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Miitta Rantakari

The role of lakes in carbon cycling in boreal catchments

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List of original publications and author's contribution

This thesis is based on the following publications. These publications are referred in the text by the Roman numerals (I-VI). The author's contribution is explained separately for each article. In addition, some previously unpublished results and figures are included in this study.

- I **Rantakari, M.**, Kortelainen, P., Vuorenmaa, J., Mannio, J. and Forsius, M. (2004): Finnish Lake Survey: The Role of Catchment Attributes in Determining Nitrogen, Phosphorus, and Organic Carbon Concentrations. *Water, Air, & Soil Pollution: Focus*, 4(2-3): 683 – 699.
- II Kortelainen, P., Pajunen, H., **Rantakari, M.** and Saarnisto, M. (2004): A large carbon pool and small sink in boreal Holocene lake sediments. *Global Change Biology* 10: 1648 –1653.
- III **Rantakari, M.** and Kortelainen, P. (2005): Interannual variation and climatic regulation of the CO₂ emission from large boreal lakes. *Global Change Biology* 11: 1368 – 1380.
- IV Kortelainen, P., **Rantakari, M.**, Huttunen, J., Mattsson, T., Alm, J., Juutinen, S., Larmola, T., Silvola, J. and Martikainen, P.J. (2006): Sedimentary respiration and lake trophic state are predictors of large CO₂ evasion from small boreal lakes. *Global Change Biology* 12: 1554 – 1567.
- V **Rantakari, M.** and Kortelainen, P. (2008): Controls of total organic and inorganic carbon in randomly selected Boreal lakes in varied catchments. *Biogeochemistry* 91:151 –162.
- VI Juutinen, S., **Rantakari, M.**, Kortelainen, P., Huttunen, J.T., Larmola, T., Alm, J., Silvola, J. and Martikainen, P.J. (2009): Methane dynamics in different boreal lake types. *Biogeosciences* 6:209 – 223.

Author's contribution

- I M. Rantakari and P. Kortelainen jointly planned the study. Water quality and catchment data was processed jointly by M. Rantakari and J. Vuorenmaa. M. Rantakari was responsible for statistical analyses of data and the interpretation of the results together with P. Kortelainen. M. Rantakari wrote the first version of the manuscript, which was commented by the other writers. M. Rantakari then finalized the paper.
- II The selection of the study lakes was performed jointly by M. Rantakari and P. Kortelainen. M. Rantakari was responsible for processing water quality and catchment data and for the statistical analyses of data. All authors jointly interpreted the results. P. Kortelainen and M. Rantakari performed the extrapolation of the results over Finland and over the whole boreal region. P. Kortelainen wrote the first version of the manuscript, which was commented by the other writers. M. Rantakari was responsible for the tables and figures of the manuscript.
- III M. Rantakari was responsible for planning the study and for processing water quality and catchment data. M. Rantakari made the statistical analyses of data. M. Rantakari and P. Kortelainen jointly interpreted the results. M. Rantakari wrote the first version of the manuscript, which was commented by P. Kortelainen.

- IV The selection of the study lakes was performed jointly by M. Rantakari and P. Kortelainen. M. Rantakari took part in sampling and was responsible for processing the water quality and catchment data and for the statistical analyses of data. P. Kortelainen and M. Rantakari jointly interpreted the results. P. Kortelainen and M. Rantakari took care of extrapolation of the results over Finland and over the whole boreal region. P. Kortelainen wrote the first version of the manuscript, which was commented by the other writers.
- V M. Rantakari was responsible for planning of the study and for processing water quality and catchment data. M. Rantakari made the statistical analyses of data. M. Rantakari and P. Kortelainen jointly interpreted the results. M. Rantakari wrote the first version of the manuscript, which was commented by P. Kortelainen.
- VI The paper was initiated and planned jointly by the authors. The selection of the study lakes was performed jointly by M. Rantakari and P. Kortelainen. M. Rantakari took part in sampling and was responsible for processing water quality and catchment data and for categorizing the lake data. The results were interpreted jointly by the writers. S. Juutinen wrote the first version of the manuscript, which was commented by the other writers.

The role of lakes in carbon cycling in boreal catchments

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Lakes are an important component of ecosystem carbon cycle through both organic carbon sequestration and carbon dioxide and methane emissions, although they cover only a small fraction of the Earth's surface area. Lake sediments are considered to be one of the rather permanent sinks of carbon in boreal regions and furthermore, freshwater ecosystems process large amounts of carbon originating from terrestrial sources. These carbon fluxes are highly uncertain especially in the changing climate.

The present study provides a large-scale view on carbon sources and fluxes in boreal lakes situated in different landscapes. We present carbon concentrations in water, pools in lake sediments, and carbon gas (CO_2 and CH_4) fluxes from lakes. The study is based on spatially extensive and randomly selected Nordic Lake Survey (NLS) database with 874 lakes. The large database allows the identification of the various factors (lake size, climate, and catchment land use) determining lake water carbon concentrations, pools and gas fluxes in different types of lakes along a latitudinal gradient from 60°N to 69°N.

Lakes in different landscapes vary in their carbon quantity and quality. Carbon (C) content (total organic and inorganic carbon) in lakes is highest in agriculture and peatland dominated areas. In peatland rich areas organic carbon dominated in lakes but in agricultural areas both organic and inorganic C concentrations were high. Total inorganic carbon in the lake water was strongly dependent on the bedrock and soil quality in the catchment, especially in areas where human influence in the catchment is low. In inhabited areas both agriculture and habitation in the catchment increase lake TIC concentrations, since in the disturbed soils both weathering and leaching are presumably more efficient than in pristine areas.

TOC concentrations in lakes were related to either catchment sources, mainly peatlands, or to retention in the upper watercourses. Retention as a regulator of the TOC concentrations dominated in southern Finland, whereas the peatland sources were important in northern Finland. The homogeneous land use in the north and the restricted catchment sources of TOC contribute to the close relationship between peatlands and the TOC concentrations in the northern lakes. In southern Finland the more favorable climate for degradation and the multiple sources of TOC in the mixed land use highlight the importance of retention.

Carbon processing was intensive in the small lakes. Both CO_2 emission and the Holocene C pool in sediments per square meter of the lake area were highest in the smallest lakes. However, because the total area of the small lakes on the areal level is limited, the large lakes are important units in C processing in the landscape. Both CO_2 and CH_4 concen-

trations and emissions were high in eutrophic lakes. High availability of nutrients and the fresh organic matter enhance degradation in these lakes. Eutrophic lakes are often small and shallow, enabling high contact between the water column and the sediment. At the landscape level, the lakes in agricultural areas are often eutrophic due to fertile soils and fertilization of the catchments, and therefore they also showed the highest CO_2 and CH_4 concentrations. Export from the catchments and in-lake degradation were suggested to be equally important sources of CO_2 and CH_4 in fall when the lake water column was intensively mixed and the transport of substances from the catchment was high due to the rainy season. In the stagnant periods, especially in the winter, in-lake degradation as a gas source was highlighted due to minimal mixing and limited transport of C from the catchment.

The strong relationship between the annual CO_2 level of lakes and the annual precipitation suggests that climate change can have a major impact on C cycling in the catchments. Increase in precipitation enhances DOC export from the catchments and leads to increasing greenhouse gas emissions from lakes. The total annual CO_2 emission from Finnish lakes was estimated to be 1400 Gg C a^{-1} . The total lake sediment C pool in Finland was estimated to be 0.62 Pg , giving an annual sink in Finnish lakes of 65 Gg C a^{-1} .

Keywords: lakes, organic carbon, inorganic carbon, CO_2 , CH_4 , catchments, climate change, boreal region

1 Introduction

Boreal headwater catchments are dominated by coniferous forests and peatlands, which have high carbon (C) pools in vegetation and soil. Humid climate and low temperatures retard complete decomposition and favor the accumulation of organic matter on soil surface. Streams provide a loss pathway for C via lateral transport downstream, typically draining to lakes. The threats of climate change have led researchers to seek wider understanding of the carbon balances on earth and the role of lakes in ecosystem carbon cycling. Freshwater ecosystems have often been neglected as potentially important components in element cycles on global or even regional scales because they cover only a small fraction of the Earth's surface area. However, lake sediments are considered to be one of few permanent sinks of C in the boreal region and furthermore, freshwater ecosystems contribute significantly to regional C balances by transferring terrestrially fixed C to the atmosphere (Richey *et al.* 2002, Hanson *et al.* 2004). Algesten *et al.* (2004) estimated that a majority of the total organic carbon (TOC) entering Swedish freshwater ecosystems was mineralized in lakes. In the northern boreal region, lakes cover 7% of the total surface area (defined from MODIS data by Myneni *et al.* 2001) and may have a considerable impact on the role of this biome as a sink or source of atmospheric CO₂.

Organic and inorganic C occur in boreal lakes as particulate organic and inorganic carbon (POC, PIC), dissolved organic and inorganic carbon (DOC, DIC) and gaseous forms (free CO₂ and CH₄). Total inorganic carbon TIC is the sum of DIC and PIC. Correspondingly, total organic carbon is the sum of DOC and POC. DIC (HCO₃⁻, CO₃²⁻) is related to gaseous C (free CO₂) via carbonate equilibria (Wetzel 1983). The relative proportions of these three inorganic forms of C are dependent on pH and to a lesser extent on temperature (Stumm and Morgan 1981).

Bicarbonate (HCO₃⁻) originates mainly from weathering reactions in soil. The chemical weathering of rock material, mainly carbon-

ate and silicate minerals, produces bicarbonate ions (HCO₃⁻) and consumes CO₂ of atmospheric origin (Gaillardet *et al.* 1999). In weathering of silicates, C in HCO₃⁻ originates exclusively from the atmosphere and in weathering of carbonates both from carbonate mineral and from the atmosphere (Gaillardet *et al.* 1999). The soil CO₂ needed in weathering reactions is mainly derived from respiration of organic matter, but ultimately is of atmospheric origin, fixed during photosynthesis (Cole *et al.* 2007). The resulting bicarbonate ion (HCO₃⁻) is the dominant form of DIC in most lakes and rivers. Studies of the sources or the fate of TIC in lakes have been limited. HCO₃⁻ concentrations in natural waters are higher in catchments with geochemically reactive alkaline bedrock than in catchments with weathering-resistant bedrock (Lahermo *et al.* 1996). TIC from the catchments can be transported to lakes via surface water or groundwater flow.

The biogeochemical processes in lakes, including the production and consumption of greenhouse gases, are closely linked to surrounding terrestrial ecosystems, because lakes receive allochthonous organic matter and nutrients from their catchment area. In Finland, streams in managed headwater catchments transport on average 4600 kg km⁻² TOC annually (Kortelainen *et al.* 1997) and the undisturbed forested catchments slightly more, 6200 kg km⁻² a⁻¹ (Kortelainen *et al.* 2006). Similar results have been reported in Sweden (e.g. Laudon *et al.* 2004; Ågren *et al.* 2007). The transport of TIC via streams is also noteworthy, 420 - 1400 kg km⁻² a⁻¹ in boreal catchments (Rantakari *et al.* 2010). Due to within-lake decomposition of allochthonous C, lakes are generally supersaturated with CO₂ and CH₄ (Kling *et al.* 1991; Kling *et al.* 1992; Cole *et al.* 1994; del Giorgio *et al.* 1999; Hope *et al.* 1996; Huttunen *et al.* 2002b; Kortelainen *et al.* 2000; Striegl *et al.* 2001). There is also some evidence that CO₂ can be transported to lakes via streams and rivers (e.g. Dawson *et al.* 2001; Hope *et al.* 2001; Cole and Caraco 2001; Jones *et al.* 2001; Billett *et al.* 2004; Teodoru *et al.* 2009) and both CO₂ and CH₄ also via groundwater flow (Striegl and Michmerhuizen 1998; Riera *et al.* 1999; Stets

et al. 2009). The crucial difference between the formation of CO₂ and CH₄ in lakes is that CO₂ is an end product of aerobic respiration, whereas formation of CH₄ always requires anaerobic conditions. CO₂ is produced under aerobic conditions both in lake sediments and in the water column, whereas the production of CH₄ in lake sediments is a microbial process that requires anaerobic conditions. In the sediment surface and in the water column CH₄ can be consumed by methanotrophs, a process contributing to the oxygen deficiency of the water column (Rudd and Hamilton 1978; Liikainen *et al.* 2002; Kankaala *et al.* 2006).

