University of Alberta

GREENHOUSE GAS PRODUCTION IN EXPERIMENTAL RESERVOIRS FLOODING UPLAND BOREAL FOREST

by

Cory J.D. Matthews ©

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Abstract

The FLooded Uplands Dynamics EXperiment (FLUDEX) at the Experimental Lakes Area (ELA) assessed the relationship between the amount of organic carbon (OC) flooded during reservoir creation and the net production of the greenhouse gases (GHGs) carbon dioxide (CO_2) and methane (CH_4) in reservoirs. Three upland boreal forest subcatchments, with OC storage in soils and vegetation ranging from 41 100 to 66 000 kg C ha^{-1}, were CO_2 and CH_4 sinks prior to flooding, but were sources of CO_2 and CH_4 to the atmosphere after flooding. Reservoir GHG production was unrelated to amounts of subcatchment OC storage, but was affected by labile C available for decomposition. CO_2 production decreased during the first three flooding seasons, but increases in CH_4 production kept the global warming potential of reservoir emissions constant. The FLUDEX results indicate GHG effects of boreal reservoirs may be largely due to changes in CH_4 cycling between the undisturbed and flooded landscapes.

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Chapter 1: Greenhouse gases, reservoirs, and the boreal ecoregion

General introduction

Carbon dioxide (CO_2) and methane (CH_4) act as greenhouse gases (GHGs) in the earth's atmosphere, trapping radiative energy from the earth and subsequently causing global temperature increases and other climatic changes (IPCC, 2001). Atmospheric concentrations of CO_2 and CH_4, the two most abundant GHGs emitted through human activities, have been increasing at 0.3 to 0.4% and 0.7 to 1% per year, respectively (Khalil and Rasmussen, 1990; Dlugokencky *et al.*, 1994), although the current rate of CH_4 increase is declining (Prather *et al.*, 2001). The majority of CO_2 released to the atmosphere comes from fossil fuel combustion, and oil and natural gas burning are among anthropogenic sources of CH_4 (IPCC, 2001).

In an effort to reduce CO_2 and CH_4 emissions to the atmosphere, hydroelectric power generation has become an attractive alternative to thermal power generation because it is widely accepted as a carbon-free source of energy (Hoffert *et al.*, 1998; Victor, 1998). However, Rudd *et al.* (1993) hypothesised that reservoirs created for all purposes (hydroelectricity production, flood control, irrigation, etc.) are sources of CO_2 and CH_4 to the atmosphere because following flooding, bacteria begin to decompose organic carbon (OC) stored in flooded plants and soil complexes, converting it to CO_2 and CH_4, which are then released to the atmosphere. Furthermore, terrestrial plants no longer assimilate carbon through photosynthesis, and terrestrial soils stop consuming CH_4. The *net* effect of reservoir creation on atmospheric CO_2 and CH_4 concentrations incorporates both the pre- and post-flood carbon dynamics of the flooded landscape.

Several studies have since focused on estimating emissions from reservoirs in temperate and tropical regions, and have found that all reservoirs emit both CO_2 and CH_4 to the atmosphere (Duchemin *et al.*, 2000; Duchemin *et al.*, 1995; Galy-Lacaux *et al.*, 1997; Galy-Lacaux *et al.*, 1999; Kelly *et al.*, 1997; Scott *et al.*, 1999; Campo and Sanchluz, 1998; Rosenberg *et al.*, 1997). Average emissions from temperate reservoirs range from 220 to 3450 mg CO_2 m^{-2} day^{-1} and 3 to 79 mg CH_4 m^{-2} day^{-1}, while average emissions from tropical reservoirs are 2900 to 4460 mg CO_2 m^{-2} day^{-1} and 65 to 1140 mg CH_4 m^{-2} day^{-1} (St. Louis *et al.*, 2000). However, extensive pre-flood CO_2 and CH_4 emissions data from these studies (except for Kelly *et al.*, 1997 and Scott *et al.*, 1999) is lacking, so our understanding of the net effect of reservoir creation on landscapes is incomplete.

Global reservoir surface area is estimated to be approximately 1.5 million km^2, with hydro reservoirs accounting for 25% of the total area (St. Louis *et al.*, 2000). With global reservoir surface area approaching that of natural lakes (Shiklomanov, 1993), reservoirs are currently estimated to be responsible for 7% of the global warming potential (GWP) of all anthropogenic GHG emissions (St. Louis *et al.*, 2000). In four Canadian provinces alone (British Columbia, Manitoba, Ontario, and Newfoundland and Labrador), reservoir surface area is estimated to be 73,000 km^2 (St. Louis *et al.*, 2000). Most of these reservoirs exist in the boreal ecoregion, a major component of the global carbon cycle.

The boreal ecoregion encircles the northern hemisphere and covers 11% of the earth's land surface (1.5 billion hectares) (Bonan and Shugart, 1989), with 20% of that area being comprised of peatlands (2.6 million ha) (Apps *et al.*, 1993). The boreal ecoregion represents one of the major continental reservoirs of carbon (Schlesinger, 1997; IPCC 2001); short growing seasons, along with cold temperatures and moist soil conditions, result in accumulations of organic material on the forest floor. The boreal ecoregion contains 26% of the global carbon stored in vegetation, 43% of global OC stored in surface litter, 12% of the total world soil OC, and contributes 11% of global net primary productivity (Schlesinger, 1997). Peatland areas of the boreal ecoregion contain about 31% of total OC stored in soils globally (Schlesinger, 1997). Finally, dry boreal upland soils are an important sink for atmospheric CH_4 (Crill, 1991; Amaral and Knowles, 1997). Therefore, largescale reservoir creation in boreal landscapes can especially impact global carbon dynamics due to the loss of terrestrial sinks for both CO_2 and CH_4, and to the mineralization of large stores of OC in the vegetation and soils in these landscapes.

The FLooded Uplands Dynamics EXperiment (FLUDEX) at the Experimental Lakes Area (ELA) in northwestern Ontario was designed to assess the impact of reservoir creation on carbon cycling in the boreal forest landscape. This whole ecosystem manipulation experiment, involving the creation of three reservoirs in upland boreal forest subcatchments, was initiated as a companion experiment to the ELA Reservoir Project (ELARP). A major objective of the ELARP was to determine if reservoirs are significant sources of atmospheric GHGs by monitoring net ecosystem carbon exchange in a lowland boreal wetland prior to and after flooding. The wetland, which provided a worst-case scenario for long-term decomposition and GHG production due to large OC stores held in peat, changed from being a small carbon sink of approximately 7 g C m^{-2} yr^{-1} before impoundment to a relatively large carbon source of 130 g C m^{-2} yr^{-1} to the atmosphere after impoundment (Kelly *et al.*, 1997). Continued monitoring of dissolved CO_2 and CH_4 in the reservoir surface waters show that levels are still well above background, eight years after initial flooding (V. St. Louis, University of Alberta, Edmonton; personal communication).

Results from the ELARP led researchers to hypothesize that minimizing the percentage of peatland flooded should, on the long-term, reduce GHG emissions because, theoretically, CO_2 and CH_4 emissions should be directly related to the amount of OC available for decomposition upon flooding. A major objective of the FLUDEX was to examine the effects of flooding upland forest subcatchments that varied in OC stored in vegetation and soils on carbon cycling in that landscape, and to compare these findings with those of the flooded ELARP wetland, which was characterized by much larger stores of OC than those found in the uplands.

Within the overall framework of the FLUDEX, the goal of this thesis is to quantify CO_2 and CH_4 production in the experimental reservoirs and to gain an understanding of the processes associated with this production. Carbon cycling processes investigated were CO_2 and CH_4 production in the flooded soils, CO_2 and CH_4 emissions from the reservoir surface via surface diffusion and ebullition, and CO_2 and CH_4 entering and leaving the systems through various inputs and outputs. Together, this information was used to determine whether CO_2 and CH_4 production by reservoirs is related to the amount of OC flooded.

This thesis consists of two research chapters. The first (Chapter 2) investigates gas exchange at the air/water interface as estimated by three common techniques. It evaluates and compares the performance of the techniques, and makes recommendations on the most suitable for use in the reservoir environment in which the study takes place. The second (Chapter 3) is the focus of this thesis, and investigates CO_2 and CH_4 production in the three FLUDEX reservoirs. Chapter 3 focuses on the second and third years of flooding, while incorporating pre-flood and first year post-flood FLUDEX results (Joyce, 2001). Finally, a concluding chapter (Chapter 4) relates FLUDEX results to the ELARP (Kelly *et al.*, 1997) and reservoir GHG issues in general, and identifies possible avenues of future research.

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Chapter 2: A comparison of three techniques used to measure diffusive gas flux from heterogeneous aquatic surfaces

Introduction

Rising atmospheric carbon dioxide (CO_2) and methane (CH_4) concentrations are of concern because of their global warming potential (GWP) (Lashof and Ahuja, 1990). Numerous studies have focused on determining both anthropogenic and natural sources of these gases (IPCC, 2001). Among aquatic sources of CO_2 and CH_4 are some natural lakes (Kling *et al.*, 1991; Kling *et al.*, 1992; Anderson *et al.*, 1999), beaver ponds (Wehenmeyer, 1999; Roulet *et al.*, 1997; Yavitt and Fahey, 1994; Ford and Naiman, 1987), rice paddies (Ziska *et al.*, 1998; Kumaraswamy *et al.*, 1997; Nouchi *et al.*, 1994) and reservoirs (St.Louis *et al.*, 2000; Galy-Lacaux *et al.*, 1997, 1999; Duchemin *et al.*, 1995; Kelly *et al.*, 1997).

Reliable quantification of CO_2 and CH_4 fluxes from aquatic surfaces is necessary to accurately assess their contributions to increasing levels of atmospheric CO_2 and CH_4. Three common approaches to quantifying diffusive gas fluxes from aquatic surfaces are: 1) the thin boundary layer (TBL) equation and a gas tracer, sulfur hexafluoride (SF_6), to measure a *gas transfer velocity* (or *k*), 2) the TBL equation and wind speed to estimate *k* using empirical relationships between wind speed and gas exchange, and 3) static floating chambers (FCs) that directly measure flux. All three approaches have been applied to large, open bodies of water, although FCs are usually favored in small, sheltered areas only.

SF_6 is commonly used to estimate *k* in lake and ocean surfaces (Wanninkhof *et al.*, 1985, 1987; Cole and Caraco, 1998; Clark *et al.*, 1995). SF_6 is an ideal gas exchange tracer because it is biologically and chemically inert in water, so the only factor governing its concentration in surface waters is physical exchange with the atmosphere. *k* calculated from SF_6 evasion rates can be resolved daily or integrated over longer periods of time. Once k_{SF_6} is determined, *k* values of other gases can be estimated (Jähne *et al.*, 1987), and their fluxes subsequently determined using the TBL equation. The use of SF_6 to calculate *k* values is limited, however, to well-mixed waters that result in uniform surface concentrations of SF_6.

The gas transfer velocity is commonly estimated using wind speed measurements and one of several empirical wind speed/gas exchange relationships (Sellers *et al.*, 1995;

Duchemin *et al.*, 1999; Kelly *et al.*, 1997) derived from studies performed in wind/wave tunnels, large lakes, and oceans (Liss and Merlivat, 1986; Wanninkhof, 1992; Smethie *et al.*, 1985). The estimated *k* is then used to determine *k* for a given gas, for which the flux is then estimated using the TBL equation. *k* estimates from wind speed do not incorporate certain important factors that affect gas exchange, such as rain (Ho *et al.*, 2000; Banks *et al.*, 1984), surface films (Goldman *et al.*, 1988), and penetrative convection (Crill *et al.*, 1988; Soloviev and Schlussel, 1994). In low-wind environments (< 2 to 3 m/s), when these parameters have a relatively greater importance in determining gas transfer (Livingstone and Imboden, 1993; Cole and Caraco, 1998), fluxes calculated using the TBL equation and wind speed derived *k* values are more likely to be incorrect.

Static FCs are regularly used to determine gas emissions from aquatic surfaces (Duchemin *et al.*, 2000; Duchemin *et al.*, 1995; Ford and Naiman, 1987; Galy-Lacaux *et al.*, 1997, 1999; Kelly *et al.*, 1997; Weyhenmeyer, 1999). Floating chambers measure emissions directly and both spatial and temporal variations in gas flux can be determined by placing individual chambers in numerous locations on the water surface at different times. Problems associated with FCs include: 1) the creation of small microenvironments that prevent factors such as wind and rain from affecting the air-water boundary layer; 2) chamber-induced changes in atmospheric pressure overlying the water surface; 3) alteration of the air-water concentration gradient as gas builds up in the chamber (Conen and Smith, 2000; Healy *et al.*, 1996); and 4) bubbles emitted from sediments, or atmospheric air in windy conditions, entering the chamber (Duchemin *et al.*, 2000).

The FLooded Uplands Dynamics EXperiment (FLUDEX) at the Experimental Lakes Area (ELA), northwestern Ontario, was initiated to quantify CO_2 and CH_4 emissions from three experimental reservoirs that flooded upland boreal forest varying in amounts of organic carbon stored in soils and plants. The experimentally created FLUDEX reservoirs were very small (< 1 ha) with short water residence times (~6 to 10 days), and were characterized by low, heterogeneous winds and considerable physical obstruction from trees, not only protruding from the reservoir, but also in the surrounding forest. Here we compare the 1) TBL equation and SF_6 derived *k*, 2) the TBL equation and wind speed estimated *k*, and 3) FCs as approaches for quantifying diffusive gas flux from the surface of one of the experimental reservoirs.

Site description and methods

Study Site

This study was conducted on the experimental reservoir that flooded a primarily upland jack pine (*Pinus banksiana*) and birch (*Betula papyrifera*) forest (with intermediate organic carbon storage relative to the other two reservoirs) in the boreal ecoregion at the ELA (Figure 2.1). The reservoir was created by constructing a 229 m dam along the low-lying contour of the catchment, and pumping water into the catchment from a nearby oligotrophic lake (Roddy Lake) using a high-volume diesel pump. The surface area of the reservoir was 0.5 ha, with an average depth of 0.9 m and volume of 4270 m^3. Water was pumped continuously at a rate of ~10 L/s, resulting in a water residence time of ~6 days (K. Beaty, Freshwater Institute, Winnipeg; unpublished data). Outflow water exited the reservoir via a V-notch weir at a rate similar to the inflow rate. The reservoir was filled in late May and drained in late September in both 2000 and 2001. We compared CO_2 and CH_4 flux estimates on three occasions, twice late in the flooding season (August 2000 and September 2001), and once just after the reservoir was filled (June 2001).

Calculation of instantaneous diffusive flux

Theory of gas exchange – the stagnant film model and the thin boundary layer equation

Liss and Slater (1974) describe a two-layer model of diffusive gas exchange between air and water. The *stagnant film model* assumes the main body of each fluid is well mixed and the main resistance to gas transport is molecular diffusion across the interfacial layers of the gas and water phases (the model assumes resistance to gas transfer is in the water phase). The main factors affecting the diffusion rate of a gas across the layer system are 1) the gas concentration gradient between the water and air and 2) the gas transfer velocity (*k*), defined as a piston velocity, or the depth of water in which the gas concentration in water has equalized with atmospheric concentration per unit time. Gas flux across the air/water interface can be described by the thin boundary layer (TBL) equation:

$$F = k(C_{sur} - C_{eq}) \tag{1}$$

Figure 2.1: Aerial view of the reservoir three years after flooding (photograph: J. Shearer, Freshwater Institute, Winnipeg). Yellow circles represent dissolved SF_6 sampling sites; red squares, dissolved CO_2 and CH_4 sampling sites; white triangles, FC positions; and blue square, anemometer position.

where F is gas flux across the air-water interface, C_{sur} is the concentration of gas in the surface water, and C_{eq} is the concentration of the gas in the atmosphere. In our study, CO_2 and CH_4 fluxes were estimated using dissolved surface water concentrations of CO_2 and CH_4 (C_{sur}) and k values calculated from SF_6 evasion rates and wind speed measurements.

Surface CO_2 and CH_4 concentrations – sample collection and analysis

Surface water CO_2 and CH_4 concentrations were measured at four sites in the reservoir (Figure 2.1). Two sites were overlying water deeper than 1 m, whereas the other two sites were overlying water less than 0.5 m deep. For each of these water depths, we chose a site that was in an open area of the reservoir, and another that was sheltered by flooded trees. This was done to examine differences in surface concentrations in open vs. sheltered areas of the reservoir and in surface waters close to and far from flooded soils, where decomposition of organic matter primarily occurred (Joyce, 2001; Chapter 3, this thesis). Surface water CO_2 and CH_4 samples were collected in 160 ml Wheaton glass serum bottles capped with butyl rubber stoppers baked overnight at 56°C. 8.9 g of potassium chloride (KCl) was added to each bottle as a preservative (Hesslein *et al.*, 1991). Bottles were evacuated and then backfilled with 10 ml of ultra high purity (UHP) N_2 gas to provide a headspace. To collect a sample, bottles were submersed ~10 cm below the water surface and punctured with an 18-gauge needle. *In situ* atmospheric pressure and water temperature were recorded.

All water samples were analyzed for CO_2 and CH_4 within 24 hours of collection. Sample bottles were placed on a wrist-action shaker for 10 minutes to equilibrate gases between the liquid phase and N_2 headspace. 0.2 mls of headspace was injected through an injection port using a pressure lok gas-tight syringe into a Varian 3800 gas chromatograph (GC). CO_2 and CH_4 were detected by a flame ionization detector (FID) at 250°C, using UHP hydrogen as a carrier gas through a hayesep D column at 80°C. A ruthenium methanizer converted CO_2 to CH_4. Six to seven gas standards ranging from 75 to 6000 ppm for both CO_2 and CH_4 (supplied by Praxair and Linde-Union Carbide) were used to calibrate the GC. A Varian Star Workstation program integrated peak areas. Standard calibration curves with an $r^2 > 0.99$ were accepted for analyses and a standard was analysed after every 10 samples to check the GC calibration. Duplicate injections were performed on ~10% of samples to ensure reproducibility of results. Gas concentrations were corrected for temperature and barometric pressure differences between sample collection and gas analyses.

In August 2000, surface water CO_2 and CH_4 sampling was done three times daily at 7:00, 13:00, and 20:00 to determine diel concentration patterns. Midday sampling was omitted during June and September 2001 comparison studies (see below). Concentrations measured from the four sites taken twice or three times per day (8 to 12 samples) were averaged to obtain an average daily concentration of CO_2 and CH_4 in surface waters.

Gas transfer velocities (k) calculated from SF_6 loss

Theory. The use of SF_6 to calculate *k* in water surfaces was developed by Wanninkhof *et al.* (1985, 1987) and has since been used in numerous gas exchange experiments (Upstill-Goddard *et al.*, 1990; Clark *et al.*, 1995; Cole and Caraco, 1998). SF_6 is added into a body of water, where it is theoretically biologically and chemically inert (Wanninkhof *et al.*, 1991). Over time, there is a decrease in dissolved SF_6 concentration as the gas escapes to the atmosphere. This gas loss can be converted to a *k*. In the reservoir, the decrease in SF_6 concentration was also due to dilution from inflow water. Ho *et al.* (2000) developed a method of quantifying the dilution effect. Briefly, *k* in a system with inflow is defined by:

$$k = \frac{h}{\Delta t} \ln \frac{C_i}{C_f} - \frac{hP}{V} \qquad (2)$$

where *h* is mean water depth, C_i and C_f are the initial and final concentration of a gas over a time period, Δt, *P* denotes the pumping rate, and *V* is the water volume.

