The importance of winter for carbon emissions from boreal lakes

Cecilia Larsson

The importance of winter for carbon emissions from boreal lakes

Cecilia Larsson

Abstract

The aim of this study was to investigate the importance of winter season for the production of carbon dioxide (CO_2) and methane (CH_4) in humic and clear-water boreal aquatic systems. The study was conducted in 16 experimental ponds in northern Sweden during the winter of 2013. Half of the ponds had a higher concentration of dissolved organic carbon (DOC). CO_2, CH_4, DOC and dissolved inorganic carbon (DIC) were measured repeatedly under the ice from January to April. The results show that CO_2 was accumulated continually during winter. No difference in winter accumulation were found between humic and clear ponds. CH_4 was rarely accumulated in neither humic nor clear ponds, and was not an important part of the gas flux at spring ice melt. At ice melt, the flux from humic ponds accounted for 1.6 g C m^{-2} and 1.7 g C m^{-2} from clear ponds, which was equivalent for 15.6% respective 100% of the annual gas emissions. On a whole-year basis humic ponds acted as a source of 10.3 g C m^{-2}, while clear ponds acted as a sink of 14.7 g C m^{-2}. 76 mg m^{-2} d^{-1} DOC was consumed in humic and 59 mg m^{-2} d^{-1} DOC in clear ponds while the DIC accumulation was 125 mg m^{-2} d^{-1} in humic and 118 mg m^{-2} d^{-1} in clear ponds. This study stresses the importance of ice-covered boreal aquatic systems as a significant parts of the global carbon cycling.

Key words:carbon dioxide, methane, winter accumulation, boreal lakes, dissolved organic carbon

Table of contents

1 Introduction and aim

The importance of winter for emissions of carbon dioxide (CO_2) and methane (CH_4) from boreal lakes has received more attention during recent years because of their significant role in the global carbon cycle. CO_2 and CH_4 are produced in lake water and large concentrations of these gases build up during winter in ice-covered lakes. During the spring ice melt, the gases are emitted to the atmosphere which is of great importance for the annual gas emissions from lakes (Huttunen et al. 2002, Karlsson et al. 2013). Higher dissolved organic carbon (DOC) content is believed to give higher production of CO_2 (Ojala et al. 2011, Riera et al. 1999) but for CH_4 the results are generally the opposite (Juutinen et al. 2009, Ojala et al. 2011, Riera et al. 1999).

1.1 Aim
The aim of this study was to investigate the importance of the winter season for the production of CO_2 and CH_4 in humic and clear-water boreal aquatic systems.

Three specific questions were addressed:
1) How much CO_2 and CH_4 has been accumulated under ice at ice melt?
2) How much CO_2 and CH_4 is emitted during spring ice melt?
3) What is the importance of the ice melt for the annual carbon emission of the lakes?

To conduct this study an experimental pond system containing 16 experimental pond sections were used. Half of the ponds have a higher content of DOC, which makes it possible to compare the production of CO_2 and CH_4 in water with different DOC content but with exact surrounding conditions.

1.2 Background
Carbon in different forms plays an important role in the earth's ecosystems. It is an important "brick", building up both inorganic and organic structures and it works as an carrier of energy, trace substances and metals. It is also part of the most important buffer system on earth and a climate regulator (Broberg and Jansson 1994, IPCC 2007). In order to predict future global climate it is important to understand all natural processes that are involved in the cycling of carbon on earth.

The atmospheric concentration of CO_2 has increased from around 280 ppm before the industrial era to over 384 ppm in 2008. Meanwhile, CH_4 has increased from a pre-industrial value of around 715 ppb to 1774 ppb in 2005 (IPCC 2007). About half of this increase is represented by the anthropogenic emissions. The other half is accumulated in terrestrial and oceanic ecosystems. Anthropogenic sources stands for 9.1 Pg C yr^{-1} of which 5.0 Pg C yr^{-1} is accumulated in ecosystems and the remaining 4.1 Pg C yr^{-1} is accumulated in the atmosphere and causes an enhanced greenhouse gas effect. Recent estimates suggest that inland waters transport, mineralize and bury ~2.7 Pg C yr^{-1}. This is similar to the size of the terrestrial carbon sink of 2.8 Pg C yr^{-1}, while marine sequestration accounts for 2.2 Pg C yr^{-1} (Battin et al. 2009).

Boreal lakes play a central role in the global carbon cycle while transforming terrestrial carbon to CO_2 and CH_4 and emitting these greenhouse gases (GHG) to the atmosphere

(Battin et al. 2009, Tranvik et al. 2009). The global carbon cycle has historically consisted of two active boxes, oceans and land, and has been connected to the third box, atmosphere, through gas exchange (Bolin 1981, Siegenthaler and Sarmiento 1993). As models developed, more processes were added to make them more advanced, but inland waters were still rarely included in these models (e.g. Parton et al. 1994, Foley et al. 1996, Canadell et al. 2000, Cramer et al. 2001). Although, as mentioned earlier recent studies does consider lakes as an important source of GHGs (e.g. Cole et al. 2007, Battin et al. 2009). These new findings give boreal lakes an important function in the global carbon cycle. Biogeochemical processes in lakes are closely linked to the terrestrial ecosystems due to the fact that they receive allochthonous carbon (carbon from outside the aquatic systems, e.g. plant and soil material) from streams, ground water and surface water (Hope et al. 1996).

Carbon dioxide in boreal lakes is produced by respiration in water and sediments (Casper et al. 1999) or by photo-oxidation of organic material (Cole et al. 2007). Supersaturation of CO_2 in lakes can also originate from inflow of supersaturated ground water from the catchment (Riera et al. 1999, Stets et al. 2009). CO_2 is the most important greenhouse gas and stands for around 70% of the enhanced greenhouse effect. CH_4 stands for around 20% but has about 25 times stronger effect on the climate (Cole et al. 2007). Lakes are commonly net sources of CO_2 and CH_4 to the atmosphere but can simultaneously bury organic carbon in their sediments (Cole et al. 2007). The main pathway in the exchange of CO_2 between air and water are molecular diffusion in the air-water interface (Casper et al. 1999). CO_2 is highly soluble and high concentrations can therefore be accumulated at depth in lakes (Casper et al. 1999). Lakes can display a uptake of CO_2 due to a high primary production (Schindler et al. 1972) and therefore act as a sink of carbon (Casper et al. 1999). However, several studies has shown that boreal lakes more often are net sources of CO_2 to the atmosphere (Cole 1999, Cole et al. 2000, Huttunen 2003).

