculated as

$$(3) \quad D_b = [1.33 + (0.055 T)] \times 10^{-5}$$

and

$$(4) \quad z_b = 10^{(2.56 - (0.133 U_{10}))},$$

where T is the water temperature ($^{\circ}\text{C}$) at the surface and U_{10} the wind speed at 10 m height (m s^{-1}). The value for U_{10} was obtained by multiplying the measured wind speed at a height of 1.0 m above the lake surface by a factor of 1.22 (Crusius & Wannikhof 2003). This approach does not take into account any stability effects.

2.4 CO₂ flux measurements

2.4.1 Eddy covariance technique

The CO₂ exchange between the lake surface and the atmosphere was measured

with the EC technique (II, V). A platform for the EC equipment was moored approximately 280 m from the northwest end of the lake and 35 m from the eastern shore (Fig. 1). The platform consisted of three rafts attached to each other to form a triangle, with each side about 5 m in length. The EC measurement tower (1.5 m) was set up on the platform's angle pointing to the longest fetch.

The measurement system consisted of a Metek ultrasonic anemometer (USA-1; Metek GmbH, Elmshorn, Germany), which measured the three wind components and virtual temperature, coupled with a closed-path IR gas analyser (IRGA, LI-7000; Li-Cor Inc., Lincoln, NE, USA), which measured the CO₂ and H₂O mixing ratio. The micrometeorological fluxes of CO₂ were calculated as covariances between the CO₂ mixing ratio and vertical wind speed according to commonly accepted procedures (Aubinet et al. 2000). The upward fluxes were defined as positive. In addition to the flux calculation used in II, the spectral correction method (Moore 1986, Horst 1997, Massman 2000, 2001) was introduced in calculations of the fluxes in V. Furthermore, data quality selection also evolved between II and IV and new criteria for turbulent mixing and wind direction were added (see below). Both II and IV share some features of data selection. First, the momentum flux must be directed downwards; second, flux instationarity was required to remain below 0.3 (Foken & Wichura 1996); third, the skewness and kurtosis of vertical wind speed and CO₂ concentration were required to remain within the range of [-2,2] and [1,8], respectively (Vickers & Mahrt 1997). In II, data only from the longest fetch were accepted, i.e. from 290°–350°, whereas in V both wind directions along the lake were

approved, i.e. 110°–170° and 290°–350°. In V, to ensure sufficient turbulent mixing, a threshold value for standard deviation of vertical wind speed (σ_w) was empirically determined as described in Launiainen et al. (2005). In comparison to the threshold values of 0.07 m s⁻¹ and 0.11 m s⁻¹ for the two different setups in Launiainen et al. (2005), the threshold value in Lake Valkea-Kotinen was much higher, i.e. $\sigma_w > 0.3$ m s⁻¹, above which the variation in CO₂ flux decreased drastically. These data quality criteria were set to ascertain that the requirements of steady-state turbulent flow were satisfied and that the fluxes represented the lake-atmosphere exchange.

Due to the differences in data calculation and quality selection there are two divergent CO₂ flux estimates for 2003 in II and V. Those in V were regarded as more reliable and used in further discussion.

2.4.2 Boundary-layer method (BLM)

The CO₂ exchange between the lake and the atmosphere (II, III) was also estimated from the concentration difference between the lake surface and the overlying air ($C_{sur} - C_{eq}$) and using the gas transfer velocity (k) according to the equation

$$(5) \quad F_{CO_2} = k (C_{sur} - C_{eq}).$$

The value of k for the gas can be computed if it is known for another gas, using the dependence of k on the Schmidt number (Sc):

$$(6) \quad \frac{k_{gas1}}{k_{gas2}} = \left(\frac{Sc_{gas1}}{Sc_{gas2}} \right)^{-n}.$$

Gas exchange velocities are usually normalized to $Sc = 600$, which is the Schmidt number of CO_2 at 20 °C in freshwater and is referred to as k_{600} . The Schmidt number is the ratio of the kinematic viscosity of water and the molecular diffusion coefficient of the gas and is a function of temperature. The Schmidt number for CO_2 was calculated from Jähne et al. (1987) and for k_{600} the empirically determined equation by Cole & Caraco (1998) was used:

$$(7) \quad k_{600} = 2.07 + 0.215 U_{10}^{1.7}.$$

Thus, k_{CO_2} could be calculated with equation

$$(8) \quad k_{CO_2} = k_{600} \left(\frac{Sc_{CO_2}}{600} \right)^{-n},$$

where n is 0.67 determined for low-wind speed conditions and taken from Jähne et al. (1987).

2.5 Methanotrophy

Methanotrophic activity was measured weekly from 12 June to 16 October 2002 and five times during the following winter and spring. Lake water from depths of 0, 2, 4 and 6 m taken with the Limnos sampler was transferred into dark 2-L bottles that were carefully flushed with water from the sampling depth before filling and then closed with glass stoppers to avoid air headspace. In the laboratory, CH_4 oxidation was measured as a linear decrease in CH_4 concentration in sterile glass syringes (SAMCO Interchangeable, S. Murray & Co., Old Woking, Surrey, England; 50-mL volume). Ten syringes for each sampling depth were filled half full (25 mL) with the lake water, carefully avoiding air bubbles,

and closed with three-way stopcocks, and the connection between the plunger and the syringe was covered by Parafilm (American National Can Group, Chicago, IL, USA). For each depth, the concentration of CH_4 was analysed from three syringes immediately after filling. The other syringes were incubated in darkness in temperatures simulating those measured in the field (± 2 °C), and their CH_4 concentration was measured after 4, 8 and 24 h of incubation. Only those time series with a significant linear decrease in CH_4 ($p < 0.05$) were accepted as the results of methanotrophic activity, whereas unchanged CH_4 concentration during 24 h indicated that no methanotrophic activity had occurred.

2.6 Free-water approach for determination of primary production and community respiration

Continuous measurements of surface water CO_2 concentration were used in an effort to compute the planktonic primary production and community respiration of the lake ecosystem (IV). The surface water CO_2 concentration was measured, as described in section 2.2.3. The change in surface water CO_2 concentration is comprised of the biological exchange between living organisms and water (g) and the physical fluxes of surface water CO_2 between air (F_a) and the deeper water layers (F_u). The mass balance of CO_2 in the surface water layer above depth h_b is

$$(9) \quad g(t) = - \int_{h_b}^0 \frac{dC(h,t)}{dt} dh - F_a + F_u,$$

where $C(h,t)$ is the CO_2 concentration in the water as a function of depth (h) and time (t). The fluxes F are positive when

they are upwards. F_a was calculated using the BLM as described in 2.4.2. Since about 60 % of the volume of Lake Valkea-Kotinen is below 1.0 m and the measurements were conducted during the autumn turnover, F_u was estimated as 60% of the F_a . The factor g is comprised of photosynthesis (p) and respiration (r); when p is larger than r , g is positive.

The photosynthetic rate and, hence, primary production in brown-water lakes can be limited by irradiance and thus a saturating Michaelis-Menten-type dependence of p on photosynthetically active radiation (PAR, 400–700 nm) (I) was applied. Respiration was assumed to be determined by temperature (T) and the daytime respiration rate was set equal to the nighttime rate (e.g. Carignan et al. 2000). Thus, g can be formulated as

$$(10) \quad g = p - r = \frac{p_{max}}{I+b} - r_0 Q_{10}^{T/10},$$

where p_{max} is maximum photosynthesis, b the half-saturation constant and r_0 is basal respiration. Q_{10} was assumed to be 2.0 (Reynolds 1984). The values of the parameters of p_{max} , b and r_0 were estimated by minimizing the residual sum of squares.

2.7 Additional measurements

The profile of the water temperature was measured with a string of temperature sensors (Vemco, Halifax, NS, Canada) with various depth combinations (9–13 sensors at 0.2–4.5 m) over the years; the logging interval varied from 15 min to 1 h. The water temperature was also measured at the depths of continuous CO₂ concentration measurements with Philips KTY81-110 temperature probes (Philips Semiconductors, Eindhoven, The

Netherlands). The strength of the stratification was estimated as a Brunt-Väisälä stability frequency (N_s) (s⁻¹) calculated from the density gradient ($\partial\rho_w/\partial z$) across 0.2–1.5 m (or 0.5–1.5 m in III), using the equation:

$$(11) \quad N_s = \sqrt{\frac{g}{\rho_w} \frac{\partial\rho_w}{\partial z}},$$

where g (m s⁻²) is the acceleration due to gravity, ρ_w (kg m⁻³) the water density and z (m) the depth. The dissolved O₂ profile was measured weekly during open-water periods and monthly in winter 2005–2006 with a YSI 55 dissolved oxygen meter (Yellow Springs).

3. RESULTS

3.1 Stratification of the lake

The temperature stratification of the lake followed the same general pattern every study year. The isothermal phase in spring after ice-out was very short or absent and thus the lake often lacked the complete spring turnover (Fig. 2, Fig. 3 in I). The surface water warmed up very quickly and a steep temperature gradient was formed in a matter of days. The mixing depth, determined as where the temperature gradient reached the value of 1 °C m⁻¹ the first time, was occasionally very shallow, i.e. 0.5 m, and based on the daily average temperatures, 1-m mixing depths were a common occurrence in June and July (Fig. 3 in III). Stratification sometimes started to break up already in August and the autumn turnover occurred by mid-October. The mixing continued until freeze-over. Figure 2 is shown as an example of the annual

temperature profiles over the years 2005 and 2006.

The O₂ profile of Lake Valkea-Kotinen confirmed incomplete spring turnover and only in spring 2007 was the bottom of the lake aerated (not shown). The anoxic boundary ascended until July–August

reaching 2 m every study year, after which it descended until the autumn turnover. Figure 3 is shown as an example of the annual O₂ profiles over the years 2005 and 2006. A high under-ice O₂ concentration due to primary production was seen in April 2006 and discussed in III.

