Biogeochemistry (2008) 91:151–162
DOI 10.1007/s10533-008-9266-8

Controls of organic and inorganic carbon in randomly selected Boreal lakes in varied catchments

Miitta Rantakari · Pirkko Kortelainen

Received: 12 February 2008 / Accepted: 9 November 2008 / Published online: 23 December 2008

Abstract Organic and inorganic carbon concentrations in lakes and the links to catchment and water quality were studied in variable landscapes using the Finnish Lake Survey data base including 874 randomly selected lakes sampled during autumn overturn. The median total organic carbon (TOC) in these boreal lakes was 7.8 mg l^{-1}, the median total inorganic carbon (TIC) 1.6 mg l^{-1} and the median partial pressure of CO_2 (pCO_2) 900 µatm. When the data was divided into subgroups according to land use in the catchment, the proportion of TIC of the total carbon (TC) in lakes was highest (31%) in agricultural areas and lowest (10%) in peatland areas. Elevated TIC concentrations were associated with agricultural land in the catchment, whereas elevated TOC concentrations were observed in lakes with high peatland proportion in the catchment. Two contrasting important sources of CO_2 in lakes were identified on the basis of statistical analysis of the data; weathering processes in the catchments and decomposition of organic matter. CO_2 was also strongly associated with total nutrients TN and TP, implying the importance of quality of organic matter and availability of nutrients for the decomposition processes.

M. Rantakari (✉) · P. Kortelainen
Finnish Environment Institute, P.O. Box 140, 00250 Helsinki, Finland
e-mail: miitta.rantakari@environment.fi

P. Kortelainen
e-mail: pirkko.kortelainen@environment.fi

Keywords Total organic carbon · Total inorganic carbon · Carbon dioxide · Boreal lakes · Catchments

Introduction

Organic and inorganic carbon occur in boreal lakes as particulate organic and inorganic carbon (POC, PIC), dissolved organic and inorganic carbon (DOC, DIC) and gaseous forms (free CO_2 and CH_4). Dissolved inorganic carbon (HCO_3^-, CO_3^{2-}) is related to gaseous carbon (free CO_2) via carbonate equilibria (Wetzel 1983). The relative proportion of these three inorganic forms of carbon are dependent on pH and to a lesser extent temperature (Stumm and Morgan 1981).

Large rivers have been shown to transport large quantities of inorganic carbon into ocean (e.g. Raymond and Cole 2003; Striegl et al. 2007; Raymond et al. 2008), but the role of total inorganic carbon (TIC) in lakes has received less interest (Dillon and Molot 1997). Bicarbonate (HCO_3^-) originates mainly from weathering reactions in soil. The chemical weathering of rock material, mainly carbonate and silicate minerals, produces bicarbonate ions (HCO_3^-) and consumes CO_2 of the atmospheric origin (Gaillardet et al. 1999). The soil CO_2 needed in weathering reactions is mainly derived from respiration of organic matter, but ultimately of the atmospheric origin fixed during photosynthesis (Cole et al. 2007). The resulting bicarbonate ion (HCO_3^-) is the dominant form of dissolved inorganic carbon in most lakes and rivers. However, an important source of CO_2 in lakes with longer residence times is also the decomposition of organic matter in situ (Sobek et al. 2003; Kortelainen et al. 2006), either by microbial utilization or photo-oxidation (e.g. Salonen and Vähätalo 1994; Granéli et al. 1996).

Dissolved organic carbon (DOC) is supplied to aquatic ecosystems from both external (allochthonous) and internal (autochthonous) sources. Autochthonous sources include the primary production of algae and macrophytes, whereas allochthonous DOC is derived from the surrounding terrestrial ecosystem. Organic carbon budgets of lakes show that external loading often dominates over internal production (e.g. Canham et al. 2004). However, when production in the littoral zone is added to the carbon budget, at least some clearwater lakes can be net autotrophic (Andersson and Kumblad 2006).

Land use of the catchment affects the quantity and bioavailability of dissolved organic matter (DOM) moving from terrestrial ecosystems into streams (Findlay et al. 2001). The differences in the ultimate origin of DOM combined with differential transformation during transport may result in significantly different behavior of autochthonous versus allochthonous DOM (Findlay and Sinsabaugh 2003). Allochthonous DOM has often experienced biogeochemical reactions before entering the lake ecosystem. Thus, on average it is less labile than DOM recently produced within the system (Sinsabaugh and Findley 2003). Compared to total organic carbon (TOC), only few studies have described the sources and behavior of TIC in natural waters. A few studies have focused on both organic and inorganic forms of carbon in running waters (e.g. Neal and Hill 1994; Palmer et al. 2001; Dawson et al. 2002, 2004; Johnson et al. 2006; Billett et al. 2007; Striegl et al. 2007; Walvoord and Striegl 2007), but very few in lakes (Dillon and Molot 1997).

This study is based on a randomly sampled database of 874 lakes representing a wide range of size, water quality, catchment land use, and covering a large geographical area, altogether 51% of the total lake area of Finland. Using this extensive data, we identify the concentrations and the relative importance of different forms of carbon (inorganic vs. organic) in lakes surrounded by forests, peatlands and agricultural land, and furthermore, study the potential sources and most important predictors of TOC, TIC and CO_2.