CH_4 is only produced in anaerobic environments, mainly in anoxic sediments but also in anoxic parts of the water column (Casper et al. 1999). CH_4 has at least four different pathways from lakes to the atmosphere; ebullition flux, diffusive flux, storage flux and flux through aquatic vegetation. Ebullition means that CH_4 is transported directly from the sediment to the atmosphere and with little CH_4 oxidation in the water column. Of the CH_4 entering the water column or oxic sediments a large proportion is oxidized by methane-oxidizing bacterias. The part of CH_4 that is not oxidized will most likely escape the lakes through diffusive flux. In stratified lakes there can be a build-up of CH_4 in anoxic sediments and this storage will be released during lake turnover, mainly during spring and fall, as storage flux. The last pathway is plant-mediated flux via vegetation in the littoral zone and is seldom included in measurements of CH_4 flux. Ebullition is measured to stand for 50-60% of the flux while diffusive flux stands for 10-50% and storage flux stands for 0-45% (Bastviken et al. 2004).

Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) are the predominant carbon inputs into lake ecosystems, and the importance of these inputs varies between lake location and hydrology (Tranvik et al. 2009). DOC concentration is particularly important in lakes; increased DOC concentrations decrease light penetration which is important for the photosynthesis of the lake. The decreased light penetration is regarded to especially affect the benthic primary production due to the fact that benthic algae are light limited. This means that the increased DOC concentrations stand for a double effect when both repressing

the primary production and enhancing the respiration (Ask et al. 2012, Cole et al. 2007). The repression of the primary production decreases net ecosystem production (NEP) resulting in increased emissions of CO_2 from lakes to the atmosphere (Ask et al. 2012).

Comparative studies of differences between clear and brown-water lakes and their contribution of CO_2 and CH_4 are few. However, the flux of CO_2 is found to be around two times higher from humic lakes than from clear-water lakes. Humic lakes is in addition a steady source during the open-water season, while clear-water lakes are shifting more between undersaturation and supersaturation (Ojala et al. 2011, Riera et al. 1999). For CH_4 the pattern is not as fully understood as for CO_2. In a North American study the concentration of CH_4 were only slightly above detection level and highest in humic lakes after ice melt (Riera et al. 1999). In an Finnish study the CH_4 flux were 21-27% higher from clear-water compared to humic lakes (Ojala et al. 2011). Another Finnish study explored the variability in annual CH_4 flux and found that the fluxes were highest from humic lakes (around three times higher than from clear-water lakes). They also found that the morphology was important, having the highest concentrations in small, shallow humic lakes (Juutinen et al. 2009).

During winter the GHGs is accumulated under the ice and the ice melt is found to be of relatively big importance to the annual emissions. This spring pulse of GHGs could contribute to between 12 to 55% of the annual emissions from boreal lakes and the relative importance of winter is therefore especially interesting to study (Demarty et al. 2011, Huttunen et al. 2002, Huttunen et al. 2003, Karlsson et al. 2013, Michmerhuizen et al. 1996). CO_2 appear to be the main supplier of GHGs to spring emissions and in some lakes no CH_4 has been found at all. CH_4 is, as described before, often oxidized before entering the surface water (Demarty et al. 2011) and a large proportion is emitted through ebullition (Bastviken et al. 2004), which makes it hard to measure properly. The general seasonal patterns of CO_2 and CH_4 in lakes is that the gas accumulates under ice during winter. When ice melt occurs the surface water contains a high concentration of GHGs which are rapidly degassed during spring. During summer stratification CO_2 and CH_4 decrease in the epilimnion due to diffusive flux to the atmosphere, phytoplankton uptake and CH_4 oxidation. Meanwhile, GHGs builds up in the hypolimnion. At autumn turnover the concentration is once again high in the surface water (Riera et al. 1999).

2 Material and methods

2.1 Study site
All measurements were carried out at Röbäcksdalen, Umeå where Umeå University have twenty experimental ponds. The first section with pond 1-8 are heated by +3° C above ambient temperature during summer, and in four of them DOC is added (figure 1). The water with DOC comes from the nearby humic stream Pålböleån. Pond 9-12 is a control section not measured in this study. The last section with pond 13-20 have the ambient temperature on the water and in four of them DOC is added as well. The heating of the ponds during summer is not believed to impact the winter values. Water with DOC is added until the ponds are ice-covered to imitate a natural system were terrestrial DOC is only added during the ice-free season. The ponds are 8 x 10 meter and 1,7 meters deep. The fact that the measurements were conducted in these ponds instead of natural lakes makes it easier to

compare the formation of CO_2 and CH_4 in water with different DOC concentrations but with comparable catchment characteristics and surroundings.

2	1	
4DOC	3 DOC	Heated
6	5	
8 DOC	7 DOC	
10	9	
12	11	
14 DOC	13 DOC	
16	15	Ambient
18 DOC	17 DOC	
20	19	

Figure 1. Experimental ponds where measurements were conducted. Pond 1-8 are heated with +3° C during summer and in four of the ponds DOC is added. Pond 9-12 are control ponds not measured in this study. Pond 13-20 have the ambient temperature and in four of them DOC is added as well.

