Factors controlling carbon gas fluxes in boreal lakes

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ABSTRACT

Despite their small surface area on Earth, freshwater ecosystems have recently been recognized as important components of the global carbon budget. The external loading of terrestrial organic carbon enhances the net heterotrophy in lake ecosystems, leading to CO$_2$ supersaturation in most of the world’s lakes, and lacustrine water bodies are therefore clear sources of carbon to the atmosphere.

The present study provides information on carbon gas (CO$_2$ and CH$_4$) concentrations and fluxes from three large dimictic lakes in southern Finland with contrasting water quality: Lake Pääjärvi (a humic lake), Lake Ormajärvi (a clear-water lake) and the Enonselkä basin in Lake Vesijärvi (an urban clear-water lake basin). The lakes were intensively sampled throughout the open-water period for general limnology as well as for biology to determine the processes behind the gas fluxes. Greenhouse gases determinations were based on surface water concentrations and gas accumulation in floating closed chambers. Fluxes were analysed at different times of the year, during the stratification period (summer) and mixing periods (spring and autumn). The gas transfer velocities ($k_{600}$) of CO$_2$ and CH$_4$ were related to wind speed during the mixing periods. The study years contrasted each other, i.e. the summer of 2004 was rainy, whereas the summer of 2005 was warm with precipitation close to the long-term average, allowing a comparison of the lake response to different weather conditions.

In this study, the greatest carbon gas evasions from the lake surfaces were measured during the spring and autumn mixing periods. The wind speed had a stronger effect on the gas transfer velocity ($k_{600}$) of CO$_2$ and CH$_4$ in spring than in the autumn. However, there was distinctive gas exchange variability during the summer after rain events. In the humic Lake Pääjärvi, the high precipitation resulted in a large peak in CO$_2$ and CH$_4$ fluxes, which contributed 46% and 48% to the annual fluxes of CO$_2$ and CH$_4$, respectively. In the clear-water Lake Ormajärvi, the contribution of the rainy period to carbon gas fluxes was 39% and 37% for CH$_4$ and CO$_2$, respectively. The response of the clear-water lake to the high precipitation was not as immediate as in the humic lake, but the outcome was more radical, since before the rainy period the lake took up more carbon than was released to the atmosphere, but as a consequence of the rains the situation was reversed. The urban lake basin, with anoxic hypolimnion, was a source of CO$_2$ and CH$_4$ even though the oxidation of CH$_4$ in the water column was intensive during the stratification period.
A clear association between biological mineralization processes and carbon fluxes was observed in the humic lake, contrary to the clear-water lake. In the humic lake, CO$_2$ was equally produced and released during the open-water period, except during the summer flux peak after the rainy period, whereas in the clear-water lake there was an excess of CO$_2$ production. Precipitation generated variability in epilimnetic and metalimnetic concentrations of carbon gases and DOC at the time when the lakes showed their strongest stability. Moreover, changes in biological processes were only observed at the surface, which indicates that the excess of CO$_2$ and CH$_4$ were flushed into the lake from the surrounding terrestrial soil or the littoral area.

The summer precipitation clearly increased the carbon emissions to the atmosphere, since when omitting the summer flux peaks in the humic and the clear-water lake, the CO$_2$ fluxes were closer to those measured in the urban lake basin during the summer of average precipitation, and close to average fluxes measured in large Finnish lakes. However, CH$_4$ fluxes were always higher in the urban lake basin, indicating the long history of eutrophication and anoxia. The importance of the lakes in recycling terrestrial carbon was expressed by comparing the lake fluxes with the net ecosystem exchange (NEE) of the forested and peatland catchment areas. The carbon gas (CO$_2$ and CH$_4$) flux from humic Lake Pääjärvi was 4%, that from clear-water Lake Ormajärvi 2% and from Enonselkä basin 7% of the terrestrial NEE of the whole catchment area, demonstrating that lakes also release carbon produced in their catchment areas.

Estimates of the global warming potential (GWP) of greenhouse gas emissions from the studied boreal lakes indicated that the contribution of CH$_4$ to the carbon fluxes was higher in the urban lake basin (33%), followed by the clear-water lake (13%) and the humic lake (7%). Thus, the lacustrine GWP is influenced by human activity. Human-induced nutrient loading into lakes enhances autochthonous production and the decomposition of organic matter, which may generate large emissions of CH$_4$, as was seen in the urban study lake.
LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications, which in the text are referred by their Roman numerals:


IV López Bellido, J., Tulonen, T., Kankaala, P. & Ojala, A. Concentrations of CO₂ and CH₄ in water columns of two stratified boreal lakes during a year of atypical summer precipitation (Revised Manuscript in Biogeochemistry)

In addition to the results of the original publications, the thesis also includes unpublished data.

The publications are reproduced with the permission of the American Geophysical Union (I), the American Society of Limnology and Oceanography, Inc. (II) and Environmental Pollution, Elsevier Ltd, Editorial Production (III).
Author’s contribution:

I  A. Ojala and P. Kankaala planned the experiments and supervised the work. **J. López Bellido** finalized the plan and together with T. Tulonen performed the field and laboratory work and analysed the data. **J. López Bellido** wrote the article with the contributions by P. Kankaala and T. Tulonen. The text was commented on and revised by A. Ojala. **J. López Bellido** was responsible for the flux calculations, tables and figures of the article.

II A. Ojala and P. Kankaala planned the data collection and supervised the work. **J. López Bellido** planned the work and together with T. Tulonen carried out the field and laboratory work. The first version of the manuscript was written by A. Ojala, after which the writing responsibility was handed over to **J. López Bellido**, who also analysed the data. The manuscript was commented on by P. Kankaala, T. Tulonen and J. Huotari. **J. López Bellido** was responsible for the calculations, tables and figures of the article.

III  **J. López Bellido** planned the work and A. Ojala supervised it. **J. López Bellido** performed the field and laboratory work and analysed and interpreted the data. E. Peltomaa analysed the gases and commented on the article. **J. López Bellido** wrote the article with a contribution by A. Ojala. **J. López Bellido** was responsible for the calculations, tables and figures of the article.

IV  A. Ojala and P. Kankaala planned and supervised the work. **J. López Bellido** and T. Tulonen performed the field and laboratory work. **J. López Bellido** analysed and interpreted the data and wrote the manuscript, which was commented on by T. Tulonen, P. Kankaala and A. Ojala. **J. López Bellido** was responsible for the calculations, tables and figures of the article.
ABBREVIATIONS

C  carbon
CO₂  carbon dioxide
CH₄  methane
BLD  boundary-layer diffusion model
FC  floating chamber
ΔCO₂  flux of CO₂ from the lake to the atmosphere calculated with the BLD
ΔCH₄  flux of CH₄ from the lake to the atmosphere calculated with the BLD
FC CO₂  flux of CO₂ from the lake to the atmosphere estimated with the FC
FC CH₄  flux of CH₄ from the lake to the atmosphere estimated with the FC
pCO₂  partial pressure of CO₂
Pt  platinum
DOC  dissolved organic carbon
PP  primary production
BP  bacterial production
CR  community respiration
NEE  net ecosystem exchange
GWP  global warming potential
1. INTRODUCTION

The importance of inland waters in the carbon cycle tends to be unnoticed in models of terrestrial ecosystems and global climate, partly because of the small area covered by lacustrine and riverine ecosystems, i.e. they make up only 3% of the total continental area (Downing et al. 2006). However, they are very active sites in the transport and storage of carbon of terrestrial origin (Cole et al. 2007, Tranvik et al. 2009). The high production of organic carbon in terrestrial systems and the relatively low soil activity results in high concentrations of dissolved organic carbon (DOC) in the soil water (Thurman 1985). Climate, hydrology, landscape morphometry (Rasmussen et al. 1989), the drainage ratio (catchment area to lake area (CA:LA) ratio), as well as the coverage of peatlands, wetlands and forests dictates the magnitude of organic carbon load from the catchment into streams and lakes (Kortelainen 1993, Hope et al. 1996, Mattsson et al. 2003). Cole et al. (2007) estimated that half of the carbon annually entering freshwater ecosystems will never reach the oceans. Some proportion of the organic carbon of autochthonous as well as allochthonous origin is sequestered in lake sediments (Dean & Gorham 1998, Kortelainen et al. 2004, Benoy et al. 2007, Downing et al. 2008, Tranvik et al. 2009), but bulk of it is mineralized to carbon dioxide (CO₂) and methane (CH₄) (Kortelainen et al. 2000, Striegl et al. 2001, Huttunen et al. 2002, Algesten et al. 2005, Sobek et al. 2009, Gudaz et al. 2010, Einola et al. 2011), leading to carbon gas supersaturation in the water column (Kling et al. 1991, 1992, Sobek et al. 2003, Alin & Johnson 2007). Thus, the mineralization of organic carbon in freshwater ecosystems plays an important role in the global carbon cycle.

CO₂ and CH₄ are among the most important greenhouse gases in the atmosphere. Since preindustrial times, the atmospheric concentrations of CO₂ and CH₄ have respectively increased from approx. 270 ppm to 379 ppm (parts per million) and from approx. 700 ppb to 1 774 ppb (parts per billion) (Barnola et al. 1987, Watson et al. 1990, Denman et al. 2007). Lakes can be either sources or sinks of CO₂ and CH₄ depending on the surface water gas concentrations in relation to atmospheric equilibrium concentration. For instance, Cole et al. (1994) found that most lakes worldwide are supersaturated with CO₂ and thus act as sources of CO₂. Most of the CO₂ in aquatic ecosystems is transported by turbulent diffusion in the water column or
horizontal advection. Vegetation along the land-water boundary is a dynamic buffer and source for the load of allochthonous and autochthonous carbon to lakes (Larmola et al. 2003). The lacustrine net production of CO$_2$ in lake water is the result of the photosynthesis of inorganic carbon and respiration of organic carbon in different parts of the lake. However, CO$_2$ exchange displays strong seasonal variation within lakes, and the role of a lake as a sink or source of CO$_2$ can therefore vary (Anderson et al. 1999, Kelly et al. 2001). The variation in CO$_2$ exchange is regulated by physical forces and photosynthetic activity, which is strongly controlled by irradiance. Thus, lakes in northern regions typically serve as sources of CO$_2$ during the spring and autumn, and if they act as sinks, this occurs during the summer (Riera et al. 1999, Huotari et al. 2009).

CH$_4$ is produced by the reduction of CO$_2$ or by acetoclastic methanogenesis in anaerobic sediments (Kelly et al. 1992, Shulstz & Conrad 1996, Avery et al. 1999, Chasar et al. 2000), and is transported by turbulent diffusion, advection, ebullition or through plants to the atmosphere (e.g. Rudd & Campbell 1974, Kuvila et al. 1988, Chanton & Whiting 1995, Kankaala et al. 2003, Bergström et al. 2007, Walter Anthony et al. 2010). While CH$_4$ concentrations are lower than those of CO$_2$, it is a highly potent greenhouse gas in the atmosphere. It has an approximately 25 times greater global warming potential (GWP) than CO$_2$ in the 100-year time horizon (Meehl et al. 2007). Globally, lakes contribute about 6–16% of the total natural CH$_4$ emissions (Juutinen et al. 2009, Bastviken et al. 2004, 2010). Recent studies have even revealed that CH$_4$ emissions of inland waters offset about 25% of the carbon sink on land (Bastviken et al. 2011). Moreover, the ebullition of CH$_4$ could globally increase CH$_4$ fluxes from lakes, especially if permafrost thaws as predicted in future warming scenarios. Thermokarst lakes influenced by thermokarst erosion were found to be 7.5-fold higher in CH$_4$ point-source emissions than non-thermokarst lakes (Walter et al. 2007). Freshwater ecosystems produce more CH$_4$ during warm summer conditions and/or when the oxygen concentration drops. Most CH$_4$ is produced in lake sediments when oxygen is no longer present (anoxic conditions). In addition to CH$_4$ production, anoxia leads to the accumulation of other reduced compounds, such as ferrous iron and hydrogen sulphide, and to the release of ammonia and orthophosphate (Ahlgren et al. 1994,
As a result of the decomposition of organic compounds, CO$_2$ and CH$_4$ concentrations in the hypolimnion can also increase. Annually, from 7% up to 75% of sedimented carbon can be mineralized to CO$_2$ and CH$_4$ (Jones & Simon 1980, Kelley et al. 1990, Gälman et al. 2008). Thus, especially shallow eutrophic lakes with an anoxic hypolimnion are potential sources of CH$_4$ to the atmosphere, whereas emissions from less productive lakes with high oxygen levels can be negligible due to effective CH$_4$ oxidation by methanotrophic bacteria in the oxic/anoxic boundary layer (Rudd & Campbell 1974, Harrits & Hanson 1980, Rudd & Taylor 1980, Liikanen 2002, Kankaala et al. 2006).

The boreal region contains about 30% of the global 304 million lakes rich in organic matter (Molot & Dillon 1996, Downing et al. 2006). Lakes in Finland are mainly surrounded by forested catchment with a variable peatland proportion (Kortelainen 1993, Kortelainen & Rantakari 2000). As a consequence, 60% of the approximately 190 000 lakes in Finland are regarded as brown-water lakes with considerable amount of carbon loading (Kortelainen 1993). Lakes located in areas close to ice marginal eskers are often clear in water colour. However, lakes in semi-natural or rural settings have been seriously perturbed, especially in Southern Finland, and changes in water quality due to human-induced nutrient loading have led to the increasing accumulation of phosphorous and nitrogen, as well as carbon (e.g. Särkkä 1979, Kansanen & Jaakkola 1985, Kansanen 1985, Meriläinen & Hamina 1993, Simola et al. 1996, Itkonen et al. 1999, Keto & Tallberg 2000). The nutrients can be bound to dissolved organic matter (DOM), but they can become available in food webs through microbial decomposition or through photochemical reactions as a result of exposure to ultra violet radiation (UVR) (Vähätalo & Salonen 1996, Mopper & Kieber 2000, Vähätalo 2000). In humic lakes the latter reactions can take only place in the uppermost 5–10 cm of the lake water column, whereas in clear-water lakes the reactive irradiance can penetrate much deeper. Through these processes, the production of carbon gases can be accelerated (Gjessing & Gjerdahl 1970, Chen et al. 1978, Miller & Zepp 1995, Granéli et al. 1996, 1998, Gao & Zepp 1998, Miller & Moran 1997, Moran & Zepp 1997, Zafiriou et al. 2003).