Jähne *et al.* (1987) showed that gas transfer velocities of different gases are related in the following manner:

$$\frac{k_{\text{gas1}}}{k_{\text{gas2}}} = \left(Sc_{\text{gas1}} / Sc_{\text{gas2}}\right)^{-n} \qquad (3)$$

where *n* is considered to be 0.67 for transfer over a smooth water surfaces with low wind (Jähne *et al.*, 1984), and *Sc* is the Schmidt number for each gas (the ratio of kinematic viscosity of water and the gas diffusion coefficient) (Jähne *et al.*, 1987). *Sc* for SF_6, CO_2, and CH_4 were calculated with formulas from Wanninkhof (1992):

$$Sc_{SF_6} = 3255.3 - 217.13t + 6.8370t^2 - 0.086070t^3 \tag{4}$$

$$Sc_{CO_2} = 1911.1 - 118.11t + 3.4527t^2 - 0.041320t^3 \tag{5}$$

$$Sc_{CH_4} = 1897.8 - 114.28t + 3.2902t^2 - 0.039061t^3 \tag{6}$$

where t = temperature in °C. Once k_{SF_6} was determined using equation (2), k_{CO_2} and k_{CH_4} were determined using equations (3, 4, 5, and 6). k_{CO_2} and k_{CH_4}, along with the dissolved surface water concentrations of CO_2 and CH_4, were used to calculate the flux of these gases across the air-water interface using equation (1).

Method – SF_6 addition and quantification of surface SF_6 concentrations. Two 2-L plastic bottles were filled with ~1 L of reservoir water. The bottles were compressed to expel the remaining air and then capped with a butyl rubber septum. Pure SF_6 gas was pumped into the bottles through the septum using a needle attached to a tank regulator until there was obvious positive pressure in the bottles. Each bottle was vigorously hand-shaken for approximately two minutes to dissolve the SF_6 into the water. The SF_6 solution was immediately introduced to the reservoir by submerging and emptying the bottles from a canoe as it was paddled around the water surface.

SF_6 concentrations were uniform throughout the reservoir surface approximately four days after addition. Surface water was then sampled daily at 10 sites (Figure 2.1) using evacuated 60 ml Wheaton glass serum bottles capped with butyl rubber stoppers and backfilled with a 5 ml UHP N_2 headspace. An 18-gauge needle was used to puncture the rubber septum approximately 5 cm below the water surface. *In situ* atmospheric pressure and water temperature were recorded at sampling time.

All samples were analysed for SF_6 concentration two to four hours after collection. Sample bottles were placed on a wrist-action shaker for 10 minutes, allowing essentially all (> 99%) of the dissolved SF_6 to enter the headspace (Upstill-Goddard *et al.*, 1990; Wanninkhof *et al.*, 1991). 0.1 ml of headspace was injected into the GC using a pressure-lok glass syringe. A 90% argon/10% methane mixture was used as a carrier gas, and SF_6 was separated in a molecular sieve column kept at 80°C. SF_6 was detected with an electron capture detector (ECD) set at 300°C. Four SF_6 standards ranging from 1 to 25 ppb were made by diluting a 100 ppb standard supplied by Matheson Gas Co. into 5 L Tedlar gas bags (Alltech). GC calibration curves were always linear through zero ($r^2 > 0.99$). A Varian Star Workstation program integrated peak areas. Duplicate injections were performed on ~5% of samples to ensure reproducibility of results. Gas concentrations were corrected for temperature and barometric pressure differences between sample collection and gas analyses.

Gas transfer velocities (k) estimated from wind speed

Theory. The relationship between wind speed and gas transfer across water surfaces has been examined in-depth (Cole and Caraco, 1998; Wanninkhof *et al.*, 1985; Upstill-Goddard *et al.*, 1990; Clark *et al.*, 1995; Livingstone and Imboden, 1993; Watson *et al.*, 1991; Wanninkhof, 1992). Several empirical relationships have been determined from experiments in wind tunnels, lakes, and the ocean (Liss and Merlivat, 1986; Wanninkhof *et al.*, 1985; Smethie *et al.*, 1985).

The relationship used to calculate instantaneous flux from wind speed in this study is that used by Hamilton *et al.* (1994), which was determined from SF_6 evasion and wind speed data collected on a small sheltered lake at the ELA (Lake 302) (Wanninkhof *et al.*, 1991). Wind speeds on Lake 302 were measured 1 m above the water surface, as they were in this study. Hamilton *et al.* (1994) used the following relationships for k_{600} if wind speeds were < 3 m/sec:

$$k_{600}(cm/hr) = 0.76u \qquad (7)$$

where u is the in situ wind speed (m/s) and k_{600} is the gas transfer velocity calculated from SF_6 loss, normalized to a Sc number of 600. k_{CO_2} for wind speeds < 3 m/s was calculated:

$$k_{CO_2}(cm/hr) = k_{600}\left(\frac{600^{0.67}}{Sc_{CO_2}{}^{0.67}}\right) \qquad (8)$$

where k_{CO_2} is the gas exchange coefficient for CO_2, and Sc_{CO_2} is the Schmidt number for CO_2 at *in situ* temperature. k_{CH_4} was determined using equation (8) replacing Sc_{CO_2} with Sc_{CH_4}. Flux rates for both gases were then determined using the calculated k values and measured dissolved surface water CO_2 and CH_4 concentrations using equation (1).

Method – wind speed measurements. Wind speeds were recorded using an anemometer (RM Young Company) placed 1 m above the water surface on a floating raft located centrally in the reservoir in a small open area cut amongst the trees (Figure 2.1). Wind speeds were stored as 15 minute averages from measurements taken every 10 seconds by a Campbell Scientific CR10 data logger in August 2000. In June 2001, wind speeds were recorded as hourly averages from measurements taken every 10 seconds. These values were then averaged to obtain average daytime (7:00-1800), nighttime (19:00-6:00), and 24 hour wind speeds. Daily average wind speeds were used in equation (7). Wind speeds were not measured in September 2001.

Direct measurement of flux – floating chambers (FCs)

Theory. Gas flux across water surfaces can be measured directly using static FCs by monitoring the build up of gases emitted into the chamber over a period of time. Linear rates of increase in chamber gas concentrations are used to calculate flux rates. Flux rates measured in several or more FCs are then used to estimate gas exchange over a larger area.

Method – chamber deployment and sample collection. Floating chambers (16.4 L) were made from blue polycarbonate water-cooler bottles with the bottoms removed. The bottles were embedded through a 45 cm square and 3 cm thick Styrofoam sheet float so that the bottom of the chamber was flush with the underside of the foam. A 25 cm long 2 mm I.D. tygon tube was attached to a rubber septum in the side of the chamber via an 18-gauge needle. The free end was fitted with a three-way valve for sample collection. Prior to deployment, the insides of chambers were dried with paper towels and flushed out by waving them in the air. Four chambers were set out at ~8:00 and 16:00 each day in August 2000 at the same four locations sampled for surface CO_2 and CH_4 concentrations (Figure 2.1). We increased our sampling effort to six chambers in June and September 2001 (Figure 2.1). Air samples were drawn from the chamber through the tygon tube at ~0, 20, 40, and 60 minutes after deployment using 5 ml plastic syringes capped with 3-way valves.

FC air samples were analysed for both CO_2 and CH_4 on the same GC as water samples, except air samples were injected into a 1 ml sample loop within two to three hours of collection and four to five standards ranging from 75 to 1000 ppm for CO_2 and 1.6 to 75 ppm for CH_4 were used to calibrate the GC. Chamber CO_2 and CH_4 concentrations were plotted against time and regression analysis was performed to determine both the linearity of the relationship and the gas emission rate. Because of ebullition and occasional breaking of the seal between the chamber and water surface, some sample runs were rejected when r^2 for the relationship was < 0.85 for both CO_2 and CH_4. On occasions when bubbles appeared to have entered the chamber midway through a run (indicated by a sudden increase in chamber CO_2 or CH_4 concentration), an emission rate was determined by examining the slope of the line before and after the apparent disturbance. If the slopes of the lines were similar, then the average of the two slopes was used as the emission rate.

Other studies have rejected chamber runs if the initial concentration of gas in the chamber was not close to the presumed atmospheric concentration (Duchemin *et al.*, 1999; Duchemin *et al.*, 1995). However, this was not a criterion in this study. Air samples taken above the reservoir over 2000 and 2001 indicated that both CO_2 and CH_4 concentrations are consistently above average global atmospheric concentrations. Individual chamber results were accepted if initial concentrations were within 10 to 20% of the mean initial concentration of all chambers deployed in the same run. Accepted fluxes from chambers deployed in the morning and afternoon were first averaged separately, and then averaged together to obtain an average daily flux estimate.

Results

Surface CO_2 and CH_4 concentrations

Dissolved surface CO_2 and CH_4 were always greater than atmospheric equilibrium concentrations during all three comparison studies (Table 2.1). Surface CO_2 concentrations were similar during all three comparisons, but CH_4 concentrations were much lower in June 2001 just after flooding than during the two studies performed at the end of the flooding period (Table 2.1). While there was some variation in CO_2 and CH_4 concentrations amongst the four sites, there were no significant concentration differences or noticeable spatial

Table 2.1: Mean dissolved surface CO_2 and CH_4 concentrations (μmol L^{-1}; ± std dev) for the three study periods.

	August 2000		June 2001		September 2001	
	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
7:00	144 ± 28	5.12 ± 2.1	142 ± 20	1.22 ± 0.40	159 ± 23	4.37 ± 1.7
13:00	127 ± 24	4.65 ± 1.9	—	—	—	—
20:00	111 ± 28	4.64 ± 1.9	123 ± 24	1.24 ± 0.44	143 ± 37	4.36 ± 1.9
Overall	127 ± 32	4.88 ± 2.0	132 ± 23	1.23 ± 0.40	151 ± 30	4.36 ± 1.7

patterns between deep/shallow or sheltered/open areas.

Morning CO_2 concentrations (146.1 ± 24.2 μmol L^{-1}) were significantly higher than evening concentrations (121.6 ± 29.7 μmol L^{-1}) ($p < 0.001$; paired t-test; t = 5.26; n = 25), most likely due to photosynthesis in the reservoir. Morning CH_4 concentrations (3.57 ± 2.38 μmol L^{-1}) were not significantly different than evening concentrations (3.36 ± 2.21 μmol L^{-1}) ($p = 0.35$; paired t-test; t = 0.944; n = 25). Midday CO_2 and CH_4 concentrations equaled the average of morning and evening concentrations in August 2000, so morning and evening values were averaged to obtain concentrations representative of the entire day for all three comparison studies.

SF_6 concentrations and calculated k values

Four days after addition, SF_6 concentrations at ten locations over the entire reservoir surface varied typically less than 10 to 15%, but occasionally over 20%. For comparison, Upstill-Goddard *et al.* (1990) saw spatial heterogeneity in SF_6 concentrations in a small lake in which lateral variations occasionally exceeded 40%, whereas Wanninkhof *et al.* (1987) recorded lateral variations around 5%. A vertical mixing study conducted in July 2001 showed SF_6 to be present at four depths (1 cm, 10 cm, and 25 cm above the flooded soil, and 10 cm below the water surface) in the water column 24 hrs after addition, and fairly uniform throughout the water column 120 hrs after addition (C. Matthews *et al.*, unpublished data).

While daily decreases in SF_6 concentration occurred (during all three comparison studies, SF_6 surface concentrations declined exponentially with time, as previous studies have documented) (Cole and Caraco, 1998; Clark *et al.*, 1995) (Figure 2.2), daily k values were sometimes negative (Table 2.2). This occurred on days when the measured decrease in SF_6 concentration was less than that expected from dilution by inflow water. Daily k_{600} (experimental k_{SF_6} standardized to a Sc number of 600 for comparison purposes) were –0.40 to 0.66 cm hr^{-1} in August 2000, –0.52 to 1.1 cm hr^{-1} in June 2001, and 0.18 to 0.98 cm hr^{-1} in September 2001 (Table 2.2). SF_6 was well mixed vertically (as described above); therefore, diffusion of SF_6 from surface waters into lower bottom waters is not likely a factor in the observed surface SF_6 decline.

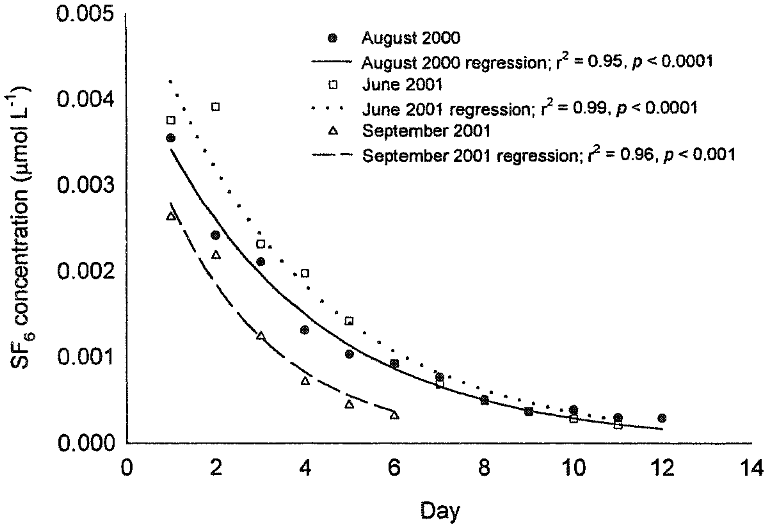

Figure 2.2: Exponential decline of surface water SF_6 concentration over the duration of the comparison studies.

Table 2.2: Gas transfer velocities (normalized to k_{600}) calculated from SF_6 loss and wind speed during two 10-day comparison studies (italicized values are those used in flux calculations). FC k values were calculated from FC fluxes and dissolved surface and atmospheric concentrations of CO_2 and CH_4, and then normalized to k_{600}.

	August 2000			June 2001		
	k_{600} (cm hr^{-1})			k_{600} (cm hr^{-1})		
Day	SF_6	wind	FC	SF_6	wind	FC
1	0.60	*0.49*	2.0	-0.52	*0.025*	1.2
2	-0.065	*0.23*	0.82	1.1	*0.067*	1.5
3	0.60	*0.19*	0.97	0.16	*0.066*	1.6
4	0.34	*0.22*	1.2	0.64	*0.099*	2.0
5	-0.092	*0.26*	1.7	0.56	*0.089*	2.1
6	0.041	*0.21*	1.4	0.36	*0.37*	3.7
7	0.66	*0.25*	2.0	0.45	*0.071*	2.3
8	0.38	0.35	2.7	0.28	*0.037*	1.1
9	-0.40	*0.32*	1.8	0.25	*0.11*	2.3
10	0.31	*0.30*	1.8	0.25	*0.27*	4.5
Overall	*0.21*	———	———	*0.31*	———	———

When *k* values were determined for five to ten day periods, the loss of SF_6 due to surface gas evasion was always evident. The *k* values for the duration of each comparison study were 0.21 cm hr^{-1} in August 2000, 0.31 cm hr^{-1} in June 2001, and 0.70 cm hr^{-1} in September 2001. These values are four to ten times less than *k* values on larger lakes determined using SF_6 (Table 2.3).

CO_2 and CH_4 fluxes calculated using k derived from SF_6 additions

Daily CO_2 flux estimates based on SF_6 derived *k* values (over the duration of each comparison study) and daily surface CO_2 concentrations (average of morning and evening values) ranged from 180 to 580 mg CO_2 m^{-2} d^{-1} in August 2000, from 300 to 470 mg CO_2 m^{-2} d^{-1} in June 2001, and from 790 to 1370 mg CO_2 m^{-2} d^{-1} in September 2001 (Figure 2.3). Daily CH_4 flux estimates ranged from 2.5 to 6.8 mg CH_4 m^{-2} d^{-1} in August 2000, from 0.84 to 2.0 mg CH_4 m^{-2} d^{-1} in June 2001, and from 6.9 to 19 mg CH_4 m^{-2} d^{-1} in September 2001 (Figure 2.4). Day to day variations in flux estimates were low because the same *k* was used for the entire comparison period and day to day fluctuations in dissolved CO_2 and CH_4 were minimal.

Wind speed and estimated k values

Wind speeds never exceeded 1 m s^{-1}, and ranged from 0 to 0.85 m s^{-1} in August 2000 and June 2001. August 2000 average wind speeds (0.41 ± 0.16 m s^{-1}) were 3.3 times greater than June 2001 average wind speeds (0.12 ± 0.09 m s^{-1}). Average daytime wind speeds (0.24 ± 0.02 m s^{-1}) were significantly higher than average nighttime wind speeds (0.080 ± 0.02 m s^{-1}) ($p = 0.003$; paired t-test on power transformed wind speeds; $t = -5.72$; $n = 20$). Daily *k* values calculated from wind speed were similar to SF_6 derived *k* values for the overall period, but were not similar to daily SF_6 derived *k* values (Table 2.2).

CO_2 and CH_4 fluxes calculated using k derived from wind speed

CO_2 flux estimates ranged from 118 to 621 mg CO_2 m^{-2} d^{-1} in August 2000 and 26.7 to 536 mg CO_2 m^{-2} d^{-1} in June 2001 (Figure 2.3). CH_4 flux estimates ranged from 1.9 to 7.2 mg CH_4 m^{-2} d^{-1} in August 2000 and 0.08 to 2.1 mg CH_4 m^{-2} d^{-1} in June 2001 (Figure 2.4).

Table 2.3: Gas transfer velocities estimated on the three FLUDEX reservoirs, two lakes at the ELA, and other lakes in the U.S. and U.K. All k values were determined using SF_6 and are normalized to k_{600}.

Location	Surface Area (ha)	k_{600} (cm hr^{-1})	Reference
High C reservoir, ELA, Ontario	0.69	0.70	Chapter 3, this thesis
Intermediate C reservoir, ELA, Ontario	0.50	0.49	Chapter 3, this thesis
Low C reservoir, ELA, Ontario	0.66	0.91	Chapter 3, this thesis
Sutherland pond, New York	4.1	~3.2*	Clark *et al.*, 1995
Lake 658, ELA, Ontario	8.4	2.7	Matthews *et al.*, unpublished data
Lake 302, ELA, Ontario	13	1.5 – 5	Wanninkhof *et al.*, 1991
Dozmary Pool, UK	14	~ 5.4*	Upstill-Goddard *et al.*,1990
Mirror Lake, New Hampshire	15	2.7	Cole and Caraco, 1998
Siblyback Lake, UK	56	~6.7*	Upstill-Goddard *et al.*,1990
Rockland Lake, New York	100	~2.5*	Wanninkhof *et al.*, 1985

*represents average of published values

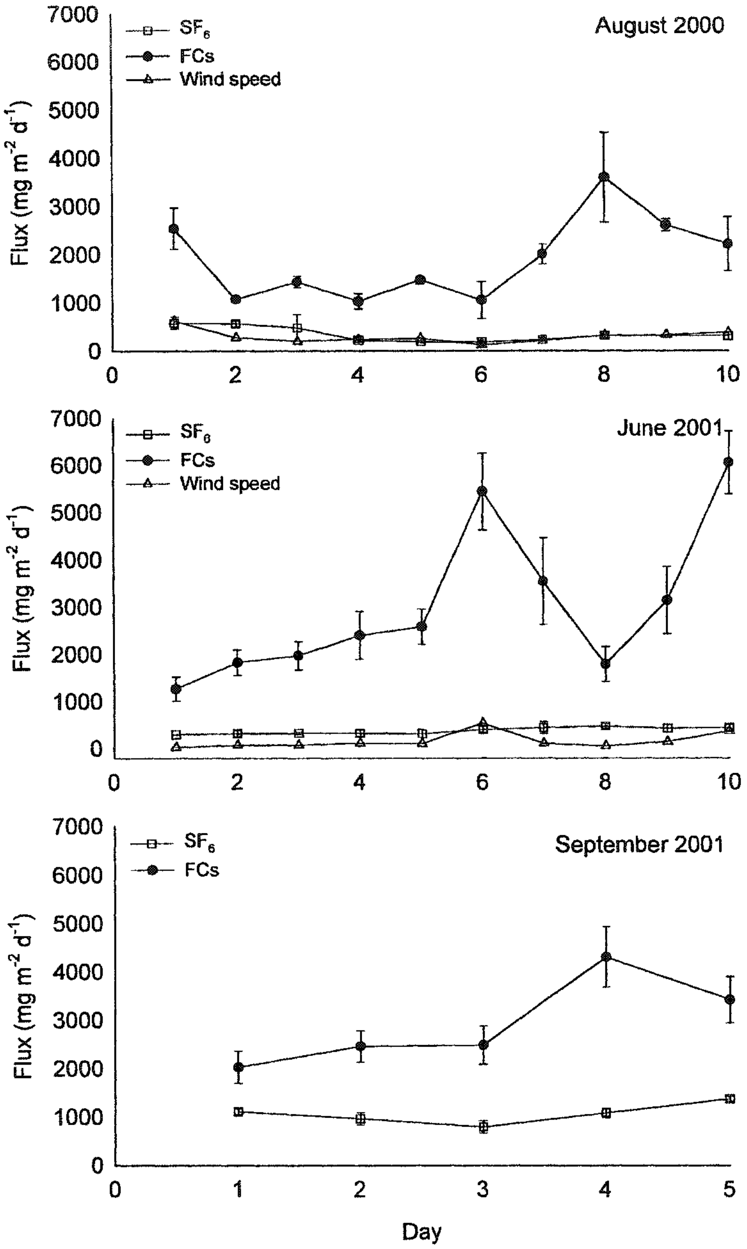

Figure 2.3: Mean (± SE bars) diffusive CO_2 flux from a small reservoir estimated using three techniques.