2.2 Field work

The ponds were sampled for CO_2, CH_4, DIC, DOC, O_2, temperature, ice thickness and depth. The sampling was done every second or third week from the end of January to mid-April through a hole in the ice. Water was collected with a Ruttner sampler (0.5 meter long, 5 cm diameter) from 0.5 meter below the ice. For DOC, DIC and CH_4 samples, a 250 ml polyethene bottle for each pond were overfilled with water without creating any air bubbles. Three 60 ml polyethene syringes per pond were filled with water and used for CO_2 measurements using a headspace equilibrium technique (Cole et al. 1994). 20 ml of each sample was disposed and filled up with 20 ml of air. Additionally, the ice thickness and water depth was measured for each pond and O_2 concentrations and temperature was measured at 0.5 meter using a oxygen-temperature meter (ProODO, YSI Inc.) Samples were stored in cooler bags until they were prepared at the laboratory the same day. The same type of samples were taken the previous ice-free season and that data was available to get a yearly budget of CO_2, CH_4 and DOC.

2.3 Laboratory analyses

For the DIC and CH_4 samples, 22 ml glass gas chromatography (GC) vials containing 50 μl 1.2 M HCl and were flushed with N_2-gas for three minutes, were filled with 4 ml of sample water from the polyethene bottles. It was important that the water injected to the vials did not contain any air bubbles. The samples were analyzed using a gas chromatograph (Clarus 500, Perkin-Elmer Inc.). For DOC analysis, water from the polyethene bottles was used, and filtered using burnt (550° C, 1 hour) 0.45 μm GF/F filters. 50 ml Falcon tubes were rinsed with the filtered lake water and then filled up with 40 ml water. The samples were acidified with 500 μl 1.2 M HCl to stop microorganisms to grow and to get rid of DIC from the water. DOC samples were stored cold until they were analyzed with a combustion chamber (IL-550 TOC-TN analyzer, Hach Lange Gmbh). DIC, DOC and CH_4 were analysed the same month as the sampling was conducted.

CO_2 measurements were conducted on the same day as sampling. The three shaken syringes containing 40 ml of the water from each pond were used. Syringes were shaken for one minute to equilibrate air and water phase, and left for another minute to stabilize. The headspace gas was transferred to a plastic syringe, and the partial pressure of CO_2 (pCO_2) was analyzed using a infrared gas analyzer (IRGA 5000 ppm, EGM-4, PP-Systems Inc.). Measured values were calibrated against CO_2 standard gases. The concentration of CO_2 in the water in each syringe was calculated from the concentration of pCO_2 in the headspace using Henry's law (Cole et al. 1994) and the ideal gas law. The reading of atmospheric pCO_2 was done every sampling day, to be used for the calculation of CO_2. Additionally, temperature of the water samples was measured and used for calculations of CO_2 concentration.

2.4 Flux estimations

The diffusive flux of CO_2 and CH_4 during the ice-free season was calculated on the basis of surface water concentrations using Fick's law (Jonsson et al. 2008). The diffusive flux F (mol m^{-2} d^{-1}) between the water surface and the atmosphere was calculated as:

$$F = k \ x \ (C_{water} \ x \ C_{equ}) \tag{1}$$

where k is the gas transfer coefficient (cm h^{-1}), C_{water} is the measured surface concentration of CO_2 and CH_4 and C_{equ} is the air-water equilibrium concentration. The k_{600} is the gas transfer coefficient at a certain temperature with a Schmidt number (Sc) of 600. Mean temperature values were collected from a weather station at the nearby Umeå airport (Statistiska centralbyrån 2012). K for gas fluxes was therefore calculated from k_{600} (Jähne et al. 1987):

$$k = k_{600} \ (Sc_t/Sc_{600})^n \tag{2}$$

Sc_t for the measured temperature was calculated as done by Wannikhof (1992) and the exponent n was assumed to be -0.5 since all water surfaces were supposed to be rippled (Jonsson et al. 2008). Fluxes from the ponds were reliant on a wind-dependent k_{600} function (cm h^{-1}) (Cole and Caraco 1998):

$$k_{600} = 2.07 + 0.215 \ U_{10}{}^{1.7} \tag{3}$$

U_{10} is the wind speed at a height of 10 meters and these data was collected from Umeå airport. Ice-free season was estimated to last between 1th May to 1th November (184 days), the ice-covered season between 1th November to 15th April (166 days) and the ice melt with spring outgassing was estimated to last between 15th April to 1th May (15 days). Emission of CO_2 and CH_4 at ice melt were estimated as the difference in concentration between the last sampling occasion under spring ice and the first open water sampling the previous ice-free season.

2.5 Statistics and other calculations

For statistical comparison between humic and clear ponds at ice melt, Student's t-test were performed at a α-level of 0.05. Uncertainties are always presented as the standard deviation (±SD). Microsoft Office Excel was used for statistics and for graphical presentations.

To investigate the relationship between DIC accumulation and DOC comsumption in the ponds during winter, the daily accumulation and consumption rate were calculated by taking the difference in total amount of DIC and DOC between the first sampling at winter and the

last sampling where a increasing trend were seen. In April the ponds started to melt and the system was not totally intact, therefore the value from measurements in mid-March was used. The sums were divided by the amount of days between the two sampling occasions.

3 Results

3.1 Water chemistry and physical parameters

The results in this section are mean values based on six sampling occasions during January to April 2013 (table 1). O_2-values from one sampling occasion in Febuary are excluded due to technical failure. Water temperature was around 2.2-2.3 °C and did not differ significantly between the two types of ponds before ice melt (t-test, p = 0.5). DOC-values before ice melt differed significantly (t-test, p = 0.02) and were about two times higher in humic than in clear-water ponds. The mean value in all ponds during the winter season was 6.6 ± 3.6 mg L^{-1}. DIC-values did not differ significantly between humic and clear ponds (t-test, p = 0.1) and mean value in all ponds during the winter season was 7.1 ± 2.7 mg L^{-1}.

Table 1. Mean values with standard deviation (± 1 SD) for O_2, water temperature, DOC and DIC during the winter season.