We hypothesize that in different land use patterns primary drivers controlling the concentrations of TOC and TIC vary. Furthermore, we hypothesize that in complex catchment systems with wide variation in land use, the concentrations of TOC and TIC in lake water are not closely related because of multiple allochthonous sources and several factors regulating TOC, TIC and pCO$_2$ in lakes.

Methods

The data set is based on a Nordic lake survey conducted in the autumn of 1995 (Henriksen et al. 1996; Mannio et al. 2000; Rantakari et al. 2004). Altogether 874 lakes were selected 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 km^2 were 1:1:4:8, respectively. All of the lakes >100 km^2 were included. Larger lakes were emphasized, because lakes >10 km^2 represent over 65% of the total lake area in Finland. One water sample was taken from the middle of the lake during the autumn overturn from depth of 1 m. During autumn circulation a single sample most representatively reflects the water quality of the lake. An extensive seasonal lake survey (Kortelainen et al. 2006) showed that in 1 m samples CO_2 concentrations were only slightly elevated in autumn compared to spring and summer but were significantly lower than in winter samples. Surface water samples of this data also showed low seasonal variability in TOC concentrations as well as in total carbon (TC) concentrations (P. Kortelainen, unpublished). Therefore, autumn sample can be considered as representative for the open water period.

Samples for TIC were taken into airtight glass bottles and placed in coolers while in transit to the laboratories. TIC was measured in the laboratory using infrared spectroscopy. CO_2 concentrations were calculated from measurements of TIC and pH with correction for in situ water temperature (Stumm and Morgan 1981; Butler 1982; Kling et al. 1992). Partial pressure of CO_2 (pCO$_2$) was calculated from CO_2 concentration using the appropriate Henry's law constant, corrected for temperature and atmospheric pressure (Plummer and Busenberg 1982). The equilibrium pCO_2 values in the lake water were calculated with Henry's law, assuming the atmospheric mixing ratio of 360 ppmv for 1995 (IPCC 2001). HCO_3 was calculated as the difference between TIC and CO_2. The concentrations of CO_3^{2-} were assumed to be negligible, since the maximum pH in this data set was 7.9. Similarly, the proportion of CH_4 in these lakes was assumed to be negligible, because when CH_4 in different seasons was measured in the subset of 209 lakes that were selected from Nordic Lake Survey database of 874 lakes, the proportion of CH_4 of TIC in autumn was less than 0.5% (Juutinen et al. 2009).

TOC was analyzed from unfiltered samples by oxidation to CO_2 followed by IR-measurement. Total nitrogen (TN) was analyzed colorimetrically after oxidation to NO_3–N, the sum of NO_3–N and NO_2–N colorimetrically by autoanalyzer after reduction to NO_2–N, NH_4–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 (PO_4–P) by spectrophotometric determination, calcium (Ca) and magnesium (Mg) were determined by flame atomic adsorption/ICP-MS, silicate (SiO_2) by a colorimetric method or by FIA and sulfate (SO_4) by ion chromatography (Henriksen et al. 1996; Mannio et al. 2000).

The catchment areas of the lakes were determined from topographic maps. The catchment boundaries were digitalized, and combined with land use data using the Arc View georeferencing software. The land use data is based on satellite images interpretation. Catchment area and lake area were determined, as well as proportions of peatland, (consisting of open peatlands and forests on peatland); forests on mineral soil; agricultural land, (consisting of cropland and pasture); water (consisting of the lake itself and the upstream water bodies); and built-up area in the catchments. The location of the lake in the south-north direction was expressed as latitude (geographical coordinates, minutes and seconds). The catchments were situated between latitudes 60 and 69°N (Fig. 1).

The relationships between lake water TOC, TIC or pCO_2 and catchment characteristics or lake water quality were studied by principal component analysis

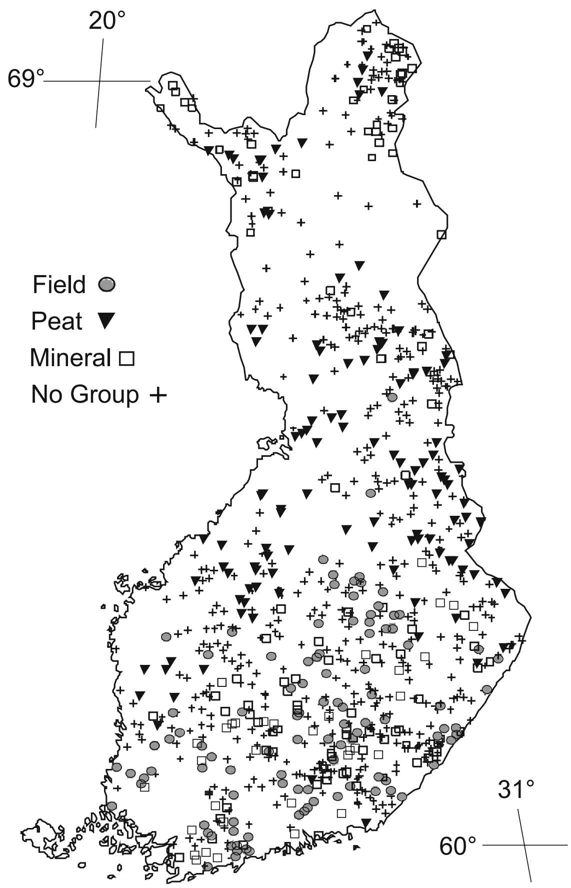

Fig. 1 The locations of the study lakes: ▼ subset PEAT (peatland > 35% and agricultural land < 8%), ● subgroup FIELD (agricultural land > 10% and peatland < 12%), □ subgroup MINERAL (forests on mineral soil > 75%, agricultural land < 7% and peatlands < 7%), + the rest of the study lakes (not belonging to any of the subgroups above)