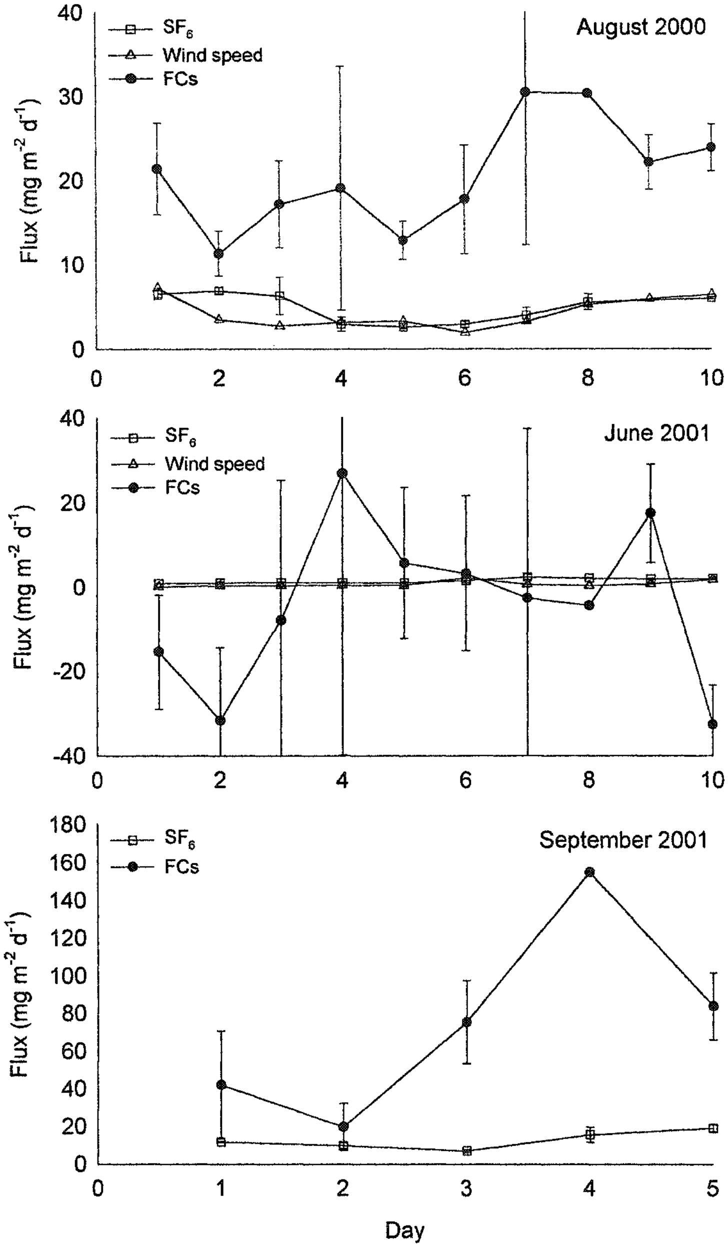

Figure 2.4: Mean (± SE bars) diffusive CH_4 flux from a small reservoir estimated using three techniques.

Wind speeds varied little throughout each comparison study, so day to day variation in fluxes estimated using wind speed derived *k* values was low.

Floating chamber CO_2 and CH_4 fluxes

Almost 100% of the CO_2 and approximately 70% of the CH_4 FC flux measurements were accepted based on the criteria described in the methods (Table 2.4). CO_2 fluxes estimated from FC measurements ranged from 1030 to 3600 mg CO_2 m^{-2} d^{-1} in August 2000, from 1260 to 6050 mg CO_2 m^{-2} d^{-1} in June 2001, and from 2030 to 4310 mg CO_2 m^{-2} d^{-1} in September 2001 (Figure 2.3). CH_4 fluxes estimated from FC measurements ranged from 13 to 30 mg CH_4 m^{-2} d^{-1} in August 2000, from –33 to 27 mg CH_4 m^{-2} d^{-1} in June 2001, and from 20 to 155 mg CH_4 m^{-2} d^{-1} in September 2001 (Figure 2.4).

There was considerable within reservoir variation amongst the fluxes measured by the four to six individual chambers during a given run, especially for CH_4 (Figures 2.3 and 2.4). There were no significant trends in measured flux related to depth of water below the chamber or whether or not the chamber was in the open or sheltered by flooded trees (p = 0.11; ANOVA; F = 2.07; n = 198). Morning and afternoon flux estimates were not significantly different (p = 0.70; ANOVA; F = 0.544; n = 25). Flux estimates based on individual FC measurements also varied more from day to day than fluxes based on SF_6 and wind speed derived *k* (Figures 2.3 and 2.4). FC CO_2 flux estimates were strongly correlated to wind speed (Figure 2.5).

During the June 2001 comparison study, FCs consistently showed that the reservoir surface was consuming CH_4 while simultaneously emitting CO_2 to the atmosphere (Figure 2.4). During the period for which negative fluxes of CH_4 were measured using FCs, CH_4 levels in the reservoir were ~50 times higher than atmospheric equilibrium.

Agreement between the three approaches

Because *k* values calculated from SF_6 loss and wind speed were similar, agreement between flux estimates based on the two techniques was good. SF_6 derived estimates of CO_2 flux were 1.3 ± 0.6 (August 2000) and 3.5 ± 2.1 (June 2001) times greater than CO_2 fluxes estimated from wind speed, and were 1.3 ± 0.5 (August 2000) and 3.3 ± 2.1 (June 2001) times greater for CH_4 flux estimates (Table 2.5). SF_6 derived estimates of gas flux were often

Table 2.4: Percentage of chamber runs accepted for CH_4 and CO_2 flux estimates.

	Number chambers deployed	% accepted
CO_2		
August 2000	92	96
June 2001	95	97
September 2001	60	96
CH_4		
August 2000	92	75
June 2001	95	59
September 2001	60	72

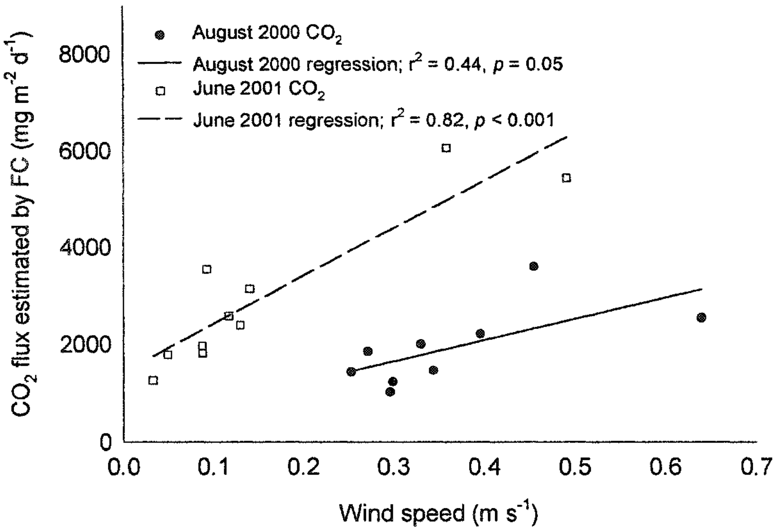

Figure 2.5: Relationship between daily average FC CO_2 flux estimates and daily average wind speed.

Table 2.5: Mean CO_2 and CH_4 fluxes (mg m^{-2} d^{-1}; ± SD) estimated from 1) the TBL equation and *k* values calculated using both SF_6 and wind speed, and 2) FC measurements.

	CO_2			CH_4		
	TBL		FC	TBL		FC
	SF_6	wind		SF_6	wind	
August 2000	339 ± 160	293 ± 137	1930 ± 791	4.80 ± 1.7	4.22 ± 1.8	19.7 ± 8.1
June 2001	377 ± 67	163 ± 161	3000 ± 1600	1.46 ± 0.54	0.67 ± 0.68	-4.18 ± 19.1
September 2001	1060 ± 210	n/a	2940 ± 918	12.5 ± 4.7	n/a	75.0 ± 51.4

higher than wind speed derived estimates due to the slightly higher *k* values calculated from SF_6 evasion.

Generally, CO_2 flux estimates from FC measurements were much higher and more variable than fluxes obtained using the SF_6 or wind speed derived *k* values during all three comparison studies (Figure 2.3; Table 2.5). FC CO_2 flux estimates were 6.1 ± 3.0 (August 2000), 8.2 ± 3.4 (June 2001), and 2.8 ± 0.8 (September 2001) times greater than those based on SF_6 determined *k* values (Table 2.5), and 6.9 ± 2.7 (August 2000) and 22.7 ± 6.9 (June 2001) times greater than those based on wind speed.

FC CH_4 flux estimates were also higher during the August 2000 and September 2001 comparison studies (Figure 2.4, Table 2.5). FC estimates were 4.8 ± 2.0 (August 2000) and 2.2 ± 15 (September 2001) times greater than SF_6 flux estimates and 5.6 ± 2.5 (August 2000) times greater than wind speed derived flux estimates. FC CH_4 flux estimates during the June 2001 comparison were –6.8 ± 13 times those estimated from SF_6 determined *k* values and –9.3 ± 51 times those estimated from wind speed (Table 2.5).

When CO_2 and CH_4 flux estimates by FCs are regressed against flux estimates using SF_6 derived *k* values (Figure 2.6), the resulting r^2 values were low (0.002 to 0.26 for CO_2 and 0.14 to 0.26 for CH_4) and none of the regressions were significant (Table 2.6). The results are similar when FC estimates are regressed against wind speed derived flux estimates (Figure 2.7, Table 2.6).

Discussion

Comparison of the SF_6 and wind speed approaches to determining k

Gas transfer velocities calculated on the reservoir using SF_6 and those estimated from wind speed were similar and both sets of values are lower than *k* values obtained for larger lakes (Table 2.3). Because effects of wind and precipitation on gas exchange are dampened by surrounding forest and trees protruding from the water surface, reservoir *k* values were expected to be much lower than those of larger, exposed water surfaces.

Similar *k* values based on SF_6 and wind speed measurements meant that both approaches produced similar estimates of CO_2 and CH_4 fluxes, despite findings that other wind speed/gas transfer relationships inadequately approximate gas exchange at low wind

Table 2.6: Statistical comparison of slopes of linear regressions between each method to a theoretical 1:1 slope.

Gas	Regression	r^2 of regression	*p* regression	*p* comparison to 1:1 line*
CO_2				
August 2000	SF_6 and FC	0.0020	0.32	<0.001
June 2001	SF_6 and FC	0.26	0.57	<0.001
September 2001	SF_6 and FC	0.15	0.67	<0.001
August 2000	FC and wind	0.19	0.07	<0.001
June 2001	FC and wind	0.82	<0.01	<0.001
CH_4				
August 2000	SF_6 and FC	0.0030	0.51	<0.001
June 2001	SF_6 and FC	0.00012	0.81	<0.001
September 2001	SF_6 and FC	0.23	0.91	<0.001
August 2000	FC and wind	0.02	0.05	<0.001
June 2001	FC and wind	0.008	0.79	<0.001

*$p < 0.05$ indicates the slopes of the regression lines are significantly different from the slope of the 1:1 line

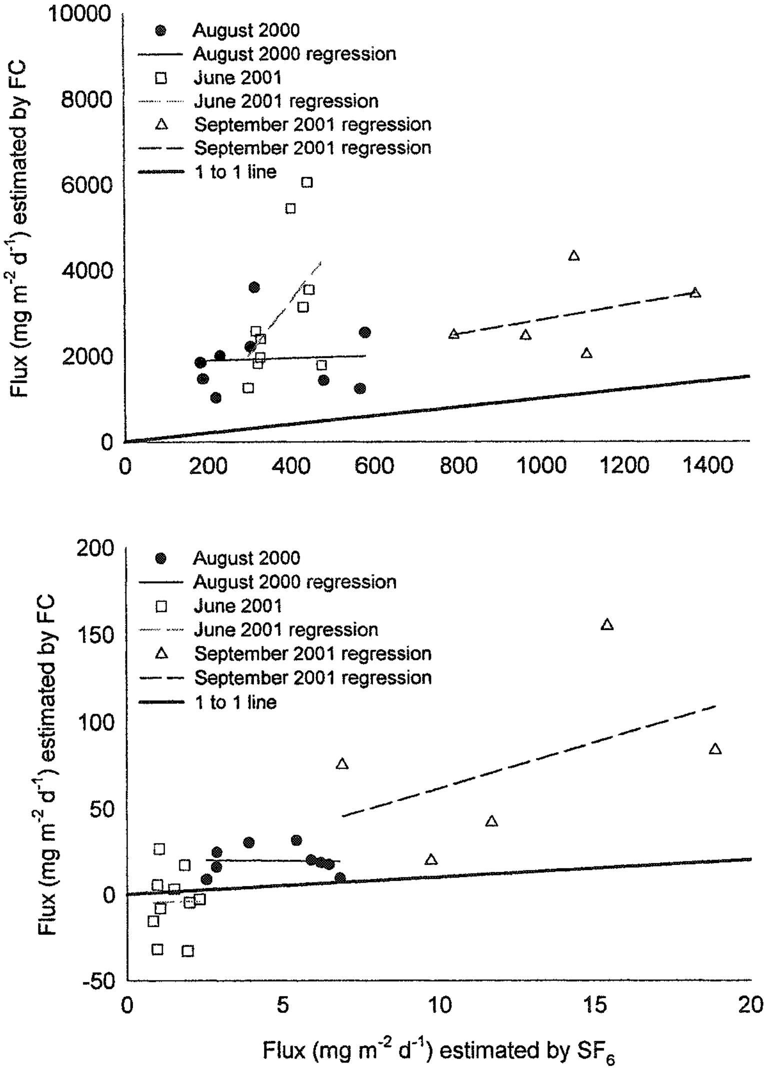

Figure 2.6: Relationship between CO_2 (top graph) and CH_4 (bottom graph) fluxes estimated from SF_6 derived *k* values and FC flux measurements. r^2 of the regressions and *p* values are listed in Table 2.6.

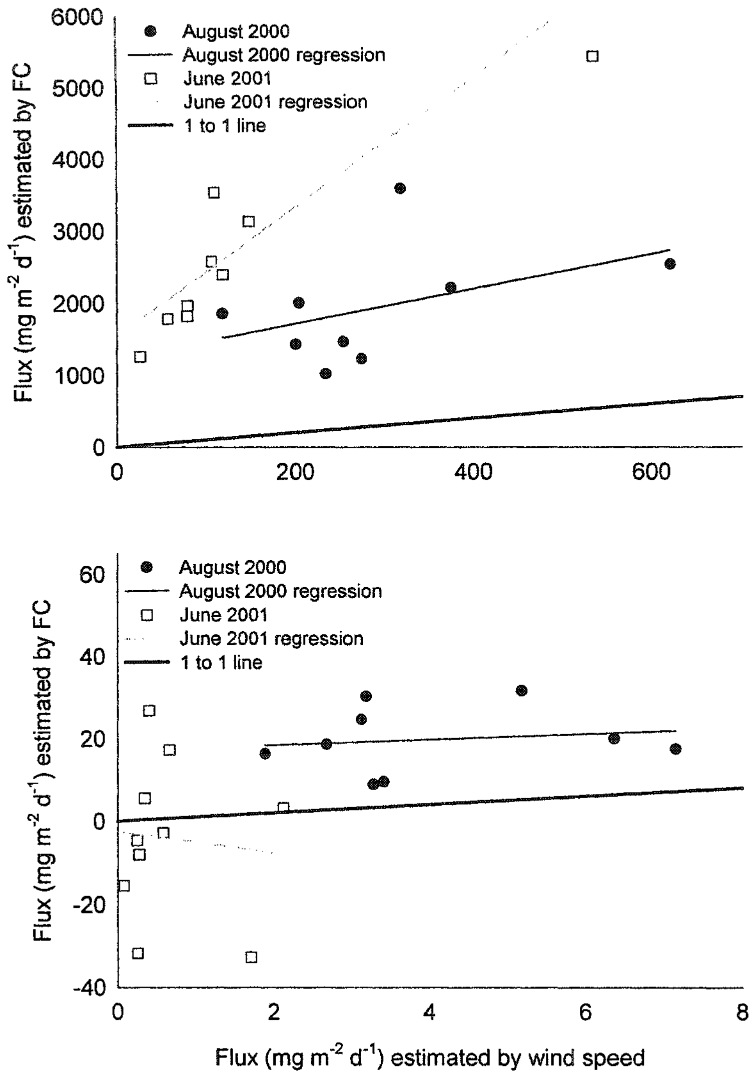

Figure 2.7: Relationship between CO_2 (top graph) and CH_4 (bottom graph) fluxes estimated from wind speed derived *k* values and FC flux measurements. r^2 of the regressions and *p* values are listed in Table 2.6.

speeds such as those characteristic of our site (Cole and Caraco, 1998; Liss and Merlivat, 1986; Wanninkhof, 1992; Clark *et al.*,1995; Wanninkhof *et al.*, 1985). The difference in the estimates that we did observe, though, could be due to an underestimation of *k* using wind speed, or to an overestimation of *k* indicated by SF_6 loss.

Underestimation using wind speed – possible sources of error

Exclusion of factors other than wind speed that affect gas transfer. Wind speeds measured in the reservoir were 3.3 times higher during August 2000 than during June 2001. SF_6 and wind speed derived CO_2 and CH_4 flux estimates agreed much more closely during August 2000, when wind speeds were higher, than during June 2001, when wind speeds were lower (Table 2.5).