The general pattern in deep boreal lakes is that complete mixing of the water column occurs twice a year, e.g. lakes turn over in
early spring and at the end of the autumn. This dimictic pattern has profound impacts on ecosystem functioning as well as on lake–atmosphere interactions. For example, mixing re-supplies nutrients from the hypolimnion for algal production in the euphotic zone, and ensures the re-oxygenation of hypolimnetic waters and profundal sediment surface. During summer stratification the steep thermocline limits gas and nutrient exchange between epilimnetic and hypolimnetic layers, whereas the ice cover in winter efficiently prevents gas exchange between the lake surface and the atmosphere (Striegl et al. 2001). In the autumn, circulation is mainly driven by wind force and heat loss from the lake water column, while in the spring, circulation is governed by the lake temperature increase when the surface water warms up in conjunction with the continuing increase in the air temperature (Wetzel 2001). In addition, as circulation proceeds, the temperature difference between the surface and bottom layers disappears. This means that the water density in most lakes becomes homogeneous throughout the water column. These events, which are important for the seasonal variation in carbon emissions (CO₂ and CH₄) in lake ecosystems (Michmerhuizen et al. 1996, Riera et al. 1999), have been considered to occur rapidly in small lakes, whereas large lakes can circulate for weeks (Wetzel 2001).

The onset and duration of the turnover period is mainly determined by weather conditions, which can result in high interannual variation in carbon gas fluxes. For instance, in Finnish lakes the median interannual variation in autumnal CO₂ fluxes was found to be two-fold in a six-year data set with single samplings during the spring, summer and autumn (Rantakari & Kortelainen 2005). However, an insufficient sampling frequency may have influenced the results concerning annual variability. In the humic studied lake, the daily fluxes in the autumn were clearly lower than in the spring, but the autumnal fluxes contributed on average 27% and the spring flux on average 12% of the total annual flux. This ostensible discrepancy was probably due to the difference in the duration of seasonal turnover periods, the autumn turnover being considerably longer in boreal lakes. The magnitude of the flux also depends on the gas transfer velocity affected by the particular properties of the micro boundary layer between air and water, but mainly depending on wind speed (Liss & Slater 1974, Cole & Caraco 1998, Crusius &

In the boreal zone, projections of global climate change also indicate diverse effects on freshwater ecosystems, but a common prognosis for the Fennoscandia region is increased precipitation leading to an increase in nutrient inputs. The input and lacustrine dynamics of allochthonous carbon are highly controlled by hydrological events such as snowmelt and heavy rains, when a large fraction of the annual influx of allochthonous materials may enter in a short period of time (Sinsabaugh & Findlay 2003). Thus, climate change resulting in changes in hydrology would have immediate effects on carbon transport. Carbon gas emissions to the atmosphere can be enhanced, especially after extreme rain events (Rantakari & Kortelainen 2005, Marotta et al. 2009, Einola et al. 2011). Accordingly, a rise in air and water temperature may stimulate primary production, leading to a higher phytoplankton biomass and deposition rate. Finally, this could lead to oxygen depletion, e.g. hypoxia and anoxia (Harris 1986, Davidson 1991, Chapman 1992, Seip & Reynolds 1995, Wetzel 2001, Weyhenmeyer 2001), thus enhancing anaerobic decomposition and methanogenesis in the sediments, which in turn could lead to the build up of large concentrations of dissolved CH$_4$, especially in the summer (Rudd & Hamilton 1978, Bartlett et al. 1988, Sobek et al. 2003, Bastviken et al. 2004). Moreover, the predicted change in the duration of the ice-free season and stratification period (Shindler 2001, Hayhoe 2006) and the increase in wind speed, affecting the lake-atmosphere gas exchange rate (Cole and Caraco 1998, MacIntyre et al. 1995, Crusius & Wanninkhof 2003), are of importance. Thus, changes in seasonality as well as in the frequency of extreme events will affect aquatic ecosystems and their surrounding catchment areas, making lakes vulnerable to changes and potentially increasing their emissions of CO$_2$ and CH$_4$ to the atmosphere.

The purpose of this study was to quantify the atmospheric exchange of CO$_2$ and CH$_4$ in three boreal lakes and the factors controlling the gas fluxes. The lakes studied were the humic Lake Pääjärvi and the clearwater lakes Ormajärvi and Vesijärvi (Enonselkä basin), the last one being anthropogenically more disturbed. The controlling factors investigated included the biological carbon assimilation of inorganic carbon and the release of gases through mineralization processes during stratification
and mixing periods. We also examined the influence of weather events, especially the effect of wind speed and extreme precipitation, on gas exchange between the lake and atmosphere. We anticipated that in terms of carbon fluxes, water colour, e.g. the load of allochthonous carbon, plays a crucial role in the boreal zone, and hence we compared these dynamics in a humic lake vs. clear-water lake systems.

**Aims of the study**

The general aim of this research was to obtain a better understanding of the factors controlling the carbon fluxes in lakes, a typical ecosystem type in Nordic countries and elsewhere in the boreal zone, by quantifying the fluxes from lakes differing in nutrient status and dissolved organic carbon concentration. Three large lakes in southern Finland, Lake Pääjarvi (2004 – 2005), Lake Ormajärvi (2004) and Enonselkä basin in Lake Vesijärvi (2005), were intensively sampled throughout the open-water periods for general limnology and biology and for CO$_2$ and CH$_4$ fluxes. The fluxes of these greenhouse gases were usually determined on the basis of surface water concentrations and gas accumulation in floating closed chambers. To reveal the seasonal cycles in fluxes the sampling was carried out at different times of the year, including stratification (II, III, IV) and mixing periods (I). In addition, during one of the study years, in 2004, the summer precipitation doubled in Southern Finland from the long term average, 200–220 mm, to 413 mm. This extra rain rendered it possible to study the lake response to an extreme weather event (II) and compare it with a dry year, 2005 (III).

The specific objectives of this thesis research were:

i) To assess the importance of the mixing periods (spring and autumn) for atmospheric carbon gas fluxes in a dimictic humic lake;

ii) To compare the carbon concentrations and fluxes during the summer stratification from three boreal lakes differing in nutrient status and the concentration of dissolved organic carbon (DOC);

iii) To analyse the lake response in terms of carbon gas fluxes during an extreme weather event, e.g. high summer precipitation;
iv) To obtain a better understanding of the factors regulating the carbon gas fluxes of aquatic ecosystems typical of the boreal zone in Finland.

2. MATERIALS AND METHODS

2.1. Study sites

The studied sites were three boreal dimictic lakes in southern Finland. The humic Lake Pääjärvi (61°04’N, 25°08’E) and the clear-water Lake Ormajärvi (61°06’N, 24°58’E) are located in the Lammi region and are headwaters of the Kokemäenjoki River basin draining to the Bothnian Sea in the northern part of the Baltic Sea (Fig. 1). Both lakes are situated so close to each other (within a distance of < 5 km) that they experience similar weather conditions. The third studied water body was the southern most basin, Enonselkä, of Lake Vesijärvi (61°05’N, 25°35’E). Similar to Lake Ormajärvi, Lake Vesijärvi is a glacial drift lake, but belongs to Kymijoki River basin draining to the Gulf of Finland. The lake is located next to the city of Lahti, approx. 35 km from Lammi. In addition to the Enonselkä basin, Lake Vesijärvi has three other main basins: Kajaanselkä, Laitialanselkä and Komonselkä (Fig. 1).
Figure 1. Locations of A) Lake Pääjärvi B) Lake Ormajärvi and C) Lake Vesijärvi–Enonselkä basin. The maps indicate the bathymetry and land use around the lakes. The black dot indicates the deepest part of the lake where sampling was carried out. Bathymetry maps courtesy: S. Anttila (Lakes Pääjärvi and Ormajärvi) and S. Kajander (Enonselkä basin).
Lake Pääjärvi

L. Pääjärvi, with a surface area of 13.4 km$^2$, is one of the deepest lakes in Finland (Fig. 1A); the maximum and mean depths are 87 m and 14.4 m, respectively (Ruuhijärvi 1974). The catchment area (199 km$^2$) is dominated by coniferous forest of pine and spruce (59%), agricultural land (18%) and peatland (11%) (Hakala et al. 2002). The catchment area to lake area (CA:LA) ratio is 15. The soil around the lake consists of till and bedrock outcrops (50%), glaciofluvial material (25%), and fine-grained deposits (25%) (Valpola & Ojala 2006). Aquatic plants, emergent as well as submerged, are sparse (Kansanen & Niemi 1974). Since the 1960s, the water level in L. Pääjärvi has been regulated by 0.8 m (maximum) to prevent the harmful effects of spring floods on agricultural fields. As a result of the lowering of the water level, the reprocessing of allochthonous organic matter in the shallow shores has intensified (Simola & Uimonen-Simola 1983). However, the sedimentation rate varies between 0.3–2.0 mm yr$^{-1}$, which is common in Finnish lakes (Pajunen 2004). L. Pääjärvi is ice covered from December to early May, but the water column remains oxygenated down to the bottom throughout the year. During the summer, the thermocline lies between 5 to 10 m (Tulonen 2004) and the euphotic zone (~4 m) is shallower than the epilimnion (Jasser & Arvola 2003). Due to the high proportion of peatlands in the catchment area, the lake water is brown in colour (100 mg Pt L$^{-1}$) with a mean DOC concentration of 12.3 mg L$^{-1}$ (range 10–22 mg L$^{-1}$) (II). The concentrations of total phosphorus and chlorophyll $a$ indicate low productivity, whereas total nitrogen concentrations are high (II, IV, Table 1). The lake is apparently phosphorus limited according to the Redfield ratio of nitrogen and phosphorus and nutrient addition experiments (Arvola et al. 1996). As urbanization in the drainage basin is low (0.4%), the lake is mainly used for recreation, e.g. swimming, boating and fishing. However, due to diffuse nutrient loading associated with agricultural activities, the lake became more eutrophic prior to the mid-1990s (Hakala & Arvola 1994). Since then, the rate of eutrophication has slowed. Nowadays, L. Pääjärvi is oligomesotrophic and represents a deep lake mainly affected by agriculture and related activities (Simola & Arvola 2005).

Lake Ormajärvi

L. Ormajärvi, with a surface area of 6.53 km$^2$, is a shallower lake (Fig. 1B) with a maximum and mean depth of 30 m and 10.7
m, respectively. The catchment area (116 km$^2$) is dominated by coniferous forest (55%), agricultural land (26%) and peatland (6%) (Huitu & Mäkelä 1999). In comparison to the other study lakes, L. Ormajärvi has the highest CA:LA ratio (Table 1). Around the lake, the soils types are glaciofluvial material (50%), till (30%), bedrock outcrops (10%), fine-grained deposits (30%), and minor peat deposits (Valpola & Ojala 2006). Extensive littoral zones and a high diversity of aquatic plants are characteristic of this clear-water lake, where emergent and submerged plants as well as isoetid species are especially abundant (Huitu & Mäkelä 1999). Moreover, L. Ormajärvi is known for its regular cyanobacterial blooms. The lake is ice covered from December to early May and the water column down to the bottom remains oxygenated throughout the year, although the conditions in the hypolimnion close to the bottom are severely hypoxic in late summer and autumn ($O_2 < 2$ mg L$^{-1}$). Effluents from a dairy, piggery and domestic sewage were discharged untreated into the lake up until the 1970s. Together with agricultural activities, this led to an increase in sedimentation, which had remained stable at 1.5 mm yr$^{-1}$ for almost 200 years (Anttila 1967, Valpola & Ojala 2006). Today, L. Ormajärvi is a recipient of treated municipal wastewaters from about 5 000 inhabitants. The lake water is clear (20 mg Pt L$^{-1}$) with a mean DOC concentration of 7.6 mg L$^{-1}$ (range 5.3–10.2) (II). In comparison to L. Pääjärvi, L. Ormajärvi has a thicker euphotic zone, i.e. 6 m. Total concentrations of nitrogen and phosphorus are in the range typical of mesotrophic lakes (II, IV). However, chlorophyll $a$ concentrations are indicative of higher productivity (II). The pH values are slightly higher than in Lakes Pääjärvi and Vesijärvi (II, III, IV, Table 1).

**Lake Vesijärvi, Enonselkä basin**

Enonselkä, with a surface area of 26 km$^2$, is a large but a relatively shallow basin at the south end of L. Vesijärvi surrounded by the city of Lahti (Fig. 1C). The maximum and mean depths of the water body are 33 m and 6.8 m, respectively (Keto, 1992). The catchment area (84 km$^2$) is dominated by urban areas (28%), where 89% of the population lives, and forest (31%), agricultural land (7%) and peatland (1%). The lake water in the basin occupies approx. 30% of the area (Table 1, Fig. 1) (S. Kajander, personal communication). Thus, the Enonselkä basin can be regarded as one of the most urban water bodies in Finland. The CA:LA ratio is very low, i.e. only 3.2, and the retention time 9 years, i.e. the
longest among the study sites (Table 1). The basin is ice covered from December to early May. Unlike L. Pääjärvi and L. Ormajärvi, the oxygen concentrations in Enonselkä basin are low during stratification and the basin has suffered from hypolimnetic anoxia, with oxygen values < 1 mg L$^{-1}$. L. Vesijärvi, and in particular the Enonselkä basin, was severely polluted from loading of industrial and domestic wastewaters until the middle of 1970’s (Keto 1982). After the sewage was diverted in 1976 the basin slowly recovered but cyanobacterial blooms did not cease until the late 1980s, concomitant with the mass removal of coarse fish (Horppila et al. 1998). Following large-scale fishing in 1989–1993, the basin changed from a highly eutrophic and turbid system to a mesotrophic system with clearer water. Presently, the water colour is 30 mg Pt L$^{-1}$ and the mean DOC concentration is between 6–7 mg L$^{-1}$ (III). The Secchi depth is 3.5 m (Horppila et al. 1998) and the depth of the euphotic zone is 6 m, i.e. the same as in L. Ormajärvi. The phosphorous reserves in the sediment of the lake are still substantial (3 mg P g$^{-1}$ dry sed.; Hartikainen et al. 1996). The sediment accumulation rate in the deep of the Enonselkä basin has been estimated to be 40–50 mm yr$^{-1}$ (Liukkonen et al. 1997). High concentrations of total phosphorous indicate that the productivity of the lake compared to Lakes Pääjärvi and Ormajärvi is higher; however, the chlorophyll a concentrations were slightly lower than in L. Ormajärvi (II, III, IV, Table 1)
Table 1. Morphological and chemical characteristics of the studied lakes. Mean chemical values are from May to October in 2004 (Lakes Pääjärvi and Ormajärvi) (II, IV) and in 2005 (Lake Vesijärvi - Enonselkä basin) (III).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lake Pääjärvi</th>
<th>Lake Ormajärvi</th>
<th>Lake Vesijärvi Enonselkä basin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake area LA (km$^2$)</td>
<td>13.4</td>
<td>6.53</td>
<td>26</td>
</tr>
<tr>
<td>Catchment area CA (km$^2$)</td>
<td>199</td>
<td>116</td>
<td>84</td>
</tr>
<tr>
<td>CA:LA</td>
<td>15</td>
<td>18</td>
<td>3.2</td>
</tr>
<tr>
<td>Mean depth (m)</td>
<td>14.4</td>
<td>10.7</td>
<td>6.8</td>
</tr>
<tr>
<td>Maximum depth (m)</td>
<td>87</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td>Retention time (yr)</td>
<td>3.3</td>
<td>2.9</td>
<td>9.0</td>
</tr>
<tr>
<td>Lake volume ($\times 10^6$ m$^3$)</td>
<td>206</td>
<td>67</td>
<td>176</td>
</tr>
<tr>
<td>Forest (%) in the catchment area</td>
<td>59</td>
<td>55</td>
<td>31</td>
</tr>
<tr>
<td>Peatland (%) in the catchment area</td>
<td>11</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Agricultural land (%) in the catchment area</td>
<td>18</td>
<td>26</td>
<td>7</td>
</tr>
<tr>
<td>Urban area (%) in the catchment</td>
<td>0.4</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>Proportion of lake water area in the whole catchment (%)</td>
<td>6.7</td>
<td>5.6</td>
<td>30</td>
</tr>
<tr>
<td>Other (%) (small scale industry/industry/parks/small lakes/summerhouses)</td>
<td>4.9</td>
<td>4.4</td>
<td>3</td>
</tr>
<tr>
<td>Total Nitrogen, TN ($\mu$g L$^{-1}$)</td>
<td>1351</td>
<td>756</td>
<td>740</td>
</tr>
<tr>
<td>Total Phosphorous, TP ($\mu$g L$^{-1}$)</td>
<td>9.90</td>
<td>16.9</td>
<td>59.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.20</td>
<td>7.50</td>
<td>7.15</td>
</tr>
<tr>
<td>DOC (mg L$^{-1}$)</td>
<td>12.3</td>
<td>7.60</td>
<td>*6-7</td>
</tr>
<tr>
<td>Chl a ($\mu$g L$^{-1}$)</td>
<td>4.41</td>
<td>8.10</td>
<td>7.80</td>
</tr>
<tr>
<td>Water colour (mg Pt L$^{-1}$)</td>
<td>100</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