(PCA), correlation and stepwise multiple regression analysis (PROC FACTOR, PROC CORR and PROC REG; SAS Institute 2001). Catchment characteristics (catchment area, lake area, proportions of peatland, forests on mineral soil, agricultural land, water and built-up area in the catchment and latitude) or water quality variables (TOC, TIC, TN, the sum of NO_3–N and NO_2–N, NH_4–N, TON, TP, Fe, Ca, Mg, SiO_2, SO_4) were used as independent variables. Most of the concentration and catchment data were transformed into natural logarithms or square roots in order to improve the normality of the distributions. Similar regression models for TOC as a function of catchment characteristics of these 874 randomly selected lakes were presented by Rantakari et al. (2004).

In the regression analysis, cases with the absolute value of studentized residual exceeding three were excluded.

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 number of lakes in each subset, because very different number 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 (Table 1).

Results

Total organic carbon

The size of the lakes ranged from 0.04 to 1, 538 km^2, the median lake size being 0.22 km^2. The median TOC in this data set was 7.8 mg l^{-1} (range 0.4–34 mg l^{-1}) (Table 1). Proportion of TOC of TC was highest in the subset PEAT (90%) and lowest in the subset FIELD (69%) (Fig. 2). The proportion of peatlands correlated positively with lake water TOC in the whole dataset and in the subset PEAT (Table 2). However, in the subsets MINERAL and PEAT agricultural land in the catchment showed stronger correlation with TOC than peatlands, and

Table 1 Median characteristics of lakes and catchments in the whole data set, and in the subsets FIELD (agricultural land > 10%, peatland < 12%), PEAT (peatland > 35%, agricultural land < 8%) and MINERAL (forests on mineral soil > 75%, agricultural land < 7%, and peatlands < 7%)

n	Whole data set 874	FIELD 120	PEAT 117	MINERAL 119
Lake area (km^2)	0.22 (0.04–1,500)	0.41 (0.04–180)	0.12 (0.04–43)	0.090 (0.04–32)
Catchment area (km^2)	4.6 (0.08–52,000)	7.3 (0.16–17,000)	3.4 (0.23–1,300)	1.5 (0.18–370)
Water (%)	8.8 (0.2–43)	9.6 (0.3–35)	5.2 (1–42)	9.7 (1–24)
Agricultural area (%)	2.3 (0–53)	19 (11–53)	0.2 (0–7)	0 (0–6.5)
Forest on mineral soil (%)	65 (10–98)	64 (32–83)	48 (10–61)	85 (76–98)
Peatland (%)	14 (0–84)	3.0 (0–11)	44 (36–84)	2.9 (0–6)
Built-up area (%)	0.09 (0–39)	0.60 (0–39)	0.01 (0–0.3)	0.03 (0–13)
CA/LA	16 (2.1–6,800)	13 (2.7–6,800)	25 (2.2–1,500)	12 (2–640)
TOC (mg l^{-1})	7.8 (0.4–34)	8.1 (0.6–18)	10 (1.3–34)	6.2 (0.4–22)
TIC (mg l^{-1})	1.6 (0.1–12)	3.6 (0.1–8.2)	1.1 (0.2–7.3)	1.5 (0.25–12)
pCO_2 (μatm)	900 (75–5,800)	1,200 (140–4,000)	810 (160–1,300)	930 (260–2,000)
Water color (Pt mg l^{-1})	60 (3.8–500)	40 (3.8–200)	100 (5–360)	35 (3.8–500)
pH	6.7 (3.8–7.9)	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)	270 (−170–980)	80 (−80–590)	100 (−20–970)
TN (μg l^{-1})	430 (60–2,500)	600 (82–1,800)	460 (150–1,800)	340 (60–790)
TON (μg l^{-1})	380 (46–2,100)	500 (69–1,300)	430 (120–1,800)	300 (46–770)
TOC:TON	25 (5.5–77)	19 (5.7–34)	30 (9.5–77)	24 (5.5–56)
TP (μg l^{-1})	13 (1–200)	23 (4–100)	18 (4–88)	9.0 (1–100)
TOP (TP-PO_4)(μg l^{-1})	12 (1–180)	17 (3–58)	15 (2.5–75)	7.8 (1–55)
Fe (μg l^{-1})	360 (2.5–5,000)	310 (40–3,500)	760 (20–3,400)	180 (2.5–3,400)
Ca (mg l^{-1})	2.8 (0.2–45)	5.7 (1.7–45)	1.7 (0.2–10)	2.5 (0.4–12)
SiO_2 (mg l^{-1})	2.8 (0.05–21)	2.5 (0.05–17)	2.6 (0.1–18)	2.9 (0.1–10)