With decreasing wind speeds, other phenomena that induce surface turbulence, such as penetrative convection (Crill *et al.*, 1988) and rain (Ho *et al.*, 1997; Banks *et al.*, 1984), become increasingly important in affecting gas transfer (Cole and Caraco 1998). These factors are not incorporated into estimates of gas exchange based on wind speed. Precipitation was minimal during the August 2000 and June 2001 comparison studies. However, differential heating and cooling at the water surface can be a dominant factor in gas exchange in low wind environments (Soloviev and Schlussel, 1994). During the day, solar radiation heats the water, creating convective currents and inducing turbulence at the water surface. At the same time, evaporation occurs at the water surface, having a cooling effect and inducing further turbulence. Crill *et al.* (1988) showed penetrative convection to generate 3 to 200 times greater surface turbulence than that generated by wind on a lake surface. The extent to which penetrative convection may have enhanced gas exchange in the reservoir is not known; however, if thermal convection increased gas transfer, wind speed estimated *k* would be less than actual *k*.

Anemometer position. Wind speeds measured at one central location were assumed to be characteristic of the entire reservoir surface. If this were not the case, *k* derived from wind speed measurements could either underestimate or overestimate actual *k*. Measured wind speeds were not likely greater than overall reservoir wind speeds because the anemometer location was moderately sheltered, as was much of the reservoir. However, one relatively small exposed margin of the reservoir repeatedly experienced higher winds than the anemometer location. If wind speeds at the exposed location were incorporated into overall reservoir wind speed estimates, the estimated *k* value may have more closely approximated the SF_6 calculated gas transfer rates.

Overestimation of k using SF_6 – possible sources of error

In the reservoir environment, SF_6 could possibly overestimate *k* due to loss of SF_6 via mechanisms other than surface gas exchange. The loss via inflow dilution in the reservoir is accounted for (equation [2]). SF_6 loss via sedimentary ebullition can be important because SF_6 is much more soluble in gas than in water. SF_6 concentrations in bubbles may be up to 200 times that dissolved in water (Wanninkhof *et al.*, 1992). However, SF_6 concentrations in bubbles collected periodically at our sites over the 2000 and 2001 flooding seasons were always below detection.

Binding of SF_6 to organic matter or sediments in the reservoir would have drawn SF_6 out of solution. Although no work was done to investigate the potential of SF_6 to sorb onto organic matter in this study, several other studies found this not to occur (Wanninkhof *et al.*, 1985; Watson *et al.*, 1991; Wilson and MacKay, 1996). We believe that any SF_6 losses via ebullition or binding to organic matter are negligible and not important in causing an overestimate of gas transfer (*k*).

SF_6 k values – concerns

Despite lower wind speeds in June 2001 (as with wind speeds measured at the reservoir site, wind speeds at the ELA meteorological site [about 1 km from the reservoir] in August 2000 were about 3.7 times greater than those in June 2001 [K. Beaty, Freshwater Institute, Winnipeg; unpublished data]), the overall *k* obtained for that period from SF_6 was higher than *k* obtained for August 2000 using SF_6 (the SF_6 derived *k* for September 2001 was even higher; however, reservoir wind data for that period are not available for comparison). The dilution correction applied in calculations of *k* was based on inflow rate measurements made during each period, so any dilution changes between August 2000 and June 2001 were accounted for and are not likely a factor in explaining the difference between the calculated *k* values. Rain induced surface turbulence is also an unlikely explanation for the differences in calculated *k*, as precipitation during both comparison studies was negligible.

Comparison of FC flux estimates to estimates based on SF_6 and wind speed

There was no agreement between fluxes estimated with FCs and those estimated from SF_6 and wind speed derived *k* values. FCs consistently estimated much higher and more variable fluxes of both CO_2 and CH_4 than the other two approaches. Duchemin *et al.* (1999) found that FC estimates were 200 to 300% higher than wind speed based TBL estimates in shallow zones (< 3.5 m depth) of a large reservoir. Mean FC flux estimates of CO_2 in June and September 2001 and of CH_4 in August 2000 and September 2001 at our sites (Table 2.5) are higher than average regular emissions of CO_2 (2300 ± 250 mg m^{-2} d^{-1}) and CH_4 (10 ± 0.5 mg m^{-2} d^{-1}) from other studied reservoirs (Duchemin *et al.*, 1999). To support fluxes estimated by FCs, gas transfer velocities in the reservoir would approach those characteristic of much larger, open water surfaces (Tables 2.2 and 2.3). We believe that fluxes measured using FCs overestimate the true flux.

Flux overestimation using FCs – possible sources of error

Chamber induced turbulence. Chamber deployment and subsequent disturbances during sampling and movement by wind likely caused increased turbulence on the water surface. Despite low wind speeds within our sites, chambers were light and were constantly moving, dragging the 45 cm square float around the water surface. The high correlation of FC CO_2 flux estimates with wind speed indicate that wind driven chamber induced turbulence may be important in enhancing gas exchange (or could simply reflect higher gas fluxes at higher wind speeds).

In high wind environments where waves are present, chamber-induced turbulence is probably negligible in affecting overall gas exchange (in fact, sheltering effects of chambers probably become important in hindering flux in turbulent conditions). However, on calm surface waters of the reservoir, any disturbance causing a decrease in the stagnant surface boundary layer thickness might be important in altering gas exchange, especially when aqueous gas concentrations are much higher than atmospheric concentrations.

Furthermore, because our FCs were not covered in reflective material, solar radiation penetrating the plastic sides of the chamber may have increased the temperature of the chamber air, causing convection induced turbulence in the surface waters and increased gas flux. Unfortunately chamber air temperature was not monitored in our study.

Time of deployment. Flux overestimation by FCs may be a function of time of chamber deployment. Flux measurements occurred during the day when stronger winds and thermal induced turbulence were likely to bias fluxes toward higher values.

FCs were deployed in the early morning and late afternoon when wind speeds were on average significantly higher than at night, whereas flux estimates based on *k* values obtained using SF_6 and wind speed incorporate both day and night periods. Gas transfer may be more than twice as high during the day than during the night (daytime $k = 0.18$ and nighttime $k = 0.080$; calculated using the mean day and night wind speeds and equation [7]).

Convective currents created by evaporation and solar heating during the day induce turbulence at the water surface, effectively reducing surface boundary layer thickness. If thermal convection increased gas transfer during times of FC deployment, FC measurements would overestimate gas transfer over a 24 hr period.

Chamber placement effects. FCs were deployed along treeless corridors cut to form canoe paths through the reservoir, where wind could induce more surface turbulence than in densely treed areas of the reservoir where chamber placement was not feasible. Some of the bias in high FC flux estimates could be the result of chamber deployment in more open areas, whereas SF_6 *k* estimates incorporate the whole reservoir, which was mostly treed, and wind speeds used in flux measurements were measured in a relatively sheltered area.

Ebullition effects. If bubbles high in CO_2 and CH_4 originating from sediments entered chambers at a steady rate, diffusive CO_2 and CH_4 fluxes would be overestimated. At maximum ebullition rates (C. Matthews *et al.*, unpublished data), about 0.01 mg CO_2 and 0.05 mg CH_4 could enter the chamber over the 1 hr deployment period. Typical increases in chamber CO_2 over the deployment period ranged from 2.2 to 4.8 mg and ebullition, had it occurred at a maximum rate, could only account for ~0.3% of the observed increase. Typical increases in CH_4 over the deployment period ranged from 0.02 to 0.05 mg, so ebullition could have been important in causing overestimates of CH_4 flux using FCs. However, chambers showing abrupt increases in either CO_2 or CH_4 concentration (indicative of bubble contamination) were not included in flux calculations.

Chemical enhancement effects. At high pH (> 8.5) reactions of CO_2 with water and hydroxide ions draw CO_2 across the boundary layer at an increased rate (Goldman and Dennett, 1983; Bolin, 1960; Smith, 1985). While chemical enhancement of gas exchange is not accounted for using *k* values based on SF_6 and wind speed measurements, reservoir pH was 5.9 ± 0.1, so chemical enhancement would not have occurred. Furthermore, the FC method gave inflated estimates of CH_4 evasion, which cannot be explained by chemical enhancement.

FC flux estimates – other concerns

Variation in fluxes. The high variation in fluxes estimated amongst chambers in a given sampling run occurred even though surface CO_2, CH_4, and SF_6 concentrations were fairly uniform throughout the reservoir. There is no clear explanation for the observed variability, as emissions did not correspond to water depth and were not related to chamber position within the reservoir. While FCs are considered ideal for the sheltered environment in which this study took place (Duchemin *et al.*, 1999; Kelly *et al.*, 1997), the high variability among chamber flux measurements over a small area seems unrealistic.

CH_4 uptake. In June 2001 the FC method showed the reservoir was acting as a sink for atmospheric CH_4, despite surface water concentrations that were higher than atmospheric equilibrium. The CH_4 decline in the chambers was linear and the relationship usually had an $r^2 > -0.95$. A biofilm present on or just below the water surface could theoretically oxidize CH_4 trapped in the chamber headspace. However, daily CH_4 fluxes alternated between positive and negative throughout the 10-day comparison, making the theory of a hypothetical CH_4 oxidizing film questionable because it would have to have been transient from one day to the next. An experiment showed syringes used to collect FC air samples did not leak CH_4 over the time between sample collection and analysis (R. Hesslein, Freshwater Institute, Winnipeg; unpublished data). The observed negative fluxes may be indicative of an error inherent to FCs.

Underestimation of k by the SF_6 and wind speed approaches – possible sources of error

For FC flux estimates to agree with flux estimates based on both SF_6 and wind speed, SF_6 and wind speed derived flux estimates would have to increase about 6 and 13 times, respectively. Given this necessary increase and good agreement between *k* values measured using SF_6 and estimated from wind speed, it is unlikely that flux underestimation by these approaches is responsible for the observed discrepancy with the FC flux estimates. Nevertheless, both the SF_6 and wind speed approaches of determining *k* could possibly have resulted in underestimated fluxes. The likelihood of underestimated fluxes based on wind speed is discussed above. Ways by which SF_6 could have underestimated fluxes are described below.

Value of n. Assigning an inappropriate value to *n* in equation (3) would have resulted in erroneous calculations of k_{CO_2} and k_{CH_4} from k_{SF_6}. Jähne *et al.* (1987) experimentally determined $n = 0.67$ at very low wind speeds when the boundary was approximated by a smooth surface. With the formation of a rough surface, *n* decreased to 0.5 and remained constant at moderate wind speeds. Ledwell (1984) performed wind-wave tunnel experiments and found $n = 0.5$ at moderate wind speeds as well. In this study, *n* was assigned a value of 0.67 because the wind speeds measured were always extremely low. Given the observed differences between FC and SF_6 based flux estimates, we recalculated the SF_6 estimates using $n = 0.5$. While this value likely represents an impossible extreme for this environment (waves were rarely present in the reservoir), Clark *et al.* (1995) found $n = 0.57 \pm 0.07$ in a small pond at wind speeds slightly higher than those in this study. The new calculations, a theoretical maximum flux estimate, increased CO_2 and CH_4 flux estimates by ~9% and 8%, respectively, an increase not great enough to span the observed difference between FC and SF_6 based flux estimates.

Dilution correction. The use of SF_6 to estimate gas exchange in a system with a low water residence time and a very low gas exchange rate (as in the reservoir) is limited by how accurately the observed loss of SF_6 can be partitioned between gas exchange and dilution. Assuming complete dilution throughout the reservoir may be an oversimplification if inflowing water mixed heterogeneously within the reservoir, in which case the dilution term in equation (2) would account for too large a portion of the observed decrease in SF_6, and thereby lower the value of *k* below its actual value. However, this is not likely a problem because SF_6, CO_2, and CH_4 concentrations were uniform throughout the reservoir, indicating the water body was well-mixed. Furthermore, *k* values were determined for the duration of each comparison study, a time span that allowed assumed dilution rates (100%) to most closely be approximated.

General conclusions

SF_6 worked well as a gas exchange tracer in a small body of water with a short water residence time, but only over periods of time spanning days. In this study, daily SF_6 derived *k* values could not be calculated because of the low gas transfer velocities and short water residence time in the reservoir. Therefore, SF_6 use in sheltered water bodies with short water residence times is valid only with careful interpretation of SF_6 loss due to dilution and when a high sampling frequency is maintained.

Estimates of *k* based on wind speed agreed surprisingly well with SF_6 *k* measurements. Generally, wind speed is considered unreliable for estimating *k* in shallow and sheltered environments. Despite the agreement between the SF_6 and wind speed determinations of *k*, in low wind environments with physical obstructions, *k* estimates based on wind speed exclude other factors such as rain that may generate relatively high levels of surface turbulence and are important causes of gas exchange. Wind speed based estimates of gas flux from such environments should be treated as minimum estimates of gas evasion.

Floating chambers are considered ideal for the environment in which this study took place. However, the results of this study suggest that floating chambers overestimate gas flux in extremely low wind environments (except for June 2001 CH_4 fluxes). Floating chambers are usually criticized for creating stagnant micro-environments that dampen effects of wind and other factors affecting the boundary layer, thereby inhibiting gas transfer in wavy environments. On calm water bodies, however, the opposite may occur. Physical disturbance of the boundary layer during and throughout deployment of the chambers may act to enhance gas transfer. Furthermore, caution must be exercised concerning the timing of FC deployment so as not to bias flux estimates. More research needs to be conducted using FCs on calm water surfaces to better understand factors causing inflated flux estimates.

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Chapter 3: Carbon dioxide (CO_2) and methane (CH_4) production in small reservoirs flooding upland boreal forest

Introduction

In addition to the many environmental and socio-economic consequences of reservoir development, reservoirs have most recently been identified as sources of the greenhouse gases (GHGs) carbon dioxide (CO_2) and methane (CH_4) to the atmosphere (Duchemin *et al.*, 2000; Duchemin *et al.*, 1995; Galy-Lacaux *et al.*, 1997; Galy-Lacaux *et al.*, 1999; Kelly *et al.*, 1997; Scott *et al.*, 1999; Campo and Sanchluz, 1998; Rosenburg *et al.*, 1997). In a recent review of the global contribution of reservoirs to the atmospheric pool of CO_2 and CH_4, St. Louis *et al.* (2000) estimate GHG emissions from reservoirs may be equivalent to as much as 7% of the total global warming potential (GWP) of other anthropogenic carbon emissions.

While concern about CO_2 and CH_4 emissions from reservoirs has led to emissions monitoring in existing reservoirs, to understand the overall *net* effect of reservoir creation on GHG flux to the atmosphere, carbon fluxes in both the undisturbed, natural ecosystem prior to flooding and the flooded landscape must be measured (St. Louis *et al.* 2000; Kelly *et al.*, 1997). All reservoirs studied to date emit CO_2 and CH_4 to the atmosphere, but often forests or wetlands flooded to create reservoirs are sinks of atmospheric carbon.

The Experimental Lakes Area Reservoir Project (ELARP) (Kelly *et al.*, 1997) experimentally flooded a boreal wetland after two years of pre-flood measurements of carbon exchange between the wetland and the atmosphere. Prior to flooding, the wetland was a natural carbon sink of approximately 7 g C m^{-2} yr^{-1}, while after flooding, it became a relatively large source of 130 g C m^{-2} yr^{-1} to the atmosphere. This change was attributed to the loss of the photosynthetic CO_2 sink upon death of the flooded vegetation, as well as the microbial production of CO_2 and CH_4 from decomposition of plant tissues and peat. In flooding a wetland, a worst case scenario was created for long-term carbon GHG emissions due to the large organic carbon (OC) stores held in peat.

Results from the ELARP led researchers to hypothesize that minimizing the amount of OC available for decomposition in the flooded landscape should, on the long-term, reduce GHG emissions from reservoirs. A companion experiment to the ELARP, the FLooded Uplands Dynamics EXperiment (FLUDEX), was designed to address this hypothesis. The FLUDEX consisted of three experimental reservoirs flooding upland boreal forest subcatchments that varied in OC stores in soils and vegetation. The main objectives of the GHG portion of the FLUDEX were to: 1) quantify OC stores in soils and vegetation in each forested subcatchment prior to flooding; 2) quantify soil respiration and CH_4 fluxes from the soils of each subcatchment prior to flooding; and 3) quantify CO_2 and CH_4 production in each reservoir after flooding, and to understand the processes related to this production.

Site description and methods

Site description

The FLUDEX is located at the Experimental Lakes Area (ELA), situated in the Precambrian shield landscape of lakes, wetlands, and upland boreal forest in northwestern Ontario, Canada. Three boreal forest subcatchments that differed in amounts of OC stored in vegetation and soils were chosen for flooding: a moist/high OC forest (High C) (Figure 3.1), a dry/intermediate OC forest (Intermediate C) (Figure 3.2), and a very dry/low OC ridge-top forest (Low C) (Figure 3.3). All sites were dominated by an 18-yr-old fire regenerating jack pine (*Pinus banksiana*) and birch (*Betula* spp.) forest at the time of flooding.

The High C subcatchment was 0.74 ha and was characterized by two forest communities of similar area: a moist jack pine forest, with an under-story of Labrador tea (*Ledum groenlandicum*), *Sphagnum* spp., and leatherleaf (*Chamaedaphne calyculata*) and a drier upland area dominated by jack pine and *Polytrichum* spp. feather mosses (Heubert, 1999). The subcatchment had an average soil depth of 41 cm (Boudreau, 2000) and occasionally had pools of standing water. The High C subcatchment had the largest OC stores of the three subcatchments (66 000 kg C ha^{-1}), with about 58% OC in soils and 42% OC in above ground vegetation (Table 3.1).

The Intermediate C subcatchment was 0.50 ha and consisted of dense jack pine forest with a sparse understory of birch, alder (*Alnus* spp.), and blueberry shrub (*Vaccinium* spp.), and an extensive ground cover of various mosses and herbs (Heubert, 1999). The soil was well drained and had an average depth of 39 cm (Boudreau, 2000). The Intermediate C subcatchment had intermediate levels of stored OC (52 600 kg C ha^{-1}), with the majority in above ground vegetation (53%). The remaining OC (47%) was stored in soils (Table 3.1).