Type	O_2 (mg L^{-1})	Temp water (°C)	DOC (mg L^{-1})	DIC (mg L^{-1})
Humic ponds	4.8 ± 3.0	2.3 ± 0.6	8.8 ± 3.6	6.4 ± 2.7
Clear ponds	5.5 ± 2.8	2.2 ± 0.5	4.3 ± 1.4	7.7 ± 2.6

The O_2 concentration was lowest at the end of February and the beginning of March, and started thereafter to increase (figure 2). The concentration was around 1 mg L^{-1} higher in clear than in humic ponds, but did not differ significantly (t-test, p = 0.1). Mean values during winter for all ponds at single sampling occasions were between 6.3 ± 2.1 mg L^{-1} and 4.6 ± 3.0 mg L^{-1}.
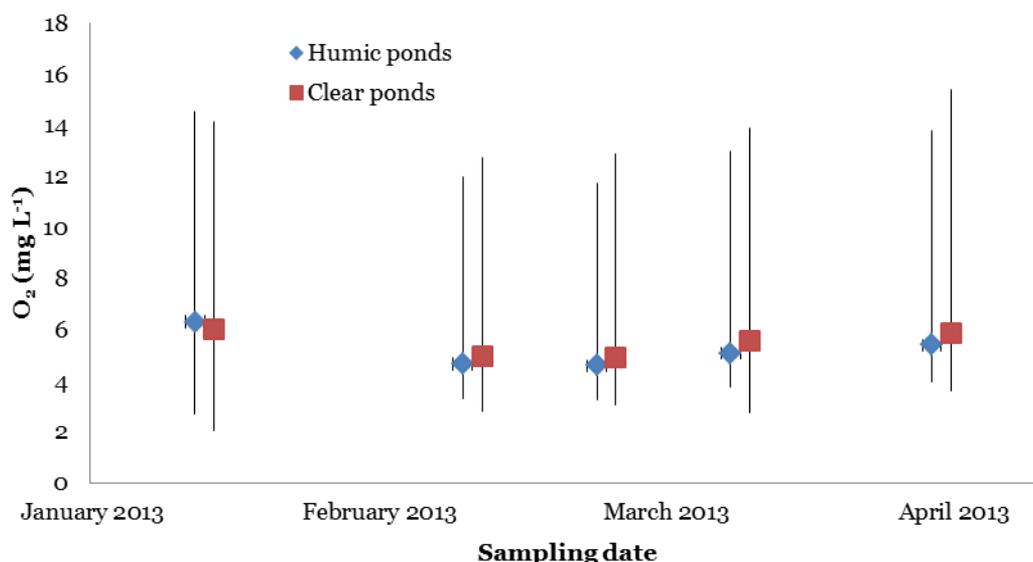

Figure 2. Mean (± 1 SD) O_2-values for the winter season in humic and clear ponds.

3.2 Accumulation during winter

The CO_2 concentration showed the same pattern in both types of ponds with concentrations around 1.5 mg L^{-1} in January, increasing values to the highest concentrations in end-March

and thereafter decreasing concentrations (figure 3). The CO_2 concentration was initially higher in ponds with DOC, but higher in clear ponds in mid-winter. No statistical difference were found between the two types of ponds at ice melt (t-test, p = 0.6). Values from one sampling occasion in February are excluded from figure 3 due to technical failure.
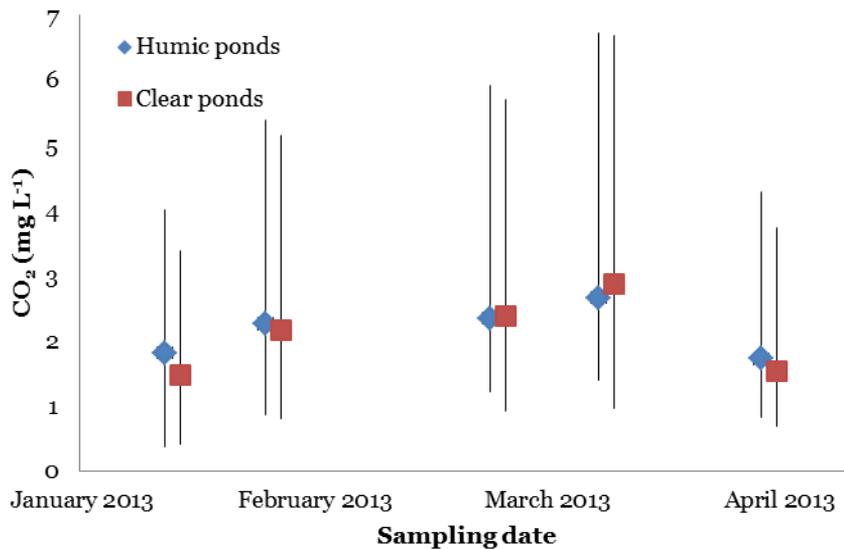

Figure 3. Mean (± 1 SD) CO_2-values for the winter season in humic and clear ponds.

The CH_4 concentration was slightly above detection level during the whole winter, and showed a marginally increasing trend (figure 4). Clear ponds showed the highest values before ice melt but the difference between the two types of ponds at ice melt was not significant (t-test, p = 0.4).
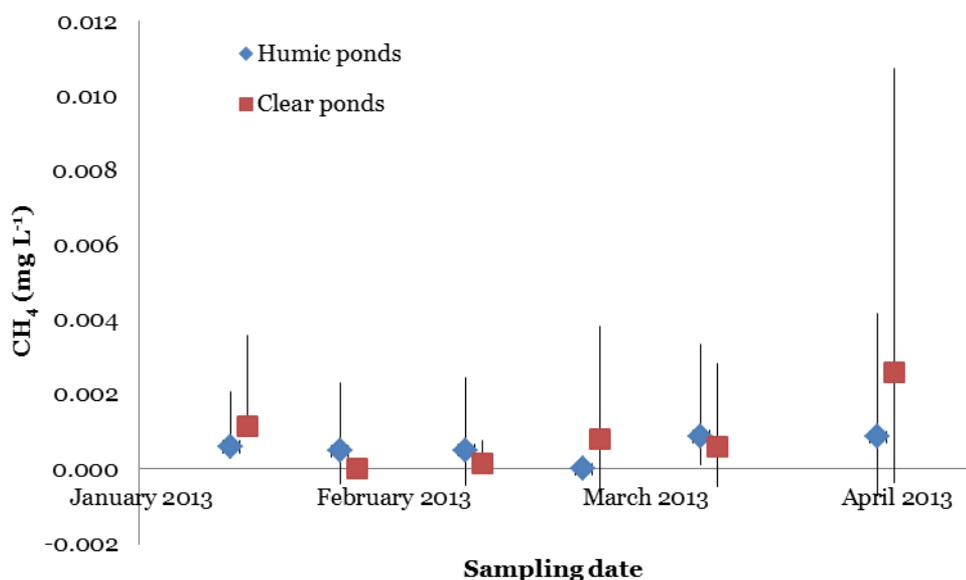