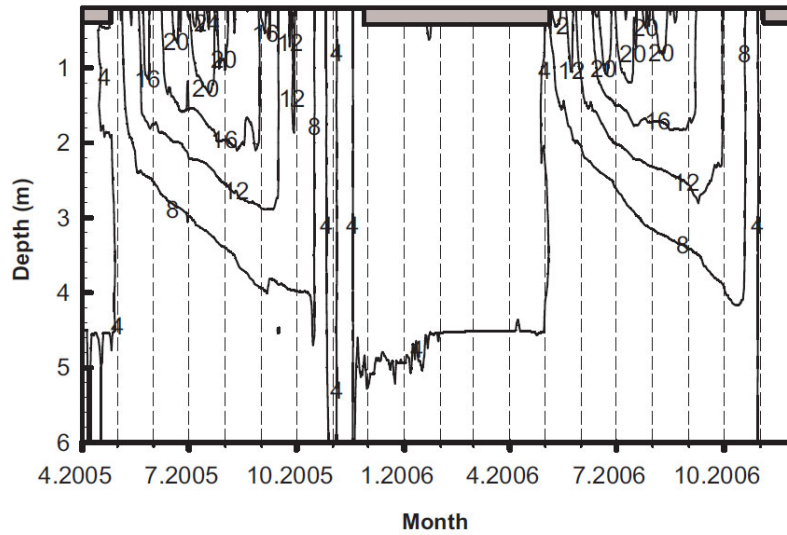


Figure 2. Temperature (°C) stratification pattern in Lake Valkea-Kotinen in 2005–2006 (III). Grey bars represent the ice-covered times.

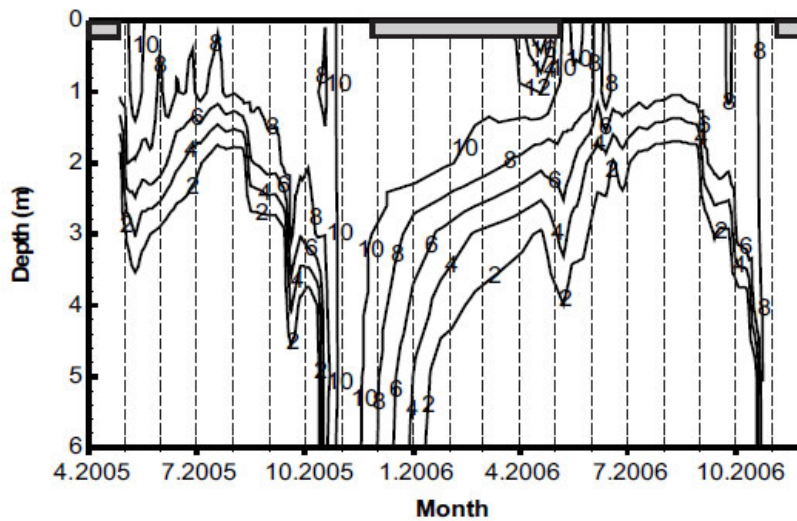


Figure 3. Oxygen (mg L⁻¹) stratification in Lake Valkea-Kotinen in 2005–2006. Grey bars represent the ice-covered times.

3.2 CH₄ dynamics and flux to the atmosphere

The surface water CH₄ concentration ranged from 0.005 mmol m⁻³ in early winter to 3.0 mmol m⁻³ at the onset of autumn turnover, but compared with the atmospheric concentration, the lake surface was always supersaturated with CH₄. The CH₄ concentration in the hypolimnion increased in parallel with anoxia, so that the maximum concentration of 236 mmol m⁻³ was recorded at 6 m in mid-September when only the uppermost 2 m in the lake were oxygenated. At that time the surface

water CH₄ concentration was 3.0 mmol m⁻³ (Fig. 4). The oxygenated layer was < 2 m in late August when there was a CH₄ peak (3.4 mmol m⁻³) at 2 m. The CH₄ storage in the water column was maximal in mid-September (1890 mol CH₄ per lake) when it was > 80% higher than CH₄ storage under the ice (I). The spring turnover during both study years was incomplete, and the O₂ concentration near the bottom (6 m) did not increase above the detection limit (Fig. 3 in I). However, the CH₄ concentration at 6 m was lowest, i.e. 17 μmol m⁻³, in spring 2002 after ice melt.

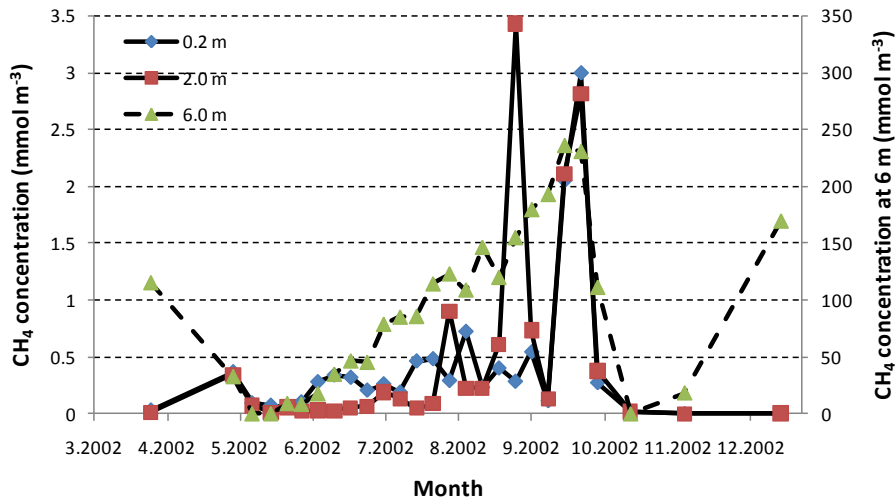


Figure 4. CH₄ concentration at depths of 0.2 m, 2.0 m and 6.0 m in Lake Valkea-Kotinen in 2002. Note the different y-axis for the depth of 6 m.

During the ice-free period, CH₄ was continuously released from the lake surface to the atmosphere (Fig. 5). From late April to late August, the CH₄ efflux rate varied between 0.1 and 0.8 mmol CH₄ m⁻² d⁻¹, but the highest effluxes (1.2–5.1 mmol CH₄ m⁻² d⁻¹) were measured from mid-September to early October during the autumn turnover. Overall, the efflux rates estimated with the BLD correlated significantly with the

chamber measurements ($r^2 = 0.91$), but the peak values with the BLD, especially during the autumn turnover, were only about half of those with the chamber measurements. The CH₄ flux measured with the chambers and integrated over the open-water period gave a total flux of 0.11 mol CH₄ m⁻² yr⁻¹.

The CH₄ efflux by ebullition from the sediment was most probably insignificant

in this lake, because no gas bubbles were trapped in subsurface funnels ($n = 8$) during a 3-week period in July 2003 (Huotari unpubl. data).

The highest methanotrophic activities were always measured at the oxic–anoxic interfaces (Fig. 6). The highest activities were measured at 6 m after the incomplete spring turnover ($6\text{--}18 \text{ mmol CH}_4 \text{ m}^{-3} \text{ d}^{-1}$), but during the summer and winter stratification periods, no activity was measured at that depth, presumably

because of O_2 limitation. At 4 m, methanotrophic activity was observed from June to mid-July and again from the onset of autumn turnover in September to mid-October and during the next winter and spring from March to May. In the epilimnion, methanotrophic activity was measured at 2 m from late June to mid-October ($0.04\text{--}1.8 \text{ mmol CH}_4 \text{ m}^{-3} \text{ d}^{-1}$) and at the surface water layer ($0\text{--}0.3 \text{ m}$) from July to mid-October ($0.02\text{--}1.3 \text{ mmol CH}_4 \text{ m}^{-3} \text{ d}^{-1}$).

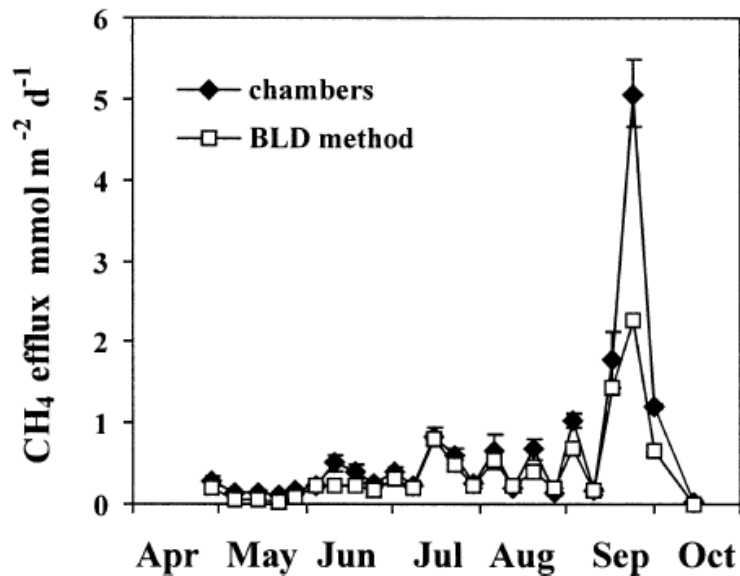


Figure 5. Methane efflux from Lake Valkea-Kotinen in 2002 determined with two different methods (I). © 2006, by the American Society of Limnology and Oceanography, Inc.

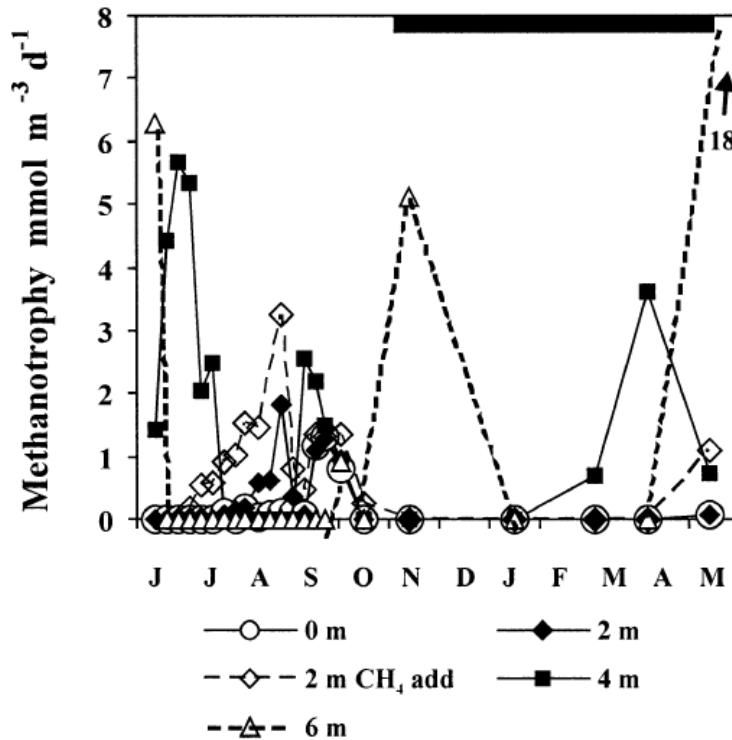


Figure 6. Methanotrophy ($\text{mmol CH}_4 \text{ m}^{-3} \text{ d}^{-1}$) in the water of Lake Valkea-Kotinen measured from June 2002 until May 2003 at 0-, 2-, 4- and 6-m depths. At 2 m, results after CH_4 addition to the water samples are also given. Black horizontal bar on the top denotes ice cover (I). © 2006, by the American Society of Limnology and Oceanography, Inc.