When the surface waters of lakes are supersaturated with dissolved greenhouse gases with respect to the atmospheric equilibrium, the excess gases are conducted to the atmosphere by molecular diffusion, enhanced by the physical movement of water (MacIntyre *et al.* 1995). High episodic greenhouse gas emissions can take place from northern lakes in spring after ice melt when the gases accumulated in the water column during ice cover period are rapidly released to the atmosphere (Michmerhuizen *et al.* 1996; Huttunen *et al.* 2001a; Huttunen *et al.* 2002a; Striegl *et al.* 2001; Huotari *et al.* 2009). Lakes as sources of CO₂ and CH₄ to the atmosphere have attracted increasing interest in the last decade (e.g. Kling *et al.* 1991; Cole *et al.* 1994; Hope *et al.* 1996; del Giorgio *et al.* 1997; Kratz *et al.* 1997; Cole and Caraco 1998; Striegl and Michmerhuizen 1998; Riera *et al.* 1999; Sobek *et al.* 2003; Sobek *et al.* 2005). Lakes have also been shown to be strongly supersaturated with CO₂ and CH₄ relative to the atmosphere in Finland (e.g. Kortelainen *et al.* 2000; Striegl *et al.* 2001, Huttunen *et al.* 2001a, Huttunen *et al.* 2002b). Although concentration of CH₄ in the atmosphere is low compared to that of CO₂, the global warming potential of CH₄ is up to 25-fold higher than that of CO₂.

Finland is a sparsely populated country where, settlements are mainly concentrated in the south. Southern coastal areas are characterized by lowlands with clay soils and the western coastal areas also by high peatland proportion. Agriculture is intensive in the coastal areas where the lake density is low. The southern

inland region is characterized by large chain-like watercourses and the topography is more variable than in coastal areas. In the Lake District in central and eastern Finland agriculture is also common, although it covers only about 5% of the total land area. The northern parts of Finland are typically sparsely inhabited and are characterized by high proportion of peatlands.

Lakes cover 10% of the total area of Finland. Large lakes dominate the total surface area, although small lakes are numerous. The number of lakes over 10 km² is 326, whereas there are 187 582 lakes in the size range 0.0005 km² – 10 km². However, the proportion of large lakes (>100 km²) of the total lake area is ~40% and of lakes over 10 km² 64% of the total lake area (Raatikainen and Kuusisto 1990). Finnish lakes are shallow; the mean depth of the lakes 10-100 km² has been estimated to be only 6.1 m and the mean depth further decreases towards the smaller lakes. In the smallest lakes (<0.01 km²) the mean depth is only 2.0 m (Kuusisto 1992; Kuusisto and Hakala 2007). Therefore, large lakes also dominate the total volume of Finnish lakes, 68% of the total water volume is in lakes over 100 km² (Kuusisto 1992).

Finnish lakes are mainly surrounded by forested catchments with a variable peatland proportion and therefore the lakes typically have high TOC and color values due to high loads of terrestrially fixed C transported to freshwater ecosystems (Kortelainen 1993). Peatlands cover one third of the total land area in Finland and over half of that area has been drained for forestry purposes. Dissolved organic matter (DOM) input into lakes can be highly dynamic; a large fraction of the annual flux may enter during a relatively brief time period. Much of this dynamics is controlled by hydrologic events such as snowmelt or storms (Sinsabaugh and Findlay 2003). Half of the annual runoff and leaching from Finnish forested catchments has been estimated to occur in spring although the spring period represents only 10-15 % of the whole year (Kortelainen *et al.* 1997).

There are clear patterns of DOM concentration and flux related to regional climate, either directly through hydrologic effects or indirectly through vegetation, when for example humid

climate favors formation of the dense vegetation and wetlands which store carbon in vegetation and soil (Sinsabaugh and Findlay 2003). On a global scale the variability in lake water DOC was best predicted by altitude, mean annual runoff and soil carbon density (Sobek *et al.* 2007). Although at a regional scale DOC export from terrestrial soils is enhanced by increasing runoff (e.g. Mulholland 2003) in a global study runoff was strongly negatively related to lake water DOC concentrations (Sobek *et al.* 2007). Globally, precipitation and runoff are higher in high altitudes leading to low soil carbon density and lake water residence times and in the long run, depleted soil organic carbon pool (Sobek *et al.* 2007). In a regional scale increasing runoff will lead to the greater DOC export at least until the soil DOC pool is depleted. The strong relationship between DOM export and runoff suggests that climate change can have a great impact on DOM export. Increase in precipitation might increase DOM fluxes, whereas increasing evaporative demand under a warmer climate might offset the effect of increasing precipitation (Mulholland 2003).

Land use, such as agriculture and forestry, can cause eutrophication of lakes by increasing leaching of phosphorus and nitrogen into lakes (Cooke and Prepas 1998; Kortelainen *et al.* 1997). Eutrophied lakes can have potentially high CO₂ and CH₄ emissions, attributable to the large supply of easily degradable organic matter from primary production in their sediments (Casper *et al.* 2000; Huttunen *et al.* 2001b).

1.1 Objectives of this study

Studies on aquatic carbon fluxes in the catchment (carbon sources, outgassing and sequestration) have mainly been carried out in forested, uninhabited areas and with small datasets, making comparison of the results difficult in the wider context and providing limited overview to generalize the findings to larger areas. The main aim of this study was to provide a comprehensive picture of carbon sources and sinks in lakes using a large randomly selected dataset.

The key aims of this study were:

1. To identify catchment characteristics affecting C (TOC, TIC, CO₂ and CH₄) concentrations in lakes.
2. To measure burial of carbon into the lake sediments in order to obtain an estimate for the total stock of carbon in Finnish lakes and identify the lake types with the most efficient carbon sinks.
3. To identify lake types with the highest CO₂ and CH₄ emissions.
4. To study C fluxes in lakes of different sizes to identify size-dependent differences in processes.
5. To compare the role of catchment in regulating lake water C concentrations in different regions in Finland.
6. To identify processes affecting CO₂ and CH₄ concentrations in lakes in different seasons.
7. To study effects of climate change on CO₂ emission from lakes.
8. To upscale the results of atmospheric CO₂ fluxes from lakes and burial of C into lake sediments over the whole boreal region.

2 Materials and methods

2.1 The datasets

The different data are described in Table 1.

The effects of different geographical regions and land use/land cover types on C concentrations in lakes were studied using the spatially extensive and randomly selected Nordic Lake Survey (NLS) database that covers the latitudinal gradient from 60°N to 69°N (I, V). The NLS database includes 874 Finnish lakes selected at random from the national lake register using stratified random sampling with unequal sampling fractions, with the requirements that a minimum of 1% of the population of lakes within any county/ region was included and that the proportions of lakes in size classes 0.04–0.1, 0.1–1, 1–10 and 10–100 km² were 1:1:4:8, respectively. All of the lakes >100 km² were included. The chemical and physical characteristics of the lakes, lake morphometry and catchment characteristics were determined.

Table 1. Description of the datasets.

Dataset	n	Sampling season for water	Sample depths	Publication
Nordic lake survey (NLS)	874	F	1m	I,V
All > 100km ² lakes in Finland	37	V,W,Su,F	1m,X/2,X-1m	III
Sample from NLS	122	(sediment samples)		II
Sample from NLS, gas lakes (GL)	177	V,W,Sp,Su,F	1m,X/2,X-1m,X-20cm	IV,VI

F, fall; W, winter; Su, Summer; Sp Spring; X, maximum depth

The data was divided into subsets according to different land use in the catchments: (1) A subset with high peatland proportion >35% and low agricultural land proportion <8% (PEAT). (2) A subset with high agricultural land proportion >10% and low peatland proportion <12% (FIELD). (3) A subset with high proportion of forests on mineral soil >75% and low proportions of agricultural land <7% and peatlands <7% (MINERAL). Cutoffs for the subsets were made using three criteria: (1) A sufficient number of lakes in each subset to enable proper statistical analysis. (2) Approximately equal numbers of lakes in each subset, because very different numbers of cases could lead to interpretation difficulties in statistical analysis. Therefore, in each subset cutoffs were chosen to give about 120 lakes. (3) Different medians/averages of land use variables between subsets (V).

Moreover, southern (south of latitude 64°) and northern (north of latitude 64°) Finland were considered separately. Southern Finland represents an area with mixed land use, including varying patterns of managed forests, agricultural areas and settlements, whereas northern Finland represents an area with little agriculture or settlements and large areas of forests and peatlands and with higher percentages of old forests and undisturbed peatlands. In northernmost Finland bedrock outcrops and tundra-like vegetation are also common.

In order to examine factors controlling the variation in CO₂ and CH₄ concentrations and fluxes to the atmosphere from boreal lakes, 177 lakes (GL) were randomly selected from the NLS data base. The seasonal depth profiles from the deepest point of the lake were collected four times a year (before and after ice melt, at the end of the summer stratification and

after fall overturn) from four depths (1 m, the middle of the water column, 1 m above the sediment and 20 cm above the sediment) in order to clarify the roles of lake water and sediments as sources of CO₂ and CH₄ (IV,VI).

To provide a more comprehensive picture of TIC and CO₂ in large lakes, all the lakes >100 km² in Finland were sampled for TIC in 1998 and 1999. The seasonal depth profiles were collected from three depths (1 m, the middle of the water column, 1 m above the sediment). All of the lakes >100 km² belong to a water quality monitoring programme carried out since 1965 by Regional Environment Centres of Finland and are thus sampled regularly. However, TIC measurements are not part of the monitoring programme, whereas alkalinity measurements are. In order to compare the CO₂ concentrations in the lakes in different years, the regression models were developed based on TIC measurements from the years 1998 and 1999 using alkalinity as dependent variable. TIC and CO₂ concentrations were calculated for the years 1996, 1997, 2000 and 2001. To study the effect of climatic factors on CO₂ fluxes we utilized air temperature and precipitation data from 44 weather stations spread evenly throughout the country (III). The lake area-specific CO₂ emission estimates from GL and all the lakes >100 km² were used for scaling up an estimate for the boreal region as a whole (IV).

In order to study average Holocene C pools in sediments, 122 lakes were selected from the NLS data base. The selection of lakes was weighted towards large lakes, which represent a majority of the total lake area in Finland. Holocene sediment volumes were estimated from information collected with an acoustic sounder in lakes larger than 2 km² and by coring in smaller lakes. Acoustic sounding pro-

files were used to estimate the area covered by different lake bottom types and the amount of gyttja systematically at intervals of 150 m in large lakes, whereas the thicknesses of the gyttja layers were determined by coring and field observations in the case of the small lakes (II).

2.2 Water chemistry

In the NLS data the samples for TIC were taken into airtight glass bottles and placed in coolers while in transit to the laboratory. TIC was measured in the laboratory using infrared spectroscopy (V). For the subset of 177 lakes (GL) from the NLS data, water samples (30 ml) for the determination of TIC and CH₄ were carefully withdrawn by means of a hypodermic needle from the silicone tube of the Ruttner water sampler into 50 ml polypropylene syringes equipped with three-way stopcocks. CO₂ samples were acidified in the field with sulfuric acid (1 ml, 20% v/v) and the samples were placed in coolers while in transit to the laboratories of the universities of Kuopio and Joensuu in order to avoid light exposure and to minimize temperature changes. Gas concentrations were analyzed the day after sampling with a headspace equilibration technique (McAuliffe 1971). Water samples were equilibrated by adding 30 ml N₂ gas to each syringe and shaking them vigorously for 3 minutes. CO₂ concentrations of the N₂ headspaces were analyzed with gas chromatographs equipped with thermal conductometric detectors (IV). For both NLS and GL data, CO₂ concentrations were calculated from measurements of TIC and pH with correction for actual water temperature (Stumm and Morgan 1981; Butler 1982; Kling *et al.* 1992). Partial pressure of CO₂ ($p\text{CO}_2$) was calculated from CO₂ concentrations using Henry's law constants, corrected for temperature and atmospheric pressure (Plummer and Busenberg 1982). The equilibrium CO₂ concentration in the lake water was calculated using Henry's law, assuming the atmospheric mixing ratio of 361 ppmv for the year 1996 and taking into account the annual increase of 1.5 ppmv a⁻¹ (IPCC 2001) and the elevation of the lake. CO₂ supersaturation ratio was calculated by dividing

the actual lake CO₂ concentration by the CO₂ concentration in equilibrium with the atmospheric CO₂ content (IV,V).