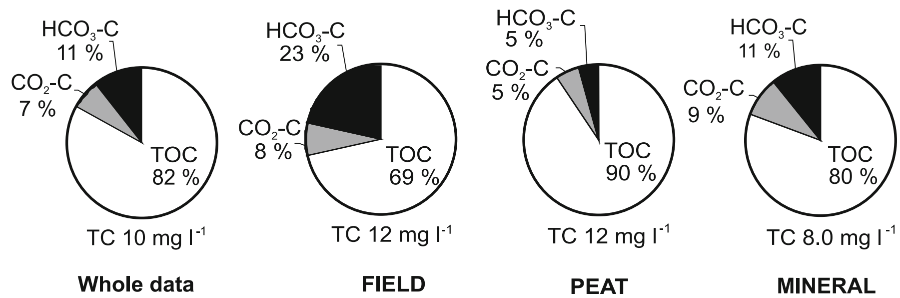

Fig. 2 The relative contribution (%) of each C-species to the total C concentration in the whole dataset and in the subsets PEAT, FIELD and MINERAL (see Fig. 1 for explanation of abbreviations)

Table 2 Pearson correlation coefficients between log[TOC] and catchment and water quality variables for the whole dataset and for the subsets FIELD, PEAT and MINERAL

n	Whole data 814	FIELD 120	PEAT 117	MINERAL 119
pH	−0.371***	−0.195*	−0.476***	−0.588***
Peatland (%)	0.340***	NS	0.243**	NS
Agr. land (%)	0.182***	NS	0.270**	0.246**
Water (%)	−0.433***	−0.563***	−0.395***	NS
Built-up (%)	NS	NS	NS	NS
CA/LA	NS	0.398***	0.202*	NS
Color (Pt mg l^{-1})	0.888***	0.804***	0.904***	0.887***
TN (μg l^{-1})	0.744***	0.721***	0.513***	0.762***
TON (μg l^{-1})	0.774***	0.711***	0.583***	0.857***
TP (μg l^{-1})	0.688***	0.395***	0.573***	0.697***

See Table 1 for explanation of abbreviations

Significant coefficients * $P < 0.05$, ** $P < 0.001$, *** $P < 0.0001$ are shown, *NS* not significant

furthermore, in the subset FIELD catchment to lake area ratio (CA/LA) had a positive relation with TOC (Table 2; Fig. 3a). Upstream water bodies were negatively related to TOC (Table 2; Fig. 4), as was already shown by Rantakari et al. (2004). Correlation coefficients between TOC and the upstream lake percentage were better in agricultural areas than in peatlands or mineral soils (Table 2).

TOC:TON ratio and water color differed between subsets (Table 1). In the subset PEAT, the median water color and TOC:TON ratio were highest, and significantly lower TOC:TON and color values were recorded in both the FIELD and FOREST subsets, suggesting differences in the quality of lake water organic matter. In PCA analysis, TOC was strongly associated with TN and TON in the subset MINERAL but the connection was less clear in the subsets PEAT and FIELD (Fig. 3a–c).

Total inorganic carbon

The median TIC in this data set was 1.6 mg l^{-1} (range 0.1–12 mg l^{-1}) (Table 1), and the average pH was 6.7 (range 3.8–7.9), indicating that TIC in the lakes consists of bicarbonate and free CO_2. The proportion of TIC of TC was the highest, 31%, in the subset FIELD. The subsets PEAT and FIELD had the same average TC concentration (12 mg l^{-1}), but there were considerable differences in the proportions of inorganic and organic carbon. Organic carbon dominated in both subsets but the proportion of TIC of TC was significantly higher in the subset FIELD (31%) than in the subset PEAT (10%) (Fig. 2).

Bicarbonate dominated alkalinity in these lakes, and consequently alkalinity explained 95% of the variability of TIC in the whole dataset (Fig. 5). As well as alkalinity, TIC was closely related to Ca, Mg and SO_4 (Table 3, Fig. 4). When testing the relationship between TIC and land use in the catchment we found that agricultural land and built-up land in the catchment correlated positively with TIC concentrations, whereas peatlands correlated negatively with TIC (Table 3; Fig. 4). TIC correlated positively with pCO$_2$ in the whole dataset and in all the subsets (Table 4), but had non-significant correlations with TOC in the whole dataset and in all the subsets (Table 3).