Figure 4. Mean (± 1 SD) CH_4-values for the winter season in humic and clear ponds.

The DIC and DOC followed a opposite pattern, i. e. when DOC was consumed during winter, more DIC was formed through respiration (figure 5). In absolute numbers 76 mg m^{-2} d^{-1} DOC was consumed in humic ponds and 59 mg m^{-2} d^{-1} DOC in clear ponds (t-test, p = 0.3). The

DIC accumulation was 125 mg m^{-2} d^{-1} in humic ponds and 118 mg m^{-2} d^{-1} in clear ponds (t-test, p = 0.7).
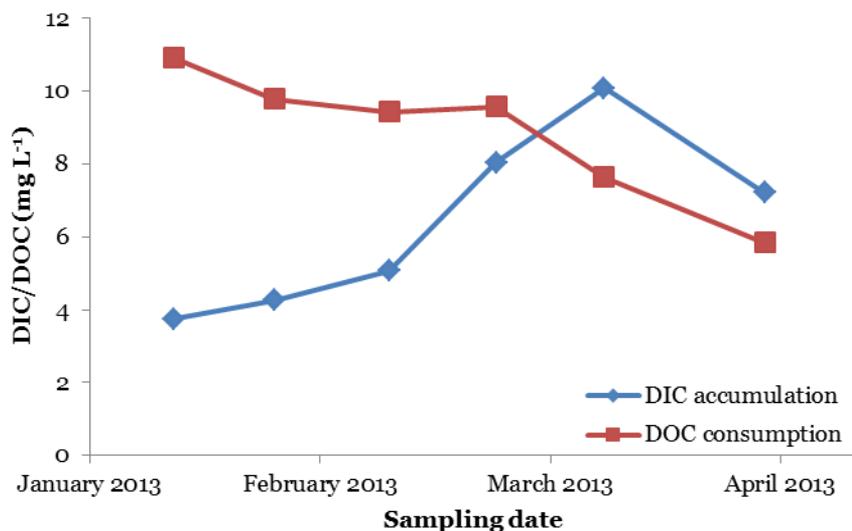

Figure 5a. Mean (± 1 SD) DIC and DOC concentrations in humic ponds.
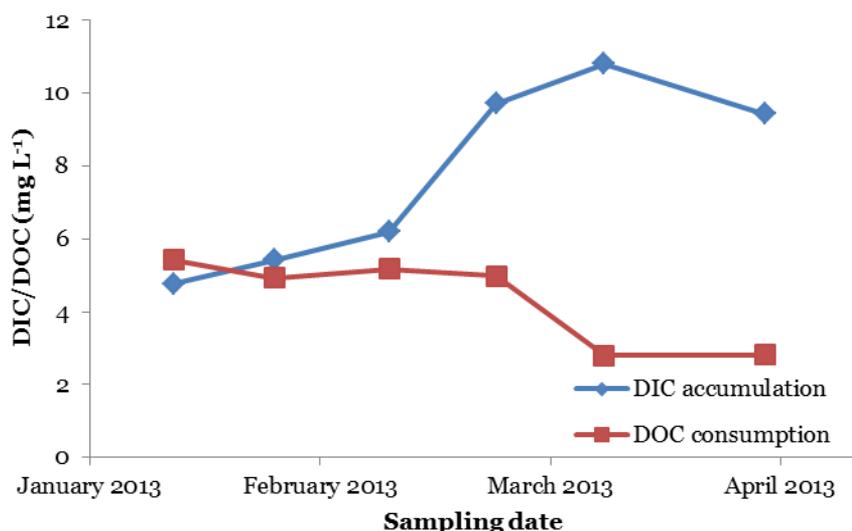

Figure 5b. Mean (± 1 SD) DIC and DOC concentrations in clear ponds.

3.3 Flux at ice melt and yearly carbon budget

Humic ponds were emitting CO_2 and CH_4 during the whole summer, while clear ponds acted as a sink for carbon (figure 6). Clear ponds emitted slightly more carbon than humic ponds at ice melt. On a whole-year basis humic ponds acted as a source of 10.3 g C m^{-2}, while clear ponds acted as a sink of 14.7 g C m^{-2}. The relative importance of spring ice melt for the whole year carbon budget was 15.6% for humic ponds and 100% for the clear ponds. CO_2 was the predominant gas at spring ice melt and attributed for 99.9% in humic ponds and 99.8% in clear ponds.
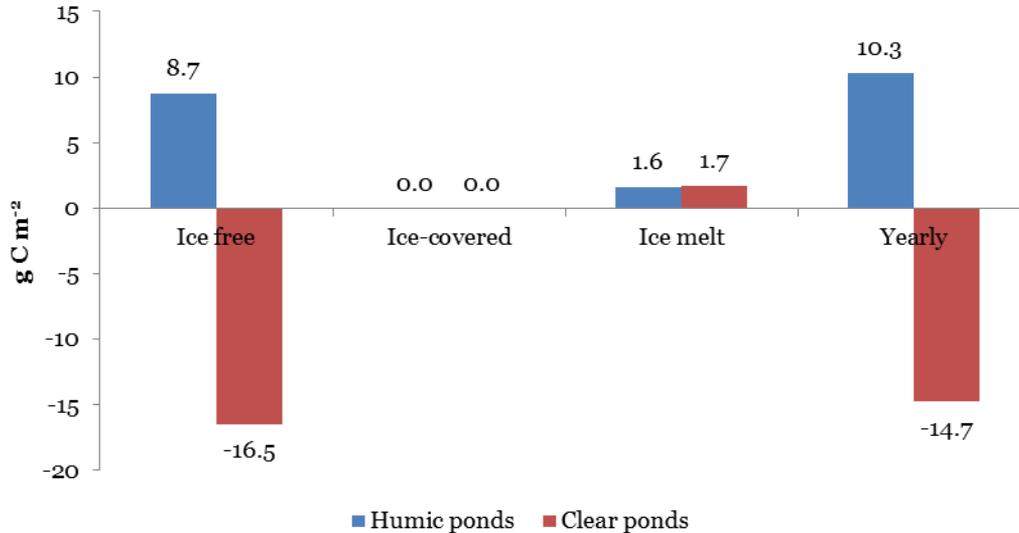
Figure 6. Emissions from the experimental ponds during a whole year.