*Rantakari and Kortelainen (2005)
2.2. Weather conditions during the study years

The weather conditions differed considerably between the study years, 2004 (studies in L. Pääjärvi and L. Ormajärvi) and 2005 (Enonselkä basin – L. Vesijärvi), especially for summer precipitation. The mean air temperature during 2004 was 4.4 °C, and for the period from June–August, 14.4 °C. Thus, the mean annual and summer temperatures were close to the long-term (1971–2000) mean values of 4.0 °C and 15 °C, respectively. The highest mean and maximum daily air temperatures were 18.1 °C in July and 25.3 °C in August, respectively. However, the precipitation in summer 2004 doubled to 413 mm from the long-term mean (200—220 mm), especially in late June and July. The four major rain events were on 30 June 2004 with 45.2 mm and on 27, 28, and 29 July 2004 with daily precipitation of 25.9, 50.3, and 23.1 mm, respectively (Fig. 2). The extreme rain resulted in rising water levels, i.e. in L. Pääjärvi the water level rose on average by approx. 20 cm in comparison to the long-term mean (years 1971—2000). The rise was most conspicuous in late June and in late July to early August, when the level was approx. 40 cm and 50–66 cm higher, respectively (Fig. 1C in IV). No data are available from L. Ormajärvi, but since the lakes are only a few kilometres apart, a similar range of water level rise was likely.

The year 2005 was in general warmer than usual. The mean annual air temperature in Lahti in 2005 was 6.5 °C and for the period June–August, 17.5 °C. Thus, the mean annual temperature was close to long-term mean of 6 °C in the Lahti region (1971–2000). However, the summer temperature was 2.2 °C higher than the long-term average of 15.3 °C. The highest mean and maximum daily air temperatures were 24.3 °C and 29.4 °C in July. August 2005 was rainy, with monthly precipitation of 121 mm. The highest daily precipitation of 29.9 mm was recorded on 5 August (Fig. 2). The total summer precipitation was 236 mm, which was close to the long-term mean of 245 mm in Lahti region.
2.3. Sampling

The lakes were sampled weekly for carbon gases and for physical, chemical and biological measurements between 8 a.m. and 11 a.m. (solar time; Greenwich Mean Time +2). L. Pääjärvi was always sampled at the beginning and L. Ormajärvi in the middle of the working week (II, IV). Samples were always taken from the deepest part of the lakes. The maximum depth at the sampling sites was 46 m in L. Pääjärvi, 26 m in L. Ormajärvi and 30 m in Enonselkä basin. In 2004, L. Pääjärvi and L. Ormajärvi were already sampled soon after the ice-out and sampling continued until the autumn turnover in November (II, IV). Enonselkä basin was sampled from mid-May to October 2005 (III). Daily water samples were taken in L. Pääjärvi during the autumn (2004) and spring (2005) turnover periods (I).

2.4. Measurements

2.4.1. Carbon gas concentrations

Two different approaches were used to estimate flux from the lake to the atmosphere. The first approach for estimating flux was the floating chamber
(FC) technique, as explained in Kankaala et al. (2006). For the chamber measurements, four gas samples were drawn from each of three floating chambers every 10 min for 30 min using 60 mL polypropylene syringes equipped with three–way stopcocks. Each chamber (height 12.5 cm and volume 4.9 L) was made of acrylic plastic and equipped with a single sampling port and a digital thermometer. Gas concentrations samples from the FC atmosphere were analysed without any pretreatment (I, II).

The second approach was based on the gas concentration gradient (Cole & Caraco 1998). CO₂ and CH₄ concentrations were measured with the headspace equilibrium technique (papers I, II, III and IV). Samples of lake water containing dissolved CO₂ and CH₄ were taken with a Limnos sampler (2 L) to measure the concentrations throughout the water column. Two replicates of water samples (volume 30 mL) from each depth were drawn into 60 mL polypropylene syringes, which were closed with three–way stopcocks after removing any gas bubbles. The water-filled syringes were kept in crushed ice until analysis within one hour of arrival at the laboratory. For the determination of the dissolved gases from duplicated water samples, the syringes were placed in a water bath at 20 °C for 5 min before 50 mL of N₂ gas was added to the headspace of each syringe and shaken vigorously. Replicate 20 mL subsamples of well-mixed headspace gas from the syringes were injected into preevacuated, 12 mL Labco Exetainer® vials (Labco Limited, High Wycombe, Buckinghamshire, UK). Samples from the overpressurized vials were then delivered to the gas chromatograph (GC) by a Gilson 222 XL autosampler (Gilson Inc., Middleton, Wisconsin, USA) through a 1-mL Valco 10-port valve (VICI Valco Instruments Co. Inc., Houston, Texas, USA). Analyses were carried out with an Agilent 6890 N (Agilent Technologies, Santa Clara, California, USA) GC equipped with a flame ionization detector (FID) (temperature 210 °C) and a thermal conductivity detector (TCD) (temperature 120 °C, oven 40 °C, PlotQ capillary column, flow rate 12 mL min⁻¹, He as a carrier gas). The GC was calibrated with CO₂ using concentrations of 103 and 999 ppm, and with CH₄ using concentrations of 10 and 493 ppm (Oy AGA Ab, Finland). The CO₂ concentration in situ was calculated using the appropriate temperature relationships for CO₂ solubility and Henry’s Law (Plummer & Busenberg 1982).

Gas concentration measurements from the lake water were complemented with
meteorological information, standard physical, chemical, and biological analyses, such as DOC, Chl a, total nitrogen and phosphorus, and process measurements on primary and bacterial production and community respiration (Table 2).

Table 2. Methods and analyses used in this study

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Method/ Analyses</th>
<th>Described in paper</th>
<th>Reference/ Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meteorological</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind speed (m s⁻¹)</td>
<td>Recordings were taken at time intervals of 15 min and averaged over the daily sampling period</td>
<td>I, II, III, IV</td>
<td>Finnish Meteorological Institute</td>
</tr>
<tr>
<td>Precipitation (mm)</td>
<td>Daily recordings</td>
<td>I, II, III, IV</td>
<td>Finnish Meteorological Institute and Lammi Biological station</td>
</tr>
<tr>
<td>Air temperature (°C)</td>
<td>Recordings were taken hourly and averaged over the sampling period between 8 a.m. and 11 a.m.</td>
<td>I, II, III, IV</td>
<td>Finnish Meteorological Institute and Lammi Biological station</td>
</tr>
<tr>
<td><strong>Physical</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Temperature (°C)</td>
<td>Throughout the water column</td>
<td>I, II, III, IV</td>
<td>YSI 58 temperature meter (YSI Incorporated Yellow Springs, Ohio, USA)</td>
</tr>
<tr>
<td>Water level (NN + cm)</td>
<td>Continuous measurements on the shore of Lake Pääjärvi (1971–2000 and 2004)</td>
<td>IV</td>
<td>OIVA service on environment and geographic information, Finnish Environment Institute</td>
</tr>
<tr>
<td>Chemical</td>
<td>Method</td>
<td>I, II, III, IV</td>
<td>Instrument/Method</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------------------------------</td>
<td>----------------</td>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td>Oxygen (mg L(^{-1}))</td>
<td>Throughout the water column</td>
<td>I, II, III, IV</td>
<td>YSI 58 oxygen meter (YSI Incorporated Yellow Springs, Ohio, USA)</td>
</tr>
<tr>
<td>Total Nitrogen (TN) (µg L(^{-1}))</td>
<td>Sulphate digestion</td>
<td>I, II, III, IV</td>
<td>Koroleff (1979)</td>
</tr>
<tr>
<td>Total Phosphorous (TP) (µg L(^{-1}))</td>
<td>Sulphate digestion</td>
<td>I, II, III, IV</td>
<td>Koroleff (1979)</td>
</tr>
<tr>
<td>Total iron (TFe) (µg L(^{-1}))</td>
<td>Atomic absorption spectrometry</td>
<td>III</td>
<td>Varian Spectra 220 multi-element lamp atomic absorption spectrometer. (Varian Inc. Corporate Palo Alto, CA, U.S.A)</td>
</tr>
<tr>
<td>PO(_4) (µg L(^{-1}))</td>
<td>FIA system</td>
<td>I, II, IV</td>
<td>Murphy &amp; Riley (1962)</td>
</tr>
<tr>
<td>N/NO(_2)+ NO(_3) (µg L(^{-1}))</td>
<td>FIA system</td>
<td>I, II, IV</td>
<td>Wood et al. (1967)</td>
</tr>
<tr>
<td>DOC</td>
<td>Pt-catalysed high-temperature combustion</td>
<td>I, II, IV</td>
<td>Total Organic Carbon Analyzer/TOC-5000 (Shimadzu, Japan)</td>
</tr>
<tr>
<td>DIC</td>
<td>Calculated from data on CO(_2) concentration and ambient pH</td>
<td>II</td>
<td>Wetzel (2001)</td>
</tr>
<tr>
<td></td>
<td>Infrared carbon analyser</td>
<td>III</td>
<td>Salonen (1981)</td>
</tr>
<tr>
<td>pH</td>
<td>pH meter,</td>
<td>I, II, III, IV</td>
<td>Orion, model SA 720 (Thermo Fisher Scientific, Inc., Massachusetts, USA)</td>
</tr>
</tbody>
</table>
### Biological

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary production (PP)</td>
<td>14C technique</td>
<td>I, II, III, IV</td>
</tr>
<tr>
<td></td>
<td>Schindler et al. (1972)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Keskitalo &amp; Salonen (1994)</td>
<td></td>
</tr>
<tr>
<td>Bacterial production (BP)</td>
<td>14C leucine incorporation method</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td>Kirchman et al. (1985)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tulonen (1993)</td>
<td></td>
</tr>
<tr>
<td>Total community respiration (CR)</td>
<td>Winkler titration of oxygen</td>
<td>I, II</td>
</tr>
<tr>
<td></td>
<td>Mettler Toledo DL 53 Titrator (Mettler-Toledo International, Inc., Columbus, Ohio, USA)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wetzel &amp; Likens (2000)</td>
<td></td>
</tr>
<tr>
<td>Chl a</td>
<td>Hitachi F-4000 fluorescence spectrophotometry</td>
<td>I, II, III</td>
</tr>
<tr>
<td></td>
<td>Holm-Hansen &amp; Riemann (1978)</td>
<td></td>
</tr>
</tbody>
</table>

### 2.4.2. Carbon flux calculations

For the CO₂ flux calculations, replicates of the water sample from the surface (0–30 cm) were used for the boundary layer diffusion model (BLD) according to Cole & Caraco (1998) (I, II, III):

\[
\text{Flux}_{\text{CO}_2} = \alpha k \Delta \text{CO}_2 = \alpha k (C_{\text{sur}} - C_{\text{eq}}) \quad (1)
\]

where \(C_{\text{sur}}\) is the concentration of CO₂ in the water and \(C_{\text{eq}}\) is the concentration of gas the water would have at equilibrium with the overlying atmosphere. \(k\) is the transfer velocity (cm h⁻¹) and can be considered as the height of water equilibrated with the atmosphere per unit time for a given gas at a given temperature. The chemical enhancement factor \(\alpha\) was assumed to be 1 (Portielje & Lijklema 1995, Wanninkhof & Knox 1996). The dependence of \(k_{600}\) on wind speed was expressed with the equation

\[
k_{600} = 2.07 + 0.215 \times \text{ws}^{1.7}, \quad (2)
\]
where \( ws \) is the wind speed at a height of 10 m. Values attributed to the constant \( k_{CO_2} \) were calculated from \( k_{600} \), which is the \( k \) measured with SF\(_6\) and normalized to a Schmidt number (Sc) of 600. Values of \( k_{CO_2} \) were calculated from \( k_{600} \) using the equation

\[
 k_{CO_2} = k_{600}(Sc_{CO_2}/600)^n, \tag{3}
\]

where \( Sc_{CO_2} \) is the Schmidt number for \( CO_2 \) (Jähne 1987, Riera et al. 1999) and the coefficient \( n \) is -0.5 (Jähne 1987).

For the \( CH_4 \) flux, we applied the following equation of the BLD by Kling et al. (1992) and Phelps et al. (1998) (I, II, III):

\[
 Flux_{CH_4} = (D/z) \times (C_{sur} - C_{eq}), \tag{4}
\]

where \( D \) is the diffusion coefficient \((x^2/t)\) \((cm^2 \text{ s}^{-1})\), \( z \) is the boundary layer thickness \((\mu m)\), \( C_{sur} \) is the \( CH_4 \) concentration at a depth of 0–30 cm, and \( C_{eq} \) is \( CH_4 \) in equilibrium calculated with Henry’s Law, where the constant was adjusted for the surface water temperature. \( D \) and \( z \) were calculated from equations (5) and (6) according to Kling et al. (1992):

\[
 D_{(CH_4)} = [1.33 + (0.055^*T)] \times 10^{-5} \quad \text{and} \quad (5)
\]

\[
 z = 10^{[2.56 - (0.133 \times ws)]} \quad \text{and} \quad (6)
\]

The atmospheric mixing ratio used in the calculations was 372 ppmv for \( CO_2 \) and 1.75 ppmv for \( CH_4 \) (IPCC 2001) (I, II), and 379 ppmv for \( CO_2 \) and 1.77 ppmv for \( CH_4 \) (Forster et al. 2007) (III). Results of daily fluxes were expressed in mmol m\(^{-2}\) d\(^{-1}\) and annual fluxes in mol \( CO_2 \) or \( CH_4 \) m\(^{-2}\). For the calculation of the annual flux, data from daily fluxes were areally integrated over the time frame.