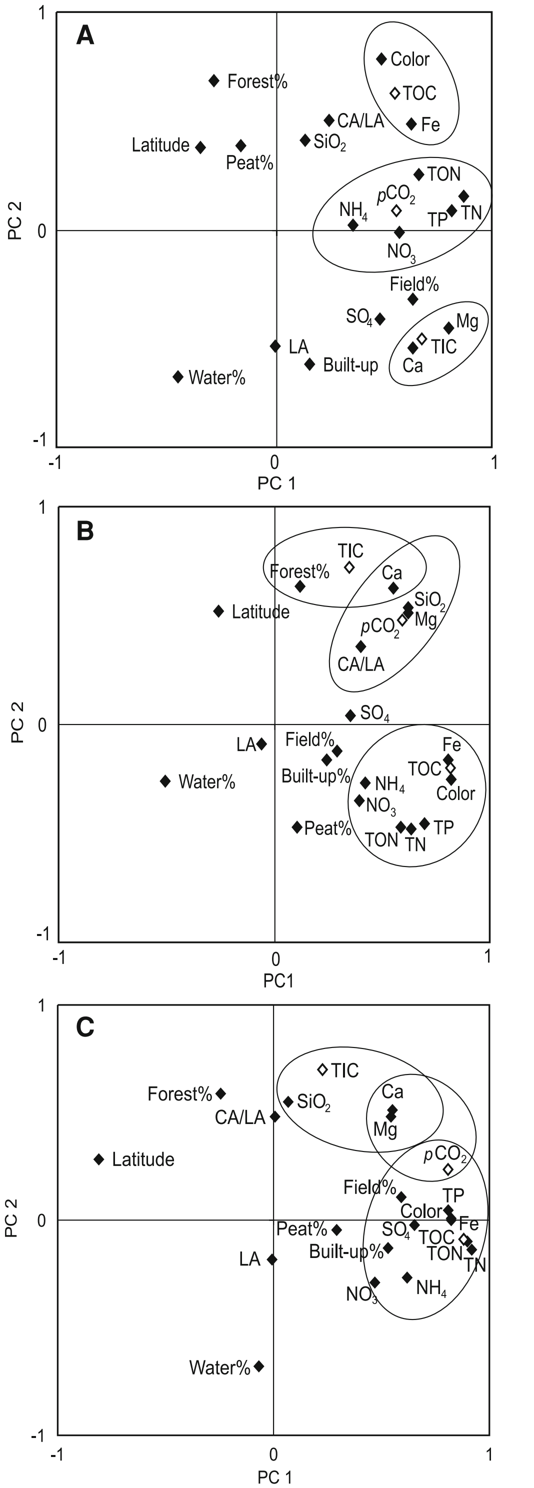

Fig. 3 The PCA analysis of the water quality and catchment variables in the subsets **a** FIELD, **b** PEAT and **c** MINERAL (see Fig. 1 for explanation of abbreviations)

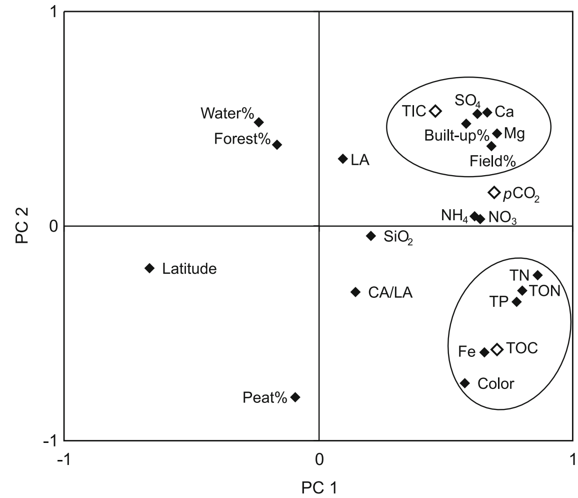

Fig. 4 The PCA analysis of the water quality and catchment variables in the whole dataset

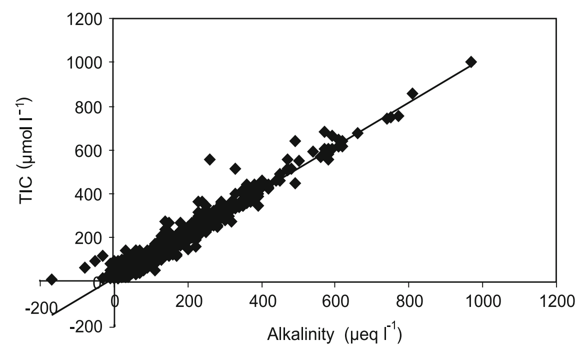

Fig. 5 The relationship between alkalinity (µeq l^{-1}) and TIC content (µmol l^{-1}) of the lake water in the whole data set ($y = 0.996x + 19.3$; $R^2 = 0.95$)

Impacts of water quality and land use on CO_2

Median pCO_2 in the data was 900 µatm (range 75–5,800 µatm) (Table 1). The highest median 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% (Fig. 2).

Principal component analysis of the data suggested that there are two major environmental drivers determining CO_2 in the lakes: on the one hand CO_2

Table 3 Pearson correlation coefficients between log[TIC] and catchment and water quality variables for the whole dataset and for the subsets FIELD, PEAT and MINERAL

n	Whole data 814	FIELD 120	PEAT 117	MINERAL 119
pH	0.679***	0.658***	0.576***	0.603***
Peatland (%)	−0.339***	−0.340***	NS	NS
Agr. land (%)	0.465***	0.519***	NS	0.250**
Water (%)	NS	NS	NS	NS
Built-up (%)	0.357***	0.390***	NS	NS
Forest (%)	NS	−0.433***	0.201*	NS
Latitude	NS	NS	0.422***	NS
TOC (mg l^{-1})	NS	NS	NS	NS
TN (μg l^{-1})	0.179***	0.394***	NS	NS
TP (μg l^{-1})	0.131***	0.468***	NS	NS
Ca (mg l^{-1})	0.810***	0.814***	0.807***	0.766***
Mg (mg l^{-1})	0.774***	0.863***	0.768***	0.705***
SO_4 (mg l^{-1})	0.354***	0.377***	NS	NS
SiO_2 (mg l^{-1})	0.266***	NS	0.445***	0.238**