3.3 CO_2 dynamics and exchange between the lake and the atmosphere

The CO_2 concentration in Lake Valkea-Kotinen showed a yearly pattern similar to that of CH_4 . The lake was also steeply stratified in terms of CO_2 from May until the autumn turnover and the spring turnover was usually incomplete (Fig. 6 in II), i.e. high hypolimnetic concentrations extended until the autumn turnover. In summer during the stratification period, the CO_2 concentrations in the epilimnion were usually less than 60 mmol m^{-3} , and at the very surface in midsummer lower than 30 mmol m^{-3} , when the concentrations at or below equilibrium were not uncommon (Fig. 7). Below the thermocline the concentration was usually more than 300

mmol m^{-3} , i.e. one order of magnitude higher than in the surface water. In the anoxic hypolimnion, the CO_2 accumulates throughout the stagnation period, so that just before the fall turnover the concentrations at the very bottom may reach 600 mmol m^{-3} (Fig. 6 in II).

The highest surface water CO_2 concentrations are usually measured in spring after ice melt, although the concentrations in autumn may reach the same level (Fig. 7). The concentration rapidly decreases close to atmospheric equilibrium in spring and often CO_2 is consumed below the equilibrium by primary producers in the surface water during spring and summer. Occasional increases in surface water CO_2 were seen throughout the summers until the greater burst of hypolimnetic CO_2 -rich water to the

surface at the onset of the break in stratification. During autumn turnover surface water CO_2 concentration remains well above the equilibrium until the lake freezes over.

The diel cycle is visible in the surface water CO_2 concentration almost throughout the growing season, slowly fading away towards freeze-over together with decreasing irradiance (Fig. 7 in III, Fig. 3 in IV). The concentration is highest in the morning after sunrise and lowest in the evening and thus clearly governed by irradiance and reflecting the metabolism of the lacustrine ecosystem. The diel cycle is sometimes blurred by pulses of CO_2 -rich

hypolimnetic water, which are due to weather changes (III). Surface water CO_2 concentrations are clearly associated with the strength of the stratification (Fig. 8). The euphotic zone and the mixing depth are restricted within the first metre of the lake surface during stratification, below which there is a high level of storage of CO_2 (Fig. 7, Fig. 6 in II). Hence, when the mixing depth increases, CO_2 from the hypolimnetic water is supplied to the surface and simultaneously, the light climate of planktonic primary producers deteriorates and productivity and carbon uptake decrease.

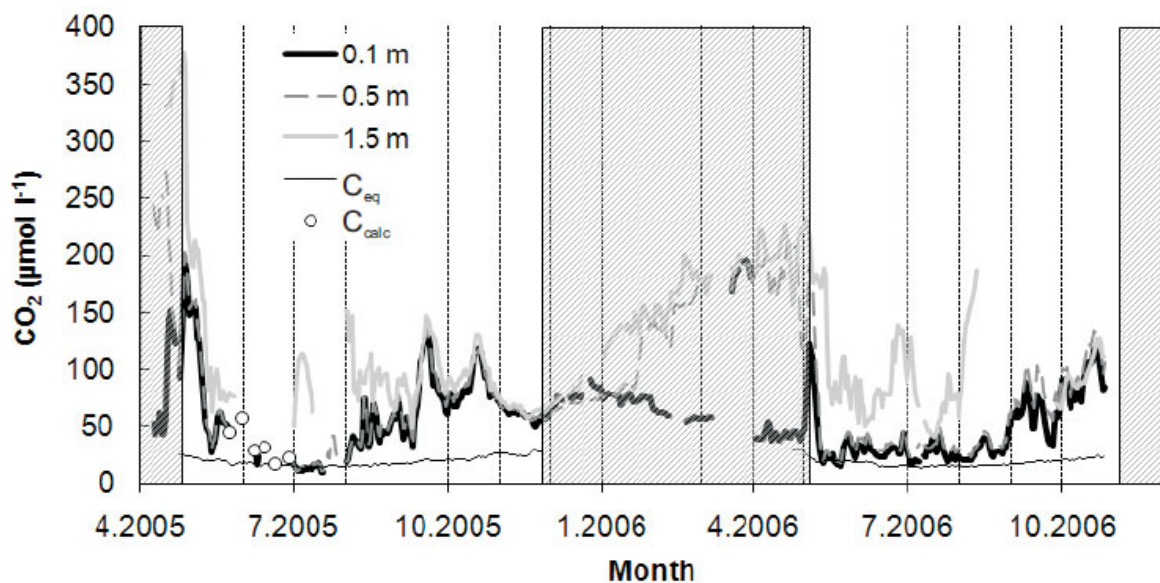


Figure 7. Daily averages of surface water CO_2 concentrations ($\mu\text{mol L}^{-1}$) at different depths, CO_2 concentrations calculated from DIC and pH (C_{calc}) and atmospheric equilibrium concentration (C_{eq}). Shaded blocks represent ice-covered periods (III).

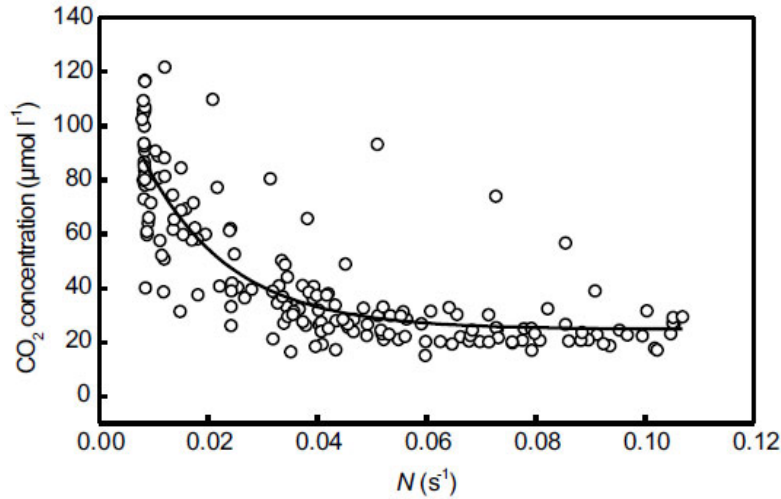


Figure 8. Relationship between surface water CO_2 concentration and stability frequency (N_s). The curve follows the first-order exponential decay function $\text{CO}_2 = 106.07\exp(-N_s/0.0157) + 24.74$ (III).

Lake Valkea-Kotinen was annually a source of CO_2 to the atmosphere. The time of the ice-out in late April or early May and the following spring turnover was quite distinct in the annual CO_2 flux dynamics, although the turnover was often incomplete and short (Fig. 9). During the summer months the lake regularly acted as a CO_2 sink, but in general the summertime variation in CO_2 fluxes was large. Occasional event-type deepening of the epilimnion due to cooling of the air temperature and often simultaneous increase in wind speed or precipitation caused bursts of CO_2 , resulting in fluxes above the normal variation. The thermocline began to deepen in late July or August and in September the lake became a continuous source of CO_2 . The autumn turnover occurred by mid-October at the latest. The ice cover in autumn, mainly consisting of congelation ice, proved to be gastight, since the ice-over days with zero fluxes are visible in the flux data (Fig. 9).

The mean annual CO_2 flux of Lake Valkea-Kotinen over the 5-yr measuring

period was $77 (\pm 11 \text{ SD}) \text{ g C m}^{-2}$. The mean daily CO_2 flux in spring, averaged over the period from ice-out until late May, was $0.31 (\pm 0.16) \text{ g C m}^{-2} \text{ d}^{-1}$ (Fig. 2 in V) and the spring period contributed $13.4\% (\pm 6.3\%)$ to the annual flux. Annually, most of the CO_2 was emitted to the atmosphere in late summer, when the thermocline was deepening, and during the autumn turnover in September–October. The mean daily CO_2 fluxes during the monthly periods from August until freeze-over were $0.52 (\pm 0.18) - 0.56 (\pm 0.22) \text{ g C m}^{-2} \text{ d}^{-1}$ (Fig. 2 in V), and this period contributed up to 77% to the annual fluxes. The flux decreased until freeze-over concomitantly with the decrease in surface water CO_2 concentration, which however did not reach atmospheric equilibrium. Differences in annual fluxes could not be associated with differences in DOC or precipitation. The length of the ice-covered period of the preceding winter correlated best with annual fluxes (V).