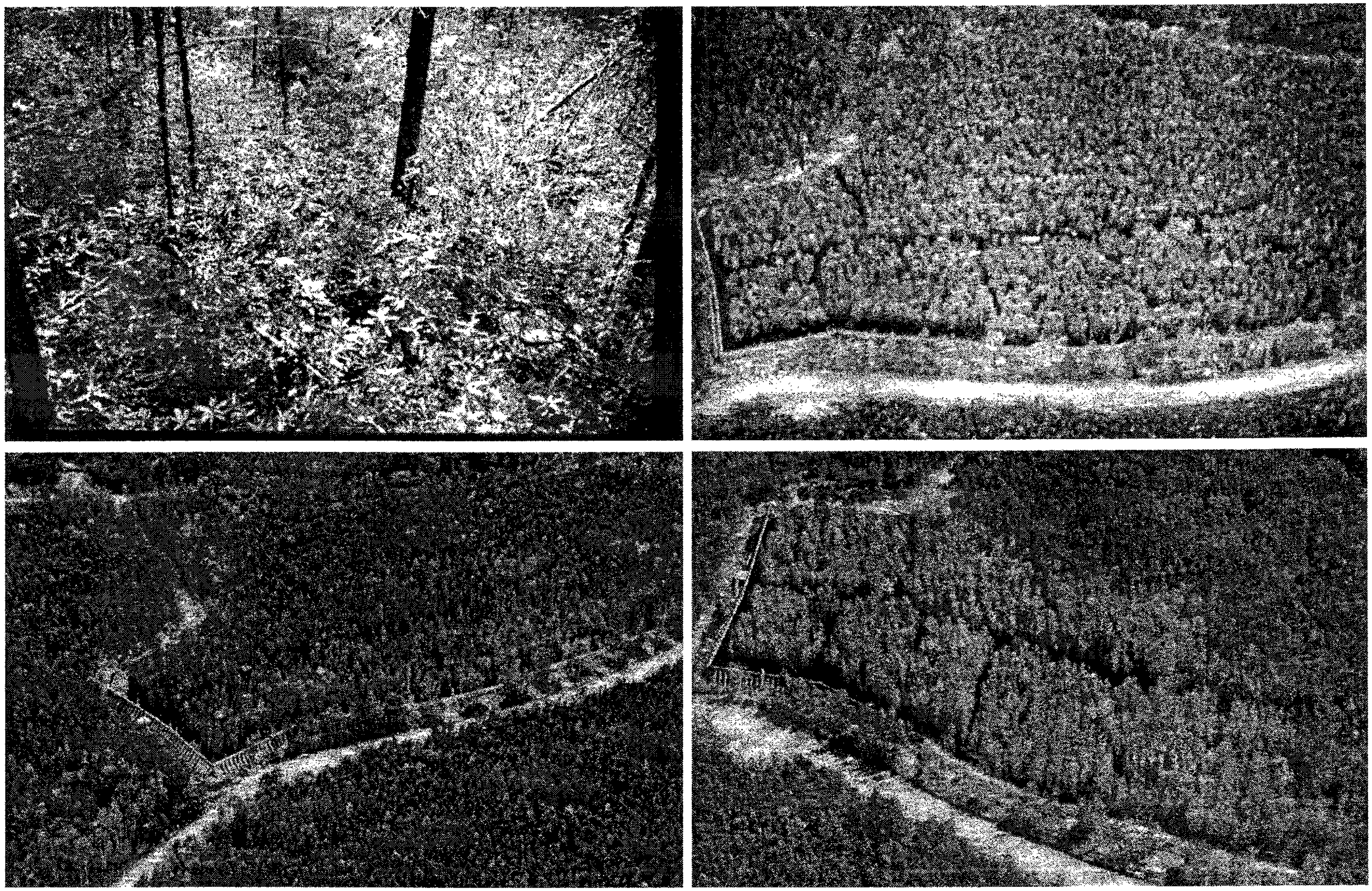

Figure 3.1: Characteristic vegetation of the High C subcatchment prior to flooding (top left) and aerial photos of the High C reservoir during the first season (top right), second season (bottom left) and third season (bottom right) of flooding.

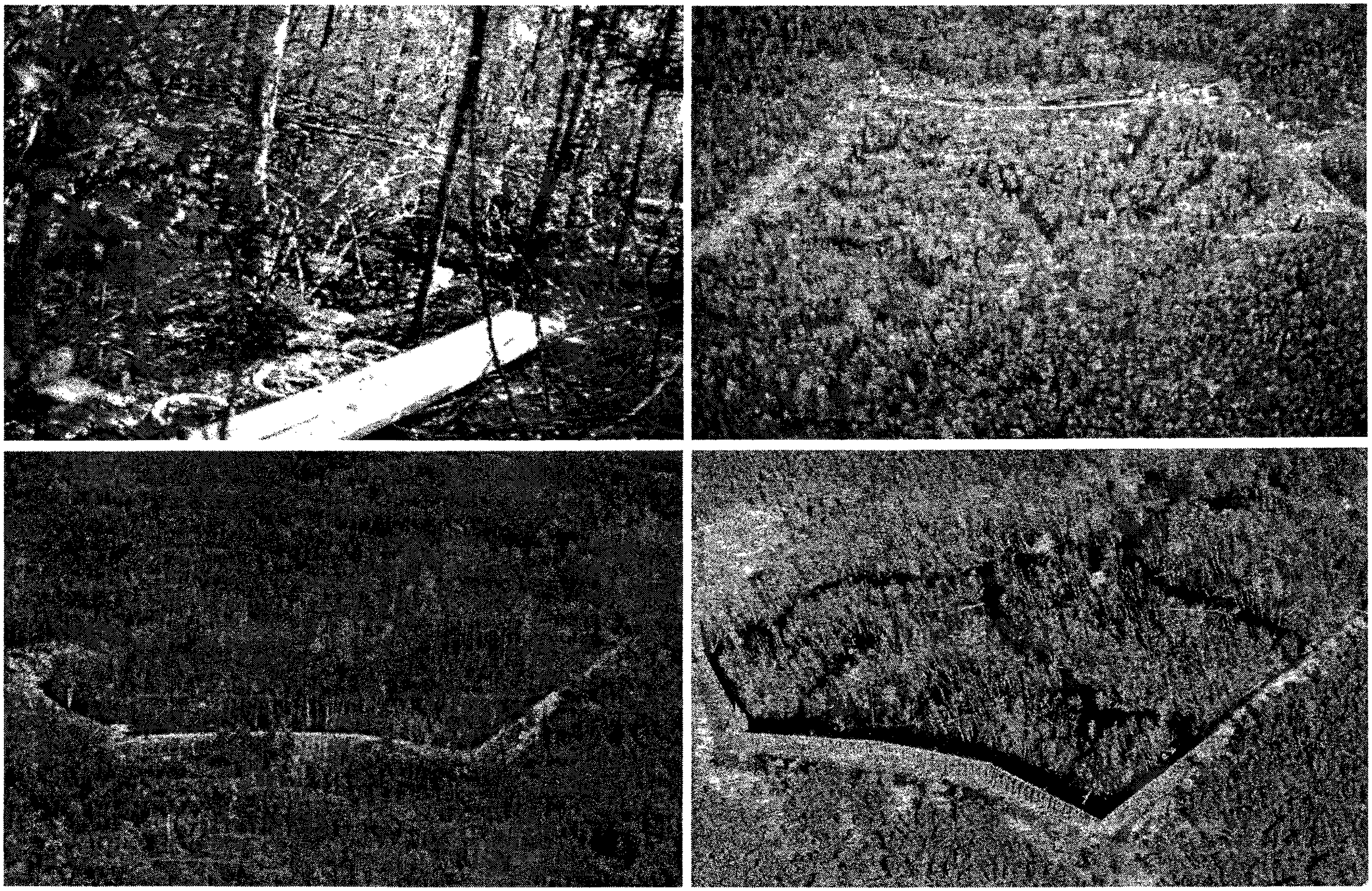

Figure 3.2: Characteristic vegetation of the Intermediate C subcatchment prior to flooding (top left) and aerial photos of the Intermediate C reservoir during the first season (top right), second season (bottom left) and third season (bottom right) of flooding.

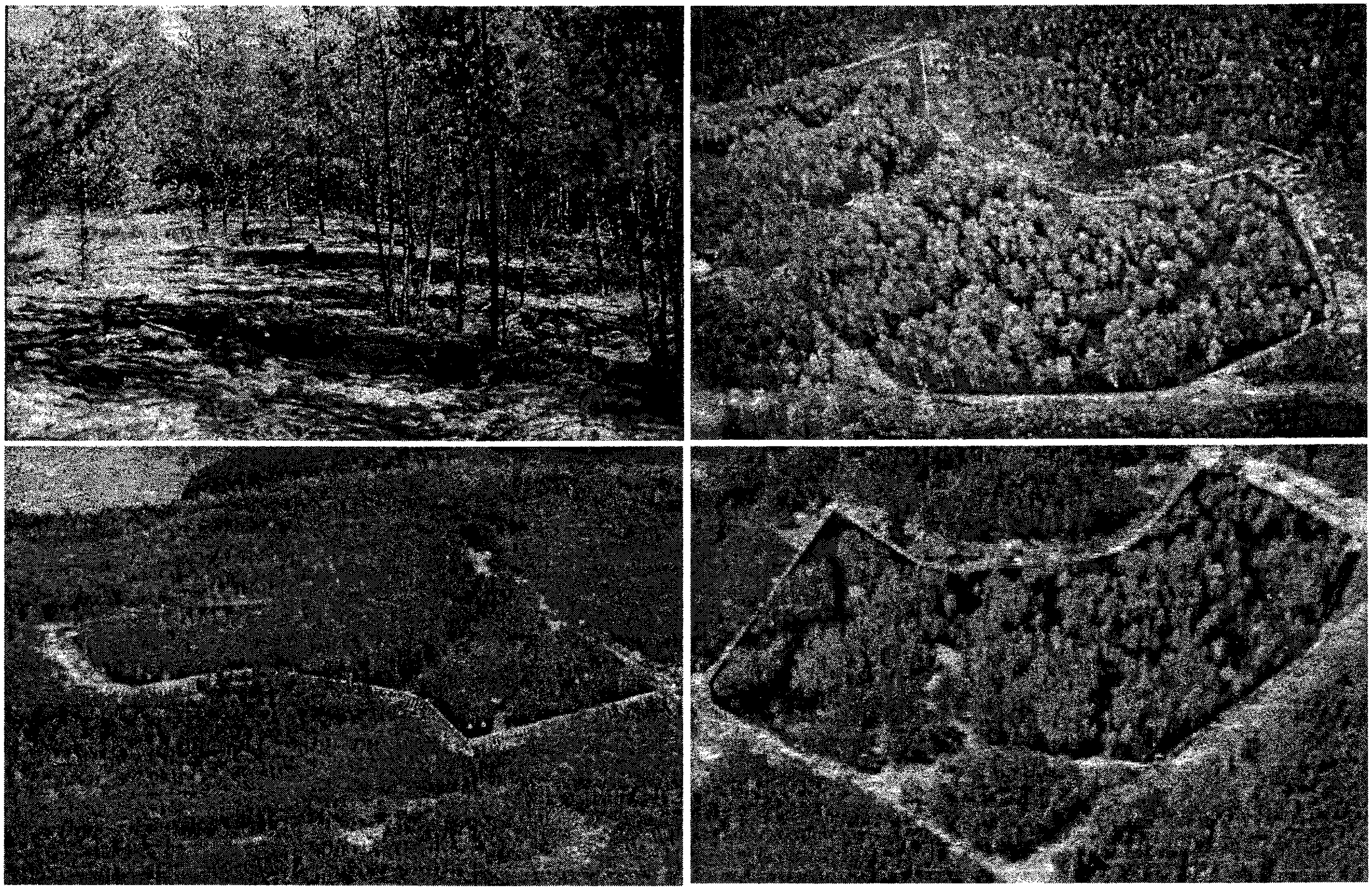

Figure 3.3: Characteristic vegetation of the Low C subcatchment prior to flooding (top left) and aerial photos of the Low C reservoir during the first season (top right), second season (bottom left) and third season (bottom right) of flooding.

Table 3.1: A summary of the carbon stores in the FLUDEX subcatchments prior to flooding. Data marked $^+$ are from Heubert 1999 and data marked * are from Boudreau 2000.

	High C Subcatchment	Intermediate C Subcatchment	Low C Subcatchment
Dominant vegetation (percent coverage)$^+$	*Pinus/Ledum/Sphagnum* (53%) *Pinus/Polytrichum* (47%)	*Pinus/Betula* (100%)	*Pinus/Vaccinium* (73%) *Polytrichum/Cladina* (27%)
Size (ha)	0.74	0.50	0.63
Range of soil depth (cm)*	6.3 to 105.0	15.6 to 90.6	0 to 69.0
Range of forest floor depth (cm)*	1.0 to 37	3.5 to 13	2.0 to 7.5
Carbon in trees (kg C ha^{-1})$^+$	26 200	27 500	19 600
in foliage	2 000	2 700	1 800
in bark	2 400	3 800	2 000
in wood	21 800	21 000	15 800
Carbon in shrubs (kg C ha^{-1})$^+$	1 400	130	200
Carbon in litter (kg C ha^{-1})*	8 900	4 300	2 300
Carbon fungal/humic layer (kg C ha^{-1})*	25 400	14 800	14 800
Carbon mineral layer (kg C ha^{-1})*	4 100	5 900	4 200
Total soil carbon (kg C ha^{-1})* (including litter)	38 400	25 000	21 300
Total carbon in above ground vegetation (kg C ha^{-1})$^+$	27 600	27 600	19 800
Total carbon (kg C ha^{-1})	**66 000**	**52 600**	**41 100**

The Low C subcatchment was 0.63 ha in area. 73% of the area was comprised of jack pine forest with stands of birch and a blueberry shrub understory. The remaining area (27%) was comprised of lichen and moss communities on exposed bedrock (Heubert, 1999). The average soil depth was 15 cm (Boudreau, 2000) and was very dry. This subcatchment contained the least amount of stored OC (41 100 kg C ha^{-1}), with 48% stored in above ground vegetation and 52% in soils (Table 3.1).

Reservoir Construction

Wooden reservoir walls were constructed along the low-lying contours of each subcatchment where the water depth was to be greater than 1 m (Figure 3.4). Upright wooden posts (10 cm × 10 cm) were bolted to bare bedrock and plywood lined with polyethylene sheeting was attached to the posts. On the inner base of the wall, concrete was poured along the bedrock and covered with plastic sheeting and backfilled with the soil removed to expose the bedrock. Gravel dikes lined with polyethylene sheeting were built where the flood depth was less than 1 m. No dikes were built where natural contours of the subcatchments were greater than the maximum height of the water.

The subcatchments were studied in their natural state in 1998, initially flooded in 1999, and again in 2000 and 2001. During the flooding season (June to September), surface water from a nearby oligotrophic lake (Roddy Lake) was drawn using a diesel pump and delivered to the subcatchments via 12.5 cm and 8 cm aluminium irrigation pipe ending in three inlets at the top of the reservoir walls (Figure 3.4). The subcatchments were flooded (Figures 3.1 to 3.3) to an average depth of 0.9 to 1.1 m, with volumes ranging from 4270 to 7120 m^3 (Table 3.2). Water exited each site via a gauged v-notch weir, and water residence times were different for each reservoir (Table 3.3). During the flooding season, water inputs (inflow, precipitation, and direct runoff), storage in soils, and outputs (outflow, dike seepage, and evaporation) were monitored to calculate a detailed water budget for each flooding season (Table 3.3). The reservoirs were emptied from October until May during the three years of study.

Pre-flood Methods

Soil CO_2 and CH_4 fluxes

Soil CO_2 respiration and CH_4 oxidation rates were measured using dark static

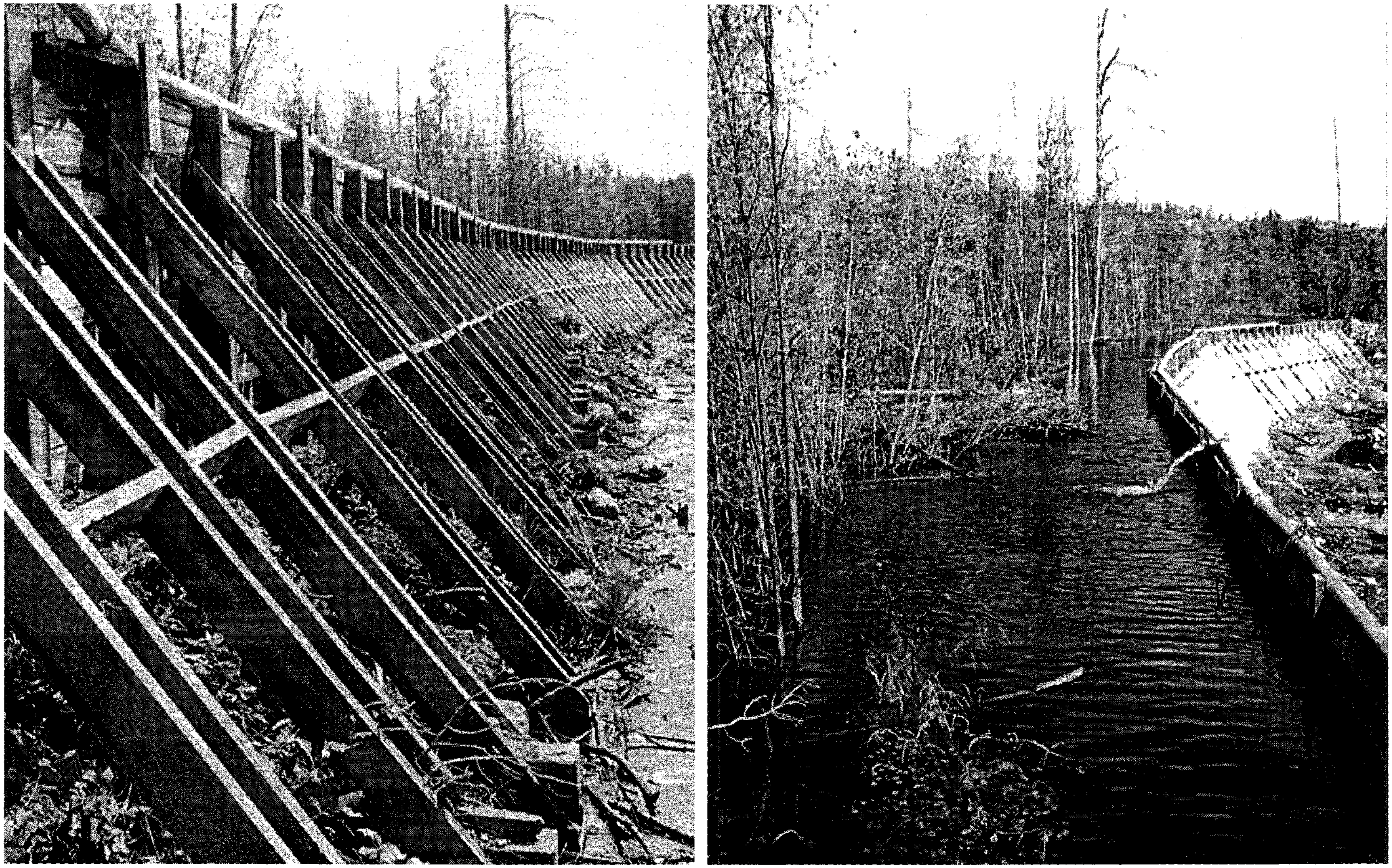

Figure 3.4: Wooden dikes built to enclose the reservoirs (left); the inflow outlet into the Intermediate C reservoir (right).

Table 3.2: A summary of the physical characteristics of the FLUDEX reservoirs (data supplied by K. Beaty, Freshwater Institute, Winnipeg).

	High C reservoir	Intermediate C reservoir	Low C reservoir
Water surface area (m^2)	7 400	5 000	6 300
Direct run-off area (m^2)	47 800	7 300	900
Total site area (m^2)	55 200	12 300	7 200
Reservoir volume (m^3)	6 870	4 270	7 120
Mean depth (m)	0.9	0.9	1.1
Length of wood dike (m)	132	92	237
Length of gravel dike (m)	102	41	94

Table 3.3. Water inputs and outputs (10^3 m^3) to the FLUDEX reservoirs in 1999, 2000, and 2001 (data supplied by K. Beaty, Freshwater Institute, Winnipeg and B. Hall, University of Alberta, Edmonton).