See Table 1 for explanation of abbreviations

Significant coefficients * $P < 0.05$, ** $P < 0.001$, *** $P < 0.0001$ are shown, *NS* not significant

was associated with Ca, Mg and SO_4 concentrations, that are linked to weathering processes in the catchment, and on the other hand CO_2 was associated with TOC, TN, TON and TP concentrations and water color, i.e. lake water organic matter concentrations (Figs. 3, 4). PCA analysis of the subsets showed variation in controls of pCO_2 in different land uses. In the subset PEAT, pCO_2 had a strong relationship with SiO_2, Mg and Ca, but did not have a close relationship with TOC, or with the different forms of nitrogen or TP. The situation was opposite in the subset FIELD, in which pCO_2 had the closest relationship with TN, NO_3, NH_4 and TP (Fig. 3a, b).

The stepwise multiple linear regression equations supported the hypothesis of two environmental drivers in regulating pCO_2 by selecting Ca representing the weathering processes and either TOC, TN or TP representing organic matter (Table 5). Additionally, SiO_2 was selected in all equations. In PCA analysis, SiO_2 was not strongly associated with the first two principal components, but mainly with the third principal component, which was characterised by positive loadings for CA/LA and SiO_2 and the negative loading for water in the catchment.

Of the water chemistry variables (besides TIC), Ca had the best correlation with pCO_2 in the whole dataset. In the subsets PEAT and MINERAL, SiO_2 and TOC, respectively, had the best correlation with pCO_2 (Table 4; Fig. 6a). TOC correlated positively with pCO_2 in the whole data and in the subsets, but in the whole dataset and in the subset FIELD, the correlation coefficients between total nutrients (TN, TP) and pCO_2 were higher than between TOC and pCO_2 (Table 4). The slopes of regression equations between TOC and pCO_2 in the subsets varied. For example with the same concentration of TOC, pCO_2 was higher in the subset FIELD than in the subset PEAT (Fig. 6b). If the subset MINERAL had been plotted in Fig. 6b, the observations would have been situated in between the subsets FIELD and PEAT.

Also, the catchment characteristics had significant correlations with CO_2. The best predictor was agricultural land in the catchment, which had a significant positive correlation with pCO_2 in the whole dataset and in the subsets FIELD and MINERAL (Table 4). Built-up land in the catchment also increased pCO_2 in lakes. The proportion of water in the catchment had a weak negative relationship with pCO_2 in many subsets (Table 4).

Discussion

Sources of total inorganic carbon

Weathering in the catchments appeared to dominate the input of TIC into lakes. The main land use types that had a positive correlation with TIC in lakes were agricultural and built-up land in the catchment. There was a strong relationship between TIC and CO_2 in

Table 4 Pearson correlation coefficients between log[pCO_2] and catchment and water quality variables for the whole dataset and for the subsets FIELD, PEAT and MINERAL

n	Whole data 790	FIELD 120	PEAT 117	MINERAL 119
Peatland (%)	−0.208***	NS	NS	NS
Agricultural land (%)	0.403***	0.325***	NS	0.398**
Built-up (%)	0.329***	NS	NS	0.337***
Water (%)	−0.217***	−0.313**	−0.286**	NS
Forest (%)	NS	NS	0.202*	NS
Latitude	−0.402***	NS	NS	−0.615***
TOC (mg l^{-1})	0.396***	0.367***	0.288**	0.698***
TN (μg l^{-1})	0.463***	0.492***	NS	0.681***
TON (μg l^{-1})	0.410***	0.245*	NS	0.670***
NH_4 (μg l^{-1})	0.420***	0.296**	0.254**	0.487***
NO_3 (μg l^{-1})	0.300***	NS	NS	0.300***
TP (μg l^{-1})	0.429***	0.432***	0.217*	0.623***
TIC (mg l^{-1})	0.649***	0.445***	0.734***	0.461***
Ca (mg l^{-1})	0.599***	0.318**	0.600***	0.551***
Mg (mg l^{-1})	0.559***	0.383***	0.540***	0.474***
SO_4 (mg l^{-1})	0.436***	NS	NS	0.506***
SiO_2 (mg l^{-1})	0.344***	0.231*	0.605***	0.230*

See Table 1 for explanation of abbreviations

Significant coefficients * $P < 0.05$, ** $P < 0.001$, *** $P < 0.0001$ are shown, *NS* not significant

Table 5 Stepwise linear multiple regression equations for log[pCO_2] for the whole dataset and for the subsets FIELD, PEAT and MINERAL

Analyzed set	Parameters						
	α	log[Ca]	log[TOC]	log[TP]	log[TN]	log[SiO_2]	R^2
Whole data	5.78	0.353[a]		0.230[b]		0.103[c]	0.53
FIELD	4.11	0.223[c]			0.401[a]	0.0998[b]	0.34
PEAT	6.34	0.301[b]				0.200[a]	0.47
MINERAL	5.64	0.302[b]	0.444[a]			0.111[c]	0.68

See Table 1 for explanation of abbreviations. The order of independent variables selected by the regression is denoted by letters[a–c]

lakes but no correlation between TIC and TOC, suggesting that decomposition of organic matter was generally not an important source for the main part of TIC, although decomposition contributed to the CO_2 content of the lakes. Billett et al. (2007) proposed different sources for DOC and CO_2 in UK peatland streams on the basis of the different ages and δ^{13} signatures of DOC and CO_2. The main part of HCO_3^- in natural waters of Finland has been proposed to originate from biogenic carbon acid taking part in weathering (Lahermo et al. 1996). This is supported by our results, because TIC in lakes correlated with Ca and Mg, which also originate mainly from weathering. TIC was better predicted by catchment characteristics than pCO_2, further suggesting that although TIC mainly enters the lakes from the surrounding catchments, CO_2 is also produced within the lake ecosystem.