The \( CO_2 \) and \( CH_4 \) fluxes calculated with the BLD (\( \Delta CO_2 \), \( \Delta CH_4 \)) were compared to emissions from the floating chambers (FC) (I, II) and changes in storage (I). For the calculation of carbon fluxes during an average summer precipitation, the carbon peak fluxes induced by the rain events were excluded (II, Table 4). Carbon fluxes from FC were calculated using linear regressions based on the concentration changes as a function of time. Only those regression equations with \( r^2 > 0.9 \) and \( p < 0.05 \) were considered. However, there was no need to exclude many measured data, i.e. in the worst case one chamber out of three was rejected when using the chosen criteria. Daily fluxes were calculated according to the ideal gas law and assuming no diurnal variation in the \( CO_2 \) and \( CH_4 \) efflux. Results were expressed in mmol m\(^{-2}\) d\(^{-1}\) (I, II). Lake \( CO_2 \) and \( CH_4 \) storage was calculated
according to Striegl & Michmerhuizen (1998). The depth profiles of CO₂ and CH₄ concentrations were integrated with depth-versus-volume data to estimate the amount of the gases within each depth interval. These amounts were then added to yield the total storage of CO₂ and CH₄. For the amount of gas stored per unit of lake surface area (mol CO₂ or CH₄ m⁻²), the whole-lake storage was divided by the lake surface area. Emissions were then estimated from the difference between the storage before and after the mixing periods (I).

2.4.3. Gas transfer velocity

The measured CO₂ and CH₄ FC fluxes were combined with the data on ΔCO₂ and ΔCH₄, and applied to formula (1) to calculate the gas transfer velocity k (cm h⁻¹) of CO₂ and CH₄ adjusted to the Schmidt number (Sc) of 600 (k₆₀₀) in formula (3) (Borges et al. 2004a, Guérin et al. 2007) (I).

2.4.4. Methane oxidation and turbulent diffusion of methane

CH₄ oxidation was derived by estimating the turbulent diffusion of CH₄ across the concentration gradient in the water column and comparing the predicted and observed concentrations (Kankaala et al. 2006) (III).

The vertical diffusion coefficients K (m² d⁻¹) were estimated from the MyLake model (Saloranta & Andersen 2004) as

\[ K = a_k (N^2)^{-0.43}, \]

where \( N^2 \) is the stability (Brunt–Väisälä) frequency (Hondzo & Stefan 1993), and

\[ N^2 = \frac{g}{\rho_w} \frac{\partial \rho_w}{\partial z} (s^{-2}), \]

where \( g \) is the gravitational constant, \( \rho_w \) is water density, \( z \) (m) is depth and \( a_k \) is parameterized by lake surface area \( A_s \) (km²).

The parameterization \( a_k = 0.00706 (A_s)^{0.56} \) was adopted from Hondzo & Stefan (1993), as well as \( N^2 \text{min} = 7.0 \times 10^{-5} \text{s}^{-2} \), which sets the upper limit for \( K \) (III).

2.4.5. Water column stability

Water column stability and mixing dynamics in L. Pääjärvi and in L. Ormajärvi were calculated as Lake Number (Ln) (Imberger & Patterson 1990) indicating processes relevant to the internal mixing of lakes induced by wind forcing (IV).

2.4.6. Global warming potential (GWP)

The global warming potential (GWP) of carbon gas emissions was calculated in CO₂
equivalents, multiplying the emissions by their GWP values over a time horizon of 100 yr, i.e. 1 for CO\(_2\) and 25 for CH\(_4\) (Meehl et al. 2007) (III).

2.4.7. Biological processes

Data from PP, BP and CR were areally integrated and expressed in mmol C m\(^{-2}\) d\(^{-1}\) and mol C m\(^{-2}\) yr\(^{-1}\) to facilitate the comparison with the fluxes (I, II, III). Otherwise, PP and CR were expressed in mg C m\(^{-3}\) d\(^{-1}\) (IV). The pelagic CO\(_2\) net production due to biological processes was calculated by subtracting the primary production from the pelagic mineralization (I, II).

3. RESULTS

3.1. Thermal stratification and oxygen conditions

3.1.1. Thermal stratification

In 2004 the ice break-up occurred on 27 April in L. Pääjärvi and on 28 April in L. Ormajärvi. In the study year 2005 the ice break-up in Enonselä basin took place on 20 April. L. Pääjärvi started to already stratify after mid-May (Fig. 1A in I), whereas the clear-water lakes stratified much later, e.g. L. Ormajärvi did not show any obvious stratification until early June and in Enonselkä basin, the water column did not stratify until mid-June. From mid-June to mid-September, temperature profiles of the water columns of Lakes Pääjärvi and Ormajärvi indicated strong stability in Lake Number values (L\(_N\) >1). In July to August, e.g. during and after the rain events, the mean L\(_N\) values were 32 in L. Pääjärvi and 35 in L. Ormajärvi (Fig. 3 in IV). During the open-water periods, water temperatures along the water column were higher in the Enonselkä basin than in Lakes Pääjärvi and Ormajärvi. The temperature in the epilimnion in Lakes Pääjärvi and Ormajärvi respectively varied from 4.0 to 21.0 °C and from 6.6 to 20.6 °C, whereas the corresponding variation in the Enonselkä basin was from 8.3 to 22.2 °C. In the hypolimnion, temperatures ranged from 3.5 to 9.2 °C in L. Pääjärvi and from 5.7 to 10.0 °C in L. Ormajärvi. In the Enonselkä basin the hypolimnetic temperatures were higher than usual in boreal lakes and varied from 8.3 to 16.0 °C (Table 3). Hypolimnetic water temperatures in deep Finnish lakes usually vary from 5.0 to 10.0 °C (Herve 2000). During the summer months (June–August) in 2004, the maximum temperature in the epilimnia of Lakes Pääjärvi and Ormajärvi were registered in August, just after the rain
event, whereas in 2005 in the Enonselkä basin the maximum temperature in the epilimnion was observed in July. The monthly means of water temperatures throughout the water column in June, July and August were 13.4 °C, 17.0 °C and 18.0 °C in L. Pääjärvi, 13.6 °C, 18.0 °C and 19.0 °C in L. Ormajärvi, and, 15.5 °C, 20.5 °C and 18.8 °C in the Enonselkä basin. The stratification in Lakes Pääjärvi and Ormajärvi began to break up in September, although in L. Ormajärvi and the Enonselkä basin there were already signs of thermocline deepening from late August onwards. Finally, Lakes Pääjärvi and Ormajärvi were in a state of complete autumn turnover in November, whereas the Enonselkä basin already reached the complete mixing state at the end of September. In 2004, L. Pääjärvi froze over on 7 December and L. Ormajärvi on 1 December. In 2005, Enonselkä basin froze over on 15 December.

3.1.2. Oxygen conditions

During the open-water period, the O$_2$ concentrations throughout the water column and especially in the hypolimnion were lower in the Enonselkä basin than in Lakes Pääjärvi and Ormajärvi (Table 3). The epilimnetic O$_2$ concentration in Lakes Pääjärvi and Ormajärvi respectively varied from 8.2 to 13 mg L$^{-1}$ and from 7.3 to 15 mg L$^{-1}$, whereas in Enonselkä basin the variation was from 4.3 to 11 mg L$^{-1}$. The decline in the epilimnetic O$_2$ concentration in the summer was especially sudden in L. Ormajärvi and coincided with the deepening of the thermocline in early August. Some decline in the metalimnetic O$_2$ concentration was observed at the same time in L. Pääjärvi, where a 2-m layer with an O$_2$ concentration of merely 7 mg L$^{-1}$ was observed (Fig. 2B in II, 2C in IV). In Enonselkä basin upon stratification, O$_2$ in the hypolimnion was rapidly depleted, and by the end of June the O$_2$ concentration had declined from 10 to 4 mg L$^{-1}$. Finally, the concentration of O$_2$ was ≤ 1 mg L$^{-1}$ from mid-July to mid-August when the thermocline began to erode, i.e. the lake turned to anoxia (Fig. 1B in III). In August after the rain event, concentrations throughout the water column in L. Ormajärvi varied from 3.5 to 8.6 mg L$^{-1}$, whereas in L. Pääjärvi the corresponding values were between 6.4 and 10 mg L$^{-1}$. The autumn turnover quickly restored the well-oxygenated conditions in all study lakes.
Table 3. Mean ± SE values of water temperature (ºC) and oxygen concentration (mg L⁻¹) throughout the water column from May to October 2004 in L. Pääjärvi and L. Ormajärvi and from May to October 2005 in Enonselkä basin. Values in parentheses indicate the range and n indicates the number of samples.

<table>
<thead>
<tr>
<th>Water layers</th>
<th>Lake Pääjärvi</th>
<th>Lake Ormajärvi</th>
<th>Enonselkä basin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (ºC)</td>
<td>O₂ (mg L⁻¹)</td>
<td>T (ºC)</td>
</tr>
<tr>
<td>Epilimnion</td>
<td>12.3 ± 0.74</td>
<td>10.1 ± 0.25</td>
<td>13.7 ± 0.81</td>
</tr>
<tr>
<td></td>
<td>n =182</td>
<td>n =182</td>
<td>n =182</td>
</tr>
<tr>
<td></td>
<td>(4.0–21.0)</td>
<td>(8.2–13.0)</td>
<td>(6.6–20.6)</td>
</tr>
<tr>
<td>Hypolimnion</td>
<td>7.4 ± 0.21</td>
<td>10.5 ± 0.22</td>
<td>8.4 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>n = 312</td>
<td>n = 312</td>
<td>n = 286</td>
</tr>
<tr>
<td></td>
<td>(3.5–9.24)</td>
<td>(6.30–13.6)</td>
<td>(5.7–10.0)</td>
</tr>
</tbody>
</table>

3.2. CO₂ and CH₄ concentrations

3.2.1. CO₂ concentration

During the summer stratification, CO₂ concentrations were higher in the hypolimnion than the epilimnion in all study lakes. In the humic L. Pääjärvi, the epilimnetic CO₂ concentrations were higher than in the clear-water lakes, whereas L. Ormajärvi had the highest hypolimnetic CO₂ concentration. In Enonselkä basin and L. Ormajärvi, the hypolimnetic concentrations were approx. 5- and 4-fold greater than the epilimnetic ones, whereas the difference between the hypolimnion and epilimnion in L. Pääjärvi was only 2-fold (Table 4).

In L. Pääjärvi, the under ice average CO₂ concentration throughout the water column was 57.5 µM, but after the ice-out the concentration averaged 83.1 µM (unpublished data/data not shown). At the beginning of May, CO₂ concentrations were 84.3 µM throughout the water column. From mid-May onwards, concentrations along the epilimnion decreased to 24.0 µM until the onset of the thermocline and concentrations, especially in the hypolimnion, began to increase up to 96.0 µM. Concentrations close to the surface followed the same pattern as in the hypolimnion until 26 July, when concentrations between the depths of 5 and 17 m began to increase to >100 µM, and
the increase continued during August. Moreover, the epilimnetic concentrations increased 3-fold in August. From September onwards, the metalimnnetic concentrations followed the hypolimnnetic ones, whereas concentrations in the epilimnion decreased to 48.0 µM (Fig. 3A). During the autumn mixing, the lake was not homogeneous at 54.0 µM until mid-November; before that, there were high concentrations below the depth of 30 m. When sampling ceased in late autumn, the CO$_2$ concentrations were 33.0 µM throughout the water column (Fig. 2A in I).

In L. Ormajärvi, the under ice average CO$_2$ concentration was 91.3 µM throughout the water column, and just after ice-out the concentration average was 21.0 µM; however, the surface (0–30 cm) CO$_2$ concentration was already below equilibrium (unpublished data/data not shown). Although L. Ormajärvi was already turning over under the ice, it is unlikely that the large accumulated reservoir of dissolved CO$_2$ could have been released to the atmosphere through the ice sheet and during the very short open-water period prior to sampling, and the bulk of the CO$_2$ was thus presumably consumed by under-ice photosynthesis. From the beginning of May there was an increasing trend in the CO$_2$ concentration at almost all depths until the autumn mixing. In the hypolimnion and metalimnion the concentrations showed a clear and constant increase, whereas in the epilimnion the concentrations in early May were low in comparison to L. Pääjärvi, i.e. 18.0 µM. During late July and August, the concentrations throughout the water column increased. The mean concentration in the epilimnion increased to ca. 70 µM in August, and was 4-fold higher than in May after spring mixing. Concentrations below the epilimnion were between 100 µM and 300 µM. By September, the concentrations in the epilimnion had decreased to 36.0 µM and the highest concentration in the hypolimnion, 379 µM, was measured during the autumn mixing period (Fig. 3B).

When the Enonselkä basin was thermally stratified there was also a clear stratification in gas concentrations. The highest CO$_2$ concentrations in the epilimnion and hypolimnion were recorded at the end of July and the beginning of August, i.e. at the time of maximum temperatures and hypoxia. At the autumn turnover, the CO$_2$ concentration was ca. 36 µM throughout the water column (Fig. 3C).

In Lakes Pääjärvi, Ormajärvi and Enonselkä basin, respectively, the surface concentrations (0–30 cm) of CO$_2$ varied
from 14.7 to 76.0 µM, from 10.6 to 67.0 µM and from 13.5 to 40.0 µM. On average, the concentrations in Lakes Pääjärvi, Ormajärvi and Enonsekkä basin were 2.29 (range 0.95–4.36), 1.71 (range 0.69–3.87) and 1.71 (range 0.72–2.46) times greater than that of the atmospheric equilibrium. Thus, CO₂ concentrations were generally above the equilibrium in all study lakes with some exceptions in each lake. In L. Ormajärvi during the spring and early summer, concentrations were below or just above the equilibrium, but at the end of the rainy period there was a sudden increase in concentrations from 18.5 to 62.0 µM. One week later the concentration dropped to 37.2 µM, and concomitantly with the thermocline deepening in early autumn, the surface CO₂ concentrations began to increase, reaching ca. 55 µM in late October. In L. Pääjärvi the high spring concentrations slowly decreased to the mid-summer minimum, which was measured on 21 July; this was the only occasion when the CO₂ concentration in L. Pääjärvi was below the equilibrium. Later, the CO₂ concentration considerably increased up to 70.0 µM, and after the rains it declined to 42.6 µM. However, the decline was slower than in L. Ormajärvi and the concentration attained was higher. In the Enonsekkä basin the only exception was 25 May, when the concentration was only 13.5 µM and below the equilibrium. During the thermocline erosion the surface concentration of CO₂ increased and the clear supersaturation persisted until the end of sampling.