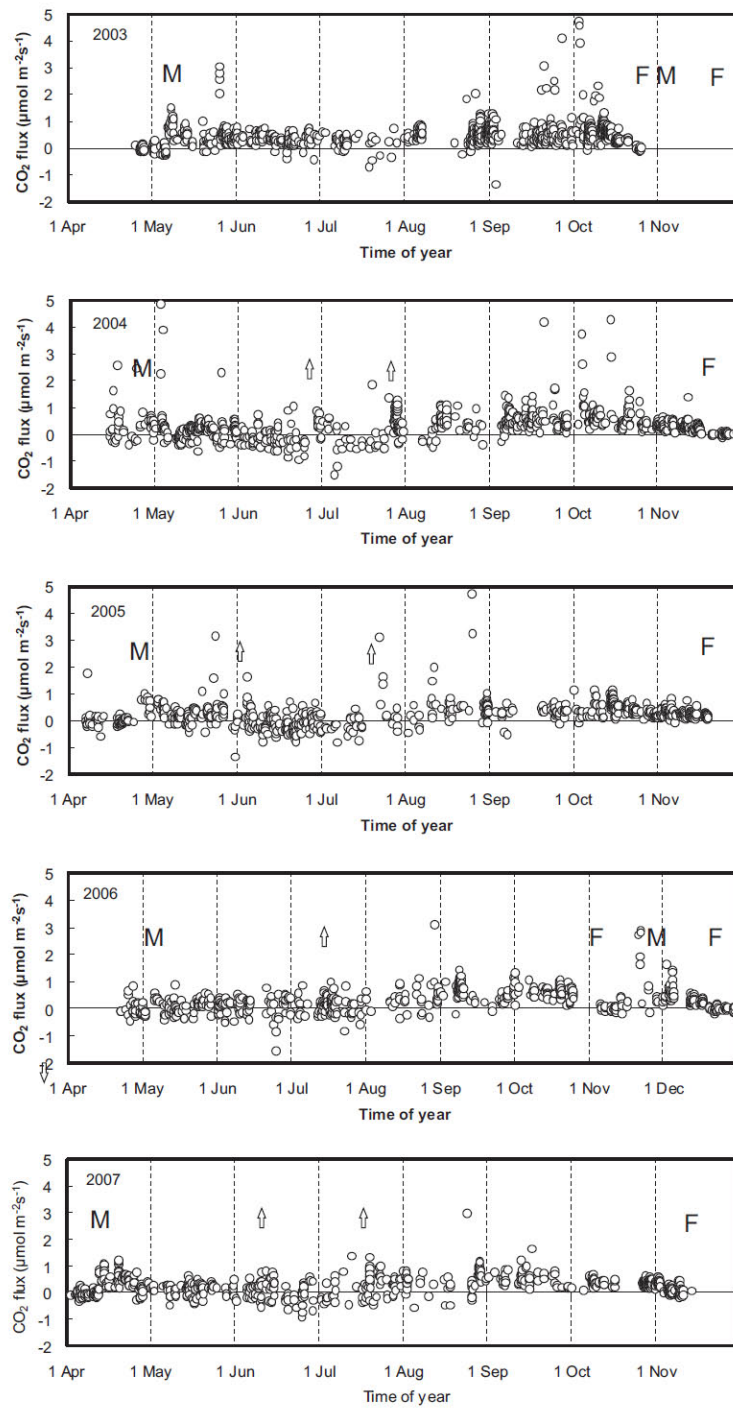


Figure 9. Half-hourly CO₂ fluxes over open-water periods of 2003–2007. Positive values indicate upward transport (emission). Capital letters M and F represent times of ice melt and freeze-over, respectively. Upward arrows represent bursts of CO₂ during summer stratification, as discussed in the text.

Since in addition to the EC measurements, the CO₂ fluxes for years 2003 (II), 2005 (III) and 2006 (III) were determined with BLM, the different methods could be compared. In II, the BLM estimate was based on a sporadic weekly sampling of the surface water CO₂ concentration, whereas in III the surface water CO₂ was measured continuously except for some gaps in the measurements, which were filled based on weekly samplings and linear interpolation. Regardless of the method used, the same seasonal pattern was found, but the EC gave higher estimates than the BLM. When all three years were included in comparison of the monthly fluxes, the EC gave flux estimates almost twice as high as those of the BLM. When year 2003 with sporadic sampling was omitted, the estimates were closer to each other but EC gave still almost 40% higher estimates than the BLM. The Pearson's correlation coefficient of the two datasets was 0.790 ($P < 0.01$).

When the datasets from III and V for year 2006 were combined, the dependence of CO₂ flux on the concentration difference (expressed here as partial pressure) was clear and it explained 37% of the variation in CO₂ flux (Fig. 10, $P = 0.000$). The factor k_{600} could be resolved from the combined dataset according the equations 5, 6 and 8. Its dependence on wind speed was unclear when the entire dataset was examined (not shown), but in autumn (September–October) the wind speed explained 39 % of the variation in k_{600} (Fig. 11). Commonly, the wind speed measured at or converted to a reference height of 10 m is used. However, the true wind speed measurements at 1.5 m above the lake surface were used, because when converting wind speeds to a height of 10 m using a logarithmic wind profile, the R² value was notably lower.

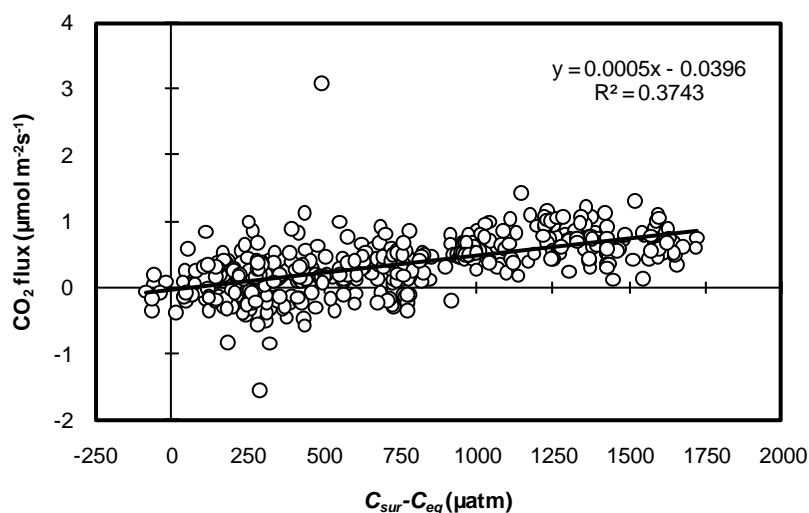


Figure 10. Relationship between CO₂ flux and the difference between pCO₂ of surface water and atmospheric equilibrium ($C_{sur} - C_{eq}$).

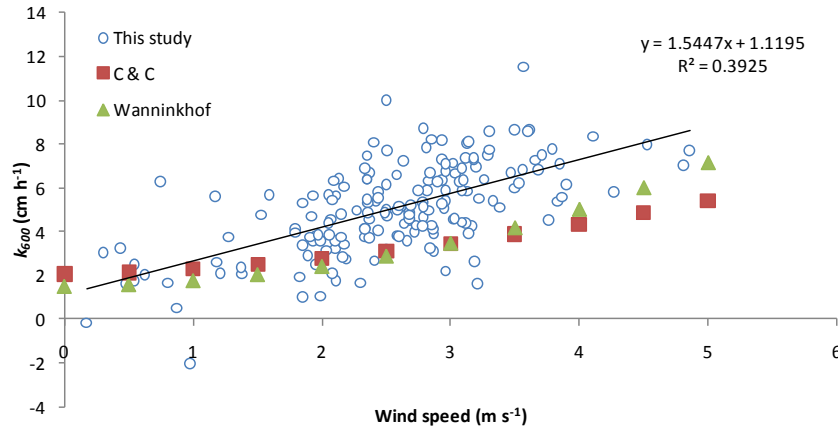


Figure 11. Relationship between normalized gas transfer velocity (k_{600}) and wind speed. The linear relationship is in the form of $y = 1.5447x + 1.1195$ and wind speed explained 39% of the variation in k_{600} . Red squares (C&C) and green triangles (Wanninkhof) represent the widely used empirically determined relationships by Cole & Caraco (1998) and Wanninkhof et al. (1985), respectively.

3.4 Free-water approach for determination of primary production and community respiration

The surface water CO_2 concentration in October 2004 showed a diel cycle clearly driven by light (Fig. 3 in IV). The net CO_2 exchange between living organisms and water (g) could be calculated from the continuous CO_2 concentration measurements with mass balance equation 9. The dependence of g on light (PAR)

(Fig. 12) could then be described with equation 10 and the parameters were estimated to be $p_{max} = 0.54 \pm 0.04 \mu\text{mol m}^{-2} \text{s}^{-1}$, $b = 59.1 \pm 13.1 \mu\text{mol m}^{-2} \text{s}^{-1}$, and $r_0 = 0.15 \pm 0.005 \mu\text{mol m}^{-2} \text{s}^{-1}$. When the light dependence of the photosynthetic rate was integrated over time the mean rate of $9.39 \pm 2.00 \text{ mmol m}^{-2} \text{d}^{-1}$ was obtained. The mean daily respiration r was estimated to be $20.5 \pm 0.14 \text{ mmol m}^{-2} \text{d}^{-1}$, resulting in a net ecosystem exchange (NEE) of $-11.1 \text{ mmol m}^{-2} \text{d}^{-1}$.

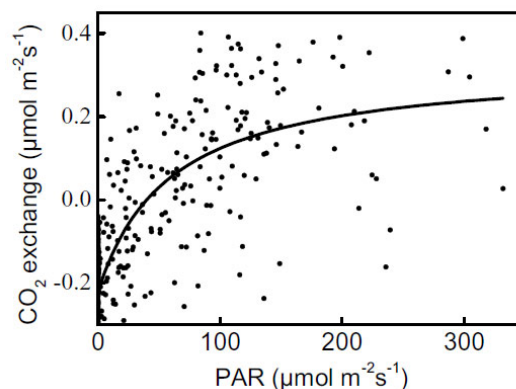


Figure 12. The Michaelis-Menten -type light (photosynthetically active radiation, PAR) dependence of CO_2 exchange between living organisms and water (IV). © 2008, by the American Society of Limnology and Oceanography, Inc.

4. DISCUSSION

As is typical of boreal brown-water lakes, Lake Valkea-Kotinen is steeply stratified and an anoxic hypolimnion is formed both in summer and winter. The very short or incomplete spring turnover, also common in Lake Valkea-Kotinen, is also a typical phenomenon in small, sheltered, boreal humic lakes, because stained humic substances rapidly absorb solar radiation and a warmer, lighter epilimnetic layer can be formed within a few days after melting of ice cover (Salonen et al. 1984, Keskitalo et al. 1998). These circulation and stratification patterns also have major effects on greenhouse gas dynamics of the lakes.

4.1 CH₄ concentration and flux

Summer stratification and winter ice cover seal the hypolimnion from the exchange of gases with the atmosphere and thus substantial amounts of both CH₄ and CO₂ can be accumulated in the hypolimnion. The seasonal dynamics of the CH₄ determined in I showed that contrary to studies stating the importance of ice melt and following spring turnover as a period of large CH₄ emissions (Michmerhuizen et al. 1996, Phelps et al. 1998), spring was the time of smallest efflux in Lake Valkea-Kotinen. Although the spring turnover was too short to re-aerate the hypolimnion in 2002, it ensured enough O₂ that instead of being emitted to the atmosphere, the CH₄ was mostly oxidized in the water column and the wintertime storage was effectively consumed. Increased primary production due to enhanced light availability in spring may have produced the O₂ needed in the biological oxidation or the CH₄ could also

have been consumed in anaerobic oxidation (Raghoebarsing et al. 2006).