Lakes in agricultural areas had higher TIC concentrations than lakes in peatland rich areas. Raymond and Cole (2003) obtained similar results in 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. Agriculture is concentrated on fine grained soils, where weathering reactions are more efficient due to greater specific surface area. Furthermore, cultivation of these soils enhances weathering by increasing the interaction with water. Correspondingly, in a large northern river

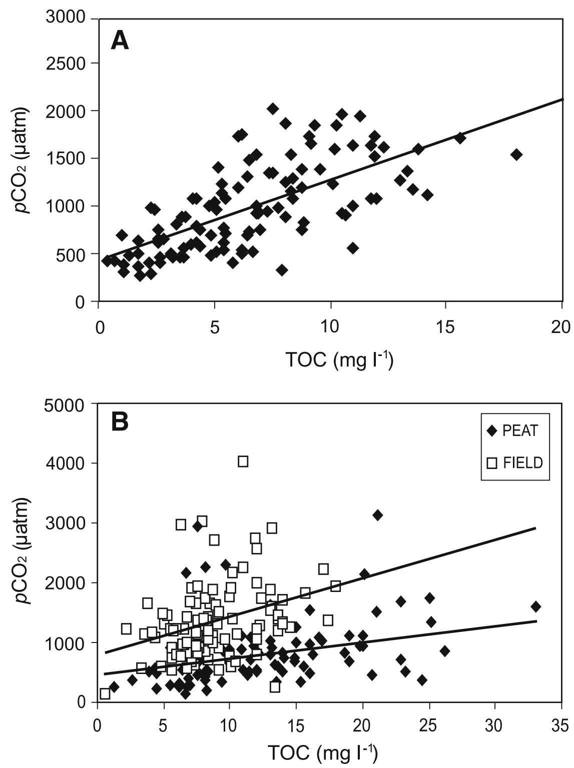

Fig. 6 The relationship between **a** the TOC content (mg l^{-1}) of the lake water and pCO_2 (µatm) in the subset MINERAL ($y = 85.0x + 420$; $R^2 = 0.49$). **b** The TOC content (mg l^{-1}) of the lake water and pCO_2 (µatm) in the subset PEAT, ($y = 25.7x + 577$; $R^2 = 0.08$) and in the subset FIELD, ($y = 64.5x + 777$; $R^2 = 0.13$)

basin, Ottawa River, 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 carbon budgets. The highest DIC in Ottawa River was recorded in a sub-basin rich in carbonates and heavily used for agriculture (Telmer and Veizer 1999).

In the PCA and correlation analysis, 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, forests on mineral soil were positively associated with TIC suggesting that mineral soils are more important sources of TIC than peatlands.

Sources of TOC in different land uses

Peatlands were proposed to be important catchment sources of TOC in the whole dataset and in the subset PEAT. However, also agricultural land in the catchment had a positive relationship with TOC concentrations in the subsets MINERAL and PEAT. TOC concentrations were relatively high in both FIELD and PEAT, but in the subset of PEAT, water color was considerably higher than in the subset FIELD, partly due to higher Fe concentrations in PEAT. In addition, the average TOC:TON-ratio was significantly lower (19 vs. 30) in the subset FIELD compared to the subset PEAT, suggesting a different origin of TOC in the lakes situated in agricultural areas compared to the lakes in peatland dominated areas. 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 low C:N rations close to the Redfield TOC:TON ratio of 6.6:1 indicate algal-derived material (Redfield et al. 1963). On the basis of the whole-lake carbon isotope additions, Bade et al. (2007) showed that algal contribution to the DOC pool was 40% in the nutrient enriched lake and 5% in the more humic lake. In humic lakes the dark water color may also limit primary production.

Finnish lakes are shallow and extended littoral zones are typical. Littoral zones are important producers of organic carbon in the lake ecosystem (Wetzel 1983), and their influence on the whole-lake C budget should not be underestimated. Lauster et al. (2006) suggested that littoral zones increase whole-lake net ecosystem production especially in eutrophic systems. In our data, the ratio of shoreline length to lake area was the most important predictor for TOC ($r = 0.40$, $P < 0.001$) in the subset FIELD. 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 formation of dense littoral vegetation. Andersson and Kumblad (2006) found that the pelagial is fed with carbon fixed by primary producers in benthic and littoral zones, and that there was a strong interaction between the habitats.

Principal component analysis and the correlation analysis showed a strong relationship between TOC and TON in the subset MINERAL suggesting a more uniform origin of organic matter compared to the subsets PEAT and FIELD. 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.