3.2.2. CH₄ concentration

CH₄ concentrations were highest in the Enonsekkä basin and concentrations in the two clear water lakes were generally higher than in the humic lake. Similarly to CO₂, the hypolimnetic concentrations of CH₄ were usually higher than the epilimnetic ones, with a slight difference in humic L. Pääjärvi (Table 4). CH₄ concentrations at the beginning of May were particularly high in L. Ormajärvi, where concentrations in the hypolimnion reached 0.80 µM. In spring in L. Pääjärvi, concentrations throughout the water column were 0.04 µM. From late May until mid-July, CH₄ concentrations decreased at all depths in L. Ormajärvi and Pääjärvi and in the Enonsekkä basin (Figs. 3 D, E, F). During late July and August in 2004, CH₄ concentrations in Lakes Pääjärvi and Ormajärvi increased throughout the water column, but especially in the epilimnion. The mean epilimnetic concentrations in August doubled from those in July in both lakes, in L. Pääjärvi from
0.04 to 0.08 µM and in L. Ormajärvi from 0.06 µM to 0.11 µM. In the end of August the concentrations began to decrease and the decrease continued until the end of the sampling period, although in L. Ormajärvi concentrations deep in the water column reached a maximum of 0.60 µM. In L. Pääjärvi, the concentration of CH₄ throughout the water column was 0.02 µM when the sampling ceased (Fig. 3A in I). In the Enonselkä basin, CH₄ did not appear until the hypolimnion had turned anoxic, whereas in Lakes Pääjärvi and Ormajärvi no correlations between O₂ and CH₄ were observed (III, IV). The highest concentrations ranging from 19.0 to 133 µM were measured at the time of peak anoxia at depths between 10 m and 20 m. Moreover, the mean CH₄ concentrations in the hypolimnion of Enonselkä basin were 121 times higher than in the epilimnion, and the highest hypolimnetic concentrations were recorded at the beginning of September. During the autumn turnover, CH₄ concentrations were 0.20 µM throughout the water column in Enonselkä basin (Fig. 3F).

The surface water concentrations (0–30 cm) of CH₄ varied from 0.007 to 0.130 µM in L. Pääjärvi, from 0.011 to 0.190 µM in L. Ormajärvi and from 0.020 to 0.460 µM in Enonselkä basin. On average, CH₄ concentrations in lakes Pääjärvi, Ormajärvi and Enonselkä basin were 13 (range 2.0–45), 21 (range 3.0–68) and 45 (range 7.0–161) times greater than that of the atmospheric equilibrium. Thus, the three study lakes were supersaturated with CH₄ throughout the measuring periods. Temporal changes in concentrations followed the same type of pattern in Lakes Pääjärvi and Ormajärvi, i.e. the concentrations were highest in July–August after the rainy period and lowest in May–June and late autumn. In comparison to CO₂, the decline in the CH₄ concentration in late August was drastic in both lakes. During the autumn turnover period, a sudden increase in the surface water CH₄ concentration was observed in the clear-water L. Ormajärvi, while in the brown-water L. Pääjärvi, the concentrations continued to decrease until the freeze up. In the Enonselkä basin, CH₄ concentrations at the surface increased from May onwards without any drastic changes. The only exception was at the beginning of September, when the concentration was 3-fold above the equilibrium.
Figure 3. Concentrations of CO$_2$ (µM) and CH$_4$ (µM) throughout the water column from May to October 2004 in Lake Pääjärvi (A, D) and Lake Ormajärvi (B, E), and the corresponding concentrations from May to October 2005 in Enonselkä basin–Lake Vesijärvi (C, F) (III) © 2011 Environmental Pollution Elsevier Ltd. Editorial Production.
3.3. Carbon gas fluxes

The carbon gas fluxes were estimated using three different methods in L. Pääjärvi (I, II). First, the estimates were based on CO\textsubscript{2} and CH\textsubscript{4} concentrations in the surface water (0–30 cm) and the results were calculated using BLD for CO\textsubscript{2} and CH\textsubscript{4}. Emissions were also estimated using FC and the change in the storage of CO\textsubscript{2} and CH\textsubscript{4} along the water column (I). Simultaneously measured fluxes with the BLD and FC methods significantly correlated during both the open-water and mixing periods, even though autumn and spring FC fluxes of CO\textsubscript{2} were respectively 40% and 70% higher than \(\Delta\text{CO}_2\), whereas the corresponding FC fluxes of CH\textsubscript{4} were 30% and 13% higher than \(\Delta\text{CH}_4\) during the mixing periods (I). During the open water period, FC fluxes of CO\textsubscript{2} and CH\textsubscript{4} were 26% and 19% higher than \(\Delta\text{CO}_2\) and \(\Delta\text{CH}_4\) in L. Pääjärvi, whereas in L. Ormajärvi the corresponding FC fluxes were 15% and 28% higher than \(\Delta\text{CO}_2\) and \(\Delta\text{CH}_4\) in L. Pääjärvi (II). The change in storage method resulted in underestimation of the fluxes (I). In the Enonselkä basin, the fluxes during the open-water period were only estimated using the BLD method (III). Thus, in this thesis summary, when comparing carbon gas emissions during the stratification period in the three study lakes, only the BLD results are applied.

3.3.1. Mixing periods

In L. Pääjärvi, the total \(\Delta\text{CO}_2\) and FC fluxes for CO\textsubscript{2} were higher during the autumn, whereas the \(\Delta\text{CH}_4\) and FC fluxes for CH\textsubscript{4} were higher during the spring (I). In the autumn, the daily \(\Delta\text{CO}_2\) and FC autumn fluxes ranged from 5.00 to 73.0 mmol C m\textsuperscript{-2} d\textsuperscript{-1} (mean = 42.3 mmol C m\textsuperscript{-2} d\textsuperscript{-1}) and from 15.7 to 73.2 mmol C m\textsuperscript{-2} d\textsuperscript{-1} (mean = 54.5 mmol C m\textsuperscript{-2} d\textsuperscript{-1}), respectively. By the end of the sampling period, the carbon gas fluxes were lower than at the onset of mixing, indicating that although complete mixing was short in duration, it was sufficient for the ventilation of CO\textsubscript{2} in the water column. In the spring, from ice-out until the onset of stratification, the average FC flux was 1.7 times higher than \(\Delta\text{CO}_2\). Daily \(\Delta\text{CO}_2\) and FC fluxes varied between 20.0 and 69.0 mmol C m\textsuperscript{-2} d\textsuperscript{-1} (mean = 43.1 mmol C m\textsuperscript{-2} d\textsuperscript{-1}) and 6.50 and 138 mmol C m\textsuperscript{-2} d\textsuperscript{-1} (mean = 71.8 mmol C m\textsuperscript{-2} d\textsuperscript{-1}), respectively. The spring mixing period was ca. one week shorter than autumn mixing, and thus the total atmospheric CO\textsubscript{2} flux was slightly lower. Total \(\Delta\text{CO}_2\) fluxes were 883 and 666 mmol C m\textsuperscript{-2} in autumn and spring, respectively,
whereas the corresponding total FC fluxes were 1223 and 1138 mmol C m\(^{-2}\) (I).

The autumnal daily flux of CH\(_4\) in L. Pääjärvi varied from 0.01 to 0.09 mmol C m\(^{-2}\) d\(^{-1}\) (mean = 0.03 mmol C m\(^{-2}\) d\(^{-1}\)) and from 0.01 to 0.07 mmol C m\(^{-2}\) d\(^{-1}\) (mean = 0.04 mmol C m\(^{-2}\) d\(^{-1}\)) for ΔCH\(_4\) and FC respectively. In spring, daily ΔCH\(_4\) and FC fluxes ranged from 0.02 to 0.09 mmol C m\(^{-2}\) d\(^{-1}\) (mean = 0.05 mmol C m\(^{-2}\) d\(^{-1}\)) and from 0.03 to 0.09 mmol C m\(^{-2}\) d\(^{-1}\) (mean = 0.06 mmol C m\(^{-2}\) d\(^{-1}\)), respectively. Total CH\(_4\) fluxes were 0.60 and 0.80 mmol C m\(^{-2}\) in the autumn and spring, respectively, whereas the corresponding total FC fluxes were 0.78 and 0.90 mmol C m\(^{-2}\) (I).

There was also some seasonality in the flux results, since the difference between the two methods was more obvious in the spring. By combining the results from BLD and FC measurements, gas transfer velocities (\(k_{600}\)) could be related to wind speed (I). Gas transfer velocities for CO\(_2\) as well as CH\(_4\) appeared to be higher in the spring than the autumn. However, wind speed only explained 52% and 67% of the variation in CO\(_2\) fluxes in the spring and autumn, respectively. The gas transfer velocity of CH\(_4\) was lower than that of CO\(_2\). Wind speed explained 80% of the variation in CH\(_4\) fluxes in the spring, but in the autumn the corresponding value was only 53%.

Of the total annual ΔCO\(_2\) flux from L. Pääjärvi, 13% was estimated to originate from the spring and 41% from the autumn mixing period. In ΔCH\(_4\) fluxes the respective proportions were 8.8% and 30%. In L. Ormajärvi, the contribution of ΔCO\(_2\) and ΔCH\(_4\) fluxes in the spring and autumn to the total annual flux were estimated at 0.5% and 62% for ΔCO\(_2\) and 9.0% and 41% for ΔCH\(_4\), respectively. In the Enonselkä basin, the contributions of spring and autumn mixing period were 1.1% and 55% for ΔCO\(_2\) and 1.2% and 63% for ΔCH\(_4\), respectively. However, in the Enonselkä basin the spring fluxes were most probably underestimated due to a 16-day delay in sampling after the ice-out.

### 3.3.2. Stratification period

The three study lakes were clear sources of CO\(_2\) and CH\(_4\) to atmosphere. During the open-water period the fluxes of CO\(_2\) were higher in the humic lake than in the clear-water lakes, whereas the fluxes of CH\(_4\) were higher in the urban Enonselkä basin than in Lakes Pääjärvi and Ormajärvi (Table 4). During the study period, the CH\(_4\) flux followed the same pattern as the CO\(_2\) flux, especially in L. Pääjärvi and Enonselkä basin. In L. Ormajärvi, a contradictory pattern between CH\(_4\) and CO\(_2\) fluxes was
observed from ice-out to late July, but from August to the end of the sampling period carbon gas fluxes followed the same trend. Moreover, in 2004 high carbon gas flux peaks were registered in mid-summer, whereas in 2005 the highest peak was observed when stratification began to erode (Figs. 4 A, B, C).

In L. Pääjärvi, the daily \( \Delta CO_2 \) fluxes during the stratification were from \(-1.40 \) to \(108 \text{ mmol C m}^{-2} \text{ d}^{-1} \) (mean = \(27.8 \text{ mmol C m}^{-2} \text{ d}^{-1} \)) and the \( \Delta CH_4 \) fluxes were from \(0.02 \) to \(0.50 \text{ mmol C m}^{-2} \text{ d}^{-1} \) (mean = \(0.08 \text{ mmol C m}^{-2} \text{ d}^{-1} \)). In mid-June, a low peak of \(26.4 \text{ mmol C m}^{-2} \text{ d}^{-1} \) in \( \Delta CO_2 \) was observed, whereas the lowest flux was recorded on 19 July. In general, from late June to late July, \( \Delta CO_2 \) and \( \Delta CH_4 \) fluxes began to increase and the respective maximum values of \(108 \text{ mmol C m}^{-2} \text{ d}^{-1} \) and \(0.50 \text{ mmol C m}^{-2} \text{ d}^{-1} \) were recorded in mid-August. By early September, \( \Delta CO_2 \) had decreased to \(37.1 \text{ mmol m}^{-2} \text{ d}^{-1} \) and \( \Delta CH_4 \) to \(0.11 \text{ mmol m}^{-2} \text{ d}^{-1} \), after which \( \Delta CO_2 \) and \( \Delta CH_4 \) continued to slowly decrease until late October (Fig. 4A).

In L. Ormajärvi, the daily \( \Delta CO_2 \) fluxes during the stratification were from \(-7.80 \) to \(49.6 \text{ mmol C m}^{-2} \text{ d}^{-1} \) (mean = \(12.6 \text{ mmol C m}^{-2} \text{ d}^{-1} \)), whereas the daily \( \Delta CH_4 \) fluxes were from \(0.02 \) to \(0.34 \text{ mmol C m}^{-2} \text{ d}^{-1} \) (mean = \(0.11 \text{ mmol C m}^{-2} \text{ d}^{-1} \)). There was a \( CO_2 \) influx or near-zero flux from the beginning of the sampling period until late July. Similarly to L. Pääjärvi, a \( \Delta CO_2 \) peak of \(26.3 \text{ mmol C m}^{-2} \text{ d}^{-1} \) was observed in August. However, the seasonal maximum was registered in late October. \( \Delta CH_4 \) fluxes fluctuated more during the sampling period and the highest rate was observed in early August (Fig. 4B).

In the Enonselkä basin, the \( \Delta CO_2 \) transfer rates varied from \(-2.50 \) to \(48.7 \text{ mmol C m}^{-2} \text{ d}^{-1} \) (mean = \(12.4 \text{ mmol C m}^{-2} \text{ d}^{-1} \)) and the \( \Delta CH_4 \) transfer rates varied from \(0.02 \) to \(1.19 \text{ mmol C m}^{-2} \text{ d}^{-1} \) (mean=\(0.24 \text{ mmol C m}^{-2} \text{ d}^{-1} \)). There was a steady increase in the \( \Delta CO_2 \) flux (slope = \(1.10, r^2 = 0.50 \)) and the \( \Delta CH_4 \) flux (slope = \(0.03, r^2 = 0.51 \)) from 31 May to 23 August, after which there was a sudden burst of \( CO_2 \) as well as of \( CH_4 \), with the highest peaks finally being registered in early September (Fig. 4C).
3.4. Rain–induced changes in carbon gas fluxes

The most notable difference between the study years was the heavy rain during the summer of 2004 compared to the warmer summer of 2005 (Fig. 2). The peaks in precipitation highlighted changes in DOC and carbon gas (CO$_2$ and CH$_4$) concentrations in the water column in Lakes Pääjärvi and Ormajärvi (Figs. 5 & 6 in IV). The increase in the gas concentrations was more noticeable in late July and August, since the cumulative capacity of the soils in the surrounding catchment was presumably exceeded, and the release of carbon was thus evident, whereas in June the soil was not yet saturated. High CO$_2$ and CH$_4$ concentrations were observed, especially in the metalimnion, and since the water column was still steeply stratified in late July–August in both lakes (Fig. 3 in IV), these gases could not originate from the hypolimnion. Throughout the water column, changes in DOC concentrations did not explain the variation in CO$_2$ concentrations during the stratification period in Lakes Pääjärvi and Ormajärvi. However, in the metalimnion of L. Pääjärvi, changes in DOC concentrations explained 78% of the variation in CO$_2$, and with the increase in the metalimnetic CO$_2$ concentration, O$_2$
concentrations decreased. The opposite was observed in L. Ormajärvi, where the CO$_2$ concentration in the metalimnion decreased as the DOC increased, and no correlation between CO$_2$ and O$_2$ was observed. In the case of CH$_4$, concentrations were positively related to DOC concentrations throughout the water column in both lakes, indicating the same lateral origin of carbon. However, the relationship was stronger in L. Pääjärvi ($r = 0.71$, $p < 0.001$) and even stronger in the metalimnion ($r = 0.90$, $p < 0.001$). Moreover, in L. Pääjärvi, CH$_4$ and CO$_2$ concentrations were positively correlated along the water column, whereas no correlation was found in L. Ormajärvi. However, the relationship was clearer in the metalimnion of both lakes (IV).