During summer stratification, three times more CH₄ was oxidized than emitted to the atmosphere, the most active depth of oxidation being between 2 and 4 m (I), thus creating an effective buffer to transport of CH₄ by turbulent diffusion from the hypolimnion to the surface. However, the surface concentrations of CH₄ were higher than at 2 m from February until mid-July, even before notable methanotrophic activity began at 2 m, implying that some of the CH₄ diffused from the hypolimnion escaped oxidation. The estimated turbulent diffusion of CH₄ across the thermocline exceeded the methanotrophy measured in the epilimnion (Fig. 7 in I), supporting the idea that surplus CH₄ at the surface is transported across the active oxidation layer. The CH₄ could also have entered the lake surface by lateral transport from the surrounding soils or littoral zone (Hofmann et al. 2010). Rain events can flush the CH₄ from the catchment to lakes, which was seen in 2004 in the larger Lake Pääjärvi nearby, where high surface water concentrations of CH₄ were measured as a consequence of heavy rains (Ojala et al. 2011). Furthermore, high concentrations of CH₄ have been measured from the riparian soil at Lake Valkea-Kotinen (Rasilo, T. et al. *manuscript*), which may increase the surface water CH₄ concentrations if transported to the lake by the surface runoff.

In summer, the hypolimnetic accumulation of CH₄ was notably higher than in winter and the highest CH₄ fluxes were measured during autumn turnover. This differs from the pattern observed in northern Minnesota and Wisconsin, where the wintertime storage of CH₄ was higher than in summer and springtime oxidation

was considered negligible compared with the efflux (Michmerhuizen et al. 1996, Striegl & Michmerhuizen 1998). However, high rates of CH₄ oxidation can occur in winter throughout the water column of eutrophic and sheltered dystrophic lakes, resulting in lowered O₂ concentration or even anoxia (Kuznetsov 1935, Rudd et al. 1976, Wetzel 2001). The estimate that 80% of the CH₄ diffusing from the sediment of Lake Valkea-Kotinen is oxidized in the water column, remainder being emitted to the atmosphere, compares well with the measurements by Striegl & Michmerhuizen (1998) who found corresponding percentages to be 62-79% in two lakes in Minnesota, USA.

4.2 CO₂ concentration and flux

The stratification-driven seasonal pattern of CO₂ dynamics was shown in III and V. As with CH₄, CO₂ accumulated in the hypolimnion during winter and summer, also resembling the pattern found in other lakes in the Boreal (Kortelainen et al. 2004), and Temperate Zones (Cole et al. 1994, Michmerhuizen et al. 1996, Cole & Caraco 1998, Riera et al. 1999). The incomplete spring turnover, which was a common occurrence in Lake Valkea-Kotinen and resulted in the high hypolimnetic CO₂ storage extending to the end of summer and was not emitted until autumn turnover, was also reported from temperate humic lakes by Riera et al. (1999). The most interesting feature of CO₂ dynamics in Lake Valkea-Kotinen is probably the summertime surface water concentration, which was occasionally lower than the atmospheric equilibrium, implying net autotrophy of the euphotic zone and from time to time a role as a carbon sink. It is almost a paradigm that

boreal humic lakes are oligotrophic systems in which heterotrophic respiration exceeds primary production and thus supersaturation of CO₂ prevails. At the time of strongest stratification, the mixing layer in Lake Valkea-Kotinen can be even shallower than the euphotic layer and surface water CO₂ can be consumed under atmospheric equilibrium by vigorous primary production. The system can occasionally support a high stock of primary producers with high annual chlorophyll *a* concentration. The algal community in Lake Valkea-Kotinen is mainly composed of flagellated species [e.g. the raphidophyte *Gonyostomum semen* (Ehr.) Diesing, chrysophytes and dinoflagellates] capable of overcoming nutrient limitation in the surface water by vertical migrations to the nutrient-rich hypolimnion, or very small eukaryotic picoplankton efficient in nutrient and light harvesting (Peltomaa & Ojala 2010). However, the surface water CO₂ is also clearly controlled by the stability of stratification (Fig. 6, Fig. 3 in V); when the mixing layer deepens the hypolimnetic injections of CO₂-rich water to the surface increase the surface water concentration and also phytoplankton can be mixed deeper than the euphotic zone, resulting in the shift from net autotrophy to heterotrophy in the surface mixing layer. Nordbo et al. (2011) showed that wind-induced mixing events during stratification are rare in Lake Valkea-Kotinen and changes in the thermocline depth are mostly governed by convection.

EC measurements of CO₂ fluxes in lakes are scarce and there are only three published reports for comparison. The pioneering work by Anderson et al. (1999) presents data over five short periods of 2–8 days during three different years from

Williams Lake in north-central Minnesota, USA. Eugster et al. (2003) had three 1–3 day field campaigns at two sites: one at Toolik Lake, Alaska, USA, and another at Soppensee, Switzerland. Jonsson et al. (2008) measured almost a complete open-water period in oligotrophic Lake Merasjärvi in northern Sweden. Anderson et al. (1999) measured decreasing CO₂ fluxes from 2.7 $\mu\text{mol m}^{-2} \text{s}^{-1}$ to slightly negative values during a week right after ice melt. Their peak fluxes in spring were little higher than in Lake Valkea-Kotinen (Fig. 7), probably reflecting the fact that there was a complete spring turnover and the site in Williams Lake was more open to wind-induced turbulence that enhanced gas transfer. Eugster et al. (2003) measured in Toolik Lake, Alaska, USA, summertime fluxes of approximately -0.005 to 0.015 $\text{mg C m}^{-2} \text{s}^{-1}$ which equal -0.42 to 1.25 $\mu\text{mol m}^{-2} \text{s}^{-1}$, and Jonsson et al. (2008) obtained fluxes of app. -800 to 1500 $\text{mg C m}^{-2} \text{d}^{-1}$ equalling -0.75 to 1.5 $\mu\text{mol m}^{-2} \text{s}^{-1}$; these are all comparable to our flux values. Compared with the traditional ways to estimate CO₂ exchange between lake and atmosphere, EC provides a clear improvement in temporal and spatial coverage of ecosystem-scale CO₂ fluxes in a lake. However, a large part of the data had to be rejected, because the main requirement of the method, i.e. a steady state turbulent flow, could not always be fulfilled. A substantial amount of data was also rejected due to unfavourable wind direction (II, V). However, the accepted data included on average 9.8% of all the measured fluxes, which equals 2.4 hours per day during five consecutive open-water periods (V). This is much more than would be feasible with the traditional labour-intensive techniques relying on gas concentration measurements or closed

chambers. In a larger lake the EC measurements would probably result in a larger proportion of acceptable data, although the source area of the measurements may significantly increase (II). Motion of the raft due to waves was not a problem in Lake Valkea-Kotinen, but in larger lakes it should be measured and taken into account in post-processing of the data, or handled through use of a stable platform.

The CO₂ flux correlated well with the surface water CO₂ concentration (Fig. 3 in V) and also with the strength of stratification (V). Consistent with the surface water CO₂ concentration measurements (III), EC showed an occasional influx to the lake, while the hypolimnetic CO₂ injections to the surface water and concomitant bursts to the atmosphere during stratification were also detected with EC (Fig. 7). Surprisingly, these bursts of CO₂ during the stratification period were similar in magnitude to the spring and autumn turnovers, but they lasted only a short period of time. Generally, summer fluxes from boreal or north temperate humic lakes are regarded to be considerably lower than during turnover periods, due to lower surface water CO₂ concentrations. Ojala et al. (2011) reported summer fluxes as high as in spring and autumn from Lake Pääjärvi, 20 km from Lake Valkea-Kotinen, and they associated the fluxes with lateral transport of CO₂ from the catchment, due to exceptional heavy rains in 2004. The effects of the same rains were also seen in Lake Valkea-Kotinen, causing two distinct bursts of CO₂ (Fig. 7).

The mean annual CO₂ flux in Lake Valkea-Kotinen, i.e. 77 $\text{g C m}^{-2} \text{yr}^{-1}$ (V), which equals 6.4 $\text{mol m}^{-2} \text{yr}^{-1}$, compares well with other published annual flux

estimates. For instance, Riera et al. (1999) obtained a flux of $6.7 \text{ mol m}^{-2} \text{ yr}^{-1}$ in a 0.5-ha bog lake in northern Wisconsin, USA using the BLM of Cole & Caraco (1998). Striegl & Michmerhuizen (1998) measured with chambers an annual efflux of $8.0 \text{ mol m}^{-2} \text{ yr}^{-1}$ from 65-ha Shingobee Lake in north-central Minnesota, and Ojala et al. (2011) 5.5 and $6.9 \text{ mol CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$, based on the model of Cole & Caraco (1998) and chamber measurements, respectively, of 13.4-km^2 Lake Pääjärvi. The long-term average in Lake Valkea-Kotinen was 30% lower than estimated for small lakes from a large sample of statistically selected lakes in Finland (Kortelainen et al. 2004). Kortelainen et al. (2004) showed that the partial pressure of CO_2 ($p\text{CO}_2$) and thus the amount of CO_2 emitted to the atmosphere is inversely proportional to lake size, which was also reported by Kelly et al. (2001), and lakes $< 1 \text{ km}^2$ annually emit on average $102 \text{ g C m}^{-2} \text{ yr}^{-1}$, i.e. $8.5 \text{ mol m}^{-2} \text{ yr}^{-1}$. Moreover, the proportion of agricultural land in the catchment and high concentrations of nitrogen (N) and phosphorus (P) predicted high CO_2 concentrations and flux, whereas the relationship between peatland proportion in the catchment and CO_2 concentration was negative. The lower fluxes in Lake Valkea-Kotinen, having a surface area of 0.041 km^2 , probably reflect the undisturbed catchment with peaty soils. The various methods used for determining the fluxes may also explain the higher estimate by Kortelainen et al. (2004); they estimated fluxes with the BLM (Cole & Caraco 1998), used a constant U_{10} value of 3 m s^{-1} to calculate the k_{600} and integrated the annual fluxes from only four annual (winter, spring, summer, autumn) concentration measurements. Although Kelly et al. (2001) stated that four evenly

distributed samples per year is enough for determining the average $p\text{CO}_2$, the continuous measurements from Lake Valkea-Kotinen showed that the annual course of CO_2 is so dynamic that it is easy to miss episodic events. Even sampling at fixed times of the day can also result in erroneous estimates of the daily averages, due to significant diel cycles in the surface water CO_2 concentration (III). Sellers et al. (1995) also pointed out the importance of frequent measurements of surface water CO_2 in estimates of CO_2 flux. Small and sheltered lakes may also be subject to lower winds and U_{10} values taken from measurements elsewhere may not be applicable to them.