Analyses of dissolved CH₄ concentrations were conducted the day after sampling in the laboratories of the universities of Kuopio and Joensuu. According to the headspace equilibration technique (McAuliffe 1971), 30 ml ultra pure N₂ gas was added to each syringe and shaken vigorously for 3 minutes. The headspace gas CH₄ concentration was quantified with a gas chromatograph (Hewlett Packard Series II and Shimadzu GC-14-A) equipped with an FI-detector. The CH₄ concentration dissolved in water was calculated from the headspace gas concentration according to Henry's law using the values after Lide and Fredrikse (1995) (VI).

All the water chemistry analyses were carried out in the accredited laboratories of the Finnish environment administration following the standard methods. TOC was analyzed from unfiltered samples by oxidation to CO₂ followed by IR-measurement. Total nitrogen (TN) was analyzed colorimetrically after oxidation to NO₃-N; the sum of NO₃-N and NO₂-N colorimetrically by autoanalyzer after reduction to NO₂-N; NH₄-N colorimetrically with hypochlorite and phenol; and organic nitrogen (TON) was calculated as the difference between total and inorganic nitrogen. Total phosphorus (TP) was measured by a colorimetric method after oxidation, phosphate phosphorus (PO₄-P) by spectrophotometric determination, calcium (Ca) and magnesium (Mg) were determined by flame atomic adsorption/ICP-MS, iron (Fe) was determined by a colorimetric method after oxidation by K₂S₂O₈, silicate (SiO₂) by a colorimetric method or by FIA and sulfate (SO₄) by ion chromatography (Henriksen *et al.* 1996; Mannio *et al.* 2000).

2.3 Calculation of the gas fluxes

The flux of CO₂ from the surface water to the atmosphere was calculated according to the equation:

$$\text{Flux}_{\text{CO}_2} = k \times (C_{\text{sur}} - C_{\text{eq}})$$

where k is piston velocity (cm h^{-1}), C_{sur} is concentration of the gas in surface water and C_{eq} is the concentration in equilibrium with the atmosphere (Cole and Caraco 1998). Piston velocity (k) can be obtained from the equation:

$$k_{\text{gas1}}/k_{\text{gas2}} = (\text{Sc}_{\text{gas1}}/\text{Sc}_{\text{gas2}})^n$$

where Sc is the Schmidt number for the relevant gas. In order to obtain values for k_{600} , which is the k measured with SF_6 and normalized to a Schmidt number (Sc) of 600, we used the empirical relationship presented by Cole and Caraco (1998):

$$k_{600} = 2.07 + 0.215 \times U_{10}^{1.7}$$

where U_{10} is the wind speed at 10 m height. Values of $k\text{CO}_2$ were calculated from k_{600} values using the equation presented by Riera *et al.* (1999):

$$k\text{CO}_2 = k_{600} \times (\text{ScCO}_2/600)^n$$

Schmidt number for CO_2 was calculated from empirical third-order polynomial fits to temperature determined by Jähne *et al.* (1987). We assumed a value of -0.67 for n (Jähne *et al.* 1987; Cole and Caraco 1998). The wind speed was assumed to be 3 m s^{-1} , which is the average long-term open water period wind speed for the inland measurement stations in Finland. These measurements are carried out at a height of 10 m and may therefore slightly overestimate the wind speed for the smallest wind-sheltered lakes.

The diffusive flux for CH_4 was calculated in analogous way than for CO_2 , except $k\text{CH}_4$ was calculated using exponent -0.5 for n according to Hamilton *et al.* (1994) and MacIntyre *et al.* (1995). The atmospheric concentration of CH_4 was assumed to be $1.72 \mu\text{l l}^{-1}$ for the year 1994 and taking into account the annual increase of 0.01% (Houghton *et al.* 2001).

To calculate the CO_2 and CH_4 emissions over the whole ice free period, the before ice out concentration was extrapolated over 0.5 months after the ice out. Similarly, the spring concentration was assumed to last for 1.5 months, the

summer time concentration for 3 months and the fall concentration over 2 months.

The CH_4 storage was calculated for the whole lakes by multiplying concentrations values by the volume of each layer assuming horizontal mixing of CH_4 . Storage change fluxes were calculated from the differences in CH_4 storage between winter and spring, and between late summer and fall assuming that the excess CH_4 was released to the atmosphere. If storage was larger during spring and fall than during late winter and late summer the larger storage was used to calculate storage flux, since the timing of the sampling might have been too early. Annual flux of CH_4 is the sum of the spring and fall storage change fluxes and the diffusive efflux over the open water period. Ebullition was not measured and it is not part of the estimate.

2.4 Statistical analyses

The influence of land use/cover on lake water C concentrations in the NLS database was studied by means of correlation, regression and principal component analysis (PCA) using the SAS 8.2 for Windows software. The regression analyses were performed by a stepwise multiple linear method (PROC REG/selection stepwise) and all cases with an absolute value of studentized residual exceeding 3 were excluded. The purpose of PCA is to transform a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible.

2.5 Extrapolation of the results over the Boreal region

The results of annual CO_2 emissions from the lakes (III, IV) and the long term C accumulation into lake sediments (II) were extrapolated over the boreal region. The boreal region was defined by using ESRI (www.esri.com) arc-data online service's vegetation map including vegetation zones: boreal sub-Arctic vegetation,

taiga and mountain vegetation of taiga. This area was then used as a mask to separate the boreal region from MODIS data (Myneni *et al.* 2001). Further, the total boreal lake area was then distributed into the five size classes using the lake size distribution of global lakes (for lakes > 1 km²; Meybeck 1995) and Finnish lakes (for lakes < 1 km²).

3 Results and discussion

3.1 Regulation of lake water C concentrations in heterogeneous catchment land use types

3.1.1 Sources of TIC

In the NLS dataset the median TIC was 1.6 mg l⁻¹ (range 0.1 – 12 mg l⁻¹) (Table 2) and the average pH was 6.7 (range 4.2 – 7.9), indicating that the majority of TIC in the lakes consisted of bicarbonate and free CO₂. Lakes in agricultural areas had higher average TIC concentrations than lakes in peatland-rich areas (Table 2). The subsets PEAT and FIELD had the same average total carbon (TC) concentration (12 mg l⁻¹) and in both subsets the greatest part of C was organic, but the proportion of TIC of TC was significantly higher in the subset FIELD (31%) than in the subset PEAT (10%) (Figure 1) (V). Agriculture is concentrated on fine grained soils, where weathering reactions are more efficient due to greater specific surface area. Cultivation of these soils enhances weathering by increasing the interaction with water. Fertilization and liming of agricultural land further increase the load of base cations and TIC from the catchments. Reactions between clay minerals and water are faster than the reactions between water and coarse-grained minerals and consequently more inorganic matter, including base cations, is leached from clay soils than from glacial till or peatlands (Lahermo *et al.* 1996). Corresponding results were found by Telmer and Veizer (1999) in the Ottawa river, where the highest DIC was recorded in a sub-basin rich in carbonates and heavily used for agriculture. In this river basin, soil respiration and carbonate weathering were proposed to

be the main sources of DIC, whereas in-river respiration and photosynthesis were not significant in the river C budgets. Similar results were obtained by Raymond and Cole (2003) in the Mississippi river basin, where the alkalinity export increased as a function of the percentage of cropland in the catchment, whereas forests in the catchment decreased the alkalinity export (V).

In the PCA and correlation analysis of NLS data (Figure 2), agricultural land and built-up land were suggested to be important catchment sources of TIC in the whole dataset and in the subset FIELD. In the subset PEAT, where on average 48% of each catchment consists of forests on mineral soils, these forests were more important sources of TIC than peatlands (V).

3.1.2 Sources of TOC

Peatlands have been recognized as an important allochthonous source of organic C to lakes (e.g. Rapp *et al.* 1985; Rasmussen *et al.* 1989; Eckhardt and Moore 1990; Kortelainen 1993; D'Arcy and Carignan 1997; Xenopoulos *et al.* 2003). Peatlands in the catchment also increased lake water TOC concentrations in this study (I, V). In the NLS data the proportion of TOC of TC was highest in the subset PEAT (90%) and lowest in the subset FIELD (69%) (Figure 1). Peatlands were proposed to be important catchment sources of TOC in the whole dataset and in the subset PEAT (I, V). However, agricultural land in the catchment also had a positive relationship with TOC concentrations, especially in forest- and peatland-rich areas (I, V). High export of organic C from agricultural areas has been reported by Correll *et al.* (2001), McTiernan *et al.* (2001) and Mattsson *et al.* (2007).

TOC concentrations in lakes were relatively high in both agricultural and peatland-rich areas (subsets FIELD and PEAT). The other water quality results, however, suggest differences in the quality of organic matter between the subsets. In the subset PEAT, water color was considerably higher than in the subset FIELD, partly due to higher Fe concentrations in PEAT. In humic lakes the dark water color may limit

Table 2. Median characteristics of lakes and catchments in the Nordic Lake Survey (NLS) data and in the subsets of southern Finland, northern Finland, FIELD (agricultural land > 10%, peatland < 12%), PEAT (peatland > 35%, agricultural land < 8%) and MINERAL (forests on mineral soil > 75%, agricultural land and peatlands 7%).

	NLS	South	North	FIELD	PEAT	MINERAL
N	874	560	314	120	117	119
Lake area (km ²)	0.22 (0.04 – 1500)	0.28 (0.04 – 1500)	0.15 (0.04 – 1100)	0.41 (0.04 – 180)	0.12 (0.04 – 43)	0.090 (0.04 – 32)
Catchment area (km ²)	4.6 (0.08 – 52000)	5.2 (0.08 – 52000)	4.0 (0.18 – 26000)	7.3 (0.16 – 17000)	3.4 (0.23 – 1300)	1.5 (0.18 – 370)
Water (%)	8.8 (0.2 – 43)	9.2 (0.3 – 43)	7.9 (0.2 – 39)	9.6 (0.3 – 35)	5.2 (1 – 42)	9.7 (1 – 24)
Agricultural area (%)	2.3 (0 – 53)	4.8 (0 – 53)	0 (0 – 27)	19 (11 – 53)	0.2 (0 – 7)	0 (0 – 6.5)
Forest on mineral soil (%)	65 (10 – 98)	68 (10 – 95)	65 (16 – 98)	64 (32 – 83)	48 (10 – 61)	85 (76 – 98)
Peatland (%)	14 (0 – 84)	8.9 (0 – 84)	24 (0 – 74)	3.0 (0 – 11)	44 (36 – 84)	2.9 (0 – 6)
Built-up area (%)	0.09 (0 – 39)	0.20 (0 – 39)	0 (0 – 13)	0.60 (0 – 39)	0.01 (0 – 0.3)	0.03 (0 – 13)
TOC (mg l ⁻¹)	7.8 (0.4 – 34)	9.1 (0.6 – 34)	6.3 (0.4 – 33)	8.1 (0.6 – 18)	10 (1.3 – 34)	6.2 (0.4 – 22)
TIC (mg l ⁻¹)	1.6 (0.1 – 12)	1.6 (0.1 – 8.2)	1.6 (0.2 – 12)	3.6 (0.1 – 8.2)	1.1 (0.2 – 7.3)	1.5 (0.25 – 12)
pCO ₂ (µatm)	900 (75 – 5800)	990 (75 – 5800)	690 (160 – 2900)	1200 (140 – 4000)	810 (160 – 1300)	930 (260 – 2000)
Water color (Pt mg l ⁻¹)	60 (3.8 – 500)	60 (3.8 – 500)	50 (3.8 – 360)	40 (3.8 – 200)	100 (5 – 360)	35 (3.8 – 500)
pH	6.7 (3.8 – 7.9)	6.6 (3.8 – 7.7)	6.9 (4.4 – 7.9)	6.9 (3.8–7.7)	6.4 (4.2 – 7.5)	6.6 (4.9 – 7.9)
Alkalinity (µeq l ⁻¹)	120 (-170 – 980)	130 (-170 – 980)	130 (-50 – 970)	270 (-170 – 980)	80 (-80 – 590)	100 (-20 – 970)
TN (µg l ⁻¹)	430 (60 – 2500)	490 (82 – 2500)	300 (60 – 2200)	600 (82 – 1800)	460 (150 – 1800)	340 (60 – 790)
TON (µg l ⁻¹)	380 (46 – 2100)	430 (70 – 1800)	280 (46 – 2100)	500 (69 – 1300)	430 (120 – 1800)	300 (46 – 770)
TOC:TON	25 (5.5 – 77)	25 (5.5 – 77)	25 (6.8 – 68)	19 (5.7 – 34)	30 (9.5 – 77)	24 (5.5 – 56)
TP (µg l ⁻¹)	13 (1 – 200)	16 (3 – 200)	11 (1 – 100)	23 (4 – 100)	18 (4 – 88)	9.0 (1 – 100)