Sources of CO_2 during the autumn high flow period

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. In solute budget constructed for the Ipswich River basin, Williams et al. (2005) found that chemical weathering was the largest source of Ca, Mg and SiO_2. In their study, and 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 CO_2 in UK peatland streams. The importance of the weathering processes in the catchment as a source of TIC and CO_2 may be overemphasized in our data due to autumn sampling. In autumn, the water discharge from the catchments is higher compared to winter and summer, and therefore, in-lake processes are expected to dominate in winter and summer, whereas the influence of the catchments is highlighted in autumn. The importance of decomposition processes as a source of CO_2 in Finnish lakes during stagnation periods was shown in Striegl et al. (2001) and Kortelainen et al. (2006).

Lake water CO_2 correlated with TOC suggesting that decomposition of organic matter is another important source of CO_2 in lakes as shown in Swedish lakes by Sobek et al. (2003). In our study, CO_2 was also strongly associated with TN, TON, NO_3, NH_4 and TP, implying the importance of the quality of organic matter and availability of nutrients for the decomposition processes.

In Finnish lakes most of the TN is organic (88% in the whole dataset). A loose connection between TOC and TON in the whole dataset and in the subsets PEAT and FIELD suggests several sources of organic matter. In the subset FIELD, a low TOC:TON ratio indicates an algal contribution. Raymond and Bauer (2001) showed that heterotrophic bacteria in the river water preferred young labile DOC over old refractory DOC, and furthermore, autochthonous carbon was preferentially utilized by bacteria compared to terrestrial DOC (Kritzberg et al. 2004). Bacterial growth on allochthonous organic carbon in lake water was also shown to be more efficient after addition of inorganic nutrient (N and P) (Reche et al. 1998). 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. Furthermore, the water soluble and bioavailable organic carbon have been shown to be higher in agricultural soils than in forest soils (Boyer and Groffman 1996).

Higher CO_2 as well as TIC in lakes in agricultural areas compared to other subgroups corroborates the hypothesis of the multiple sources of CO_2. The high availability of organic matter for decomposition in lakes contributes to high pCO_2 in the subset FIELD, but weathering is also more efficient in disturbed, fine-structured soils. 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 by available for further decomposition (Granéli et al. 1996). Part of the difference in inorganic carbon concentrations between the subsets PEAT and FIELD is due to the lower equilibrium level of lake water CO_2 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 regular liming.

The domination of decomposition processes versus weathering processes as a principal regulator of CO_2 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 pCO_2 were emphasized, whereas different processes dominated pCO_2 concentrations in the subsets. In the subset PEAT, where on average 48% of each catchment consists of forests on mineral soils (Table 1), weathering in the catchments controlled CO_2 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 CO_2, supported by the close connection with TON, NO_3 and NH_4 in the PCA analysis. Both processes were indicated to be important in the subset MINERAL. The results also indicated that more uniform is the land use in the catchment, and consequently the quality of the allochthonous organic matter, the stronger is the connection between TOC and CO_2. This is supported by the strong relationship in PCA and correlation analysis between lake water TOC and pCO_2 in the subset MINERAL, with the most uniform land use of all the subsets.

Silicate (SiO_2) correlated positively with both TIC and CO_2 and was included in the multiple regression models for CO_2. The decomposition of organic matter produces organic acids and carbon dioxide, both of which enhance weathering and thus SiO_2 concentrations. The increase in the proportion of vegetation cover increased the fluxes of weathering products such as dissolved silica in arctic Swedish rivers (Humborg et al. 2004; Smedberg et al. 2006) and furthermore, there was a positive relationship between TOC and dissolved silica in arctic rivers. For example some wetland plants have been shown to accumulate large quantities of amorphous silica (Struyf and Conley 2008). Probably due to this dual relationship, in the PCA analysis of the whole dataset SiO_2 is not associated with either of the two main principal components and has little influence on pCO_2 in lakes.

Conclusions

Organic carbon dominated the TC pool in boreal Finnish lakes. The proportion of inorganic carbon was highest in agricultural areas. Weathering was the main source of TIC in lakes, and in agricultural areas both weathering and export of inorganic carbon from the catchments was enhanced by fine structure of soils. Furthermore, due to the high pH of these lakes, a smaller part of TIC was in gaseous form.

Two contrasting sources of CO_2 in lakes could be identified in the statistical analysis of the data: weathering processes in the catchments and decomposition of organic matter were both important sources of CO_2 in boreal, Finnish lakes during autumn overturn. The importance of these two processes as the regulators of CO_2 in lakes varied in different catchment types. In agricultural areas and in the catchments of forested mineral soils, decomposition processes were suggested to be the main regulator of CO_2, whereas in peatland rich areas (on average 44% peatlands), weathering processes controlled CO_2. CO_2 was also strongly associated with total nutrients TN and TP, implying the importance of the quality of organic matter for decomposition. Highest CO_2 in lakes was recorded in agricultural areas: weathering is more efficient in disturbed, fine-structured soils, and furthermore, high availability of nutrients in these lakes enhanced both primary production and decomposition.

Acknowledgments This study was supported by the Academy of Finland. We thank Jussi Vuorenmaa for valuable help with water quality and catchment data.

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