4.3 CO_2 exchange between Lake Valkea-Kotinen and the atmosphere, obtained with different methods

The discrepancy between the fluxes modelled and the EC measurements was also evident when estimates for the years 2005 and 2006 in Lake Valkea-Kotinen were compared (III, IV). The BLM (Cole & Caraco 1998) gave annual fluxes of 3.7 and 2.5 mol m^{-2} (III), whereas the fluxes measured were 6.2 and 7.4 mol m^{-2} (IV), respectively. It is notable that the 20-day open water period from 30 November until 19 December was excluded from the flux modelled in 2006 since the measurements were stopped on 3 November due to freeze-over. Leaving this 20-day period out from the EC estimate resulted in a flux of $6.1 \text{ mol m}^{-2} \text{ yr}^{-1}$. Thus, EC resulted in 70% and 144% higher flux estimates in 2005 and 2006, respectively. The discrepancy was similar to that reported in Cole & Caraco (1998), who used different models for gas transfer velocity in Mirror Lake, New Hampshire, USA, i.e. the annual flux

estimate was 70% higher when they used wind speed- and precipitation-based calculations for gas transfer velocity than when only a wind speed-based calculation was used. This demonstrates uncertainty in the use of gas exchange models. Cole & Caraco's (1998) empirically determined relationship between wind speed and k_{600} is widely used in the scientific community, especially for studies of gas exchange under low-wind conditions. However, gas transfer is probably not dependent on wind speed, especially under low-wind conditions (Ocambo-Torres & Donelan 1994, Cole & Caraco 1998), but other factors such as heat loss are more likely to control gas exchange (MacIntyre et al. 1995).

The importance of other factors besides wind speed became evident when trying to establish the relationship between gas transfer velocity and wind speed for the combined datasets from III and V for the year 2006. The lack of general relationship was evident when the entire dataset was used, since the wind speed explained only 1.7% of the variation in normalized gas transfer velocity (k_{600}). However, when only the autumn (September–October) was considered the wind speed explained almost 40% of the variation in gas transfer velocity (Fig. 9), implying that the relationship is time-dependent and in spring and summer some other factors are more important in controlling k_{600} . However, throughout the year data a single factor could at most explain only 6% of the variation in k_{600} . The time-dependent nature of the relationship between gas transfer velocity and wind speed was also reported by López Bellido et al. (2009) from Lake Pääjärvi, who calculated the gas transfer velocities from simultaneous chamber measurements and measurements of air-

surface water CO_2 differences and found that the dependency for wind was stronger right after the ice melt during spring turnover than in autumn. Anderson et al. (1999), who determined gas transfer velocities from EC measurements and models, also concluded that “there are temporal mechanisms determining when models and measurements agree”. The relationship between k_{600} and wind speed found for the autumn data was steeper in Lake Valkea-Kotinen than as determined by Cole & Caraco (1998), and a steeper relationship was also reported by Jonsson et al. (2008). The footprint (source area) modelling over Lake Valkea-Kotinen revealed that turbulence generated above the surrounding forest is transported with wind over the lake (II) and this may partly explain the steeper relationship between k_{600} and wind speed. This is most probably a universal phenomenon and should be taken into account when estimating gas fluxes over sheltered lakes. However, these results suggest that actual measurements of turbulence of the surface water should be conducted together with flux and surface water gas concentration measurements to reveal if the gas transfer velocity can be reliably modelled from wind speed or from any other easily measured environmental variable.

In addition to the turbulence that with the concentration difference across the water-air interface are the major drivers of the gas exchange (MacIntyre 1995), the monthly averaged CO_2 flux was clearly dependent on the surface water $p\text{CO}_2$ (V). The difference between the surface water concentration and the atmospheric equilibrium explained 37% of the variation in the flux when the combined dataset was also considered (Fig. 8). This relationship in Lake Valkea-Kotinen is much stronger

than that measured with a comparable apparatus in oligotrophic Lake Merasjärvi in northern Sweden, where the amount of excess CO₂ in the surface water explained only 15% of the variation in CO₂ flux (Åberg et al. 2010). The range in surface water concentration in excess of atmospheric equilibrium in Lake Merasjärvi was only 20 µM, compared with 100 µM in Lake Valkea-Kotinen, which may partly explain the difference. In Lake Valkea-Kotinen there were several occasions in which surface water CO₂ concentration was within 30 µM above equilibrium, which implied influx into the lake. Although it may be just noise of the EC measurements, it is more likely that it was a result of the different source areas of EC and the surface water concentration measurements. EC integrated fluxes from an elusively defined area upwind from the measuring point that was, however, modelled to fit well within the lake surface area when the requirements of turbulent flow were fulfilled (II). The area occupied by the littoral flora is ~25% of the lake surface area (Keskitalo et al. 1998). Thus, the source area of the EC may have reached the shallow littoral area where the CO₂ concentration can be under atmospheric equilibrium, due to primary production of the littoral communities. The horizontal variability in the surface water CO₂ concentration was not measured in Lake Valkea-Kotinen, but its importance has been emphasized by Pace & Prairie (2005), who found daily variations in some shallow littoral areas to be 5-fold compared with the middle of the small bay of Lake Memphremagog in Quebec, Canada. The source area of the surface water CO₂ concentration measurements was much smaller than that of the EC. Different source areas of the two measurements are

probably also partly responsible for the lack of explanatory factors for k_{600} in summer, because in summer the lake most likely experiences the highest horizontal variability in surface water CO₂.

4.4 Free-water approach

The free-water approach, tested in IV for determination of primary production and community respiration in Lake Valkea-Kotinen, showed much higher metabolic rates than the traditional bottle incubations conducted as a part of ICP IM activities (IV). The difference between the two methods in determining the primary production was app. 5-fold. The difference observed in Lake Valkea-Kotinen probably was partly explained by the fact that the free-water approach gave an estimate of gross primary production, whereas the result of the ¹⁴C method is much closer to net primary production, due to the long incubation time (24 h) (Peterson 1980 and references therein). In the case of respiration, the discrepancy was even larger, i.e. the free-water approach gave an approximately 16-fold higher estimate than the bottle incubation. The same type of discrepancy was reported by Pace & Prairie (2005). The free-water method is argued to give results different from bottle incubations, because they measure different compartments of the lake, i.e. the free-water method integrates from bacteria to fish and from autotrophic picoplankton to macrophytes, resulting in estimates of total lake metabolism, including benthic, littoral and pelagic communities, whereas bottle incubation includes only the pelagic plankton enclosed in the bottle (Hanson et al. 2003, Pace & Prairie 2005). In these estimates, however, only the flux to the atmosphere is considered. The free-water

estimate can be restricted to pelagic communities only if fluxes from the euphotic zone to the air and from the deeper waters to the euphotic zone are known and if advection can be estimated. The accurate determination of these fluxes is important, as shown in Eq. 9 and thus the actual measurements of turbulence in the water are necessary to improve the reliability of the flux estimates and further the estimates of metabolic processes of the lake. The effect of advection in Lake Valkea-Kotinen could not be determined and the littoral communities may have affected the estimate of lake metabolism.

The use of the free-water approach is advisable, since the inherent problems in bottle incubations can be avoided, i.e. nutrient availability, mixing, light climate and grazing pressure remain natural. The approach can be applied in all types of aquatic systems, assuming that pH is measured simultaneously with CO₂ to calculate the mass balance of DIC in less acidic systems where bicarbonate dominates the inorganic carbon pool. In choosing the applied light response model carefully, the approach presented here can result in ecophysiological relevant information on adaptations of phytoplankton communities under natural conditions.

4.5 Regional relevance

The importance of Lake Valkea-Kotinen as a site of remineralization of terrestrial carbon can be assessed when the flux is calculated per catchment area. In V, the annual CO₂ flux normalized to catchment area was 11 g C m⁻² yr⁻¹, which can be compared with estimates of the NEP of unmanaged boreal forests in corresponding temperature and

precipitation regimes (Luyssaert et al. 2007). The NEP estimates varied roughly from -50 to 200 g C m⁻² yr⁻¹ (Luyssaert et al. 2007) and thus in Valkea-Kotinen the CO₂ flux normalized to the catchment area yielded a 20% addition to the source at one end and a 5% decrease in the sink on the other end of the range and showed that the lake is potentially a very important factor in regional carbon balance. The unmanaged forest surrounding Lake Valkea-Kotinen is in the phase of late succession, but the carbon loss from catchments under forest management with fast-growing stands building up tree biomass, is probably substantially lower (Jonsson et al. 2007, Ojala et al. 2011). The carbon loss from the lake in the form of CH₄ and the long-term net sedimentation (2.8 g C m⁻² yr⁻¹; Pajunen 2004) together are only 5% of the CO₂ flux, and as minor components are not included in the comparison. However, in estimating the GWP, the flux of CH₄ from Lake Valkea-Kotinen, 0.11 mol CH₄ m⁻² yr⁻¹, equals 2.75 mol m⁻² yr⁻¹ in CO₂ equivalents and thus contributes to 30% of GWP in Lake Valkea-Kotinen. These results strongly support the message by Cole et al. (2007), Battin et al. (2009) and Tranvik et al. (2009) that inland waters make a difference in regional and global carbon cycling and should also be taken into account in larger-scale studies of rates and processes.

5. CONCLUSIONS

Stratification dynamics controlled the gas concentration and flux dynamics in Lake Valkea-Kotinen. The role of stratification was clearer in the case of CO₂; the highest fluxes occurred in spring when stable stratification had not yet formed and during

autumn turnover when stratification was lost, whereas during stable stratification in summer, the surface water CO₂ concentration could be consumed under atmospheric equilibrium by primary production, resulting in influx to the lake. When the mixing layer extended deeper, it brought CO₂-rich water to the surface, causing a sudden burst of CO₂ comparable to the fluxes in spring and autumn. The surface water CO₂ concentration correlated with the strength of stratification. The lake was a source of CH₄ throughout the open-water period, but in spring CH₄ was effectively oxidized and the highest fluxes occurred in the autumn turnover. Some CH₄ escaped oxidation during the stratification period and diffused to the surface, resulting in small variations in summertime fluxes.