4 Discussion

CO_2 was accumulated in both humic and clear ponds during the whole winter, showing the highest values in mid-March with around 2.5 mg L^{-1}. The concentration of CO_2 and CH_4 increases until end-March and then show a small decrease, while O_2 show the opposite trend. This might be due to thawing of the ice at the sides of the ponds in early spring which gives a outgassing of CO_2 and an influx of O_2 during the rest of the winter. Another factor that can influence the result is that the last sampling was not done exactly before and after the ice melt occurred due to weak ice. The amount of gas that eventually is built up should however not make a major difference in the results. Many studies have calculated the potential spring flux by using the amount of accumulated gas and the amount of gas at atmospheric equilibrium. Many lakes are however supersaturated with CO_2 giving an overestimation in the result (Demarty et al. 2011). In this study the amount of gas in the water after ice melt was used instead of the atmospheric equilibrium, which probably is a better method for estimating the spring flux.

When comparing with results from studies conducted in natural lakes, the results from this study equals the lowest range of measured concentrations of CO_2. In a Canadian study concentrations from 0.6 to 4.8 mg L^{-1} CO_2 was found (Riera et al. 1999), while in Finland the measured concentration was 3.2 mg L^{-1} CO_2 (Kortelainen et al. 2006) and in Sweden 5.6-28.1 mg L^{-1} CO_2 (Karlsson et al. 2013). The ponds do not have as much organic rich sediment as many natural lakes and therefore not as much available organic matter that can form CO_2 and CH_4 under the ice during winter. This might explain why the values are slightly lower than from the studied natural lakes. Another reason might be that the ponds have started to taw at the last sampling occasion. At the sampling before, in late March, was the mean value 2.9 mg L^{-1} CO_2 in humic ponds and 2.6 mg L^{-1} CO_2 in clear ponds which still is in the lower range but closer to other reported studies.

The DIC concentration during the winter were similar in both types of ponds, but the DOC concentration were slightly higher in humic ponds. The concentrations could be interpreted

9

as a rough measurement of DIC accumulation and DOC consumption. This may mean that the DOC consumption is of a lower importance for DIC accumulation in clear ponds than in humic ponds and that the carbon that is mineralized in clear ponds comes from for example the sediments. The difference in DOC consumption is however not significant and the study is too limited to conclude which type of carbon controls the mineralization. The ponds will probably act more as natural lakes in a few years when the organic carbon pool in the sediments is greater. The pelagic habitats in clear-water lakes are more dependent on a constant supply of organic carbon while the respiration in benthic habitats can sustain at winter thanks to the pool of organic carbon accumulated at bottom. This is likely why the DOC consumption is slightly less important in clear ponds (Karlsson et al. 2008).

The concentration of CH_4 were slightly above detection level the whole winter in this study. Other studies show results that are to some extent higher, 0.08-6.9 mg L^{-1} CH_4 (Karlsson et al. 2013) and 0.004-0.7 mg L^{-1} CH_4 (Riera et al. 1999). Much of the CH_4 that is produced in anoxic sediments is oxidized when entering the water column or transported via ebullition (Bastviken et al. 2004) and the fact that only diffusive flux is measured in this study makes the results conservative. Measuring ebullition, and also flux through aquatic vegetation, would give a more comprehensive result. However, for a study of this size it was only possible to measure the diffusive flux. As mentioned before anoxic sediments are needed for the formation of CH_4 and the ponds do most likely have good O_2 conditions during the whole winter. O_2 is not measured in the bottom layer but the values in the water column are far from anoxic during the whole winter which prevents CH_4 production. The main reason for the low CH_4 values might, as for CO_2, be that the ponds have limited amounts of organic rich sediment compared to natural lakes. Even though CH_4 has around 25% stronger effect on the climate compared with CO_2 (Cole et al. 2007) it is clear that the emissions of CH_4 from the ponds are of little concern. In this study CH_4 was responsible for only 0.06-0.2% of the annual gas emission. This is in line with other findings from boreal systems. Huttunen et al. (2003) reported that CH_4 accounted for 0.4-6% and Demarty et al. (2011) reported results where CH_4 accounted for 0.2-6.5% of the spring gas flux.

The ice melt period had a great importance to the annual carbon cycle, especially for the clear ponds where it accounted for 100% of the annual outgassing. This is a result that is, to my knowledge, rather unusual. The fact that the clear ponds act as carbon sinks on an annual basis makes it even more remarkable. Lakes can act as sinks part of the year due to high primary production (Casper et al. 1999) but the majority are net sources on an annual basis. Karlsson et al. (2013) quantified the annual gas flux in twelve subarctic lakes and in three of them the spring ice melt switched the lakes from being a small sink to a small net source. In the humic ponds, the spring ice melt accounted for 16% of the annual carbon emissions and this is more in line with other studies. Three recent studies have found that the spring ice melt stand for 30-52% (Demarty et al. 2011), 13-29% (Huttunen et al. 2003) and 11-55% (Karlsson et al. 2013). This means that the flux at spring ice melt is a important event for the annual gas emissions that has to be included in estimations of global carbon cycles.