In all the studied lakes the DOC concentrations were high, but the quality of the DOC was presumably different in L. Ormajärvi and in Enonselkä basin with low water colour (II, III). The influence of the rain event was clearly observed in Lakes Pääjärvi and Ormajärvi with the extra loading of DOC during the summer. Not only did epilimnetic DOC concentrations increase in both lakes, but there was also a clear increase in metalimnetic concentrations (Fig. 3 in II, and 5 & 6 in IV). In L. Pääjärvi, DOC concentrations increased during the rain event along the water column, and the highest concentration of 22.2 mg L$^{-1}$ was measured between the depths of 5 and 10 m after the rain event. In L. Ormajärvi, DOC concentrations increased between the surface and 10 m depth during the rainy period, with the maximum being 10.2 mg L$^{-1}$. However, the increase took place throughout the epilimnion, not at a particular depth (IV).

Similarly, the increase in CO$_2$ and CH$_4$ concentrations was clearer in the metalimnion in L. Pääjärvi. In early June, a CO$_2$ concentration gradient with respective epilimnetic and hypolimnetic concentrations of 41.3 µM and 92.0 µM was observed. In July, changes in the metalimnetic concentrations were more obvious than in June, since the surface concentration dropped below the equilibrium and the hypolimnetic concentration increased to 114 µM. During the rain event, in late July, the metalimnetic concentration reached 100 µM, and after the rain event the concentration doubled to 217 µM. The same pattern was observed in CH$_4$ concentrations; however, the concentrations in the hypolimnion did not increase in L. Pääjärvi. During the rain event, the CH$_4$ concentration in the metalimnion reached 64.0 nM and increased up to 238 nM after the rain. The highest ∆CO$_2$ and ∆CH$_4$ fluxes occurred in mid-August, approx. 2 weeks after the heavy rains. The ∆CO$_2$ peak after the rainy period contributed 41% to the open water flux and 5% during the rain; thus,
altogether 46% of the total flux occurred during and after the rain event. The ΔCH₄ peak after the rain events contributed 48% to the annual flux (II).

In L. Ormajärvi in June–July, CO₂ concentrations in the epilimnion were lower than in L. Pääjärvi (< 20 µM). In August, the concentrations throughout the water column increased; a clear rise was observed on 25 August between 6 m and 10 m, when the concentration surged from 45.3 µM to 255 µM, i.e. a 6-fold increase, whereas in the hypolimnion the concentration was > 300 µM. In general, the hypolimnetic CO₂ concentrations varied more in L. Ormajärvi than in L. Pääjärvi. CH₄ concentrations were generally higher in L. Ormajärvi than in L. Pääjärvi, and also showed more daily variations throughout the water column (Figs. 5 & 6 in IV). The highest epilimnetic and metalimnetic CH₄ concentrations were observed after the rain events, being 190 nM and 164 nM, respectively. In contrast to L. Pääjärvi, the seasonality in ΔCO₂ and ΔCH₄ fluxes from L. Ormajärvi was not clear. However, the effect of rains and thermocline deepening gradually changed the lake from a small sink/zero flux of CO₂ to a source, whereas in the case of CH₄, the increase in the flux already appeared in July. The highest ΔCO₂ peak was registered after the rain period and contributed 35% to the annual flux, whereas 2% was contributed during the rain; thus a total of 37% of the total ΔCO₂ was registered during and after the rainy period, whereas ΔCH₄ contributed 39% to the annual flux during the rainy period (II).

3.5. Total annual fluxes and global warming potential (GWP)

The total ΔCO₂ flux during the open-water period was 5.43, 3.38 and 2.10 mol C m⁻² in Lakes Pääjärvi, Ormajärvi and the Enonselkä basin, respectively (Table 4). Thus, the total ΔCO₂ flux from L. Ormajärvi and the Enonselkä basin, respectively, was 38% and 61% smaller than from L. Pääjärvi. Moreover, the ΔCO₂ flux from L. Ormajärvi was 61% higher than from the Enonselkä basin. On the other hand, when the peaks during and after the rain event were omitted, the total ΔCO₂ fluxes from Lakes Pääjärvi and Ormajärvi were closer to that from the Enonselkä basin, i.e. the respective fluxes were 2.93 mol C m⁻² and 2.13 mol C m⁻². However, ΔCO₂ flux from L. Pääjärvi is still 38% and 40% higher than the fluxes from L. Ormajärvi and the Enonselkä basin, respectively (Table 4). Total ΔCH₄ fluxes during the open water period were 0.016, 0.021 and 0.041 mol C m⁻² in Lakes Pääjärvi, Ormajärvi and the
Enonselkä basin, respectively (Table 4). Thus, the total $\Delta CH_4$ fluxes from Lakes Ormajärvi and Pääjärvi were 49% and 61% lower than from the Enonselkä basin, respectively. Moreover, when the peaks from the rainy period were omitted, their corresponding total $\Delta CH_4$ fluxes were 0.013 and 0.008 mol m$^{-2}$. Thus, $\Delta CH_4$ fluxes were 68% and 80% smaller than from the Enonselkä basin, respectively (Table 4).

During the stratification period, the total annual global warming potential (GWP) for Lakes Pääjärvi, Ormajärvi, and Enonselkä basin was 5.60, 3.80 and 3.10 mol CO$_2$ equivalent m$^{-2}$, respectively. The annual GWP originating from CH$_4$ in the Enonselkä basin and in L. Ormajärvi was 33% and 13% respectively, whereas in L. Pääjärvi the contribution of CH$_4$ was only 7%. In L. Pääjärvi, CH$_4$ was most important in August, whereas in L. Ormajärvi the contribution was highest at the time of the lowest total fluxes, e.g. before August. Meanwhile, in Enonselkä basin the highest contribution was during the turnover period (Fig. 5 A, B, C). During the mixing periods in L. Pääjärvi, GWP was 0.90 and 0.70 mol CO$_2$ equivalent m$^{-2}$ in autumn and spring, respectively. Thus, the contribution of CH$_4$ to the carbon gas flux in spring was higher (3.0%), than in autumn (1.6%).
Table 4. Measurements of CO\textsubscript{2} and CH\textsubscript{4} concentrations (µM), total annual carbon gas fluxes (mol C m\textsuperscript{-2}) and the global warming potential (GWP, mol CO\textsubscript{2} equivalent m\textsuperscript{-2}) from the study lakes during 2004 and 2005. Carbon concentrations are from epilimnion and hypolimnion (mean ± SE). Lakes where the total annual fluxes were calculated, including the period of high summer precipitation, are indicated with (*). For comparison, calculated total emissions omitting the summer flux are presented (summer with average precipitation) (II). Data from the Enonselkä basin–Lake Vesijärvi in (III). Values in parentheses indicate the range and n indicates the number of samples.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Study lakes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon gas concentrations (µM)</td>
<td>Lake Pääjärvi* 2004</td>
</tr>
<tr>
<td>Epilimnion</td>
<td></td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>44 ± 3.07 n = 120 (15.0–98.7)</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>0.04 ± 0.006 n = 120 (0.004–0.12)</td>
</tr>
<tr>
<td>Hypolimnion</td>
<td></td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>94.3 ± 4.17 n = 96 (43.5–146)</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>0.03 ± 0.003 n = 96 (0.004–0.09)</td>
</tr>
<tr>
<td>Annual carbon gas emissions (mol C m\textsuperscript{-2})</td>
<td></td>
</tr>
<tr>
<td>ΔCO\textsubscript{2}</td>
<td>5.43</td>
</tr>
<tr>
<td>ΔCH\textsubscript{4}</td>
<td>0.016</td>
</tr>
<tr>
<td>Extreme rainy period*</td>
<td></td>
</tr>
<tr>
<td>ΔCO\textsubscript{2}</td>
<td>2.93</td>
</tr>
<tr>
<td>ΔCH\textsubscript{4}</td>
<td>0.008</td>
</tr>
<tr>
<td>Summer with average precipitation</td>
<td></td>
</tr>
<tr>
<td>ΔCO\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>ΔCH\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>Global warming potential (GWP) * (mol CO\textsubscript{2} equivalents m\textsuperscript{-2})</td>
<td>5.60</td>
</tr>
</tbody>
</table>
The total primary production (PP) and the amount of photosynthetic phytoplankton (Chl a) were 1.4 and 3.0 times higher in L. Ormajärvi than in L. Pääjärvi. Thus, the clearwater lake was more productive and therefore more active in biological inorganic carbon uptake than the humic lake (II). In L. Pääjärvi, PP was mainly high at the depth of 0–1 m. PP decreased from 117 mg m\(^{-3}\) d\(^{-1}\) to 89.1 mg m\(^{-3}\) d\(^{-1}\) in July and after the rain events, but in August the rate doubled. In L. Ormajärvi, PP was highest at 0–2 m. At the beginning of July, the highest rate, 243 mg m\(^{-3}\) d\(^{-1}\), was measured at the water surface, and during the rainy period PP decreased to 150 mg m\(^{-3}\) d\(^{-1}\). After the rain events, rates at the surface increased back to 257 mg m\(^{-3}\) d\(^{-1}\) (IV).

Similarly to PP, community respiration (CR) and thus the biological mineralization of carbon was higher in L. Ormajärvi. The total biological mineralization of organic carbon in L. Ormajärvi over the open-water period was 5.98 mol C m\(^{-2}\), i.e. 1.5 times higher than the biological uptake of inorganic carbon. In L. Pääjärvi the mineralization was 4.86 mol C m\(^{-2}\), which is 81% of that in L. Ormajärvi (II). In June, the highest activities were measured at the end of month in the uppermost epilimnetic layer (0–1 m), whereas in July CR increased in the epilimnion of both lakes. In L. Pääjärvi, the highest CR activity of 103 mg C m\(^{-3}\) d\(^{-1}\) was recorded at 0–1 m depth and in L. Ormajärvi at 1–2 m depth (172 mg C m\(^{-3}\) d\(^{-1}\)). In late July and August, after the rain event, CR increased in both lakes, particularly in L. Ormajärvi (IV).

Lakes Pääjärvi and Ormajärvi were in general net heterotrophic (R > PP). In L. Pääjärvi the pelagic CO\(_2\) net production was generally sufficient for the estimated CO\(_2\) flux; however, at the time of the peak flux in August, it was clear that the CO\(_2\) efflux could not have been due to the biological mineralization of carbon in the lake. Meanwhile, in L. Ormajärvi, CO\(_2\) fluxes were in balance with the biological processes in June, but in July–August more CO\(_2\) was produced than was discharged through the lake–atmosphere interface (II). Along the water column, no significant correlations were observed between CR and CO\(_2\) in L. Ormajärvi; however, in the metalimnion of L. Pääjärvi, CR explained 41% of the variation in CO\(_2\) concentrations (IV).

In contrast to Lakes Ormajärvi and Pääjärvi, the urban lake basin Enonselkä turned anoxic during the stratification period. Thus, the high CH\(_4\) concentrations were accompanied by high rates of CH\(_4\) oxidation. The maximum rate of oxidation was recorded at the depths of 10 m and 20 m, and especially at 10 m at the end of July and the
beginning of August. At the surface the activity was high in mid-spring and autumn (Fig. 6 in III). In the epilimnion, the oxidation of CH$_4$ correlated positively with the measured CH$_4$ concentration. The CH$_4$ was still released to the atmosphere, even though the CH$_4$ oxidation was 5 times higher than the estimated CH$_4$ flux from the sediment. The CH$_4$ emission was 17% of the amount produced through methanogenic activity, whereas 83% was oxidized. (III). In the Enonselkä basin the total primary productivity (PP) was 1.5 times higher than in the humic L. Pääjärvi, but 59% lower than in L. Ormajärvi. The highest PP was measured at the time of the strongest stratification and hypoxia, and the rate correlated with total iron concentrations (TFe). Moreover, there was a peak in bacterial production (BP) in June correlating with CH$_4$ concentrations. In the Enonselkä basin the mean and total BP during the open-water period was ca. 40–50% of PP.

4. DISCUSSION

4.1. Factors regulating carbon gas fluxes

4.1.1. Mixing and stratification of the water column

In temperate and boreal dimictic lakes, the highest carbon evasion rates have been measured during mixing periods (Kling et al. 1991, Cole et al. 1994, Riera et al. 1999). Studies in temperate lakes have demonstrated that the CH$_4$ flux is particularly high after ice-out whereas high CO$_2$ fluxes can take place in spring or autumn, depending on the depth of the lake (Michmerhuizen et al. 1996, Riera et al. 1999). CO$_2$ and CH$_4$ accumulate under ice, and the gases are rapidly lost immediately after ice-out, after which there is a decrease in epilimnetic CO$_2$ and CH$_4$ concentrations during stratification. Finally, surface concentrations of CO$_2$ and CH$_4$ increase again during the autumn turnover, when the gases accumulated in the hypolimnion are released (Dillon & Molot 1997, Riera et al. 1999). In the three study lakes the seasonality in carbon gas concentrations and fluxes followed this general pattern, but due to the short duration of the spring turnover, carbon gas fluxes in the spring were smaller than in the autumn. However, some differences were observed during a rainy summer in Lakes Pääjärvi and Ormajärvi (see 4.1.3.). In L. Pääjärvi, the highest CO$_2$ and CH$_4$ fluxes were recorded in the autumn and spring, respectively. Besides this, peaks in CO$_2$ and CH$_4$ fluxes were observed during the stratification period in mid-August after heavy rainfall. In L. Ormajärvi, the seasonal maximum of the CO$_2$ and CH$_4$ fluxes occurred during the autumn period, similarly to the Enonselkä basin. The
two different measuring techniques, namely floating chambers and calculations based on BLD models, resulted in slightly different flux estimates. For instance, in L. Pääjärvi the FC flux for CO\textsubscript{2} was 1.3 and 1.7 times higher than the flux estimated with BLD in the autumn and spring, respectively (I). The FC method has been criticized to eliminate wind force, which is important for gas exchange (Wanninkhof & Knox 1996, Cole & Caraco 1998, Raymond & Cole 2001). However, at low wind speeds, chambers yield satisfactory flux estimates (Borges et al. 2004a).