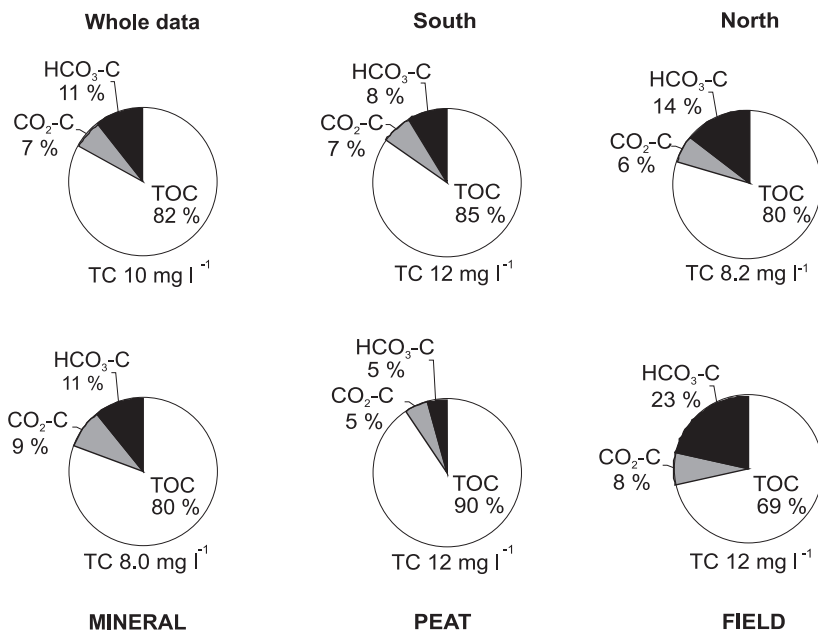


Figure 1. The relative contribution (%) of each C-species to the total C concentration in the whole dataset and in the subsets of southern Finland, northern Finland, PEAT, FIELD and MINERAL. Subset PEAT (peatland > 35% and agricultural land < 8%), subset FIELD (agricultural land > 10% and peatland < 12%), subset MINERAL (forests on mineral soil > 75%, agricultural land < 7% and peatlands < 7%) (cf. V).

primary production. Higher nutrient concentrations together with better light conditions suggest higher primary production in the subset FIELD. The average TOC:TON-ratio was significantly lower (19 vs. 30) in the subset FIELD compared to the subset PEAT (V). On the basis of the whole-lake C isotope additions, Bade *et al.* (2007) reported that algal contribution to the DOC pool was 40% in a nutrient-enriched lake and 5% in a more humic lake. DOC of algal origin has little color, compared to the colored humic substances of terrestrial DOC (Meili 1992), and furthermore, terrestrially fixed organic matter typically has a higher TOC:TON ratio compared to phytoplankton. The Redfield TOC:TON ratio of 6.6:1 indicates algal-derived material (Redfield *et al.* 1963), suggesting that the proportion of the algal derived material of TOC is higher in subset FIELD than in the subset PEAT. In the lakes surrounded by mixed land use, organic matter exported from peatlands with high TOC:TON ratio is combined with the organic material supplied from agricultural areas and with the organic material gener-

ated in primary production in lakes with higher nitrogen proportions, leading to lower average TOC/TON ratios (Figure 3).

In the subset MINERAL, the catchments are mainly forests on mineral soil, whereas in the subsets PEAT and FIELD the land use is more variable. There are also notable differences in the nutrient levels between the subsets. Because there are differences in the TOC/TON ratios of the organic matter originating from different sources, it can be assumed that the less sources the tighter is the connection between TOC and TON in lake water. A uniform origin of the organic matter in the subset MINERAL was suggested by a stronger relationship between TOC and TON in the subset MINERAL ($r=0.857$, $p<0.001$) compared to the subsets PEAT ($r=0.583$, $p<0.001$) and FIELD ($r=0.711$, $p<0.001$) (Figure 2). In Finnish lakes most of the TN is organic (88% in NLS data).

Finnish lakes are shallow and extended littoral zones are typical. Littoral zones are important producers of organic C in the lake ecosystem (Wetzel 1983), and their influence on the C

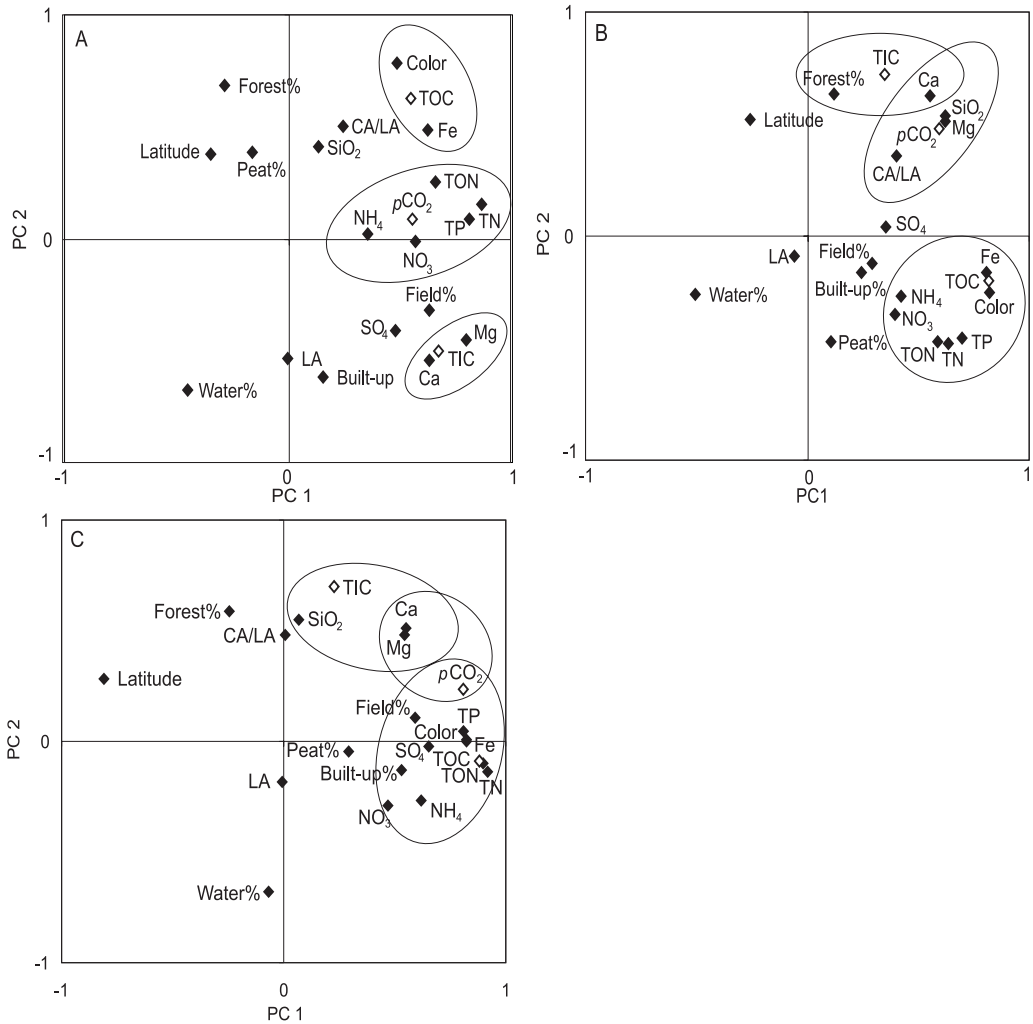


Figure 2. PCA analysis of the water quality and catchment variables in the subsets a) FIELD, b) PEAT and c) MINERAL. (See Figure 1 for explanation of abbreviations) (V).

budgets of Finnish lakes should not be underestimated. Lauster *et al.* (2006) suggested that littoral zones increase whole lake net ecosystem production especially in eutrophic systems. In the NLS data, the ratio of shoreline length to lake area was the most important predictor for lake water TOC ($r = 0.40$, $p < 0.001$) in agricultural areas (subset FIELD), where the most nutrient-rich lakes are located (V). The ratio of shoreline length to the lake area describes the shape of the lake; the greater the ratio, the more sheltered bays there are enabling the forma-

tion of dense littoral vegetation. Andersson and Kumblad (2006) found that the pelagial is fed with C fixed by primary producers in benthic and littoral zones, and that there was a strong interaction between the habitats. Biodegradable organic carbon was closely associated with the percentage of lake area covered by littoral zone in a survey of 12 lakes in Minnesota, suggesting that the aquatic macrophytes and lake surface sediments are a significant source of biodegradable organic carbon in lakes (Stets and Cotner, 2008).

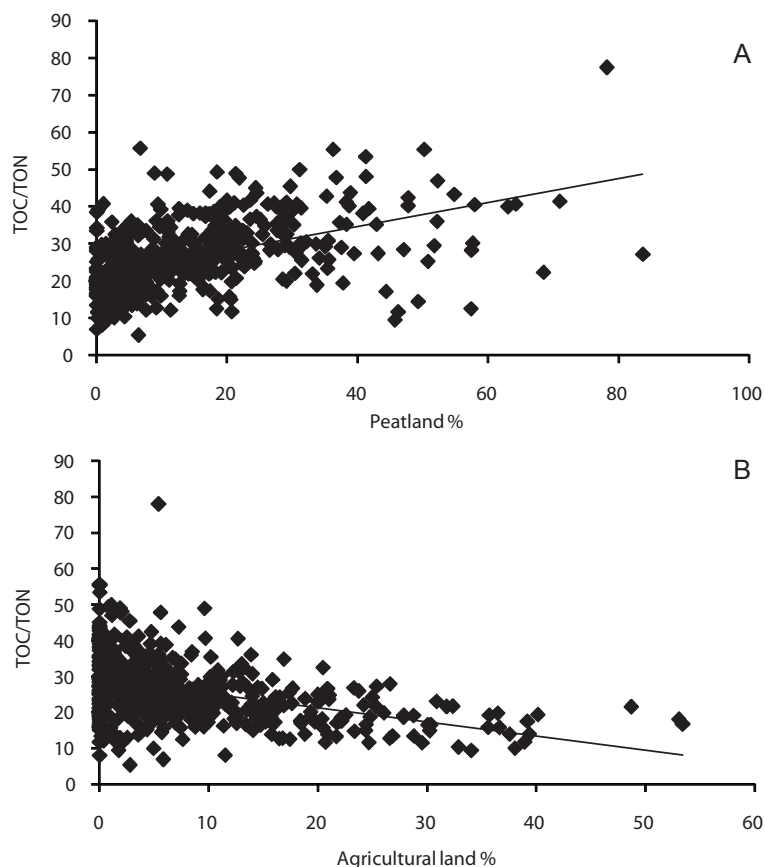


Figure 3. The relationship between a) the proportion of peatlands in the catchment (%) and the TOC/TON ratio of the lake water ($y = 0.324x + 21.7$; $R^2 = 0.25$) and b) the proportion of agricultural land in the catchment (%) and the TOC/TON ratio of the lake water ($y = -0.395x + 29.2$; $R^2 = 0.17$) in southern Finland.

3.1.3 Sources and regulation of CO_2 in lakes with variable catchments

In the different landscapes the highest median lake water pCO_2 was found in the subset FIELD (1,200 μatm), in which partial pressure was significantly higher than in the subset PEAT (810 μatm). The proportion of CO_2 of TIC varied between subsets, being highest in the subset PEAT (average pH 6.4), in which 53% of the TIC was in the form of CO_2 , and lowest in the subset FIELD (average pH 6.9), in which the proportion of CO_2 was only 25% (Figure 1). Two sources of CO_2 in lakes could be identified by statistical analysis of the data: weathering processes in the catchment, supported by the correlation between CO_2 and Ca, Mg, SiO_2 and

TIC; and the decomposition of organic matter, supported by the correlation between CO_2 and TOC, TN and TON (Figure 2). Higher CO_2 as well as TIC in lakes in agricultural areas compared to other subsets suggest both weathering and decomposition as sources of CO_2 . The high availability of organic matter for decomposition in the subset FIELD compared to the subset PEAT contributes to high pCO_2 . Raymond and Bauer (2001) demonstrated that heterotrophic bacteria in river water preferred young labile DOC over old refractory DOC, and furthermore that autochthonous C was preferentially utilized by bacteria compared to terrestrial DOC (Kritzberg *et al.* 2004). Bacterial growth on allochthonous organic C in lake water was also shown to be more efficient after addition

of inorganic nutrient (N and P) (Reche *et al.* 1998). Water soluble and bioavailable organic C has been shown to be higher in agricultural soils than in forest soils (Boyer and Groffman 1996). The strong negative correlation between percentage of water in the catchment and TOC concentrations indicates higher retention (either degradation or accumulation) of organic matter in lakes in the subset FIELD compared to the other subsets. (V).