EC proved useful in measurements of CO₂ fluxes in lakes. The result was not as continuous information on CO₂ fluxes over the lake, as anticipated due to high rejection percentage of the data, but it was still superior compared with that obtained with traditional methods. Together with continuous surface water CO₂ measurements, it revealed that the widely used gas exchange model, in which gas transfer velocity is related to wind speed, underestimates fluxes in this sheltered lake. This was probably because the flow measured above Lake Valkea-Kotinen was more turbulent than the flow with the same wind speed above larger lakes. The gas transfer velocity appeared to be time-dependent over this lake, because some factor other than wind controlled the gas exchange in summer or the large horizontal variability in surface water CO₂ concentration smeared all the relations. Careful consideration in choosing a site for

future EC studies on small lakes is suggested, however.

The free water approach for determination of primary production and community respiration also appeared useful in measuring lake metabolism, but due to the short evaluation time in autumn, further examination and comparison with the other methods is needed. Careful determination of the fluxes from the euphotic zone to the air and from the deeper layers to the euphotic layer is prerequisite of the method and the actual measurements of these fluxes should be especially considered. Advection may also be important in mass balance of CO₂ in the euphotic layer and should be kept in mind when interpreting the results.

Actual turbulence, together with flux and concentration measurements of the surface water, are necessary to improve the estimates of the relationship between gas transfer velocities and wind speed, or to determine the possible relationships with other environmental factors. Measurements of surface water turbulence would also improve the free-water approach in determining the important fluxes contributing to the mass balance of the surface water CO₂.

High levels of uncertainty remain in the importance of Lake Valkea-Kotinen in regional carbon cycling, since there are no measurements of NEP from its catchment. However, the estimates from the literature of unmanaged forests in corresponding temperature and precipitation regimes suggest that Lake Valkea-Kotinen is potentially important in recycling terrestrial carbon and emitting it into the atmosphere. Its contribution ranges from increasing the source effect of the surrounding forest by 20% to decreasing its sink effect by 5%. In Lake Valkea-Kotinen the contributions to

the GWP were 70% and 30% for CO₂ and CH₄, respectively.

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7. REFERENCES

- Åberg, J., Jansson, M. & Jonsson, A. 2010. Importance of water temperature and thermal stratification dynamics for temporal variation of surface water CO₂ in a boreal lake. *J. Geophys. Res.* 115, G02024, doi:10.1029/2009JG001085.
- Anderson, D. E., Striegl, R. G., Stannard, D. I., Micherhuizen, C. M., McConnaughey, T. A. & LaBaugh, J. W. 1999. Estimating lake-atmosphere CO₂ exchange, *Limnol. Oceanogr.* 44: 988– 1001.
- Aubinet M., Grelle, A., Ibrom, A., Rannik, Ü., Moncrieff, J., Foken, T., Kowalski, A. S., Martin, P. H., Berbigier, P., Bernhofer, C., Clement, R., Elbers, J., Granier, A., Grünwald, T., Morgenstern, K., Pilegaard, K. Rebmann, C., Snijders, W., Valentini, R. & Vesala T. 2000. Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology. *Adv. Ecol. Res.* 30: 113-175.
- Baldocchi, D. D. 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: Past, present and future, *Global Change Biol.* 9: 479– 92.
- Bastviken, D., Cole, J., Pace, M. & Tranvik, L. 2004. Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. *Global Biogeochem. Cycles* 18, GB4009, doi: 10.1029/2004GB002238.
- Battin, T. J., Luysaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A. & Tranvik, L. J. 2009. The boundless carbon cycle. *Nature Geosci.* 2, 598-600.
- Belanger, T. V. & Korzun, E. A. 1991. Critique of floating dome technique for estimating reaeration rates. *J. Envir. Engrg.* 117: 144-150.

- Butler, J. N. 1982. Carbon dioxide equilibria and their applications. Addison-Wesley Publishing Company, Reading, Massachusetts.
- Capone, D. G. & Kiene, R. P. 1988. Comparison of microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon metabolism. *Limnol. Oceanogr.* 33: 725-749.
- Carignan, R. 1998. Automated determination of carbon dioxide, oxygen, and nitrogen partial pressures in surface waters. *Limnol. Oceanogr.* 43: 969-975.
- Carignan, R., Planas, D. & Vis, C. 2000. Planktonic production and respiration in oligotrophic Shield lakes. *Limnol. Oceanogr.* 45:189-199.
- Cole, J. J., Caracao, N. F., Kling, G. W. & Kratz, T. K. 1994. Carbon dioxide supersaturation in the surface waters of lakes. *Science* 265: 1568-1570.
- Cole, J. J. & Caraco, N. F. 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF₆. *Limnol. Oceanogr.* 43: 647-656.
- Cole, J. J., Pace, M. L., Carpenter, S. R. & Kittchell, J. F. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnol. Oceanogr.* 45: 1718-1730.
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburgh, J. J. & Melack, J. 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* 10: 171-184.
- Crusius, J. & Wannikhof, R. 2003. Gas transfer velocities at low wind speed over a lake. *Limnol. Oceanogr.* 48: 1010-1017.
- DeGrandpre, M. D., Hammar, T. R., Smith, S. P. & Sayles, F. L. 1995. In situ measurements of seawater pCO₂. *Limnol. Oceanogr.* 40: 969-975.
- Downing, J. A., Prairie, Y. T., Cole, J. J., Duarte, C. M., Tranvik, L. J., Striegl, R. G., McDowell, W. H., Kortelainen, P., Caraco, N. F., Melack, J. M. & Middelburg, J. J. 2006. The global abundance and size distribution of lakes, ponds, and impoundments. *Limnol. Oceanogr.* 51: 2388-2397.
- Duarte, C. M. & Prairie, Y. T. 2005. Prevalence of heterotrophy and atmospheric CO₂ emissions from aquatic ecosystems. *Ecosystems* 8: 862-870.
- Duchemin, E., Lucotte, M. and Canuel, R. 1999. Comparison of static chamber and thin boundary layer equation methods for measuring greenhouse gas emissions from large water bodies. *Environ. Sci. Technol.* 33: 350-357.
- Eugster, W., Kling, G., Jonas, T., McFadden, J. P., Wüest, A., MacIntyre, S. & Chapin III, F. S. 2003. CO₂ exchange between air and water in an Arctic Alaskan and midlatitude Swiss lake: Importance of convective mixing, *J. Geophys. Res.* 108(D12), 4362, doi:10.1029/2002JD002653.
- Foken, T. & Wichura B. 1996. Tools for quality assessment of surface-based flux measurements. *Agric. For. Meteorol.* 78(1-2): 83-105.
- Hanson, R. S. & Hanson, T. E. 1996. Methanotrophic bacteria. *Microbiol. Rev.* 60: 439-471.
- Hanson, P. C., Bade, D. L., Carpenter, S. R. & Kratz, T. K. 2003. Lake metabolism: Relationships with dissolved organic carbon and phosphorus. *Limnol. Oceanogr.* 48: 1112-1119.
- Hofmann, H., Federwisch, L. & Peeters, F. 2010. Wave-induced release of methane: Littoral zones as a source of methane in lakes. *Limnol. Oceanogr.* 55: 1990-2000.
- Horst, T. W. 1997. A simple formula for attenuation of eddy fluxes measured with first-order-response scalar sensors. *Boundary. Meteorol.* 82: 219-233.
- Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J. & Xiaosu, D. (eds.). 2001. Climate change 2001. The scientific basis. Cambridge Univ. Press.
- Huttunen, J. T., Hammar, T., Alm, J., Silvola, J. & Martikainen, P. J. 2001. Greenhouse gases in non-oxygenated and artificially oxygenated eutrophied lakes during winter stratification. *J. Environ. Qual.* 30: 387-394.
- Huttunen, J. T., Väisänen, T. S., Heikkinen, M., Hellsten, S., Nykänen, H., Nenonen, O. & Martikainen, P. J. 2002. Exchange of CO₂, CH₄ and N₂O between the atmosphere and two northern boreal ponds with catchments dominated by peatlands or forests. *Plant Soil* 242: 137-146.