No significant difference was found between how much CO_2 and CH_4 that was produced during the winter season in humic and clear ponds. The flux at spring ice melt is also similar in the two different types of ponds. There are not many studies that compare the production of CO_2 and CH_4 and the yearly flux in clear-water and brown-water systems, but one of them conclude that the concentration of CO_2 prior to spring ice melt is ten to fifteen times higher

in brown-water lakes and that the flux at spring ice melt is around two times higher from brown-water lakes (Riera et al. 1999). The catchment in natural lakes often differ between clear-water and brown-water lakes even when they are located in the same region. Since the ponds have the same surroundings, the only difference between them is the concentration of DOC. This means that one can conclude that there are other factorsthan only the DOC concentration, for example depth and area, that determine the CO_2 production. Humic and nutrient-rich lakes are more commonly small and shallow, resulting in more efflux from small brown-water lakes (Juutinen et al. 2009). Keeping this in mind is it clear that depth and lake area are two aspects that has to be taken into account when comparing clear-water and brown-water systems. The fact that the ponds are of exact same size and with the same surroundings might be the reason that there is no difference between humic and clear ponds.

During the open-water this study show a bigger difference between humic and clear ponds. The clear ponds are a sink of CO_2 almost the whole open-water season and becomes a source first in October. The humic ponds are instead weak sinks at a few times during summer, but acts more often as sources of CO_2 and CH_4 (unpublished data). Earlier research has shown that lakes turn from net autotrophy to heterotrophy when the DOC concentration exceeds 4-6 mg C L^{-1} (Sobek et al. 2006). The clear ponds in this study has a mean DOC concentration around 4 mg C L^{-1}, meaning that they are in the zone between autotroph and heterotroph systems. Other studies found the same seasonal pattern when comparing a brown-water and a clear-water lake (Ojala et al. 2011, Riera et al. 1999). In their studies the brown-water lakes were always a source of CO_2 during the open-water season and the flux was 38-42% higher than from the clear-water lakes. The clear-water lakes acted as a sink or near-zero efflux but was a source from late summer.

4.1 Conclusions

The aim of this study was to investigate what importance the winter season has the for production of CO_2 and CH_4 in aquatic systems in the boreal area. CO_2 was accumulated successively during winter and was also a significant source of the annual gas flux, especially in clear ponds. However, CH_4 was rarely accumulating in the ponds and was not a important part of the gas flux at spring ice melt. Probably because the ponds were well-oxygenated throughout the winter. The difference between humic and clear ponds was almost absent. This result was not expected and the absence of difference might be due to the fact that the ponds are of the exact same size and that other factors, for example depth and area, are more important for the production of GHGs. During the open-water period, the difference between the two types of ponds was greater, clear ponds acted as sinks and humic ponds as sources of CO_2 and CH_4. The results from this study are important both for understanding how carbon is circulating in boreal terrestrial and aquatic ecosystems and for predicting future climate changes. Small lakes are dominating the boreal area (Juutinen et al. 2009) and play a significant role in the carbon cycling in the boreal area.

Small lakes with a seasonal ice-cover are a subject for undergoing changes in the climate. With the current warming trend in the global climate (IPCC 2007) it is believable that the length of the ice-cover will be shorter and that the build-up of GHGs during winter will be less important. However, the warming is thought to result in more vegetation, which probably will result in an increase in DOC input to lakes. This will affect the wintertime oxygen conditions and gas production in northern lakes. Further studies are needed to assess the magnitude of factors controlling the production of GHGs. To be able to use the data

regionally is it important to understand how hydrology, area, depth, groundwater and year-to-year variation are influencing the carbon cycling in boreal lakes.

5 Acknowledgements

6 References

Ask, J., Karlsson, J. and Jansson, M. 2012. Net ecosystem production in clear-water and brown-water lakes. *Global biogeochemical cycles*. 26, GB1017.

Bastviken, D., Cole, J., Pace, M. and Tranvik, L. Methane emissions from lakes: dependence of lake characteristics, two regional assessments, and a global estimate. *Global biogeochemical cycles*. 18, GB4009.

Battin, T., Luyssaert, S., Kaplan, L., Aufdenkampe, A., Richter, A. and Tranvik, L. 2009. The boundless carbon cycle. *Nature Geoscience,* 2, 598-600.

Bolin, B (Eds.). 1981. Carbon cycle modelling. Scope report no. 16. John Wiley and sons, Chichester. 390 pp.

Broberg, A. and Jansson, M (Eds.). 1994. Abiotiska faktorers karaktäristiska, funktion och omsättning i sötvatten. Limnologiska institutionen, Uppsala university, Uppsala. 76 pp.

Canadell, J. G., Mooney, H. A., Baldocchi, D. D., Berry, J. A., Ehleringer, J. R., Field, C. B., Gower, S. T., Hollinger, D. Y., Hunt, J. E., Jackson, R. B., Running, S. W., Shaver, G. R., Steffen, W., Trumbore, S. E., Valentini, R., and Bond, B. Y. 2000. Carbon metabolism of the terrestrial biosphere: a multitechnique approach for improved understanding. *Ecosystems*. 3,115–130.

Casper, P., Maberly, S., Hall, G. and Finlay, B. 1999. Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere. *Biogeochemistry,* 49**,** 1-19.

Cole, J. J., Caraco, N., Kling, G. and Kratz, T. 1994. Carbon dioxide supersaturation in the surface waters of lakes. *Science*. 265, 1568-1570.

Cole, J. J. and Caraco, N. F. 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF_6. *Limnology and oceanography*. 43, 647-656.

Cole, J. J. 1999. Aquatic microbiology for ecosystem scientists: new and recycled paradigms in ecological microbiology. *Ecosystems*. 2, 215-225.