Dark water color in the subset PEAT may also restrict the photochemical decomposition of TOC in the subsurface layers, and consequently, only a part of TOC may be available for further decomposition (Granéli *et al.* 1996). Part of the difference in inorganic C concentrations between the subsets PEAT and FIELD is due to the lower equilibrium level of lake water CO₂ in the subset PEAT, because lakes situated in catchments with large areas of peatland are typically acidic due to organic acidity (e.g. Kortelainen and Mannio 1988, Kortelainen *et al.* 1989), whereas lakes in agricultural areas are more alkaline due to chemical weathering and liming (V).

Lake water CO₂ correlated more strongly with the total nutrients (N,P) than with TOC in most cases (IV,V), further suggesting the importance of the quality of substrate and the surrounding conditions (nutrient availability, water pH, water color) for decomposition processes. Only in the subset MINERAL was TOC the best predictor of CO₂, which is most probably attributable to the very homogeneous land use in the catchments in this subset, and consequently, homogeneous quality of allochthonous C in lakes (V). Ågren *et al.* (2008a) reported differences in the quality of exported C between forests and peatland as expressed with absorbance ratio (A_{254}/A_{365}) and with DOC-specific ultraviolet absorption (SUVA₂₅₄). The bioavailability of stream water C was significantly higher in the forested catchments than in the peatland catchments (Ågren *et al.* 2008a and 2008b).

The dominance of decomposition processes versus weathering processes as a principal regulator of CO₂ concentrations in lakes varied between the subgroups, as suggested by the PCA analysis. In the whole dataset with mixed

land use the dual sources of pCO₂ were emphasized, whereas different processes dominated pCO₂ concentrations in the subsets. In the subset PEAT, weathering in the catchments controlled CO₂ probably due to the refractory nature of organic matter and the unfavorable conditions for decomposition processes (low nutrient availability and dark water restricting photo-oxidation). In the subset FIELD, decomposition mainly controlled CO₂, supported by the close connection with TON, NO₃ and NH₄ in the PCA analysis. Both processes were indicated to be important in the subset MINERAL. The results also indicated that the more uniform the land use in the catchment, and consequently the quality of the allochthonous organic matter, the stronger is the connection between TOC and CO₂ (V).

3.1.4 CH₄ concentrations in lakes with variable catchments

The lakes characterized by nutrient-rich and calcareous water had high methane concentrations and fluxes to the atmosphere. These lakes typically had a high proportion of agriculture in their catchments. High concentrations of nutrients and CH₄ in these lakes cannot be related only to the agriculture in their catchments, because agriculture was originally initiated in the most naturally nutrient rich and calcareous soils. Eutrophic lakes in agricultural areas often have dense littoral vegetation, and shallow littoral sediments have been shown to be the major contributors of CH₄ to the atmosphere on a whole lake scale (Juutinen *et al.* 2003; Bastviken *et al.* 2008). The methane concentrations in the bottom water near the sediment during the stagnation periods were highest in lakes suffering from anoxia and having the highest TP levels (Figure 4), which is in good agreement with the results of Huttunen *et al.* (2003) and Bastviken *et al.* (2004). The catchments of these lakes had significantly larger proportion of agricultural land and settlements, and significantly smaller proportions of peatlands and water than the lakes with oxic bottom water and low TP (VI).

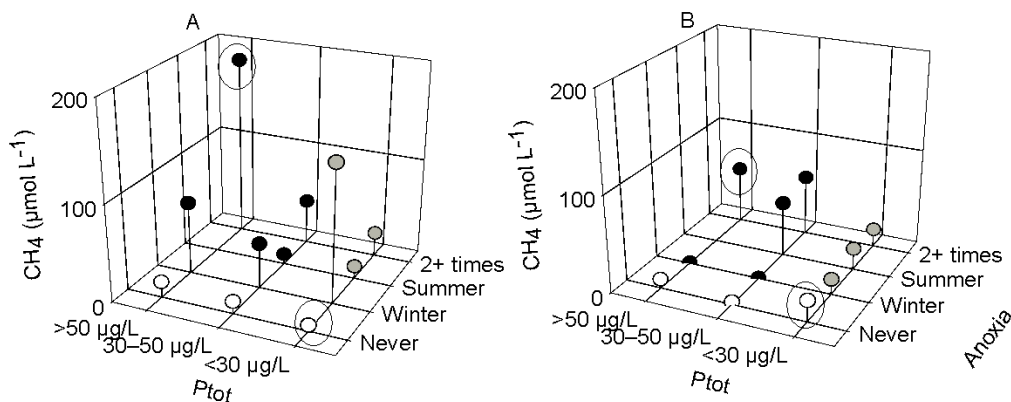


Figure 4. Mean CH_4 concentrations of the water close to the bottom in the winter (a) and the summer (b) in the lakes categorized by frequency of anoxia and total phosphorus (P_{tot}). The two extreme categories (anoxic in summer and winter, high phosphorus vs. never anoxic, low phosphorus) have been circled (VI).

3.2 Sources and concentrations of TOC, TIC and CO_2 in southern and northern Finland

Variation in land use (Figure 5) and climate in different parts of Finland lead the main catchment regulators of lake water TOC to vary in different regions (I). Studies in Finland show higher lake water TOC concentrations in the more heterogeneous catchments of southern Finland compared to northern Finland (Table 2) (I). Weyhenmeyer and Karlsson (2009) have shown that DOC concentrations in lakes increase along a latitudinal temperature gradient. The multiple sources of TOC in southern Finland have the result that the connection between the proportion of peatlands in the catchment and the TOC in the lake was stronger in northern Finland compared to the south (Figure 6) and even stronger in the northernmost part of Finland, Lapland ($R^2=0.60$) (I). Furthermore the same amount of peatlands in the catchment resulted in higher concentrations of TOC in southern than in northern Finland (Figure 6) (I; Kortelainen 1993). In northern Finland the overall transport of e.g. TOC, TN, TP and Fe from the catchments is lower (e.g. Kortelainen and Saukkonen 1998) than in the south due to longer frost and snow cover periods. The catchment-lake connection can also be expected to be tighter in Northern Finland, because seepage

lakes are more common in Lapland (17% of all lakes) than in other parts of the country (<5% of all lakes). In southern Finland chain-like watercourses are typical and as a consequence there is a weaker connection between catchment and the lake water quality.

The retention of C in upper watercourses and in the lake itself had a stronger influence on lake water TOC concentrations in southern Finland than in northern Finland (I) (Figure 7). The lakes in southern Finland have on average lower CA/LA ratios than in the north (Table 2) and therefore, the lake water retention time can be expected to be longer in southern Finland than in northern Finland. The longer retention times also enhance the retention of C in the watercourses. Furthermore, cold climate and the low nutrient concentrations in lakes may retard decomposition in the north. In the south, nutrient export to lakes can be expected to be higher due to more heterogeneous catchments enhancing decomposition. The atmospheric deposition of nutrients as well as deposition of DOC is higher in southern Finland (Vuorenmaa 2004; Lindroos et al. 2008).

Agricultural area in the catchment was an important source for lake water TN and TP in the south, whereas in northern Finland mainly peatlands supplied total nutrients to lakes (I). The quality of organic matter and availability of nutrients were important for efficient decom-

position of organic matter in lakes, because the highest $p\text{CO}_2$ concentrations both in the north and the south were observed in lakes with the highest total nutrient (TN, TP) concentrations rather than high TOC concentrations (V).

In northern Finland, lake water pH was slightly higher than in southern Finland, reflecting the more alkaline bedrock and lower acid deposition. Partly due to higher pH, $p\text{CO}_2$ in lakes was lower in the north compared to southern Finland (Table 2) and the proportion of CO_2 of TIC was lower in northern Finland (Figure 1). The higher lake water $p\text{CO}_2$ in southern Finland also reflected the more efficient degradation of organic matter in the Southern Finland due to both climate and more heterogeneous land use.

TIC concentrations were of the same magnitude in southern and northern Finland, although the highest lake water concentrations were measured in the north. In southern Finland TIC concentrations in lakes were highest in the agricultural areas, whereas in northern Finland land use of the catchment was not related to the highest values (Figure 8). However, the same or higher lake water TIC concentrations in the north compared to the south implies that catchment sources of TIC are also important in northern Finland.

In southern Finland clay and silt deposits in the coastal areas extend at best hundreds of kilometers inland, but are rare in other parts of the country. Clay deposits in coastal areas are largely used for crop cultivation and pasture, promoting the close connection between

agricultural land and TIC in southern Finland. Furthermore, base cation deposition is higher in the south. Alkalinity, TIC and base cation concentrations correlate strongly, and consequently in southern coastal areas median TIC concentrations in lakes are higher (2.0 mg l^{-1}) than in other parts of the country.

In catchments with geochemically reactive alkaline bedrock HCO_3^- concentrations in natural waters are higher than in catchments with weathering-resistant bedrock (Lahermo *et al.* 1996). In Finland the bedrock is mainly acidic, causing poorly buffered waters. In parts of southern Finland, high alkalinity of the clay deposits masks the effect of acidic bedrock underneath, whereas in northern Finland the type of bedrock determines the TIC concentrations of the surface waters because clay soils are absent. In northern Finland the mafic and ultramafic layered intrusions and areas with schist and greenstone result in well buffered, high alkalinity surface waters in parts of the region, whereas granite bedrock together with thin soils cause poorly buffered waters in some other areas (Kähkönen 1996). Therefore, in northern Finland it is difficult to predict TIC concentrations of the surface waters with land use data, because land use does not necessarily follow the type of bedrock. As a conclusion, in inhabited areas in the Boreal zone, agricultural land is an important source of TIC in lakes, whereas in the largely uninhabited areas TIC concentrations in lakes are most probably affected by the bedrock and the soil type in the catchment.

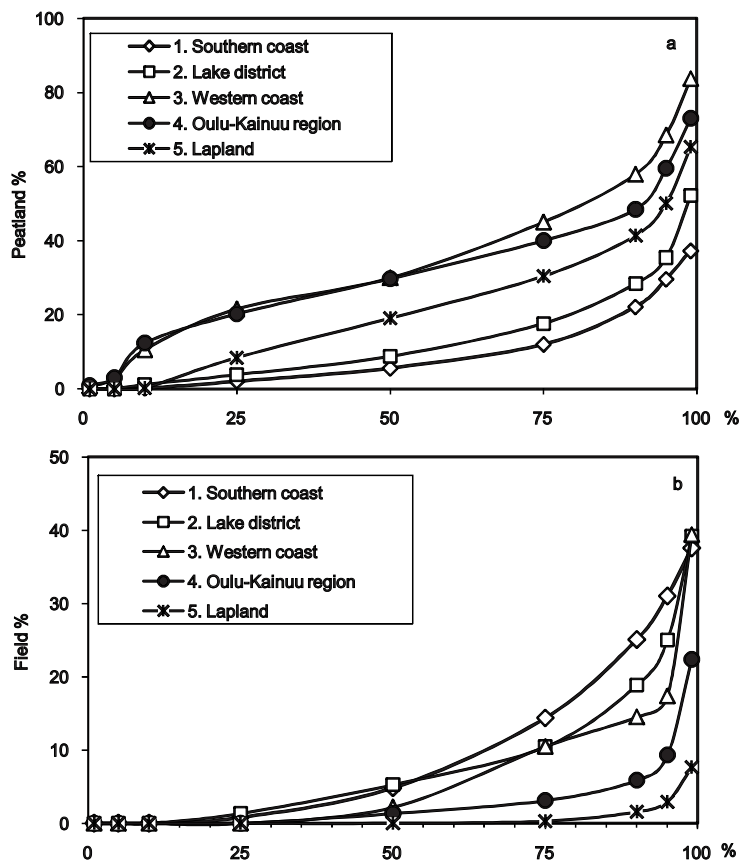


Figure 5. Percentiles of 25%, 50% (median) and 75% of a) the proportion of peatland in the catchment and b) the proportion of agricultural land in the catchment (Field) in different regions in Finland: 1) Southern coastal area, 2) Lake district in southern central Finland, 3) Western coastal area, 4) Oulu-Kainuu region in northern central Finland below the Arctic Circle and 5) Lapland north of the Arctic Circle.