- Jähne, B., Münnich, K. O., Börsinger, R., Dutzi, A., Huber, W. & Libner P. 1987. On the parameters influencing air-water gas exchange. *J. Geophys. Res.* 92: 1937–1949.
- Jonsson, A., Karlsson, J. & Jansson, M. 2003. Sources of carbon dioxide supersaturation in Clearwater and humic lakes in northern Sweden. *Ecosystems* 6: 224-235.
- Jonsson, A., Algesten, G., Bergström, A.-K., Bishop, K., Sobek, S., Tranvik, L. J. & Jansson, M. 2007. Integrating aquatic carbon fluxes in a boreal catchment carbon budget. *J. Hydrol.* 334: 141-150.
- Jonsson, A., Åberg, J., Lindroth, A. & Jansson, M. 2008. Gas transfer rate and CO₂ flux between an unproductive lake and the atmosphere in northern Sweden. *J. Geophys. Res.* 113, G004006, doi:10.1029/2008JG000688.
- Kankaala, P., Huotari, J., Peltomaa, E., Ojala, A. & Arvola, L. 2005. Methanotrophic activity in relation to primary and bacterial production in a boreal humic lake. *Verh. Internat. Verein. Limnol.* 29: 250-253.
- Kelly, C. A., Fee, E., Ramlal, P. S., Rudd, J. W. M., Hesslein, R. H., Anema, C. & Schindler, E. U. 2001. Natural variability of carbon dioxide and net epilimnetic production in the surface waters of boreal lakes of different sizes. *Limnol. Oceanogr.* 46: 1054-1064.
- Keskitalo, J., Salonen, K. and Holopainen, A.-L. 1998. Long-term fluctuations in environmental conditions, plankton and macrophytes in a humic lake, Valkea-Kotinen. *Boreal Env. Res.* 3:251-262.
- Kling, G. W., Kipphut, G. W. & Miller, M. C. 1992. The flux of CO₂ and CH₄ from lakes and rivers in arctic Alaska. *Hydrobiologia* 240: 23-36.
- Kortelainen, P., Huttunen, J. T., Väisänen, T., Mattsson, T., Karjalainen, P. & Martikainen, P. J. 2000. CH₄, CO₂ and N₂O supersaturation in 12 Finnish lakes before and after ice-melt. *Verh. Int. Verein. Limnol.* 27: 1410-1414.
- Kortelainen, P., Rantakari, M., Huttunen, J., Mattsson, T., Alm, J., Juutinen, S., Larmola, T., Silvola, J. & Martikainen, P. J. 2004. Sediment respiration and lake trophic state are predictors of large CO₂ evasion from small boreal lakes. *Global Change Biol.* 12: 1554-1567.
- Kuznetsov, S. I. 1935. Microbiological researches in the study of the oxygenous regimen of the lakes. *Verh. Internat. Verein. Limnol.* 7:562-582.
- Launiainen, S., Rinne, J., Pumpanen, J., Kulmala, L., Kolari, P., Keronen, P., Siivola, E., Pohja, T., Hari, P. & Vesala, T. 2005. Eddy covariance measurements of CO₂ and sensible and latent heat fluxes during a full year in a boreal pine forest trunk-space. *Boreal Env. Res.* 10: 569-588.
- Lide, D. R. & Fredrikse H. P. R. (eds.). 1995 CRC handbook of chemistry and physics, 76th ed. CRC Press.
- López Bellido, J., Tulonen, T., Kankaala, P. & Ojala, A. 2009. CO₂ and CH₄ fluxes during spring and autumn mixing periods in a boreal lake (Pääjärvi, southern Finland). *J. Geophys. Res.* 114, G04007, doi:10.1029/2009JG000923.
- Lyussaert, S., Inghima, I., Jung, M., Richardson, A. D., Reichstein, M., Papale, D., Piao, S. L., Schulze, E.-D., Wingate, L., Matteucci, G., Aragao, L., Aubinet, M, Beer, C., Bernhofer, C., Black, K. G., Bonal, D., Bonnefond, J.-M., Chambers, J., Ciais, P., Cook, B., Davis, K. J., Dolman, A. J., Gielen, B., Goulden, M., Grace, J., Granier, A., Grelle, A., Griffis, T., Gtünwald, T., Guidolotti, G., Hanson, P. J., Harding, R., Hollinger, D. Y., Hutya, L. R., Kolari, P., Kruijt, B., Kutsch, W., Lagergren, F., Laurila, T., Law, B. E., Le Maire, G., Lindroth, A., Loustau, D., Malhi, Y., Mateus, J., Migliavacca, M., Misson, L., Montagnani, L., Moncrieff, J., Moors, E., Munger, J. W., Nikinmaa, E., Ollinger, S. V., Pita, G., Rebmann, C., Rouspard, O., Saigusa, N., Sanz, M. J., Seufert, G., Sierra, C., Smith, M.-L., Tang, J., Valentini, R., Vesala, T. Janssens, I. A. 2007. CO₂ balance of boreal, temperate, and tropical forests derived from a global database. *Global Change Biol.* 13: 2509-2537, doi: 101111/j.1365-2486.2007.01439.x
- Massman, W. J. 2000. A simple method for estimating frequency response corrections for eddy covariance systems. *Agric. For. Meteorol.* 104: 185-198.
- Massman, W. J. 2001. Reply to comment by Rannik on "A simple method for estimating frequency response corrections for eddy covariance systems". *Agric. For. Meteorol.* 107: 247-251.
- McAuliffe, C. C. 1971. GC determination of solutes by multiple phase equilibration. *Chem. Technol.* 1: 46-51.

- MacIntyre, S., Wanninkhof, R. & Chanton J. P., 1995. Trace gas exchange across the air-water interface in freshwater and coastal marine environments. In: Matson, P. A. & Harris, R. C. (Eds.), *Biogenic Trace Gases: Measuring Emissions from Soil and Water*. Blackwell, pp. 52–97.
- Michmerhuizen, C. M., Striegl, R. G. & McDonald, M. E. 1996. Potential methane emission from north-temperate lakes following ice melt. *Limnol. Oceanogr.* 41: 985-991.
- Moore, C. J. 1986. Frequency-response corrections for eddy-correlation systems. *Bound-Lay Meteorol.* 37: 17-35.
- Mäkelä, K. 1995. Valkea-Kotinen; general features of the monitoring area. – In: Bergström, I., Mäkelä, K. & Starr, M. *Integrated monitoring programme in Finland, first national report*. Ministry of the Environment, Environmental Policy Department, Helsinki. Report 1: 16-18.
- Nordbo, A., Launiainen, S., Mammarella, I., Leppäranta, I., Huotari, J., Ojala, A. & Vesala, T. 2011. Long-term energy flux measurements and energy balance over a small boreal lake using eddy covariance technique. *J. Geophys. Res.* 116, D02119, doi:10.1029/2010JD014542
- Ocampo-Torres, F. J. & Donelan, M. A. 1994. Laboratory measurements of mass transfer of carbon dioxide and water vapour for smooth and rough flow conditions. *Tellus* 46B: 16–32.
- Ojala, A., López Bellido, J., Tulonen, T., Kankaala, P. & Huotari, J. 2011. Carbon gas fluxes from a brown-water and a clear-water lake in the Boreal Zone during a summer with extreme rain events. *Limnol. Oceanogr.* 56: 61-76.
- Pace, M. L. & Prairie, Y. T. 2005. Respiration in lakes. – In: del Giorgio, P. A. & le B. Williams, P. J. *Respiration in aquatic ecosystems*. pp. 103-121.
- Pajunen, H. 2004. Lake sediments as a store of dry matter and carbon. *Geological Survey of Finland, Report of Investigation* 160: 184-185. [In Finnish with English summary]
- Peltomaa, E. & Ojala, A. 2010. Size-related photosynthesis of algae in a strongly stratified humic lake. *J. Plankton Res.* 32: 341-355
- Peterson, B. J. 1980. Aquatic primary productivity and the ¹⁴C-CO₂ method: A history of the productivity problem. *Ann. Rev. Ecol. Sys.* 11: 359-385.
- Phelps, A. R., Peterson, K. M. & Jeffries, M. O. 1998. Methane efflux from high-latitude lakes during spring ice melt. *J. Geophys. Res.* 103: 29029-29036.
- Raatikainen, M & Kuusisto E. 1990. Suomen järvien lukumäärä ja pinta-ala [The number and surface area of the lakes in Finland]. *Terra* 102: 97-110. [In Finnish with English summary].
- Raghoebarsing, A. A., Pol, A., van de Pas-Schoonen, K. T., Smolders, A. J. P., Ettwig, K. F., Rijpstra, I. C., Schouten, S., Sinninghe Damsté, J. S., Op den Camp, H. J. M., Jetten, M. S. M. & Strous, M. 2006. A microbial consortium couples anaerobic methane oxidation to denitrification. *Nature* 440: 918-921.
- Rask, M., Holopainen, A-L., Karusalmi, A., Niinioja, R., Tammi, J., Arvola, L., Keskitalo, J., Blomqvist, I., Heinimaa, S., Karppinen, C., Salonen, K. & Sarvala, J. 1998. An introduction to the limnology of the Finnish Integrated Monitoring lakes. *Boreal Env. Res.* 3:263-274.
- Reynolds, C. S. 1984. *The ecology of freshwater phytoplankton*. Cambridge Univ. Press.
- Riera, J. L., Schindler, J. E. & Kratz, T. K. 1999. Seasonal dynamics of carbon dioxide and methane in two clear-water and two bog lakes in northern Wisconsin, U.S.A. *Can. J. Fish. Aquat. Sci.* 56: 265-274.
- Roehm, C. L., Prairie, Y. T. & del Giorgio P. A. 2009. The pCO₂ dynamics in lakes in the boreal region of northern Québec, Canada. *Global Biogeochem. Cycles* 23, GB3013, doi:10.1029/2008GB003297.
- Rudd, J. W. M., Furutani, A., Flett, R. J. & Hamilton, R. D. 1976. Factors controlling methane oxidation in shield lakes: The role of nitrogen fixation and oxygen concentration. *Limnol. Oceanogr.* 21: 357-364.
- Salonen, K., Arvola, L. & Rask, M. 1984. Autumnal and vernal circulation of small forest lakes in southern Finland. *Verh. Int. Verein. Limnol.* 22: 103-107.
- Schink, B. 1997. Energetics of syntrophic cooperation in methanogenic degradation. *Microbiol. Mol. Biol. R.* 61: 262-280.
- Schulze, E. D., Lloyd, J, Kelliher, F. M., Wirth, C., Rebmann, C., Lühker, B., Mund, M., Knohl, A., Milyukova, I. M., Schulze, W.,

- Ziegler, W., Varlagin, A. β., Sogachev, A. F., Valentini, R., Dore, S., Grigoriev, S., Kolle, O., Panfyorov, M. I., Tchebakova, N. & Vygodskaya, N. N. 1999. Productivity of forests in the Eurosiberian boreal region and their potential to act as a carbon sink – a synthesis. *Global Change Biol.* 5: 703-722.
- Sellers, P., Hesslein, R. H. & Kelly, C. A. 1995. Continuous measurement of CO₂ for estimation of air-water fluxes in lakes: An in situ technique. *Limnol. Oceanogr.* 40: 575-581.
- Sobek, S., Algestern, G., Bergström, A-K., Jansson, M. & Tranvik, L. J. 2003. The catchment and climate regulation of pCO₂ in boreal lakes. *Global Change Biol.* 9: 630-641.
- Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M. & Miller, H. L. 2007. Climate change 2007. The scientific basis. Cambridge Univ. Press.
- Stets, E. G., Striegl, R. G., Aiken, G. R., Rosenberry, D. O., & Winter, T. C. 2009. Hydrologic support of carbon dioxide flux revealed by whole-lake carbon budgets. *J. Geophys. Res.* 114, G01008, doi:10.1029/2008JG000783.
- Striegl, R. G. & Michmerhuizen, C. M. 1998. Hydrologic influence on methane and carbon dioxide dynamics at two north-central Minnesota lakes. *Limnol. Oceanogr.* 43: 1519-1529.
- Striegl, R. G., Kortelainen, P., Chanton, J. P., Wickland, K. P., Bugna, G. C. & Rantakari, M. 2001. Carbon dioxide partial pressure and ¹³C content of north temperate and boreal lakes at spring ice melt. *Limnol. Oceanogr.* 46: 941–945.
- Tranvik, L.J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack, J. M., Overholt, E., Porter, J. A., Prairie, Y., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek, S., Tremblay, A., Vanni, M. J., Verschoor, A. M., von Wachenfeldt, E. & Weyhenmeyer, G. A. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol. Oceanogr.* 54, 2298-2314
- Vickers, D. & Mahrt L. 1997. Quality control and flux sampling problems for tower and aircraft data. *J. Atmos. Ocean. Tec.* 14: 512–526.
- Wanninkhof, R., Ledwell J. R. & Broecker W. S. 1985. Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake. *Science* 227: 1224–1226.
- Wetzel, R. G. 2001. Limnology, lake and river ecosystems, 3rd ed. Academic Press, San Diego.