	High C reservoir			Intermediate C reservoir			Low C reservoir		
	1999	2000	2001	1999	2000	2001	1999	2000	2001
Inputs (10^3 m^3)									
Inflow	78.6	93	84.8	76.7	69.6	74.7	96.9	108.6	106.9
Precipitation	0.3	0.4	0.3	0.2	0.3	0.2	0.7	1.0	0.8
Throughfall	1.2	1.6	2.1	0.8	1.1	1.4	0.8	1.1	1.4
Direct run-off	4.7	12	4.9	0.7	1.8	0.8	0.06	0.2	0.09
Total water input	84.7	107	92.2	78.4	72.8	77.1	98.4	110.8	109.1
Outputs (10^3 m^3)									
Weir	60.2	80.2	64.0	60.8	57.3	63.7	33.5	42.5	51.5
Seepage	16.0	15.9	13.0	15.4	13.9	14.5	36.9	19.1	12.2
Bedrock fracture	0	0	0	0	0	0	23.1	43.4	40.8
Outflow pipe	6.9	6.9	6.9	4.3	4.3	4.3	7.1	7.1	7.1
Evaporation	1.6	1.8	1.9	1.4	1.3	1.3	1.4	1.7	1.6
Canopy interception	0.6	0.5	0.3	0.6	0.9	0.3	0.3	0.6	0.1
Total water output	85.3	105.3	86.1	82.4	77.7	84.0	102.3	114.4	113.4
% water yield	101	98	93	105	107	109	104	103	104
Residence time (days)	8.5	7.5	9.4	5.3	5.5	5.7	10.1	7.0	7.1
Water exchanges*	12.4	14.0	11.2	19.8	18.7	18.3	10.4	14.9	14.7

*equals the total water output during the flooding season divided by the reservoir volume chambers in 1998 (Joyce, 2001). Net ecosystem exchange (NEE) of CO_2 (total photosynthesis minus total respiration) was not quantified prior to flooding. CO_2 and CH_4 fluxes from subcatchment soils were also monitored in May 2000 just prior to the second season of flooding for comparison to 1998 pre-flood emissions.

Prior to flooding, transects were cut through each subcatchment to facilitate movement within the subcatchments. At each of five sites randomly chosen along these transects, three grooved plastic collars were embedded into the ground (15 collars total per reservoir). In 1998, fluxes were measured at all 15 collars in each reservoir, while in May 2000, fluxes were measured from only two of the three collars within each site (10 total per reservoir). Fluxes were measured using ~13 L static chambers constructed from 18 L polycarbonate bottles with the bottom third removed. The chambers were covered in foil to omit light and reduce heating during deployment and the neck of the chamber was blocked with a rubber stopper. To extract gas samples from the chamber, tygon tubing fitted with a 3-way valve was attached via an 18-gauge needle to a butyl rubber septum on the side of the chamber. Gas samples were taken four times over a 60 to 90 minute period by drawing air through the tygon tubing using a 5 ml syringe fitted with a 3-way valve such that it could be locked and kept air-tight until the sample was analysed for gas content approximately two to three hours later. CO_2 and CH_4 concentrations were determined using a gas chromatograph (GC) (For GC set-up and methodology, see Chapter 2, this thesis). Linear regression analyses of these concentrations with time were used to determine gas production or consumption rates.

Soil temperatures at 0, –5, –15, and –30 cm from the soil surface were measured after each chamber run using a Campbell Scientific CR10X data logger attached to copper-constance thermocouple rods permanently installed in the soils. Temperatures were logged at 30 second intervals for three minutes at two sites within each subcatchment. Vertical temperature profiles were constructed by averaging temperatures from each depth over the three minute period.

Post-flood Methods

Diffusive CO_2 and CH_4 fluxes from flooded soils were estimated using submerged chambers. Inorganic carbon inputs (DIC and CH_4 added to the reservoirs via inflow, throughfall, direct run-off) and outputs (diffusive surface fluxes of CO_2 and CH_4, DIC and CH_4 losses via outflow water, and ebullition CO_2 and CH_4 fluxes) were measured to construct an inorganic carbon (inorganic C) budget to determine net CO_2 and CH_4 production in each reservoir.

Diffusive soil CO_2 and CH_4 fluxes

Diffusive CO_2 and CH_4 fluxes from flooded soils were measured at the same collar sites used for measuring pre-flood soil respiration and CH_4 oxidation. Submerged chambers (13 L) were constructed from 18 L polycarbonate bottles with removed bottoms and were lead-weighted for stabilization. Fluxes measured using transparent chambers incorporated soil and water column respiration and photosynthetic uptake of CO_2, thereby representing a conservative estimate of soil CO_2 fluxes. Shallow site chambers were placed onto collars by hand, while deep site chambers were placed onto collars using metal poles attached to the neck of the chamber. Debris was cleared from the collar grooves before placement to ensure a tight seal between the chamber and collar. A propellor in the chamber powered by a 9-volt battery-operated motor rotated at 12 rpm to slowly mix chamber water to prevent formation of soil/water boundary layers and concentration gradients during chamber deployment. Tygon tubing fitted with a 3-way valve ran from the chamber to the water surface for sampling purposes.

Water samples were collected from chambers three times over a four to six hour period (initial, intermediate, and final) by drawing 60 ml of chamber water via the tygon tubing into a 60 ml plastic syringe. Before sampling, 30 ml of water was drawn and expelled to flush the tygon tubing. Syringe contents were transferred through a needle to a pre-evacuated 60 ml glass Wheaton bottle capped with a butyl rubber septum and backfilled with a 5 ml ultra high purity (UHP) N_2 headspace. After collection, 0.3 ml of 85% phosphoric acid (H_3PO_4) was injected into the bottles to convert all bicarbonate to CO_2 to allow measurement of total DIC in each sample (CH_4 concentration was unaffected by acid addition). DIC was measured instead of dissolved CO_2 because possible pH changes within the chamber during deployment would have affected dissolved CO_2 concentrations, confounding flux measurements. Gas concentrations in the water were determined using a GC (Chapter 2, this thesis) and production/consumption rates were determined from linear regression analysis of concentration increase or decrease with time. When the r^2 for the relationship was < 0.85, individual chamber rates were not included in calculations of overall reservoir soil fluxes. Flooded soil temperatures were measured at the same sites and depths as were pre-flood profiles.

Inorganic C inputs (inflow water, throughfall, and direct-runoff)

Inflow water was sampled for DIC and CH_4 content at only one site (entering the Low C reservoir) because carbon content in water supplying each of the three reservoirs was the same (unpublished data). Water was collected at 13:00 for three consecutive days bi-weekly in conjunction with surface water $CO_2/CH_4/SF_6$ sampling using evacuated 60 ml Wheaton bottles. Inflow samples were analysed for gas content using a GC (Chapter 2, this thesis). Inflow samples were acidified using 0.5 ml 85% H_3PO_4 and analysed to determine DIC concentrations. Entire season DIC and CH_4 inputs via inflow water were determined by multiplying average seasonal inflow DIC and CH_4 concentrations by the total season inflow water volume (Table 3.3).

Inorganic C inputs via canopy throughfall and direct run-off from the surrounding watershed were estimated by multiplying total throughfall and run-off water volumes over the flooding season (Table 3.3) by average precipitation and run-off DIC and CH_4 concentrations (precipitation data were collected at the ELA meteorological station less than 1 km from the reservoirs and were supplied by S. Page, Freshwater Institute, Winnipeg; run-off concentrations were estimated from surface run-off over a nearby reference upland catchment 114). Seasonal average DIC and CH_4 concentrations in inflow, precipitation, and run-off were used in the calculations because frequent measurements throughout the season showed them to be constant. Water was not collected at the 114 reference catchment in 2001, so average concentrations over 1999 and 2000 were used to determine run-off inputs of DIC and CH_4 into the reservoirs in 2001.

Inorganic C outputs (diffusive surface flux to the atmosphere, outflow water, and ebullition)

Diffusive surface CO_2 and CH_4 fluxes. Sulfur hexafluoride (SF_6) gas was used to determine gas transfer coefficients (*k*) at the surface of each reservoir. *k* values were then used with dissolved surface CO_2 and CH_4 concentrations to estimate diffusive fluxes of these gases to the atmosphere. For theory behind the SF_6 method, and details on SF_6 addition, sample collection and analysis, refer to Chapter 2, this thesis. SF_6 was added to each reservoir every two weeks approximately four to five days before surface sampling for dissolved CO_2 and CH_4 began. After SF_6 concentrations were uniform throughout the reservoir, surface water was collected daily to determine SF_6 concentrations at 10 sites in each reservoir. Samples were analysed within two to four hours of collection using a GC.

Dissolved surface water CO_2 and CH_4 concentrations were measured to estimate diffusive gas flux from the reservoir surfaces. For details on surface water sampling and analysis of dissolved CO_2 and CH_4 concentrations, refer to Chapter 2, this thesis. Generally, surface water samples were collected for three consecutive days every two weeks, resulting in eight sampling sets throughout each flooding season. Samples were collected ~10 cm below the surface at four sites with the following characteristics: 1) treed and deep water, 2) open and deep water, 3) treed and shallow water, and 4) open and shallow water. These sites were chosen to examine differences in surface concentrations in open vs. sheltered areas of the reservoir and in surface waters close to the sediment (< 0.5 m) and far from the sediment (> 1 m). During flooding in 2000, sampling was done three times daily at 7:00, 13:00, and 20:00 to determine if there were diel patterns in concentrations. There were diel differences in CO_2 concentrations, with morning concentrations being higher than evening concentrations. Midday concentrations equaled the average of morning and evening concentrations (unpublished data). Therefore, the midday sampling run was omitted in 2001. Morning and evening concentrations from the four locations were averaged to obtain a concentration representative of the entire reservoir over a 24 hour period.

Outflow water (weir, dike seepage and fracture flow, and drawdown) DIC and CH_4 losses. Outflow water was collected at the weir of each reservoir to determine the amount of DIC and CH_4 exiting each reservoir; sample collection and analyses procedures were the same as for inflow precedures. Because weir outflow DIC and CH_4 changed over the season, outputs via weir outflow water were determined by multiplying average bi-weekly outflow DIC and CH_4 concentrations by weir outflow water volume during the two week period and adding the bi-weekly losses to obtain an estimate of entire season loss.

Water volumes exiting via dike seepage and bedrock fracture flow (Low C reservoir, Table 3.3) were multiplied by weir outflow DIC and CH_4 concentrations to estimate DIC and CH_4 loss over the season. These estimates of inorganic C loss via seepage and fracture flow are conservative because weir outflow DIC and CH_4 concentrations were lower than DIC and CH_4 concentrations in bottom and porewaters (Joyce, 2001; Venkiteswaran, 2002) that also contributed (to an unknown extent) to seepage and fracture flow.

Total DIC and CH_4 outputs during drawdown were estimated by multiplying water column DIC and CH_4 concentration profiles taken at 120, 100, 80, 60, 40, 20 and 2 cm above the soil/water interface two to four days before drawdown began (Joyce 2001; Venkiteswaran 2002) by volumes corresponding to each of those depth profiles (determined from storage-discharge curves for each of the reservoirs [K. Beaty, Freshwater Institute, Winnipeg; unpublished data]). The amounts of C stored in each depth profile were then added to obtain the total amount of C in the reservoirs at the time of drawdown.

Ebullition – bubble traps. Five inverted 30 cm diameter plastic funnels were deployed at the water surface in each reservoir to trap bubbles originating from the flooded soils. The traps were stabilized with lead weights and fitted with square styrofoam floats (30 cm by 30 cm) and the neck of the trap was fitted with a plexi-glass cylinder capped with a butyl rubber septum. Bubble traps were deployed continuously and checked weekly to bi-weekly for bubble accumulation. Bubble volume was measured by removing the accumulated gas via the rubber septum with an 18-gauge needle on a 10 or 60 mL syringe. Fresh bubbles were collected into another bubble trap for concentration analysis by probing the flooded soils with a pole. 1 ml of fresh bubbles was then drawn from the bubble trap and injected into a 13 ml glass Wheaton bottle capped with a butyl rubber septum and containing atmospheric air. 1 ml of air was removed from the bottle before addition of the 1 ml of fresh bubbles. After each sampling event, bubble traps were cleaned, the stopper replaced, and reset. CO_2 and CH_4 concentrations in fresh bubbles were determined using a GC (Chapter 2). Bubble concentrations were multiplied by bubble volume collected over the week long period to determine ebullition CO_2 and CH_4 fluxes.

Inorganic C mass budget and net GHG (CO_2 and CH_4) production

Total inorganic C outputs (diffusive surface flux, outflow, draw-down, seepage, and ebullition flux) minus total inputs (inflow, throughfall, and direct run-off) represented the *net CO_2 and CH_4 production* by each reservoir during the flooding season. The budget approach was necessary to determine net GHG production primarily because we could not adequately estimate reservoir soil CO_2 and CH_4 emissions from submerged chamber flux measurements. Furthermore, reservoir inorganic C concentrations were dictated by water residence times in each reservoir. Because water residence times differed between reservoirs and between flooding seasons (Table 3.3), DIC/CO_2 and CH_4 concentrations (and therefore, inorganic carbon outputs via outflow losses and diffusive gas flux) were not directly intercomparable among reservoirs. Constructing an inorganic C mass budget for each reservoir allowed for differences in water residence times to be accounted for.

The total mass of inorganic C that entered and left each reservoir via inflow and outflow water was divided by the reservoir area and days flooded (giving fluxes in mg m^{-2} d^{-1}) to account for differences in reservoir size and total days flooded. CO_2 and CH_4 outputs via diffusive surface flux and ebullition were estimated by averaging bi-weekly CO_2 and CH_4 flux estimates to obtain a seasonal average flux (mg m^{-2} d^{-1}).

Results and discussion

Diffusive soil fluxes measured using submerged chambers are presented first, followed by a discussion of relative contributions of individual components included in the inorganic C mass budget, and overall net GHG production in the FLUDEX reservoirs. A general discussion of the relationship between OC storage and net GHG production, GHG production patterns over time, and the net effect of reservoir creation in boreal landscapes, follows.

Soil fluxes pre and post-flood

CO_2 soil respiration rates prior to flooding (1900 to 2400 mg CO_2-C m^{-2} d^{-1}) (Table 3.4, Figure 3.5) were similar to rates measured in other boreal and temperate forest sites (Table 3.5). During the first season of flooding, average soil CO_2 fluxes over the entire season (4200 to 9200 mg CO_2-C m^{-2} d^{-1}) were higher than pre-flood CO_2 respiration rates in all reservoirs (Table 3.6). During three weeks prior to the second flooding season (May 2000), all subcatchment soils emitted CO_2 to the atmosphere at rates four to five times lower than the actual 1998 pre-flood emissions (Joyce, 2001) (Table 3.4). Throughout flooding in 2000, soil CO_2 fluxes were much lower than in 1999, and season averages ranged from 940 to 1400 mg CO_2-C m^{-2} d^{-1}. In 2001, average season fluxes ranged from 800 to 1510 mg CO_2-C m^{-2} d^{-1} (Table 3.6). Generally, soil CO_2 fluxes measured at the individual chamber sites decreased with each season of flooding, with the exception of the High C reservoir in 2001. While average soil temperatures for each flooded season were different (i.e., soils in 2001 were 2 to 3 °C warmer than in 2000; Figure 3.6), there was no relationship between average soil temperature and soil CO_2 fluxes ($r^2 = 0.03, p = 0.32$). Average post-flood soil

Table 3.4: Soil CO_2-C and CH_4-C fluxes from the High, Intermediate, and Low C subcatchments in 1998 (pre-flood) and May 2000 (before second season of flooding). 1998 data are from Joyce (2001).

	High C subcatchment flux (mg C m^{-2} d^{-1})		Intermediate C subcatchment flux (mg C m^{-2} d^{-1})		Low C subcatchment flux (mg C m^{-2} d^{-1})	
CO_2	1998	2000	1998	2000	1998	2000
Range	1960 to 3170	215 to 975	1480 to 4160	211 to 1390	680 to 3710	178.9 to 976.9
Mean ± SD	2400 ± 530	533 ± 208	2700 ± 280	679 ± 200	1900 ± 240	540.9 ± 189.0
CH_4						
Range	–1.1 to –0.3	–6.1 to 11.8	–1.3 to –0.7	–6.3 to 5.1	–1.0 to –0.4	–9.0 to 4.5
Mean ± SD	–0.8 ± 0.2	1.1 ± 4.4	–1.1 ± 0.1	–1.1 ± 2.8	–0.7 ± 0.1	–2.6 ± 3.5

Table 3.5: Summary of soil CO_2 respiration and CH_4 oxidation rates measured in forest sites similar to the FLUDEX subcatchments. Negative values represent a flux from the atmosphere to the terrestrial ecosystem.

Forest type	Location	Age (years)	Time of year	CO_2 flux ($g\ CO_2\ m^{-2}\ d^{-1}$)	CH_4 flux ($mg\ CH_4\ m^{-2}\ d^{-1}$)	Reference
boreal	northern Ontario	18	May to September	1 to 21	0.6 to –2.6	This study (Joyce, 2001)
boreal	northern Manitoba	15 to 30	————		–0.6 to –2.4*‡	Amaral and Knowles (1997)
boreal	northern Manitoba	—	May to September	0 to 27	–0.15 to –0.75*	Savage *et al.* (1997)
temperate	New Hampshire	100	entire year	0 to 25	0.15 to –3.7*	Crill (1991)
subarctic	Québec	—	————		–0.75 to –2.3*‡	Ademsen and King (1993)
temperate	Massachusetts	66 to 84	entire year		–1.8 to –4.5*	Castro *et al.* (1995)
temperate	Massachusetts	65	spring to fall		–2.2 to –3.1*	Castro *et al.* (1994)
temperate	southern Ontario	—	April to November	2 to 15	–0.04 to –1.1	Lessard *et al.* (1994)

*calculated from published values

‡fluxes were determined from cores and mass soil samples, not on site

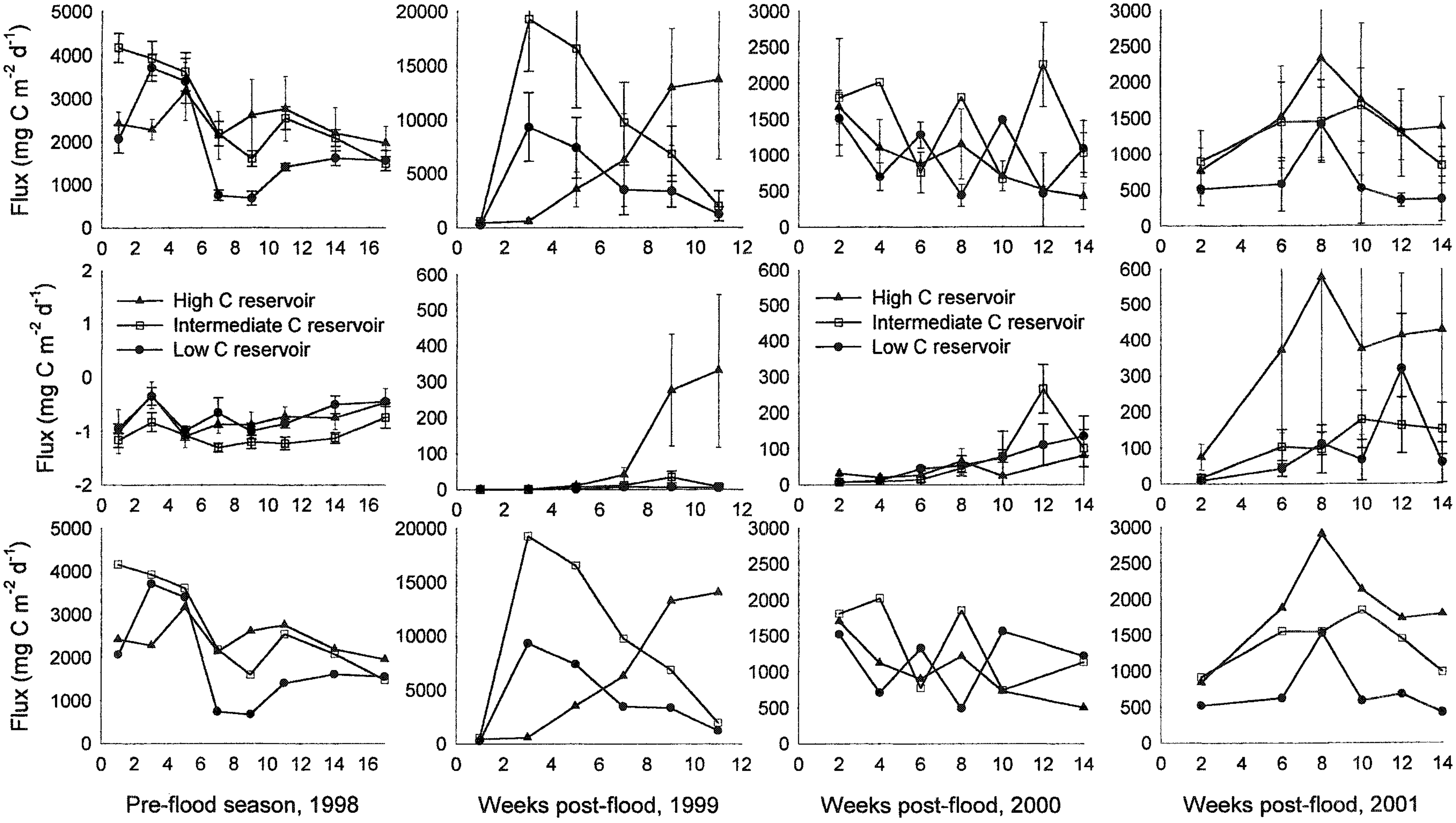

Figure 3.5: Pre-flood (1998) and submerged (1999, 2000, 2001) soil fluxes of CO_2 (top graph), CH_4 (middle graph), and total (CO_2+ CH_4) C (bottom graph) from the high, intermediate, and low C subcatchments/reservoirs. 1998 and 1999 data are from Joyce (2001).