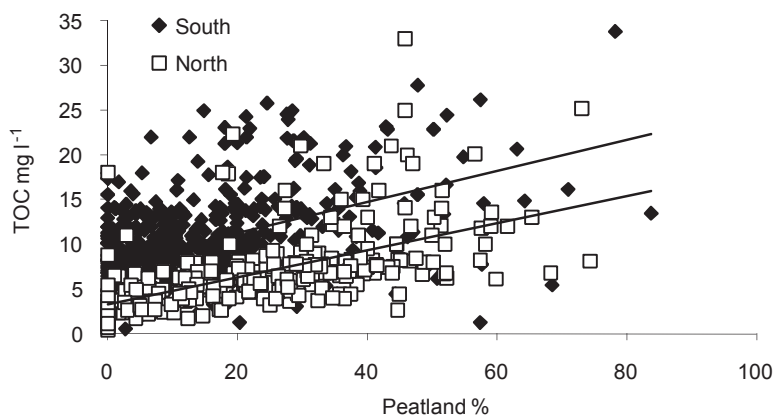


Figure 6. The relationship between the proportion of peatlands in the catchment (%) and TOC content (mg l^{-1}) of the lake water in southern Finland ($y = 0.173x + 7.83$; $R^2 = 0.23$) and in northern Finland ($y = 0.151x + 3.31$; $R^2 = 0.31$).

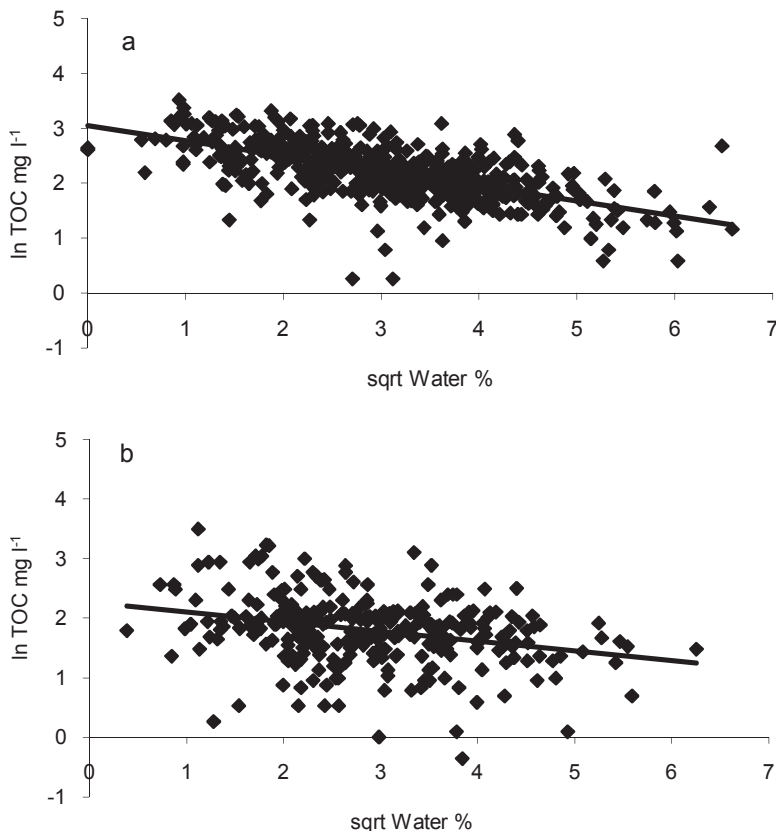


Figure 7. The relationship between the proportion of water in the catchment (%) and TOC content (mg l⁻¹) of the lake water a) in southern Finland ($y = -0.276x + 3.06$; $R^2 = 0.42$) and b) in northern Finland ($y = -0.164x + 2.27$; $R^2 = 0.09$).

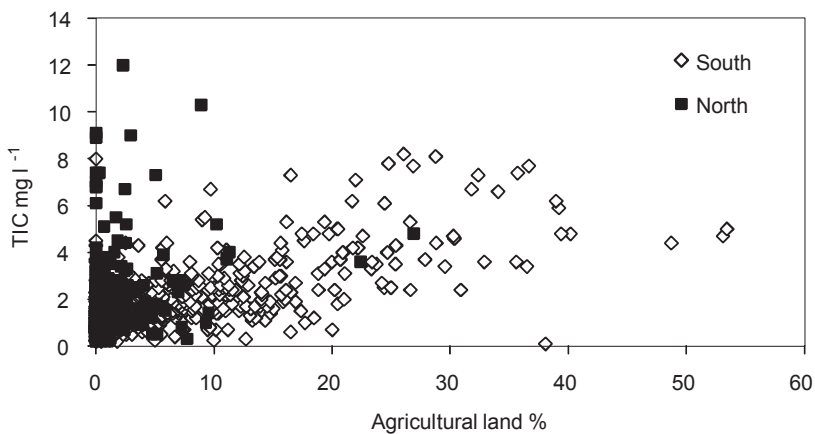


Figure 8. The relationship between the proportion of agricultural land in the catchment (%) and TIC content (mg l⁻¹) of the lake water in southern Finland and in northern Finland.

3.3 Regulation of C concentrations and fluxes in lakes of different size

The largest lakes in Finland are typically of drainage type, with many smaller lakes upstream. In the NLS data the average proportion of water in the catchment is 15% in the lakes over 10 km², but only 6.3% in the lakes under 0.1 km² (I). Control of TOC concentrations in lakes larger than 10 km² by retention was indicated by the negative correlation ($r=-0.61$) between water percentage in catchment and lake water TOC concentration (I). The catchments of the largest lakes are correspondingly large; the average size of the catchments of the lakes over 10 km² was 1500 km² (I), and furthermore, the catchments of the largest lakes (>100 km²) cover altogether 137 000 km², 45% of the total area in Finland (III). The large catchments of the large lakes embrace the average land use in Finland, whereas the small lakes are typically situated in forested upland areas, with little human activity (agriculture, settlements) (I). Despite the evidence of C retention along the lake chains before water reaches the largest lakes, the strong correlation between the annual precipitation in Finland and the average annual emission of CO₂ from the largest lakes (Figure 9) suggests that part of the organic C leached by precipitation

from the catchments is carried downstream and processed in the largest lakes (III).

The C pool in Finnish lake sediments representing the whole period after the last glaciation was 0.62 Pg and the areal C stock in lakes was 19 kg C m⁻² (II). The largest C pool was found in the middle-sized lakes (0.1-10 km²) (Figure 10). However, when the C stock was calculated per square metre of the lake area, the smallest lakes had the greatest stocks (II). Greater organic C burial in small impoundments than in large ones was also reported in U.S (Downing et al. 2008). The low areal stock in the large lakes is at least partly due to the low proportion of the total lake bottom serving as accumulation area, whereas in small lakes the whole bottom can often be classified as an accumulation area. The carbon burial efficiency in sediments has been shown to be negatively related to oxygen exposure time (Sobek et al. 2009). Many small lakes in our data are either eutrophic or humic, and both of these lake types are susceptible to oxygen deficiency (cf. VI), thus enhancing carbon burial in these lakes.

The annual CO₂ emission estimates from Finnish lakes divided into five size classes (Table 3, III, IV) and multiplied by the area of the corresponding lake size classes suggest that Finnish lakes emit annually 1400 Gg C. This is approximately 20% of the average annual C

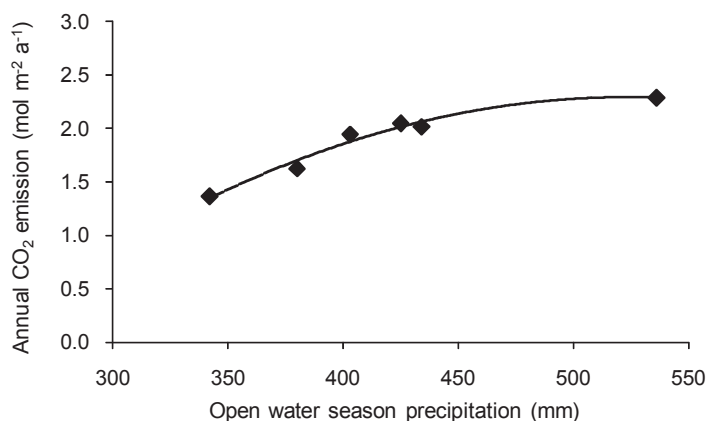


Figure 9. The relationship between combined open water season precipitation in June – October in the study year and September – October in the previous fall and the annual flux of CO₂ in 1996 – 2001 ($y = -0.0000294x^2 + 0.0301x - 5.37$, $r^2 = 0.99$, $p < 0.001$) (III).

accumulation in Finnish forest soils and tree biomass (covering 56 % of the total land area) in the 1990s (Liski *et al.* 2006). On an annual level, both CO₂ emission into the atmosphere and the burial of C into lake sediments were greater in the small lakes per unit area (Table 3) (II, IV, Pajunen 2004). The smallest lakes are often very shallow and their water volume is small, and therefore the sediment area-to-volume ratio is high leading to efficient interaction between the sediment and the atmosphere. In summer the sediment temperature in the pelagial area can be expected to be higher in shallow lakes than in deep, strongly stratified lakes, thus enhancing the degradation. However, if the C fluxes are calculated into the absolute amounts of C processed annually, the large lakes are also important conduits for C fluxes (Table 3). The longer water retention times of the large lakes compared to small lakes probably enhance the role of the large lakes as units for C processing in the catchment.

Emission into the atmosphere was a more important route for C departure from lakes than sedimentation. In the smallest lakes annual CO₂ emission was over 40 times higher than the burial of C into sediment. In the other lake size classes emission to the atmosphere was approximately 20 times higher than the sedimentation (Table 3, IV). However, as the retention times of water in shallow, small lakes are often short, the high rate of C processing

and departure is rather unexpected. A strong positive relationship between organic C loss in the catchment and mean catchment water residence time has been reported in Sweden (Algesten *et al.* 2004). It is possible that part of the CO₂ and CH₄ that is emitted to the atmosphere from the smallest lakes is not autochthonous, but transported in gaseous form from the catchment and released into the atmosphere from lakes (Striegl and Michmerhuizen 1998). Kratz *et al.* (1997) found a strong positive relationship between the sum of base cations in lakes and in their groundwater input. In this study we found a strong positive correlation between Ca and CO₂ (V), and therefore it can be posited that CO₂ can also be transported to lakes via groundwater. CO₂ originating from the decomposition processes in the catchment can also be transported to lakes via streams. The horizontal concentration gradients have shown methane to enter lakes from incoming streams or adjacent peatlands (Schmidt and Conrad 1993; Larmola *et al.* 2004; Murase *et al.* 2005; Repo *et al.* 2007; Bastviken *et al.* 2008).

The average Holocene burial of C into the lake sediments is annually low, on average only 2 g C m⁻²a⁻¹ (Table 3) (II). The amount of C that is buried is small compared to the C burial estimates from the sediment traps in small Swedish lakes (55 ± 44 g C m⁻²a⁻¹) (von Wachenfeldt and Tranvik 2008). The difference between the long term and the short term estimates suggests

Table 3. Estimated annual carbon emission into the atmosphere, average annual Holocene carbon accumulation in sediments, average annual carbon departure (CO₂ emission + carbon accumulation in sediments) and emission/accumulation ratio in different lake size classes.