In L. Pääjärvi the saturation factor for CO\textsubscript{2} varied from 0.95 and 4.36 and in L. Ormajärvi between 0.69 to 3.87 times the atmospheric pCO\textsubscript{2}, whereas in the urban lake basin, the saturation factor only varied from 0.72 to 2.46 times the atmospheric pCO\textsubscript{2}. The corresponding averages for mid-summer saturation were 2.2, 1.5 and 1.8 respectively. The saturation of CO\textsubscript{2} was higher in L. Pääjärvi, whereas in L. Ormajärvi and in the Enonselkä basin the values were within those recorded in lakes in northern Sweden, where seasonal variation was from 0.84 to 3.41 times the atmospheric pCO\textsubscript{2} and the average for the mid-summer saturation was 1.68 (Jonsson et al. 2003).

Studies in large deep lakes have shown that thermal stratification has considerable significance for the cycling of CH\textsubscript{4}, especially in terms of CH\textsubscript{4} concentrations and oxygen in the epilimnion and hypolimnion (Fallon et al. 1980, Harrits & Hanson 1980). Lakes Pääjärvi and Ormajärvi remained oxic during the open-water period and CH\textsubscript{4} concentrations were higher in the clear water lake than in the humic lake along the whole water column. In the urban lake basin, where hypoxia and anoxia prevail during summer stratification, CH\textsubscript{4} concentrations throughout the water column were higher than in Lakes Pääjärvi and Ormajärvi, especially in the hypolimnion (ca. 480 and 100 times higher, respectively). Due to more eutrophic conditions in the Enonselkä basin, the degradation of organic matter was enhanced and the autochthonous sources of organic matter contributed more to the carbon cycling in the lake (Rantakari 2010). Thus, the more productive lake sediments had a higher capacity to produce CO\textsubscript{2} and CH\textsubscript{4}, which was then reflected in the carbon gas fluxes.

Since we measured the gas fluxes with the chamber method as well as by using the BLD model, we could estimate the gas transfer velocities (k\textsubscript{600}) and relate them to wind speed. Although in L. Pääjärvi the k\textsubscript{600} values of CO\textsubscript{2} and CH\textsubscript{4} in the spring and autumn were mostly controlled by wind speed, a considerable fraction of variation remained unexplained and was related to neither rainfall nor temperature differences between
the air and water. However, wind-wave interactions, sensible heat loss, long wave back radiation and turbulence due to buoyancy fluxes that we were unable to measure probably affected the gas transfer velocity (Anderson et al. 1999, MacIntyre et al. 2001) (I). There have been few studies on the lacustrine gas transfer velocity in the boreal zone, and especially from lakes of a reasonable size. Therefore, the results were compared with small lakes in the USA and Sweden, an estuary, a tropical reservoir and a Japanese river (Crucius & Wanninkhof 2003, Borges et al. 2004b, Guérin et al. 2007, Jonsson et al. 2008, Tokoro et al. 2008). Gas transfer velocities were measured directly, i.e. using the floating chamber method, concomitantly with CO$_2$ gradient measurements in the estuary, the tropical reservoir and the river, whereas in the small lake in the USA, the study was based on the introduction of SF$_6$ and in Sweden on eddy covariance measurements. The $k_{600}$ in L. Pääjärvi was 1.3 times higher at a wind speed similar to the American lake and within the median values of the northern lake in Sweden. $k_{600}$ for CO$_2$ in autumn in L. Pääjärvi was closer to that reported from the tropical reservoir and the river and comparable to the estuary in the spring, even though in tidal systems, turbulent currents appeared to be of greater importance than in a boreal lake (I). In the spring as well as in the autumn, $k_{600}$ for CH$_4$ was comparable to the tropical reservoir. Thus, the formulation of $k_{600}$ is not only site-specific, but also time-specific (Borges et al. 2004a, Guérin et al. 2007). Moreover, $k_{600}$ from eddy covariance measurements was calculated in a small humic lake close to L. Pääjärvi. These results showed that when considering the complete data set, only 1.7% of the variation was due to wind speed, but when considering only the autumn data, wind speed explained 40% of the variation (Huotari 2011). In L. Pääjärvi, wind speed explained 67% of the variation. This was probably because L. Pääjärvi is fairly large and thus exposed to wind action, whereas the small lake was sheltered by the surrounding mature forest, and instead of wind the lake was mainly driven by convection. Thus, the gas transfer velocities of CO$_2$ and CH$_4$ in L. Pääjärvi generally correlated with wind speed, and the slope of the linear regression between the wind speed and $k_{600}$ was steeper in the spring than the autumn, whereas the opposite situation has been observed in small lakes (Cole & Caraco 1998, Jonsson et al. 2008, Huotari 2011).

4.1.2. Biological processes

Current evidence suggests that CO$_2$ emission to the atmosphere from lakes is primarily
maintained by the mineralization of allochthonous organic carbon (Jonsson et al. 2003, Duarte & Prairie 2005), which causes respiration to exceed primary production and results in net heterotrophy of the lake (del Giorgio & Peters 1994, Cole et al. 2000). We occasionally observed net uptake of CO$_2$ in the study lakes, but for the majority of the growing season the lakes were net heterotrophic. There was a rapid spring decrease in the CO$_2$ concentration in the clear-water L. Ormajärvi, which suggests that vigorous primary production had already started underneath the ice cover (Tulonen et al. 1994, Wetzel 2001, Kiili et al. 2009). The lake acted as a sink of CO$_2$ in the early summer, but switched to a source in mid-August, which lasted for the rest of the open-water period.

L. Pääjärvi as well as L. Ormajärvi and the Enonselkä basin can be considered as net heterotrophic on the basis of the measured DOC concentration, since the threshold concentration of DOC for net heterotrophy is 8 mg L$^{-1}$ (Sobek et al. 2006). However, the DOC in L. Ormajärvi and Enonselkä basin is colourless, whereas in L. Pääjärvi DOC is strongly coloured, implying that DOC in clear-water lakes may be more labile, whereas in the humic lake, DOC is presumably more recalcitrant (II, III). The increase in community respiration in the epilimnion was observed in Lakes Pääjärvi and Ormajärvi at the time when the DOC concentrations increased. In both lakes, biological processes (R-PP) were enough to explain the atmospheric CO$_2$ fluxes. During the stratification period of the rainy summer in 2004, the main differences were at the time of the summer flux peak (Fig. 6 in II). Thus, in the humic L. Pääjärvi, the CO$_2$ flux and mineralization processes were generally more closely associated than in the clear-water L. Ormajärvi. During and after the rain events, however, more CO$_2$ was emitted than could be produced biologically in the water column. In L. Pääjärvi, if the flux peak in August is omitted, 92% of the CO$_2$ emitted to the atmosphere could be explained by the biological processes.

Belowground processes are crucial for carbon cycling in littoral zones, where the key primary producers, e.g. emergent macrophytes, have a high content of structural carbon and thus decompose very slowly (Wrubleski et al. 1997). For instance, Larmola et al. (2006) suggested that nearly 40% of the accumulated litter remained on littoral site after the first 2 years of decomposition, and the first year carbon loss contributed 1 to 1.5 times to the net carbon efflux. However, in flooded areas, CO$_2$ emission to the atmosphere was almost zero, implying that CO$_2$ was dissolved in water and transported to the lake. During
decomposition in water and in sediments, part of the carbon is released as gases (CO$_2$ and CH$_4$) and part is buried in the sediments. Methanogenesis is a microbial process that can only occur in anaerobic sediments or an anoxic hypolimnion, whereas methanotrophy (CH$_4$ oxidation) requires both CH$_4$ and oxygen in freshwater environments and tends to occur in the sediment surface (Lidstrom & Somers 1984, Boon & Lee 1997) or around the thermocline, where the CH$_4$-rich hypolimnion meets the oxygen-rich epilimnion (Harrits & Hanson 1980).

In the urban Enonselkä basin, the high hypolimnetic temperature favoured decomposition and thus the production of carbon gases. Moreover, an increase in CH$_4$ concentrations followed the increase in phosphorous and iron (c.f. Roden & Wetzel 2003). During thermocline erosion and water column mixing, iron and phosphorus were re-supplied from the hypolimnion, enhancing primary production. Hence, a strong correlation was observed between primary production (PP) and iron (III). The epilimnetic iron concentration in the Enonselkä basin was 20 and 23 µg L$^{-1}$ in July and August, respectively, which should be enough to sustain algal growth for several days (Wurtsbaugh & Horne 1983). However, the results are for total iron and the fraction of iron utilizable by algae was not measured.

Iron can also favour nitrogen-fixing cyanobacteria over chlorophytes (Molot et al. 2010). This is the case in the Enonselkä basin, where cyanobacteria are usually abundant during the stratification and in August (Ojala et al. 2003). Aquatic prokaryotes can also produce siderophores, which enhance iron uptake (Wilhelm & Trick 1994, Granger & Price 1999). In 2005, the cyanobacterial genera *Aphanizomenon* and *Anabaena* were abundant in Enonselkä basin, and the latter is particularly known to produce siderophores (Clarke et al. 1987). Thus, there was a positive feedback mechanism between the processes in the anoxic hypolimnion and primary production, which was also reflected in the carbon gas concentrations (III).

In contrast to Lakes Pääjärvi and Ormajärvi, with constantly oxygenic hypolimnia, the most active layer of CH$_4$ oxidation in the Enonselkä basin was at the depth of 10 m during the summer maximum, i.e. at the thermocline. Through turbulent diffusion, CH$_4$ was transported from the hypolimnion to the surface. The correlation between BP and the CH$_4$ concentration in the epilimnion indicates that oxidation took place in the surface, but since the lake was supersaturated with CH$_4$, some CH$_4$ escaped oxidation (Fig. 6 in III). During the summer stratification, 83% of CH$_4$ was oxidized, but the CH$_4$ flux was still higher than in Lakes
Pääjärvi and Ormajärvi. The proportion of CH$_4$ oxidation in the Enonselkä basin was similar to the small humic lake Valkea–Kotinen, where the oxidation rate was 80% (Kankaala et al. 2006). In relation to the latter finding, it is important to point out that results from direct measurements of methanotrophic activity in comparison to predicted CH$_4$ concentrations (amount of CH$_4$ transported by turbulent diffusion in the water column assuming no CH$_4$ oxidation activity) have been reported to give markedly similar results. Thus, modelling calculations can be successfully applied in stratified lakes for studies on the magnitude of CH$_4$ oxidation in annual budgets (Kankaala et al. 2006)

4.1.3. Rain-induced effects

In summer 2004, the extreme rain events were followed by sudden pulses of DOC and also carbon gases (CO$_2$ and CH$_4$) in the epilimnia and metalimnia of Lakes Pääjärvi and Ormajärvi, which presumably originated from terrestrial and littoral areas (IV). The concentrations showed clear peaks, especially in L. Pääjärvi, at the same time as the peak in gas fluxes. A similar, but slightly more modest peak was observed in L. Ormajärvi. In general, during the rainy period in 2004, CO$_2$ fluxes from Lakes Pääjärvi and Ormajärvi were clearly higher than in the Enonselkä basin, which was studied in 2005. In both lakes the extreme rain event was manifested in an increase in the saturation factor of CO$_2$ as well as in CH$_4$. These findings are in accordance with those of Roehm et al. (2009), who also suggested that the interannual variability in pCO$_2$ is driven by regional precipitation patterns. Rantakari & Kortelainen (2005) additionally demonstrated in 37 large Finnish lakes that the annual CO$_2$ emission and precipitation were closely connected. Similarly, in a study on a 5-lake chain in southern Finland, high summer precipitation increased CO$_2$ emissions from small lakes (Einola et al. 2011). Moreover, in 12 coastal Brazilian lakes the mean CO$_2$ flux was enhanced 10-fold following a rain event (Marotta et al. 2009). However, our finding is somewhat contrary to Kelly et al. (2001), who could not find a single weather-related factor that could by itself exert strong enough control to show an observable effect on pCO$_2$ in oligotrophic lakes. Distinct seasonal changes in the saturation of carbon gases may be due to large variations in metabolic activity or large changes in the input of CO$_2$ or CH$_4$ with inflowing water. The seasonality in the CO$_2$ concentration in L. Pääjärvi showed differences that could reflect large changes in the input of CO$_2$ compared to L. Ormajärvi and the Enonselkä basin of Lake Vesijärvi.
Heavy rains enhance the loading of DOC and therefore stimulate bacterial production in boreal lakes (Bergström & Jansson 2000, Berggren et al. 2009). Although some stimulation of community respiration was observed in the upper water layers in both lakes (II), the increase in CO$_2$ and CH$_4$ concentrations in the lower epilimnia and especially in the metalimnia cannot be explained by increased microbial activity alone. The extra CO$_2$ and CH$_4$ in the pelagic zone, 500 m from the shoreline, were presumably due to the lateral transport of gases from the catchments and/or littoral zone. The gases originated from soils with high CO$_2$ concentrations as a result of soil respiration and weathering (Hope et al. 2004), whereas the CH$_4$ resulted from the anaerobic decomposition of organic matter. The more pronounced increase in the pelagic CO$_2$ and CH$_4$ concentrations after the rain events may have been due to more extensive shoreline flooding, since the water level was considerably higher in August than in early July, leading to more saturated soils (IV). Thus, in all three of the study lakes, lateral flows from littoral zones most likely contributed to the increased gas concentrations and finally to the carbon gas fluxes. Similarly, studies in Germany have revealed that the lateral transport of CH$_4$ from the littoral zone due to wave action results in increased epilimnetic CH$_4$ concentrations in the pelagic epilimnion (Hofmann et al. 2010). Thus, littoral zones are an important source of lacustrine CH$_4$. Moreover, the CH$_4$ flux during the summer can be higher from littoral sediments than from profundal sediments, because high sediment temperatures at shallow depths support high CH$_4$ production rates (Casper 1996). In addition to temperature, littoral zones often have greater carbon inputs, and therefore more methanogenesis.