Table 3.6: Diffusive CO_2-C and CH_4-C fluxes from flooded soils in the High, Intermediate, and Low C reservoirs in 1999, 2000, and 2001. 1999 data are from Joyce (2001).

	High C reservoir flux (mg C m^{-2} d^{-1})			Intermediate C reservoir flux (mg C m^{-2} d^{-1})			Low C reservoir flux (mg C m^{-2} d^{-1})		
CO_2-C	1999	2000	2001	1999	2000	2001	1999	2000	2001
Range	450-13700	420-1670	770-2330	580-19000	660-2260	835-1670	270-9300	440-1510	360-1410
Mean ± SD	6300 ± 3200	940 ± 520	1510 ± 1800	9200 ± 3000	1400 ± 1140	1330 ± 330	4200 ± 1750	1040 ± 620	800 ± 940
CH_4-C									
Range	0.02-280	21-81	8-270	0.3-34	8-270	18-180	0.1-7	7-140	9-320
Mean ± SD	110 ± 65	36 ± 78	370 ± 570	10 ± 5.7	66 ± 91	120 ± 150	3.3 ± 2.2	62 ± 80	130 ± 210
Total C	6410	980	1880	9210	1470	1450	4200	1100	930

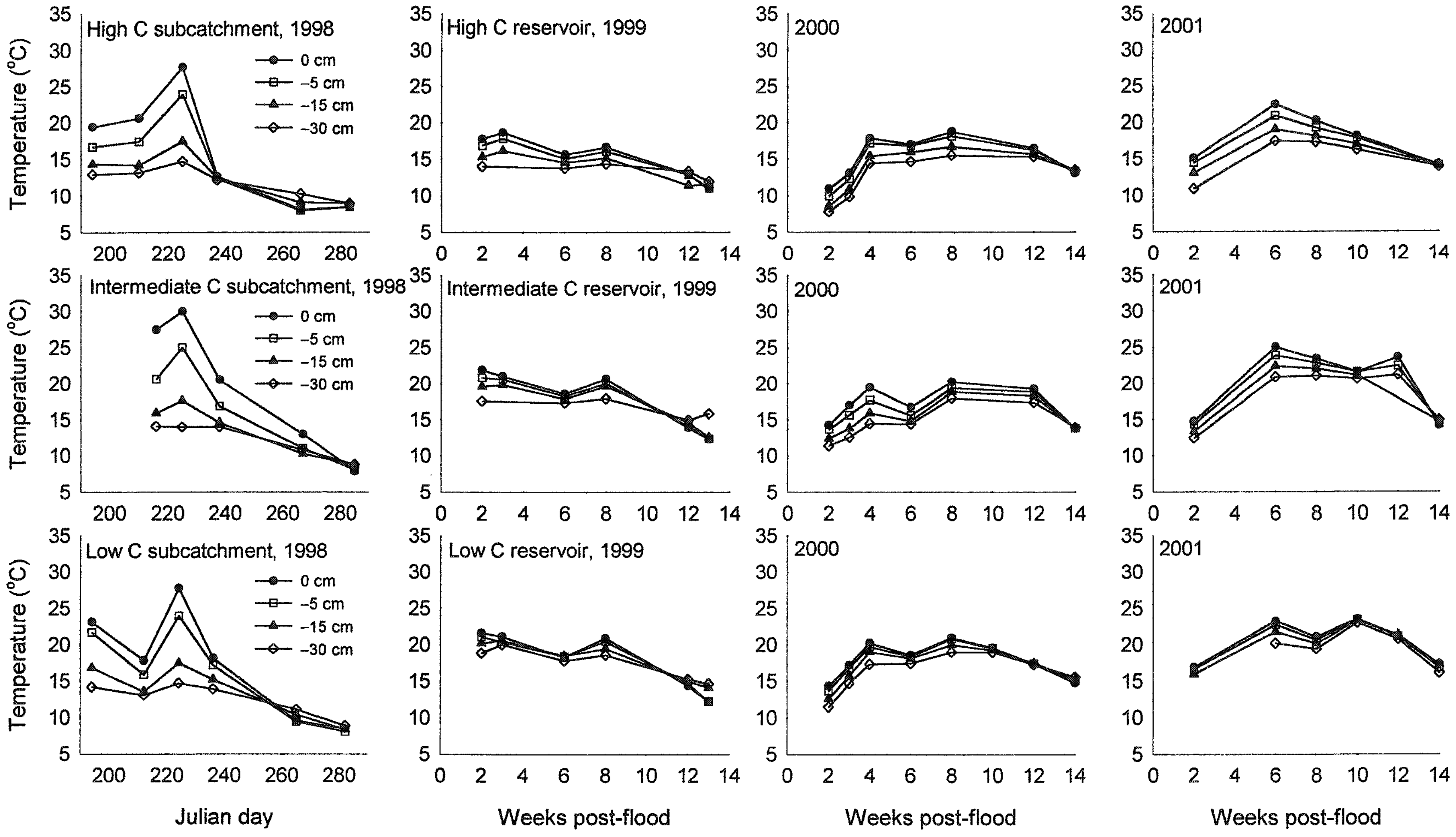

Figure 3.6: Sediment temperatures at 0, –5, –15, and –30 cm in each reservoir during the 2000 and 2001 flooding seasons. Each point is an average of six measurements from each depth at two sites within each reservoir (error bars not included to allow trends to be visible).

temperatures were strongly negatively correlated to DOC concentrations in reservoirs ($r^2 = 0.74$; $p < 0.001$).

Prior to flooding, subcatchment soils consumed CH_4 at rates of 1.1 to 0.7 mg CH_4-C m^{-2} d^{-1} (Table 3.4, Figure 3.5), similar to rates measured in other boreal and temperate forest sites (Table 3.5). All soils changed from being CH_4 sinks prior to flooding to CH_4 sources after flooding. Average flooded soil fluxes in 1999 ranged from 3 to 110 mg CH_4-C m^{-2} d^{-1} (Table 3.6). Prior to re-flooding in 2000, both the Intermediate and Low C subcatchment soils again consumed CH_4 at rates similar to pre-flood rates; however, mean CH_4 fluxes from the High C subcatchment soils in May 2000 were positive (Table 3.4). Waterlogged soils in the High C reservoir likely provided an environment conducive to methanogenesis instead of CH_4 oxidation (because water slows the diffusion of O_2 into soils), whereas both the Intermediate and Low C reservoirs were relatively well drained. Average flooded soil fluxes in 2000 ranged from 36 to 66 mg CH_4-C m^{-2} d^{-1}. In 2001, flooded soil fluxes averaged 120 to 370 mg CH_4-C m^{-2} d^{-1} (Table 3.6). Soil CH_4 fluxes generally increased with each flooding season (with the exception of the High C reservoir in 2000). There was no relationship between average soil temperatures and soil CH_4 fluxes ($r^2 = 0.18$, $p = 0.10$).

Diffusive flooded soil CO_2 and CH_4 fluxes measured at the five sites within each reservoir were highly variable (Figure 3.5). Within-site variability of CH_4 fluxes from wetlands can be very high (Moore and Knowles, 1990; Moore *et al.*, 1990; Whalen and Reeburgh, 1988; 1992; Bubier *et al.* 1993). Intra reservoir heterogeneity in soil/vegetation characteristics and microbial communities likely caused spatial variability in soil CO_2 and CH_4 fluxes. Organic carbon quality affects litter and soil decomposition rates (Meentemeyer, 1978; Aerts, 1997; Moore *et al.*, 1999; Taylor *et al.*, 1989; Melillo *et al.*, 1989). Soil was not analysed for composition of labile (e.g., carbohydrates) versus recalcitrant (e.g., lignin) C compounds. Microbial community compositions were not characterized in the soils of the subcatchments/reservoirs. Temperature also influences decomposition rates (Bartlett and Harriss, 1993; Roulet *et al.*, 1992). Reservoir soil temperatures were consistent from site to site, so spatial variability in temperature is therefore not likely a cause of the flux variation.

In this study, flux measurements were made at four to five sites within each reservoir, over an area equivalent to less than 0.01 % of the entire reservoir bottom. Standard errors were approximately 100% of the mean measurement. Due to the spatial variation in flooded soil CO_2 and CH_4 fluxes between sites within each reservoir and the small surface area from which fluxes were measured, we believe overall estimates of soil flux (i.e., decomposition rates) from each reservoir cannot reliably be scaled up from individual chamber measurements. Nevertheless, because soil flux measurements were made at the same individual sites prior to flooding in 1998 and during all three subsequent flooding seasons, they are useful in determining overall trends in soil fluxes from those specific sites over time.

Net reservoir GHG production – inorganic C mass budget approach

Due to our inability to accurately estimate whole reservoir flooded soil fluxes from individual chamber measurements, mass budgets incorporating inorganic C inputs and outputs were constructed to determine rates of net reservoir CO_2 and CH_4 production.

Inorganic C inputs (inflow, throughfall, and direct run-off)

DIC and CH_4 concentrations in inflow water were similar during all three seasons of flooding (Figure 3.7). Inflow DIC concentrations in 1999, 2000, and 2001 were 130 ± 3, 126 ± 6, and 120 ± 6 μmol L^{-1}. Inflow CH_4 concentrations in 1999, 2000, and 2001 were 0.11 ± 0.04, 0.11 ± 0.03, and 0.13 ± 0.03 μmol L^{-1}. Seasonal average DIC concentrations in precipitation were also consistent between flooding seasons, although they were variable within each season (CH_4 in precipitation was below our detection limit of 1 ppm). Average DIC concentration in precipitation over 1999 to 2001 was 40 ± 20 μmol L^{-1}. Average run-off DIC and CH_4 concentrations varied over 1999 to 2000, mostly due to the infrequent sampling regime (dictated by rainfall amounts sufficient to collect run-off from the 114 reference catchment). Average DIC concentrations were 190 ± 70 μmol L^{-1} (ranging from 140 to 240 μmol L^{-1}) and average CH_4 concentrations were 0.07 ± 0.1 μmol L^{-1} (ranging from 0 to 0.15 μmol L^{-1}).

Inflow water was the major water input into all three reservoirs ($\geq$ 90% of total inputs), and represented a higher proportion of total water inputs in the Intermediate and Low C reservoirs (96 to 98%) than in the High C reservoir (~ 90%) (Table 3.3). For all three reservoirs, inorganic C inputs via inflow water were much greater than inputs via throughfall and direct run-off (Tables 3.7 to 3.9). Throughfall water inputs were minimal compared to the overall input water volume (< 2%) (Table 3.3), and inorganic C inputs via throughfall

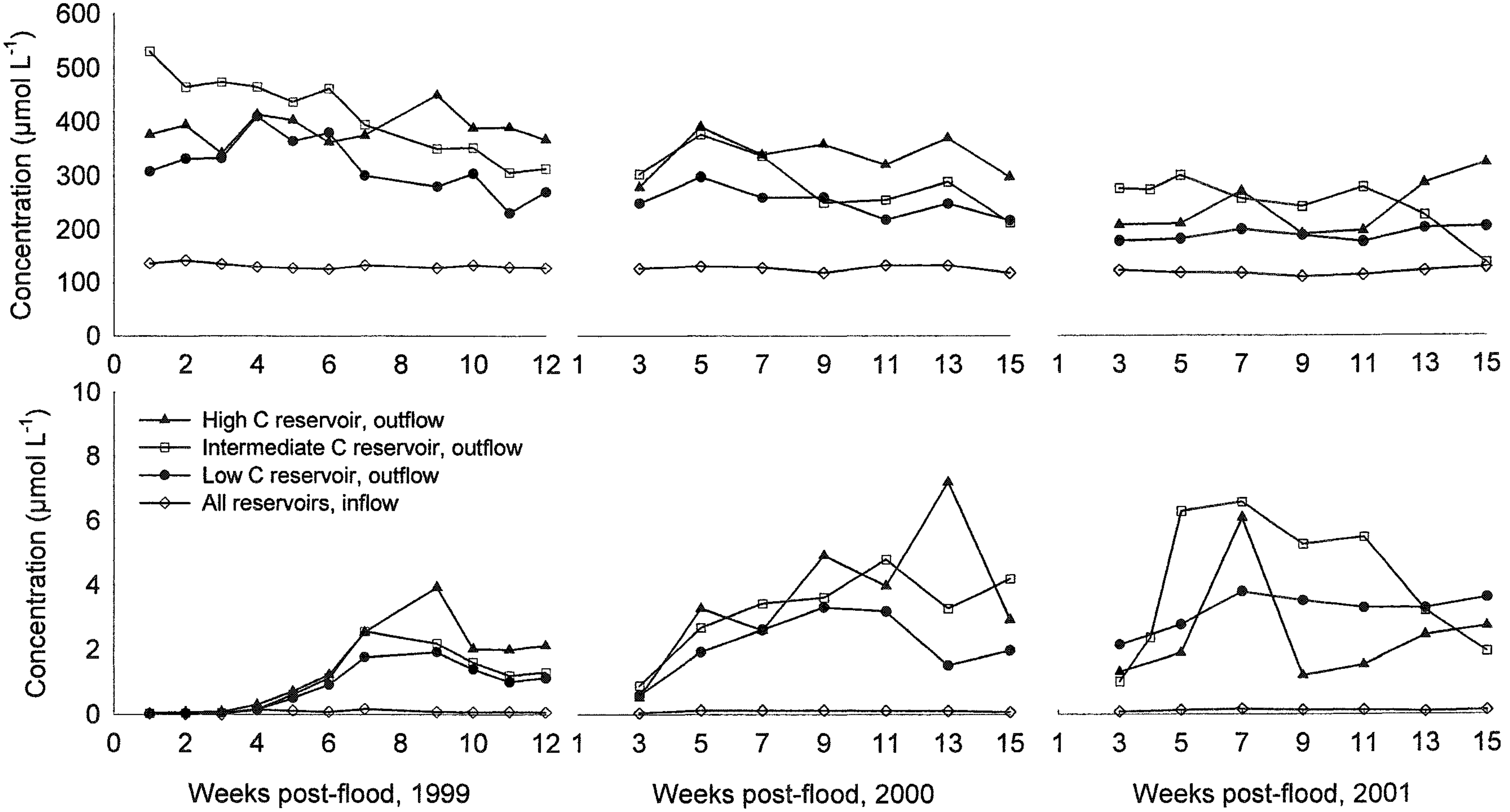

Figure 3.7: Dissolved inorganic carbon (DIC) (top) and CH_4 (bottom) entering and exiting the three FLUDEX reservoirs via inflow and outflow water during 1999, 2000, and 2001. 1999 data are from Joyce (2001).

Table 3.7: Mass balance budget of inorganic C (CO_2/DIC and CH_4) inputs and outputs (mg C m^{-2} d^{-1}) to and from the High, Intermediate, and Low C reservoirs during the flooding season 1999. Data are from Joyce (2001).

	High C reservoir			Intermediate C reservoir			Low C reservoir		
Inputs	CO_2/DIC	CH_4	Total C	CO_2/DIC	CH_4	Total C	CO_2/DIC	CH_4	Total C
Inflow	162	0	162	234	0	234	235	0	235
Throughfall	0	0	0	0	0	0	0	0	0
Direct run-off	14	1	15	2	0	2	0	0	0
Total inputs	176	1	177	236	0	236	235	0	235
Outputs									
Diffusive flux	399	2	401	287	1	288	364	2	366
(range)	(379 to 418)	(2 to 2)	(381 to 420)	(275 to 298)	(1 to 1)	(276 to 299)	(339 to 389)	(1 to 2)	(340 to 391)
Outflow[§]	501	1	502	794	4	798	457	1	458
Ebullition	0	0	0	0	0	0	0	0	0
Total outputs	900	3	903	1081	5	1086	821	3	824
(range)	(880 to 919)	(3 to 3)	(883 to 922)	(1069 to 1092)	(5 to 5)	(1074 to 1097)	(796 to 846)	(2 to 3)	(798 to 849)
Net production	**724**	**2**	**726**	**845**	**5**	**850**	**586**	**3**	**589**
(range)	**(704 to 743)**	**(2 to 2)**	**(706 to 745)**	**(833 to 856)**	**(5 to 5)**	**(838 to 861)**	**(561 to 611)**	**(2 to 3)**	**(563 to 614)**

[§] includes volume exiting the reservoir via the v-notch weir, during drawdown, via seepage under/through the reservoir walls and bedrock fractures

Table 3.8: Mass balance budget of inorganic C (CO_2/DIC and CH_4) inputs and outputs (mg C m^{-2} d^{-1}) to and from the High, Intermediate, and Low C reservoirs during the flooding season 2000.

	High C reservoir			Intermediate C reservoir			Low C reservoir		
Inputs	CO_2/DIC	CH_4	Total C	CO_2/DIC	CH_4	Total C	CO_2/DIC	CH_4	Total C
Inflow	183	0	183	204	0	204	262	0	262
Throughfall	2	0	2	2	0	2	2	0	2
Direct run-off	27	0	27	6	0	6	1	0	1
Total inputs	212	0	212	212	0	212	265	0	265
Outputs									
Diffusive flux	260	5	265	158	3	161	195	4	199
(range)	(248 to 272)	(5 to 6)	(253 to 278)	(150 to 167)	(2 to 3)	(152 to 170)	(186 to 204)	(4 to 4)	(190 to 208)
Outflow[§]	532	5	537	499	5	504	542	5	547
Ebullition	0	5	5	0	4	4	1	13	14
(range)	(0 to 1)	(2 to 8)	(2 to 9)	(0 to 1)	(2 to 6)	(2 to 7)	(0 to 1)	(10 to 17)	(10 to 18)
Total outputs	792	15	807	657	12	669	738	22	760
(range)	(780 to 805)	(12 to 19)	(792 to 824)	(649 to 667)	(9 to 14)	(658 to 681)	(728 to 747)	(19 to 26)	(747 to 773)
Net production	**580**	**15**	**595**	**445**	**12**	**457**	**473**	**22**	**495**
(range)	**(568 to 593)**	**(12 to 19)**	**(580 to 612)**	**(437 to 455)**	**(9 to 14)**	**(446 to 469)**	**(463 to 482)**	**(19 to 26)**	**(482 to 508)**

[§] includes volume exiting the reservoir via the v-notch weir, during drawdown, via seepage under/through the reservoir walls and bedrock fractures

Table 3.9: Mass balance budget of inorganic C (CO_2/DIC and CH_4) inputs and outputs (mg C m^{-2} d^{-1}) to and from the High, Intermediate, and Low C reservoirs during the flooding season 2001.