Lake size (km ²)	<0.1	0.1-1	1.0-10	10-100	>100	All lakes
Number of lakes in Finland	172 185	13 114	2 283	279	47	187 888
Total lake area (km ²) *	1671	3934	5703	7227	14 128	32 663
CO ₂ -C emission (g C m ⁻² a ⁻¹) **	102	66	56	37	25	42 ††
C accumulation (g C m ⁻² a ⁻¹) †	2.4	4.0	3.1	1.8	1.0	2.0
CO ₂ -C emission (Gg C a ⁻¹)	170	260	320	270	350	1400
C accumulation (Gg C a ⁻¹)	4	16	18	13	13	65
C departure (Gg C a ⁻¹)	174	276	338	283	363	1465
Emission/accumulation ratio	43	17	18	21	26	21

* Raatikainen and Kuusisto (1990)
 ** (III, IV)
 † Pajunen (2004) †
 †† Area weighted average

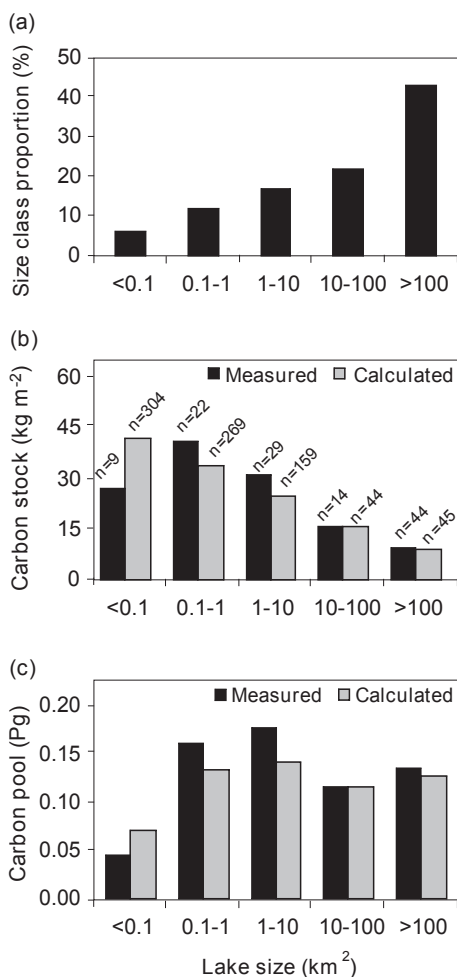


Figure 10. a) Proportion of the total lake area (LA) of Finland occupied by the five size classes (cf. Raatikainen and Kuusisto, 1990), b) distribution of sediment C stock in the five lake size classes based on values measured from the 118 lakes and calculated for the NLS lakes using equation $\sqrt{\text{Average C stock (kg m}^{-2} \text{ LA)}} = 7.01 - 0.312 \ln \text{LA (m}^2) + 0.544\sqrt{\text{Field (\%)}} + 0.402 \ln \text{Fe}_{\text{tot}} (\mu\text{g l}^{-1}) - 0.247 \ln \text{NO}_3\text{-N } (\mu\text{g l}^{-1})$ and c) total C pool in the five lake size classes in Finland. N represents number of study lakes and number of NLS lakes in the five lake size classes. Four outliers in the size class <0.1 were excluded from the measured values (II).

not only that the degradation of organic matter is efficient in lake sediments, but also that the degradation products (CO₂, CH₄) are emitted into the upper water layers and from the surface water also to the atmosphere (IV, VI). These results are in contradiction with incubation experiments in which the sediment respiration contributed only 10 % to the CO₂ emission in

oligotrophic lakes (Algesten *et al.* 2005). The contradictory results may be a consequence of different time scales; the incubation period in the cited work was 1-2 days, whereas our results mainly reflect the situation after a few months of stratification. The very low rate of the long-term burial of C suggests that the degradation continues in the sediment over a long time period. In an oligotrophic lake in Finland the annual CO₂ production of deep profundal sediment has been estimated to be 30 g CO₂ m⁻² and in shallow littoral sediment 114 g CO₂ m⁻² (Bergström *et al.* 2010).

Although methane is an important greenhouse gas its implications for the whole lake carbon budget are small. Methane concentrations in the lake pelagial area were very low especially in the large lakes in all seasons and depths, and consequently the total storage of methane in the water volume and the methane emissions were also small (VI). Pelagial methane concentrations and emissions were highest in shallow lakes, which are also the smallest lakes in the data. The high interaction between the whole water column and sediment in shallow lakes partly explains the differences, but in shallow lakes the proportion of the surface area covered with littoral vegetation can also be expected to be larger and the lake littoral areas have been shown to be large contributors of methane in previous studies (Smith and Lewis 1992; Juutinen *et al.* 2003; Kankaala *et al.* 2005; Bergström *et al.* 2007). In large and often deep lakes methane produced near the sediment during stratification can also be more susceptible to oxidation than outgassing into the atmosphere, due to more force and time needed for proper mixing of the water column (VI).

In Finland, where chain-like lake systems are very common, the smallest lakes are often situated at the top of the lake chains and it can be hypothesized that the largest particulate matter, both autochthonous and allochthonous, sediments in the first basins. Kortelainen *et al.* (1986) reported that the proportion of high molecular weight organic matter (i.e. particulate and colloidal fractions) was high in humic first order lakes with large catchments, where the retention times are short and the input of alloch-

thonous organic matter is high, whereas in the clear water first order lakes with long retention time low molecular weight organic matter (i.e. dissolved) dominated. Low molecular weight organic matter was also shown to dominate in the lower reaches of the watercourse, with an assumption that the main part of the high molecular organic matter had settled or decomposed in the upper lakes. In our study of the total C pool in the Finnish lake sediments, the Holocene sediment C stock had a strong positive correlation with the present lake water Fe content (II). Kortelainen *et al.* (1986) observed that high molecular organic matter had a strong positive correlation with total Fe concentration.

Raymond and Bauer (2001) observed in long term, dark incubations of river water that young labile DOC was first degraded and that remaining DOC was much older than the original material. Therefore, probably only the most labile and young organic matter is decomposed in the first basins of the lake chains and the older and more refractory matter flows through. The degradation of more refractory organic matter is more efficient in the larger and often more clear water basins down stream, with longer residence times and more favourable conditions for photo-oxidation. Furthermore, von Wachenfeldt *et al.* (2008) observed that flocculation of allochthonous DOC was stimulated by light, thus enhancing sedimentation of C in lakes.

3.4 Regulation of lake water carbon in different seasons

In the NLS dataset, which was sampled during the fall overturn, the input of TIC from the catchments determined the concentrations in lakes. TIC was of weathering origin, as suggested by the correlation with lake water Ca, Mg and SiO₂. The decomposition of organic matter was generally not an important source for the main part of TIC, although decomposition contributed to the CO₂ content of the lakes because in the statistical analyses there was no correlation between TIC and TOC. Furthermore, TIC was more closely linked to catchment characteristics than *p*CO₂, suggesting that although TIC mainly enters the lakes from the

surrounding catchments, CO₂ is also produced within the lake ecosystem (V).

Two sources of CO₂ in lakes during fall overturn could be identified by the statistical analysis of the NLS data: weathering processes in the catchment, supported by the correlation between CO₂ and Ca, Mg, SiO₂ and TIC; and decomposition of organic matter in the lake, supported by the correlation between CO₂ and TOC, TN and TON (V). In a solute budget constructed for the Ipswich River basin, Williams *et al.* (2005) found that chemical weathering was the largest source of Ca, Mg and SiO₂. In their study, and also in our data, the agricultural and urban areas of the catchment had strong positive correlations with base cation concentrations in the water. Billett *et al.* (2007) suggested that carbonate weathering may be an important source of DIC in UK peatland streams. The mixing of carbonate rich groundwater with low pH organic-rich peatland soil solutions can lead to the formation of significant amounts of free CO₂. They further proposed different sources for DOC and CO₂ on the basis of the different ages and δ¹³C signatures of DOC and CO₂. The importance of the weathering processes in the catchment as a source of TIC and CO₂ can be expected to be characteristic to fall. In fall, the water discharge from the catchments is often higher than in winter and summer, and therefore, in-lake processes are expected to dominate in winter and summer, whereas the influence of the catchments is emphasized in fall.

Degradation of organic matter was an important source of CO₂ and CH₄ in lakes, especially during the stratification periods, as was suggested by the strong negative correlation with O₂ saturation (IV,VI). Degradation as a source of CO₂ during winter stagnation in Finnish lakes was also demonstrated by the ¹³C content of DIC (Striegl *et al.* 2001). Lake water CO₂ had a positive correlation with TOC in both GL (IV) and NLS (V), as shown for Swedish lakes by Sobek *et al.* (2003). CH₄ in lakes also correlated with TOC (VI).

In the GL data there were measurements from four seasons, thus enabling comparison between the seasons. The PCA analysis suggests that different processes control the CO₂

and CH_4 concentrations in different seasons. In-lake degradation as an important CO_2 and CH_4 source during the stagnation periods was suggested by stronger interaction between TOC and CO_2 or CH_4 during the winter and summer than in other seasons. In fall the connection with TOC was weaker, indicating either the allochthonous source of CO_2 and CH_4 or the efficient loss of gases into the atmosphere (Figure 11). During the summer stratification the bottom water CO_2 and CH_4 had a closer connection with the total nutrients TN and TP than with TOC, probably due to the continuous supply of easily degradable fresh organic matter to the sediment. A close connection between CO_2 , TOC, TN and TP in the bottom water during winter (Figure 11) suggests a homogeneous organic matter source for degradation, which is in good agreement with stagnant winter conditions with little supply of new material. This also is in agreement with the large lakes data, in which high discharge in the fall predicted high CO_2 emission in the next spring, suggesting that the allochthonous organic matter transported to the lakes during the fall period is processed and decomposed during winter and that decomposition products (CO_2) are released with the ice melt (III, Striegl 2001). In summer the response was more rapid, and the high precipitation in the summer months predicted high CO_2 concentrations during the same summer (III).

Degradation during the stagnation periods, winter and summer, was indicated to be concentrated either in the hypolimnion or in the sediments. There was a strong vertical gradient in CO_2 and CH_4 concentrations, with the highest concentrations near the sediment and also a strong negative correlation with the O_2 saturation rate (IV, VI). The CO_2 concentrations in surface water had a strong positive correlation with the CO_2 concentrations near the sediment demonstrating that also surface water CO_2 originates partly from the hypolimnion during stagnation periods (IV). The PCA analysis showed closer connection between CO_2 and TOC in the hypolimnion than in epilimnion, further suggesting that degradation mainly occurred in hypolimnion or in sediment. CH_4 concentrations did not exhibit similar correlation between

surface water and near sediment water layers, suggesting different sources. CH_4 is typically produced in the anoxic hypolimnion and in the sediment and consumed in the oxic epilimnion by methanotrophs (Rudd and Hamilton 1978; Liikanen *et al.* 2002; Kankaala *et al.* 2006). Furthermore, the surface water CH_4 probably originated from other sediments than just below the sampling point, for example from the littoral sediments, and were transported to the sampling point due to lateral mixing of water (Bastviken *et al.* 2008) (VI).

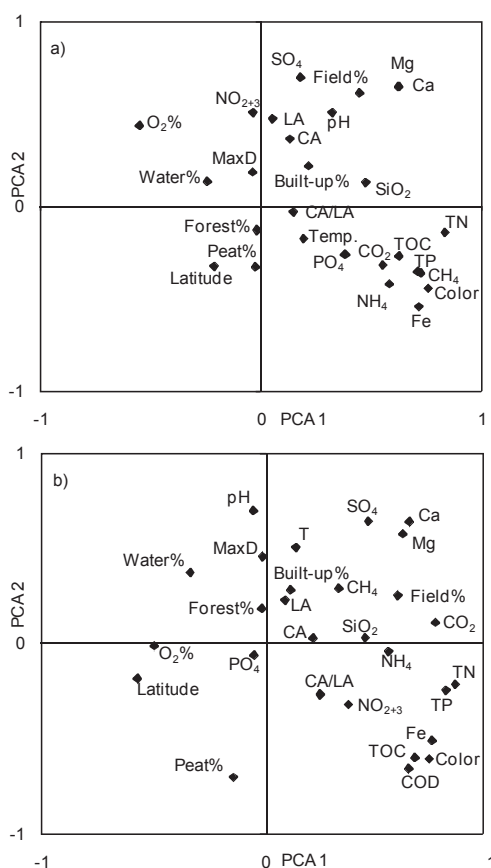


Figure 11. PCA analysis of the bottom water quality and catchment variables in the gas lakes (GL) data in the subsets a) winter and b) fall.

3.5 Extrapolation of CO₂ emission to the atmosphere and Holocene carbon pools in lake sediments

The randomly selected lake datasets of this study enable extrapolation of the results to all lakes of the boreal region. Lake size was chosen as an extrapolation tool since both areal C pool in lake sediments and CO₂ emission into the atmosphere were larger in small, shallow lakes than in large deep lakes. Furthermore, lake size can easily be determined for a representative lake population.

We estimated the total annual CO₂ emission from boreal lakes to be 47 Tg C, by multiplying the lake area specific CO₂ emission estimates (Table 3, IV) by the total area of the corresponding lake size classes in the whole boreal region. The other approach, multiplying the average Finnish CO₂ emission estimate, 42 g C m⁻², by the total area of the boreal lakes, gave an estimate of 59 Tg C a⁻¹ (IV). Globally, it has been estimated that CO₂ emission from lakes is 0.53Pg C annually (Tranvik *et al.* 2009), of which, according to our results, the Boreal lakes represent 9-11%.