Cole, J. J., Pace, M. L., Carpenter, S. R. and Kitchell, J. F. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnology and oceanography*. 45, 1718-1730.

Cole, J. J., Praire, Y., Caraco, N., McDowell, W., Tranvik, L., Striegl, R., Duarte, C., Kortelainen, P., Downing, J. and Middelburg, J. 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems,* 10**,** 172-185.

Cramer, W., Bondeau, A., Woodward, F. I., Prentice, I. C., Betts, R. A., Brovkin, V., Cox, P. M., Fisher, V., Foley, J. A., Friend, A. D., Kucharik, C., Lomas, M. R., Ramankutty, N., Sitch, S., Smith, B., White, A. and Young-Molling, C. 2001. Global response of terrestrial ecosystem structure and function to CO_2 and climate change: results from six dynamic

global vegetation models. *Global change biology*. 7, 357–373.

Demarty, M., Bastien, J. and Tremblay, A. 2011. Annual follow-up of gross diffusive carbon dioxide and methane emissions from a boreal reservoir and two nearby lakes in Quebec, Canada. *Biogeosciences*. 8, 41–53.

Foley, J. A., Prentice, I. C., Ramankutty, N., Levis, S., Pollard, D., Sitch, S., and Haxeltine, A. 1996. An integrated biosphere model of land surface processes, terrestrial carbon balance, and vegetation dynamics. *Global biogeochemical cycles*. 10, 603–628.

Hope, D., Kratz, T. K. and Riera, J. L. 1996. Relationship between P_{CO_2} and dissolved organic carbon in northern Wisconsin lakes. *Journal of environmental quality*. 25, 1442-1445.

Huttunen, J. T., Alm, J., Saarijärvi, E., Lappalainen, K. M., Silvola, J. and Martikainen, P. J. 2002. Contribution of winter to the annual CH_4 emission from a eutrophied boreal lake. *Chemosphere*. 50, 247-250.

Huttunen, J. T., Alm, J., Liikanen, A., Juutinen, S., Larmola, T., Hammar, T., Silvola, J. and Martikainen, P. J. 2003. Fluxes of methane, carbon dioxide and nitrous oxide in boreal lakes and potential anthropogenic effects on the aquatic gas emissions. *Chemosphere*. 52, 609-621.

IPPC. 2007. Climate change 2007: the physical science basis. *Intergovernmental panel on climate change.*

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.

Jonsson, A., Åberg, J., Lindroth, A. and Jansson, M. 2008. Gas transfer rate and CO_2 flux between an unproductive lake and the atmosphere in northern Sweden. *Journal of geophysical research*. 113, G04006.

Jähne, B., Munnich, K., Bosinger, R., Dutzi, A., Huber, W. and Libner, P. 1987. On the parameters influencing air-water gas exchange. *Journal of geophysical research – Oceans*. 92, 1937-1949.

Karlsson, J., Ask, J. and Jansson, M. 2008. Winter respiration of allochthonous and autochthonous organic carbon in a subarctic clear-water lake. *Limnology and oceanography*. 53, 948-954.

Karlsson, J., Byström, P., Ask, J., Ask, P., Persson, L. and Jansson, M. 2009. Light limitation of nutrient-poor lake ecosystems. *Nature,* 460**,** 506-509.

Karlsson, J. Giesler, R., Persson, J. and Lundin, E. 2013. High emission of carbon dioxide and methane during ice-thaw in high latitude lakes. *Geophysical research letters*. doi: 10.1029/2012GL054800.

Michmerhuizen, C. M., Striegl, R. G. and McDonald, M. E. 1996. Potential methane emission from north-temperate lakes following ice-melt. *Limnology and oceanography*. 41, 985-991.

Ojala, A., Bellido, J. L., Tulonen, T., Kankaala, P. and Huotari, J. 2011. Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events. *Limnology and oceanography*. 56, 61-76.

Parton, W. J., Pulliam, W. M. and Ojima, D. S. 1994. Application of the CENTURY model across the LTR network: parameterization and climate change simulations. *Bulletin of the ecological society of America*. 75, 186–187.

Riera, J. L., Schindler, J. E. and Kratz, T. K. 1999. Seasonal dynamics of carbon dioxide and methane in two clear-water lakes and two bog lakes in northern Wisconsin, U.S.A. *Canadian journal of fisheries and aquatic sciences*. 56, 265-274.

Schindler, D. W., Brunskill, G. J., Emerson, S., Broeker, W. S. and Peng, T-H. 1972. Atmospheric carbon dioxide: its role in maintaining phytoplankton standing crops. *Science*. 177, 1192-1194.

Siegenthaler, U. and Sarmiento, J. L. 1993. Atmospheric carbon dioxide and the ocean. *Nature*. 365, 119-125.

Sobek, S., Söderbäck, B., Karlsson, S., Andersson, E., Brunberg, A. K. 2006. A carbon budget of a small humic lake: an example of the importance of lakes for organic matter cycling in boreal catchments. *Ambio*. 35, 469-475.

Statistiska centralbyrån. 2012. Statistical yearbook of Sweden. A01BR1201.

Stets, E. G., Striegl, R. G., Aiken, G. R., Rosenberry, D. O. 2009. Hydrologic support of carbon dioxide flux revealed by whole-lake carbon budgets. *Journal of geophysical research-biogeosciences*. 114, GO1008.

Tranvik, L., Downing, J., Cotner, J., Loiselle, S., Striegl, R., Ballatore, T., Dillon, P., Finlay, K., Fortino, K., Knoll, L., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., Leigh McCallister, S., McKnight, D. M., Melack, J. M., Overholt, E., Porter, J. A., Prairie, Y., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek, S., Tremblay, A., Vanni, M. J., Verschoor, A. M., von Wachenfeldt, E. and Weyhenmeyer, G. A. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and oceanography*. 54, 2298–2314.

Wannikhof, R. 1992. Relationship between wind-speed and gas-exchange over the ocean. *Journal of geophysical research – Oceans*. 97, 7373-7382.