4.1.4. Lake characteristics

In boreal lakes the flow of organic matter is dominated by allochthonous DOC originating from the catchment areas, which due to humic substances determined not only the water colour but also the $p$CO$_2$ variation. A factor important to the relationship between DOC and $p$CO$_2$ is the pathway to deliver this organic carbon into the lakes (Mattson et al. 2005), which not only influences the amount but also the nature of the DOC inputs (Schiff et al. 1997). While the general importance of the allochthonous carbon load is widely recognized, its relative significance in comparison to autochthonous carbon can greatly vary from lake to lake depending on the CA:LA ratio, water residence time and the proportion of peatlands in the catchment area.
DOC concentrations in aquatic environments usually range from 0.5 to 30 mg L$^{-1}$ (Hessen & Tranvik 1998). The mean DOC concentrations in our study lakes were 12.3, 7.6 and 7.0 mg L$^{-1}$ in Lakes Pääjärvi, Ormajärvi and Enonselkä basin, respectively. In general, the catchment areas of our study lakes can be regarded as mixed in terms of land use, e.g. Lakes Pääjärvi and Ormajärvi were surrounded by forest and agricultural areas. However, the proportion of forest was higher around L. Pääjärvi, whereas around L. Ormajärvi agricultural areas were more abundant. Around the Enonselkä basin, forest and urban settings were common, and in general the basin was greatly influenced by urbanization. The carbon content in lakes that are surrounded by forest and adjacent peatlands as well as those surrounded by agricultural areas is high, although the proportion of inorganic carbon is usually higher in lakes more affected by agriculture (Rantakari 2010). On the other hand, since the study lakes were not pristine lakes, the allochthonous carbon could have originated also from several anthropogenic sources. Therefore, we could not find a clear connection between organic carbon and the CO$_2$ concentrations in the lakes (cf. Rantakari 2010). However, as a consequence of the extreme rain event, the connection became clearer (II, IV).

The geological setting of L. Ormajärvi is calcareous and the lake itself has a relatively high pH and alkalinity (II, Huitu & Mäkelä 1999). In L. Ormajärvi, the excess CO$_2$ produced by biological processes did not result in higher atmospheric fluxes, which could have been due to the transformation of DIC to carbonates (II). On the other hand, in L. Ormajärvi it is also necessary to consider the transport of organic carbon from the benthos and littoral zone as a source of the heterotrophy of the pelagic zone (II). Besides, the “extra” carbon gases discharged from Lakes Pääjärvi and Ormajärvi could have originated from groundwater, since the ground water input of inorganic carbon can be significant (Striegl & Michmerhuizen 1998).

The higher CA:LA ratio, the greater an impact in the catchment area can be expected to have on the water and sediment quality and the carbon accumulation rate in lake sediments (Mullholland & Elwood 1982). The mean carbon accumulation in sediments in Finnish lakes with a surface area between 1.0–10 km$^2$ is 0.26 mol C m$^{-2}$ y$^{-1}$, and in lakes between 10–100 km$^2$ the value is 0.15 mol C m$^{-2}$ y$^{-1}$ (Pajunen 2004), whereas the corresponding emission-to-accumulation ratios are 18 and 21, respectively (Rantakari 2010). In the urban lake basin Enonselkä the
ratio was ~ 4 times lower than typical values for lakes in the same size category, indicating that sedimentation played a more important role (III). In the clear water L. Ormajärvi and the humic L. Pääjärvi, emissions were more important. In the clear-water lake the ratio was closer to the proposed 18; however, in the humic lake the estimated ratio was 36 i.e. 1.7 times higher. Thus, larger lakes are not only sites of organic carbon mineralization but also significant emitters of carbon to the atmosphere.

Although our lakes emitted a fair amount of carbon gases, in general it is known that CO₂ and CH₄ fluxes are inversely related to lake size (Kortelainen et al. 2006, Roehm et al. 2009, Juutinen et al. 2009). In addition, surface pCO₂ concentrations in the Enonselkä basin and L. Ormajärvi were similar, even though the urban basin is 4 times larger. This indicates the long history of anthropogenic influence on the basin (III).

4.2. Annual CO₂ and CH₄ fluxes from boreal lakes and the global carbon cycle

Northern lakes in general have been demonstrated to be sources of CO₂ (Cole & Caraco 1994, Dillon & Mollot 1997, Jansson et al. 2003, Huotari 2011). In Finland, in a study on 117 randomly-selected lakes from different size classes, the average value of CO₂ emission was 3.1 mol C m⁻² from lakes with a surface area of between 10 and 100 km² (Kortelainen et al. 2006), whereas the annual CO₂ flux from the large lakes varied from 1.49 to 2.29 mol m⁻² (Rantakari & Kortelainen 2005). The latter values are ca. 58% and 32% lower than the annual fluxes from Lakes Pääjärvi and Ormajärvi, respectively, during the rainy year. However, they are within the annual value of CO₂ flux from the Enonselkä basin. When omitting the summer peaks, the fluxes of CO₂ from Lakes Pääjärvi and Ormajärvi were within the range of large lakes in Finland, and annual CO₂ fluxes from L. Ormajärvi and the Enonselkä basin were equal.

Pools of carbon stored in freshwater sediments are large; approximately 820 Pg of carbon have been stored in lake sediments during the Holocene (Einsele et al. 2001), which is comparable with the global estimates for the amount of carbon stored in forest vegetation and soils (approx. 1 146 Pg of carbon) (Dixon et al. 1994). Moreover, recent studies have shown that lateral transport and fluxes of carbon from terrestrial to aquatic systems are substantial; for comparison, they are similar in magnitude to the net ecosystem production of the terrestrial biosphere (approx. 2 Pg C yr⁻¹), and should not therefore be ignored in global carbon budgets (Randerson et al. 2002, Cole et al. 2007).
However, studies in Finland have revealed that carbon stores in lake sediments are actually smaller than earlier estimates in the boreal region, i.e. the new estimate is 78% to 84% lower (Kortelainen et al. 2004).

The net ecosystem exchange (NEE) of forests and peatlands in southern Finland is approx. 10 mol C m\(^{-2}\) yr\(^{-1}\) (Suni et al. 2003, Riutta et al. 2007). The annual CO\(_2\) and CH\(_4\) flux from Lakes Pääjärvi and Ormajärvi and from the Enonselkä basin estimated for the whole catchment area were approx. 0.40, 0.20 and 0.70 mol C m\(^{-2}\) yr\(^{-1}\), respectively. Thus, the fluxes from Lakes Pääjärvi and Ormajärvi, respectively, were 4% and 2% of the terrestrial NEE in their catchments. In the Enonselkä basin the proportion was higher (7%), which was presumably influenced by the smaller CA:LA ratio (Table 1) compared to the previously mentioned lakes. These proportions are; however, lower than observed by Huotari et al. (2011) during a five-year study in Lake Valkea–Kotinen, which is surrounded by old-growth forest (10%). Hanson et al. (2004) estimated that due to intensive forestry the forests are not mature, natural forests with low NEE but fast-growing stands building up tree biomass (Luyssaert et al. 2008). Jonsson et al. (2007) came into same conclusions in northern Sweden, where the catchment of the study lake was under intensive forestry.

Air temperatures have risen by approx. 1 °C due to the increase in greenhouse gas emissions and the accumulation of CO\(_2\) in the atmosphere during the last 50 years (IPCC 2001). In Finland the mean annual temperature increased by approx. 0.7 °C during the 20\(^{th}\) century, whereas the projected rise in the next 100 years will be from 1 to 3 °C (Jylhä et al. 2004), accompanied by an earlier onset of the spring melt and lengthening of the melting season. In our data set, the mixing period in autumn 2004 was longer than the spring melt in 2005, i.e. the autumn turnover lasted for 17 days whereas in spring the duration was only 8 days. Thus, CO\(_2\) emissions were higher during the autumn than in the spring mixing period. The estimations agreed with Piao et al. (2008), who predicted that in northern ecosystems autumns will become longer and thus carbon fluxes will increase, and the ecosystems will lose part of their capacity to take up carbon. The situation may be enhanced when taking into account the presence of CH\(_4\), e.g. our evaluation of the global warming potential...
(GWP) indicates that the contribution of CH\textsubscript{4} to carbon gas release is 3.0% during the spring and 1.6% during the autumn in L. Pääjärvi. Changes in wind speed and the frequency of strong winds will also have consequences for lake ecosystems; despite other factors also being important, the gas transfer velocity in lakes is largely determined by wind speed (I) (Wanninkhof & Knox 1996, Cole & Caraco 1998).

Although the turnover periods appeared important for carbon gas fluxes from the study lakes, on an annual basis a considerable proportion of the flux was emitted during the summer months due to the extreme rain events (II). This effect was more radical in the clear water L. Ormajärvi, which turned from a sink to a source of CO\textsubscript{2} after the rain event (II). In Finland, it has been suggested than the mean annual precipitation will increase by 0–15% by 2020, and projections for 2050 and 2080 are 30% and 40%, respectively (Jylhä et al. 2004). The increase in precipitation implies a higher lateral flux of CO\textsubscript{2} from the catchment areas and therefore higher emissions of CO\textsubscript{2} from lakes. Moreover, metabolic processes are important to carbon concentrations. For instance, aerobic respiration produces CO\textsubscript{2}, which can enhance the atmospheric emissions of CO\textsubscript{2} (Cole et al. 1994). Respiration itself may increase as a consequence of the allochthonous DOC load (Kling 1991, Striegl & Michmerhuizen 1998).

This was observed in the late summer and autumn when biological mineralization processes were enhanced by the increase in DOC during the rain events (II). Thus, L. Pääjärvi, as a typical dimictic and humic boreal freshwater ecosystem, was shown to be an important conduit of terrestrial carbon. The more productive lakes, which are often considered as carbon sinks, also appeared to be sources of carbon gas emissions. In Lakes Pääjärvi and Ormajärvi, CH\textsubscript{4} fluxes contributed significantly to the GWP in both lakes, but the highest CH\textsubscript{4} contribution was from the urban lake basin. This observation was somewhat in contrast to that by Huttunen et al. (2003), who concluded that CH\textsubscript{4} is insignificant for GWP in small boreal lakes. However, the importance of lakes for global CH\textsubscript{4} budgets has been stressed, for example, by Bastviken et al. (2004), and more recent studies in arctic permafrost with thermokarst lakes have identified enhanced CH\textsubscript{4} emissions associated with permafrost degradation as a positive feedback to climate warming (Walter et al. 2006).

Globally, inland waters are estimated to make a net contribution of approx. 0.75 Pg C yr\textsuperscript{-1} to the atmosphere (Cole et al. 2007). Of this, about 0.11 Pg of carbon represents emissions of CO\textsubscript{2} from lakes and the rest is storage in the sediments (Cole et al. 2007).
By comparison, deforestation releases 1.6 Pg C yr\(^{-1}\) (Sundquist 1993, DeFries et al. 2002). CH\(_4\) as a powerful greenhouse gas accounts for 20% of the anthropogenic greenhouse gas effect (Cicerone & Oremland 1988, Wuebbles & Hayhoe 2002). CH\(_4\) emissions from lakes account for 8 to 48 Tg yr\(^{-1}\) of CH\(_4\) released to the atmosphere (Bastviken et al. 2004, Juutinen et al. 2009). Thus, CH\(_4\) emissions from lakes are similar in magnitude to those from anthropogenic sources such as rice paddies (60 Tg yr\(^{-1}\), range from 20 to 100 Tg yr\(^{-1}\)) and biomass burning (40 Tg yr\(^{-1}\)) (Crutzen et al. 1985, Wang & Shangguan 1996).

5. CONCLUSIONS

In the three study lakes the seasonality in carbon gas concentrations and fluxes followed the general pattern of dimictic lakes in northern latitudes, but due to the brief duration of spring mixing, carbon gas fluxes in the spring were smaller than in the autumn. Moreover, some differences were observed during the rainy summer of 2004 in Lakes Pääjärvi and Ormajärvi.

Although spring mixing was a short and rapid event in comparison to that in the autumn, both mixing periods effectively liberated the carbon gases accumulated during summer stratification and during the period of ice cover. When the gas transfer velocity of CO\(_2\) and CH\(_4\) in L. Pääjärvi was plotted against wind speed, it appeared that \(k_{600}\) depends more strongly on wind speed in the spring than the autumn. Thus, the gas transfer velocity as a function of wind speed is not only site-specific but also time-specific.

The three large dimictic lakes with contrasting water quality characteristics were supersaturated with CO\(_2\) and CH\(_4\), and were therefore sources of carbon gas fluxes on an annual basis. In the humic lake, biological processes were closely connected to CO\(_2\) fluxes during mixing and stratification periods, whereas in the clear water lakes the impact of the littoral and benthic areas was more pronounced. Higher CO\(_2\) fluxes were measured in the humic lake, whereas in the clear-water lakes CH\(_4\) fluxes were of greater importance. Differences in carbon gas concentrations and fluxes between the clear-water lakes were also observed, since L. Ormajärvi was oxic throughout the open-water period and the Enonselkä basin was anoxic during summer stratification. Even though the methanotrophic activity was high in the Enonselkä basin and 83% of CH\(_4\) was oxidized to CO\(_2\), 17% was still released to the atmosphere.

Lakes as well as terrestrial ecosystems have a high capacity to store carbon; however, the magnitude of carbon fluxes
varies due to seasonal changes, especially in the presence of an extreme rain event. In 2004, the summer precipitation generated variability in carbon gas and DOC concentrations in the epilimnion and metalimnion, especially during and after the rain event when Lakes Pääjärvi and Ormajärvi showed their strongest stability. In the humic L. Pääjärvi, a high summer peak flux of CO$_2$ and CH$_4$ was responsible for nearly 50% of the annual flux after the rainy period, whereas the clear-water L. Ormajärvi switched from nearly being a sink of CO$_2$ before the rain to a clear source after the rain event. Moreover, precipitation enhanced community respiration in the surface water, but the high concentrations of DOC, CO$_2$ and CH$_4$ concentrations in deeper layers below the euphotic zone indicated the presence of lateral carbon transport, and thus strong associations between the soil/littoral system and the pelagic zone.

The carbon stores and fluxes in the study lakes varied according to the characteristics of the catchment area and previous loading history. The catchments and the lakes were influenced by a varying degree of human activity. Thus, in contrast to pristine lakes, autochthonous and allochthonous carbon originated from different sources. The CA:LA ratio also played an important role in the water and in the carbon accumulation rate. In the Enonselkä lake basin, the carbon accumulation rate was high due to the anoxic conditions, and the ratio of gas emission to accumulation was therefore low. However, carbon gas emissions were still an important route for carbon departure, although less so compared to the oxygenated Lakes Pääjärvi and Ormajärvi. On the other hand, the urban lake basin Enonselkä, with a low CA:LA ratio but a history of urban waste water loading, resulted in carbon gas emissions comparable to Lakes Pääjärvi and Ormajärvi when omitting the rainy summer peaks.

In general, the study lakes were effective in transporting and processing terrestrial carbon and emitting it to the atmosphere during the mixing periods, and especially after intensive precipitation. In the Fennoscandia region, warmer autumns are expected to be more frequent as a consequence of global climate change, which will lead to a delay in the onset of freezing and the enhancement of organic carbon loading from lake surroundings. Similarly, increased wind speeds and extremes of precipitation are very likely to increase in magnitude and frequency, and the future scenario for boreal lakes will thus be higher carbon gas fluxes and an enhanced role as a ventilator of terrestrially fixed carbon.
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