Correspondingly, we estimated the total lake sediment C pool in the boreal region to be 21 Pg by multiplying the lake area specific C stock estimates (Table 3, II) by the total area of the corresponding lake size classes in the whole boreal region. A slightly larger estimate (27 Pg) was obtained if the average lake area weighted C stock in Finnish lakes, 19 kg m⁻², was multiplied by the total area of boreal lakes. Assuming that C has accumulated in boreal lakes at a constant rate over the 10 000 years since the continental ice retreat, the annual sink in boreal lakes would be 2-3 Tg C a⁻¹ (II). Therefore, our estimation for the annual C emission from boreal lakes was on average 21-fold higher compared to the average permanent C accumulation in Holocene lake sediments (IV).

These results clearly demonstrate that lakes are important sites for C cycling in the boreal region by burying C and also by transferring terrestrially fixed C into the atmosphere. There are, however, several potential sources of error in extrapolations of this kind. First of all, our

data is restricted to lakes with a minimum size of 0.04 km². Downing *et al.* (2006) estimated that global extent of natural lakes is twice as large as previously known and dominated in area by millions of small waterbodies. If it holds true that both C accumulation and emission into the atmosphere are higher in small lakes, both calculated boreal C stock and C emission may be underestimates because the smallest lakes are not included. Secondly, results from Finnish lakes are not representative for the entire boreal region, because, for example, there are no mountainous areas in Finland, and furthermore, our acidic Precambrian bedrock is a very different setting for lakes compared to the more calcareous areas. Possible source of error are described in (IV, p. 1564).

3.6 Impacts of climate change on CO₂ emission from lakes

Climate change may further enhance the role of lakes in C cycling in boreal landscapes. The snow-covered period has shortened in the northern latitudes; in particular snowmelt occurs earlier (Lemke *et al.* 2007). As temperatures increase, the possibility of precipitation falling as rain rather than snow increases, especially at the beginning and end of the snow season and in areas where temperatures are close to freezing. The climate change scenarios predict increasing rainfall and temperature in Northern Europe, which means frequent snow melt events during winter, and increasing rain during summer (Lemke *et al.* 2007). In Finland the climate change scenarios predict that the annual mean precipitation will increase by 0–15 % by the 2020s. The corresponding increases by the 2050s are 0–30% and by the 2080s 5%–40% (Jylhä *et al.* 2004).

The annual CO₂ emission from the large lakes in Finland followed closely the precipitation pattern (III). The close connection between annual CO₂ emission and precipitation implies that CO₂ is transported to lakes from the catchments or that the organic C produced in the terrestrial ecosystem is carried to the lakes and decomposed there, generating supersaturation of CO₂. Interannual variability in pCO₂ in lakes

in Quebec was also suggested to be driven by regional patterns in precipitation (Roehm *et al.* 2009). Organic C export simulations based on climate change scenarios and neural network modelling indicate increasing DOC fluxes in Canadian rivers (Clair *et al.* 1999) and in Finnish headwater streams (Holmberg *et al.* 2003). Our results suggest that increasing precipitation will also increase CO₂ emissions from lakes.

Climate change-induced higher transport of substances to lakes can also result in eutrophication. Our results show higher CO₂ and CH₄ flux from eutrophic lakes compared to oligotrophic lakes; especially under the ice cover strongly elevated CO₂ and CH₄ concentrations were found (IV, VI). The biological, chemical and physical processes involved in organic matter mineralization consume oxygen, which can result in oxygen depletion and further accelerate the eutrophication process (III, IV).

4 Conclusions

Lakes in different landscapes vary in their C quantity and quality. In both agricultural and peatland-dominated areas C content in lakes is high, but the proportion of inorganic C in lakes is much higher in agricultural areas compared to the lakes surrounded by peatlands. Correspondingly, the organic matter quality shows differences between agricultural and peatland areas, as estimated by TOC/TON ratio. In catchments with homogeneous land use/cover there is a close relationship between TOC and CO₂ in lakes, probably due to the homogeneous quality of the allochthonous C in the lake. In the case of mixed land use the allochthonous C originates from several sources, and therefore there is no clear connection between TOC and CO₂ in lakes. Lake water TIC is strongly dependent on the bedrock and soil quality in the catchment, especially in areas where human influence in the catchment is low. In inhabited areas both agriculture and habitation in the catchment increase TIC concentrations in lakes, probably because in the disturbed soils both weathering and leaching are more efficient than in pristine areas.

TOC concentrations in lakes are related to either catchment sources, mainly peatlands, or to retention in the upper watercourses. Retention as a regulator of the TOC concentrations dominated in southern Finland, whereas the peatland sources were more important in the north. The homogeneous land use and the restricted catchment sources of TOC together with the large proportion of seepage lakes contribute to the close relationship between peatlands and the TOC concentrations in the northern lakes. In southern Finland the more favorable climate for degradation and the heterogeneous catchments leading to multiple sources of TOC highlight the importance of retention.

Both CO₂ and CH₄ concentrations and emissions were high in the eutrophic lakes. Autochthonous sources of organic matter combined with allochthonous sources contribute to the net heterotrophy also in the productive lakes. High availability of nutrients and fresh organic matter enhance degradation in these lakes. Eutrophic lakes are often small and shallow, enabling intensive contact between the water column and the sediment. At the landscape level, the lakes in agricultural areas are often eutrophic due to fertile soils and fertilization of the catchments, and therefore they also showed the highest CO₂ and CH₄ concentrations.

C processing was intensive in the small lakes. Both CO₂ emission and the burial of C into sediments per square meter of the lake area were highest in the smallest lakes. However, because the total area of the small lakes on the areal level is limited, the large lakes are important units in C processing in the landscape scale.

Both import from the catchments and in-lake degradation were suggested to be important sources of CO₂ and CH₄ in fall when the lake water column was intensively mixed and the transport from the catchment was high due to the rainy season. In the stagnant periods, especially in the winter, in-lake degradation as a gas source was highlighted due to minimal mixing and little transport of C from the catchment.

The strong relationship between the annual CO₂ level of lakes and the annual precipitation suggests that climate change can have a major impact on C cycling in the catchments. Increase

in precipitation enhances DOC and DIC export from the catchments and leads to increasing greenhouse gas emissions from lakes.

Yhteenveto

Hiili esiintyy järvissä sekä orgaanisessa että epäorgaanisessa muodossa. Orgaaninen hiili voi olla peräisin järvessä tapahtuvasta perustuotannosta tai huuhtoutua järveen ympäröivän valuma-alueen kasvillisuudesta tai maaperästä. Epäorgaaninen hiili esiintyy järvessä joko liuenneina bikarbonaateina, karbonaateina tai kaasumaisessa muodossa hiilidioksidina ja metaanina. Bikarbonaatti on peräisin maaperässä tapahtuvasta rapautumisesta, mutta hiilidioksidi muodostuu pääosin orgaanisen aineen hajoamisen seurauksena. Hapettomissa oloissa hajoamisen seurauksena muodostuu metaania.

Järvet ovat tärkeä osa ekosysteemin hiilenkiertoa, koska maaekosysteemistä huuhtoutunutta orgaanista ainesta hajoaa järvissä muodostaen ilmastoa lämmittäviä metaani- ja hiilidioksidikaasuja. Osa järvessä muodostuvasta ja ympäröivältä valuma-alueelta tulevasta hiilestä varastoituu järvien pohjasedimenttiin. Tässä tutkimuksessa selvitimme järvien roolia hiilikaasujen lähteenä ja hiilen varastona. Lisäksi tutkimme valuma-alueelta järviin tulevan hiilen alkuperää sekä hiilen eri muotojen (orgaaninen, epäorgaaninen) suhteellista osuutta erilaisissa järvissä. Tutkimus perustuu satunnaisotannalla valittuun Pohjoismaiseen järvikartoitusaineistoon, joka käsittää 874 järveä etelärannikolta pohjoisimpaan Suomeen. Laaja aineisto mahdollistaa tulosten yleistämisen Suomen ja koko boreaalisen alueen mittakaavassa.

Erityyppisillä alueilla sijaitsevat järvet poikkesivat toisistaan järveden hiilen määrän suhteen. Hiilen kokonaismäärä vedessä oli suurin maatalous- tai turvemaavaltaisilla alueilla. Turvemaavaltaisilla alueilla orgaaninen hiili oli pääasiallinen hiilen muoto järvissä, mutta maatalousvaltaisilla alueilla sekä orgaanisen että epäorgaanisen hiilen pitoisuudet olivat suuria. Metsäisillä mineraalimailla sijaitsevat järvet olivat tyypillisesti vähähiilisiä. Tutkimustulosten perusteella voitiin havaita että järvien orgaanisen hiilen pitoisuudet määräytyivät

järveä ympäröivältä valuma-alueelta, lähinnä turvemailta, tulevan kuormituksen perusteella etenkin Pohjois-Suomessa. Yläpuolisissa järvissä tapahtuva orgaanisen aineen pidentyminen hajoamisen tai sedimentoitumisen myötä oli etenkin eteläisessä Suomessa keskeinen järvien orgaanisen hiilen määrää säätelevä tekijä, mikä johtui valuma-alueiden pohjoista monipuolisemmasta maankäytöstä (maatalous, asutus) ja orgaanisen aineen hajoamiselle suotuisemmista olosuhteista etelässä. Valuma-alueen kallioperä ja maaperä vaikuttivat järvien epäorgaanisen hiilen pitoisuuksiin. Asutuilla alueilla maanviljely lisää järvien epäorgaanisen hiilen pitoisuuksia, sillä maanviljely on myös tyypillisesti keskittynyt hienojakoisille maille, joissa rapautuminen on nopeampaa.

Tämän tutkimuksen tulosten perusteella järvien rehevöityminen lisää järvien luontaisia hiilidioksidi- ja metaanipäästöjä. Orgaanisen aineen hajotus tehostuu, kun ravinteita on riittävästi saatavilla ja lisäksi rehevät järvet tuottavat runsaasti helposti hajoavaa orgaanista ainetta. Rehevimmät järvet ovat usein pieniä ja matalia, mikä tehostaa myös pohjalietteestä vapautuvien kaasujen pääsyä ilmakehään. Maatalousalueilla sijaitsevat järvet ovat usein keskimääräistä rehevempiä pelloilta huuhtoutuvien ravinteiden vuoksi. Verrattaessa hiilen prosessointia eri kokoisissa järvissä havaittiin, että orgaanisen aineen hajotus ja sedimentaatio olivat tehokkaimmillaan pienissä järvissä. Hiilidioksidi ja metaanipäästöt järvistä sekä hiilen pysyvä varastoituminen järvisedimenttiin olivat pinta-alaan suhteutettuina suurimpia pienissä järvissä. Pienten järvien kokonaispinta-ala Suomessa on kuitenkin suuriin järviin verrattuna pieni, joten kokonaispäästöiksi ja varastoiksi laskettuina myös suuret järvet ovat tärkeitä valuma-alueiden hiilenkierrossa.

Eri vuodenaikoina järvien hiilidioksidi ja metaanipitoisuuksien säätelyssä havaittiin eroja. Syksyisin, kun sademäärät usein ovat suuria ja valuma-alueelta veden mukana kulkeutuvia aineita on järvissä paljon, sekä järven sisäisissä prosesseissa syntyvillä että valuma-alueelta kulkeutuvilla hiilidioksidilla ja metaanilla oli merkitystä järvien pitoisuuksiin. Talvella, kun järven ulkopuolelta tuleva kuormitus on pieni,

järven oman hajotustoiminnan tuloksena syntyvien kaasujen määrä oli ratkaiseva. Vuosittaisen sademäärän ja järvien vuosittaisen hiilidioksidipäästöjen väliltä löydettiin voimakas riippuvuus, joka todennäköisesti johtui siitä, että sateisina vuosina valuma-alueilta huuhtoutui järviin enemmän orgaanista ainetta. Tämä tulos viittaa siihen, että jos sademäärä kasvaa ilmastomuutoksen myötä, myös luonnon lähteistä tulevat hiilidioksidipäästöt kasvavat.

Järvisedimetteihin viime jääkauden jälkeen Suomessa varastoitunut hiilimäärän arvioitiin olevan 0,62 Pg, joka on kolmanneksi suurin luonnon hiilivarasto Suomessa soiden ja metsämaiden jälkeen. Suomen järvien vuotuisiksi hiilidioksidipäästöiksi arvioitiin 1400 Gg.

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