	High C reservoir			Intermediate C reservoir			Low C reservoir		
Inputs	CO_2/DIC	CH_4	Total C	CO_2/DIC	CH_4	Total C	CO_2/DIC	CH_4	Total C
Inflow	159	0	159	198	0	198	212	0	242
Throughfall	2	0	2	2	0	2	2	0	2
Direct run-off	11	0	11	2	0	2	0	0	0
Total inputs	172	0	172	202	0	202	244	0	244
Outputs									
Diffusive flux	305	7	312	180	4	184	220	8	228
(range)	(281 to 328)	(6 to 8)	(287 to 336)	(167 to 194)	(3 to 5)	(170 to 199)	(203 to 237)	(7 to 8)	(210 to 245)
Outflow[§]	326	4	330	489	8	497	426	8	434
Ebullition	2	23	25	2	20	22	2	22	24
(range)	(1 to 3)	(14 to 32)	(15 to 35)	(1 to 3)	(9 to 31)	(10 to 34)	(1 to 2)	(15 to 29)	(16 to 31)
Total outputs	633	34	667	671	32	703	648	38	686
(range)	(608 to 657)	(24 to 44)	(632 to 701)	(657 to 686)	(20 to 44)	(677 to 730)	(630 to 665)	(30 to 45)	(660 to 710)
Net production	**461**	**34**	**495**	**469**	**32**	**501**	**404**	**38**	**442**
(range)	**(436 to 485)**	**(24 to 44)**	**(460 to 529)**	**(455 to 484)**	**(20 to 44)**	**(475 to 528)**	**(386 to 421)**	**(30 to 45)**	**(416 to 466)**

[§] includes volume exiting the reservoir via the v-notch weir, during drawdown, via seepage under/through the reservoir walls and bedrock fractures

were low for all reservoirs in all flooding seasons (Tables 3.7 to 3.9). Only the High C reservoir, with a larger watershed area than the other two reservoirs (Table 3.2), had an important water input from direct run-off (Tables 3.7 to 3.9). During all three flooding seasons, inorganic C inputs via direct run-off into the High C reservoir were ~5 times greater than similar inputs into the Intermediate and Low C reservoirs, but still represented only ~10% of the inorganic C input via inflow to the High C reservoir (Tables 3.7 to 3.9). All three water inputs were negligible sources of CH_4.

Inorganic C outputs

Diffusive surface CO_2 and CH_4 fluxes. Gas transfer velocities (*k*) measured using SF_6 were lower than those obtained on larger, open water bodies (Table 3.10). The Low C reservoir consistently had the highest *k* values; a sparse tree canopy, as well as its location on a ridge top, exposed the reservoir surface to relatively greater winds than the other two reservoirs. *k* values in 2001 were higher than in 2000 (Table 3.10), likely because needle and leaf loss from dead trees during the winter exposed reservoir surfaces to the effects of wind and precipitation, factors that enhance gas exchange (Ho *et al.*, 2000; Banks *et al.*, 1984; Cole and Caraco, 1998; Wanninkhof, 1992). *k* values were not determined in 1999. However, weekly *k* values calculated for each reservoir in 2000 were averaged and applied to 1999 surface CO_2 and CH_4 concentrations to estimate diffusive surface fluxes (*k* values determined in 2001 were not used because canopy cover was much less than in 1999, when the reservoirs were relatively much more sheltered).

In 1999, mean surface water CO_2 concentrations in the High, Intermediate, and Low C reservoirs were 260 ± 10, 290 ± 10, and 190 ± 10 μmol L^{-1} (Table 3.11). In 2000, mean CO_2 concentrations in the High, Intermediate, and Low C reservoirs were 180 ± 30, 150 ± 40, and 110 ± 30 μmol L^{-1} (Table 3.11). Mean CO_2 concentrations in 2001 were 140 ± 30, 130 ± 20, and 85 ± 10 μmol L^{-1} in the High, Intermediate, and Low C reservoirs (Table 3.11). Dissolved surface CO_2 concentrations remained fairly constant from the beginning to end of each flooded season (Figure 3.8).

In 1999, mean surface water CH_4 concentrations in the High, Intermediate, and Low C reservoirs were 1.4 ± 0.1, 0.8 ± 0.03, 0.7 ± 0.04 μmol L^{-1} (Table 3.11). In 2000, mean CH_4 concentrations in the High, Intermediate, and Low C reservoirs were 3.3 ± 2.4, 2.2 ± 1.4 and

Table 3.10: Gas transfer velocities estimated on the three FLUDEX reservoirs, two lakes at the ELA, and other lakes in the U.S. and U.K. All k values were determined using SF_6 and are normalized to k_{600}.

Location	Surface Area (ha)	k_{600} (cm hr^{-1})	Reference
High C reservoir, ELA, Ontario	0.69	0.53 (2000); 0.87 (2001)	This study
Intermediate C reservoir, ELA, Ontario	0.50	0.38 (2000); 0.57 (2001)	This study
Low C reservoir, ELA, Ontario	0.66	0.70 (2000); 1.1 (2001)	This study
Sutherland pond, New York	4.1	~3.2*	Clark *et al.*, 1995
Lake 658, ELA, Ontario	8.4	2.7	Matthews *et al.*, unpublished data
Lake 302, ELA, Ontario	13	1.5 – 5	Wanninkhof *et al.*, 1991
Dozmary Pool, UK	14	~ 5.4*	Upstill-Goddard *et al.*,1990
Mirror Lake, New Hampshire	15	2.7	Cole and Caraco, 1998
Siblyback Lake, UK	56	~6.7*	Upstill-Goddard *et al.*,1990
Rockland Lake, New York	100	~2.5*	Wanninkhof *et al.*, 1985

*represents average of published values

Table 3.11: Dissolved concentrations of CO_2 and CH_4 in surface waters of the High, Intermediate, and Low C reservoirs in 1999, 2000, and 2001. * 1999 data are from Joyce (2001).

	High C reservoir (µmol L^{-1})			Intermediate C reservoir (µmol L^{-1})			Low C reservoir (µmol L^{-1})		
CO_2	1999	2000	2001	1999	2000	2001	1999	2000	2001
Range	227 to 283	104 to 209	113 to 194	224 to 356	114 to 210	98 to 160	151 to 220	47 to 145	63 to 102
Mean ± SD	260 ± 10	180 ± 30	140 ± 30	290 ± 10	150 ± 40	130 ± 20	190 ± 10	110 ± 30	85 ± 10
CH_4									
Range	0.05 to 3.4	0.12 to 6.1	0.51 to 8.1	0.04 to 2.3	0.08 to 3.8	0.50 to 4.5	0.03 to 2.2	0.05 to 3.4	1.1 to 3.2
Mean ± SD	1.4 ± 0.1	3.3 ± 2.4	3.6 ± 3.2	0.8 ± 0.03	2.2 ± 1.4	2.5 ± 1.7	0.7 ± 0.04	1.9 ± 1.2	2.5 ± 0.8

*Differences in water residence times between reservoirs (Table 3) influenced surface water CO_2 and CH_4 concentrations, making direct inter reservoir, and to some extent, inter seasonal, comparisons of CO_2 and CH_4 concentrations invalid.

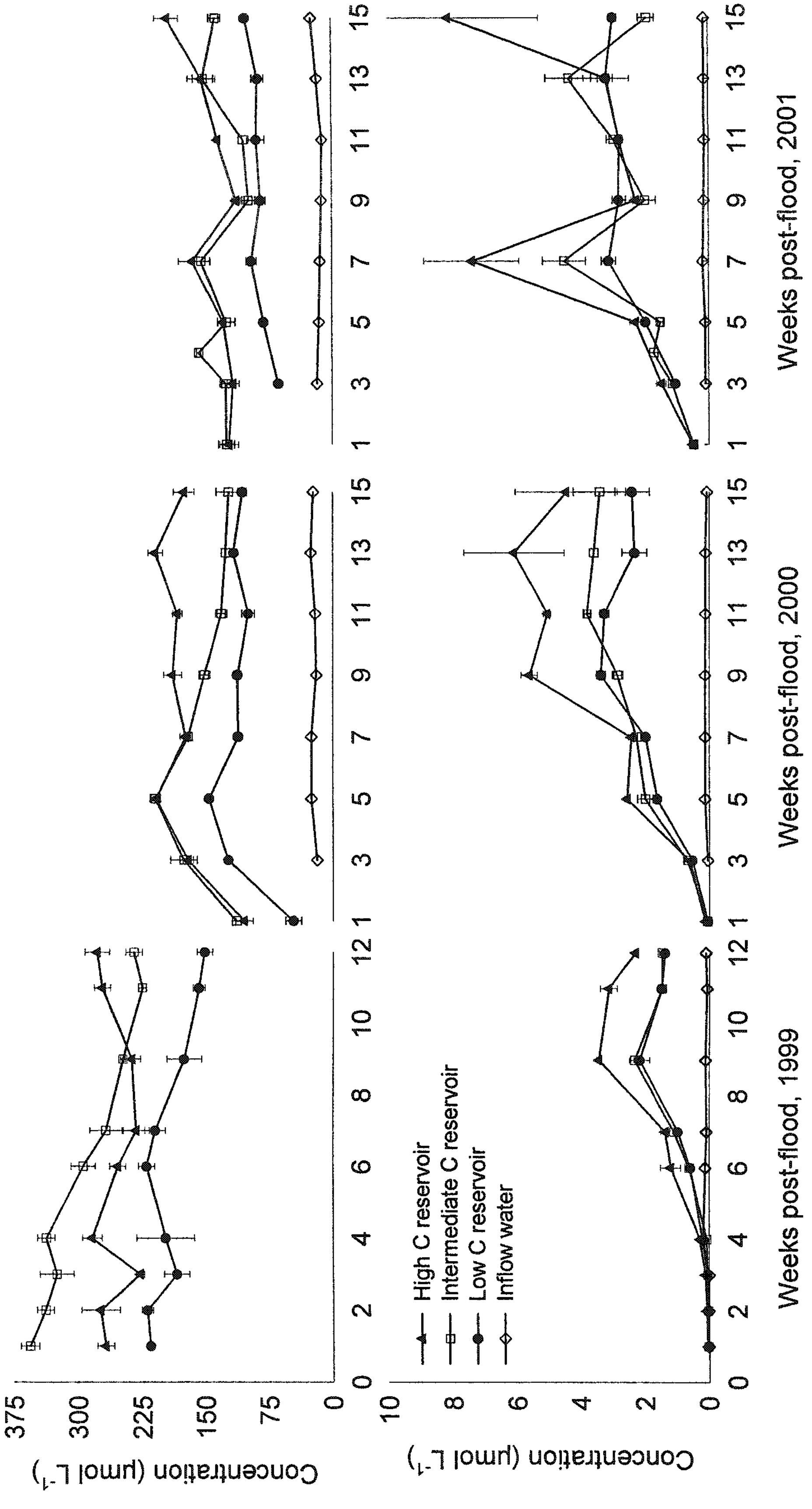

Figure 3.8: Dissolved surface concentrations of CO_2 (top) and CH_4 (bottom) in the three FLUDEX reservoirs during 1999, 2000, and 2001. 1999 data are from Joyce (2001). Dissolved CO_2 concentrations in inflow water were not measured in 1999.

1.9 ± 1.2 μmol L^{-1} (Table 3.11). In 2001, mean dissolved CH_4 concentrations were 3.6 ± 3.2, 2.5 ± 1.7, and 2.5 ± 0.8 μmol L^{-1} in the High, Intermediate, and Low C reservoirs (Table 3.11). Surface water CH_4 concentrations generally increased from the beginning to end of each flooded season (Figure 3.8).

Diffusive surface CO_2 fluxes were highest during the first year of flooding (Figure 3.9), with seasonal averages ranging from 1050 to 1460 mg CO_2 m^{-2} d^{-1}. In 2000, average CO_2 fluxes ranged from 580 to 950 mg CO_2 m^{-2} d^{-1}. Fluxes remained at about the same level in 2001, ranging from 660 to 1110 mg CO_2 m^{-2} d^{-1} (Table 3.12). Overall, CO_2 fluxes from the FLUDEX reservoirs were lower than those measured from the ELARP reservoir, reservoirs flooding boreal forest and peatlands, reservoirs flooding tropical landscapes, and beaver ponds flooding boreal forest (Table 3.13).

Diffusive surface CH_4 fluxes increased with each year of flooding (Figure 3.9, Table 3.12). CH_4 fluxes in 1999 ranged from 1.1 to 2.8 mg CH_4 m^{-2} d^{-1}. In 2000, CH_4 fluxes ranged from 3.3 to 7.1 mg CH_4 m^{-2} d^{-1}. CH_4 fluxes in 2001 ranged from 5.4 to 10.3 mg CH_4 m^{-2} d^{-1} (Table 3.12). Diffusive surface CH_4 fluxes from the FLUDEX reservoirs were lower than those measured in other temperate reservoirs, considerably lower than CH_4 fluxes measured from tropical reservoirs, but similar to those measured from boreal beaver ponds (Table 3.13).

Weir outflow, dike seepage/fracture flow, and drawdown. DIC and CH_4 weir outflow concentrations varied with each season (Figure 3.6). Season average outflow DIC concentrations in 1999 were 380 ± 40, 430 ± 75, and 320 ± 50 μmol L^{-1} in the High, Intermediate, and Low C reservoirs. In 2000, season average outflow DIC concentrations were 340 ± 40, 290 ± 60, and 250 ± 30 μmol L^{-1} in the High, Intermediate, and Low C reservoirs. In 2001, concentrations were 240 ± 50, 260 ± 25, and 190 ± 10 μmol L^{-1} in the High, Intermediate, and Low C reservoirs. Season average outflow CH_4 concentrations in 1999 were 1.1 ± 1.2, 0.9 ± 0.9, and 0.7 ± 0.7 μmol L^{-1} in the High, Intermediate, and Low C reservoirs. In 2000, season average outflow CH_4 concentrations were 3.6 ± 2.1, 3.3 ± 1.3, and 2.2 ± 1.0 μmol L^{-1} in the High, Intermediate, and Low C reservoirs. In 2001, concentrations were 2.5 ± 1.7, 4.3 ± 2.1, and 3.2 ± 0.6 μmol L^{-1} in the High, Intermediate, and Low C reservoirs.

Water losses via weir outflow, drawdown, and seepage represented 97 to 98% of

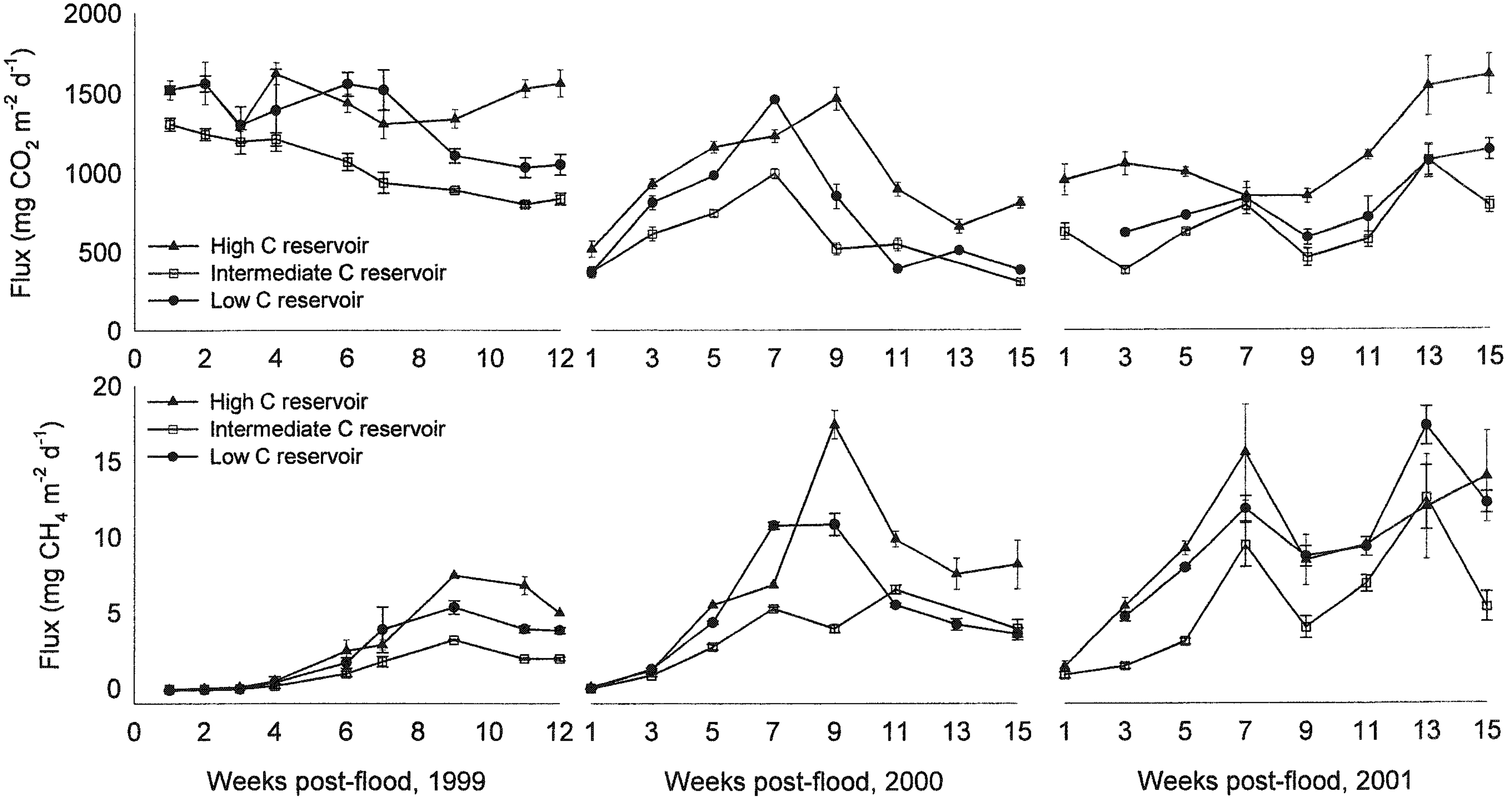

Figure 3.9: Diffusive surface fluxes of CO_2 (top) and CH_4 (bottom) from the three FLUDEX reservoirs during 1999, 2000, 2001. 1999 fluxes were estimated from surface concentration data from Joyce (2001) and using gas transfer velocities (*k*) determined during the 2000 flooding season.

Table 3.12: Diffusive surface* and ebullition CO_2 and CH_4 fluxes from the High, Intermediate, and Low C reservoirs in 1999, 2000, and 2001. 1999 fluxes were calculated using concentration data from Joyce (2001).

CO_2	High C reservoir (mg CO_2 m^{-2} d^{-1})			Intermediate C reservoir (mg CO_2 m^{-2} d^{-1})			Low C reservoir (mg CO_2 m^{-2} d^{-1})		
Diffusive	1999	2000	2001	1999	2000	2001	1999	2000	2001
Range	1290-1620	520-1460	840-1600	800-1310	300-990	380-1060	1030-1560	370-1450	580-1130
Mean ± SD	1460 ± 120	950 ± 310	1110 ± 290	1050 ± 190	580 ± 230	660 ± 220	1340 ± 220	720 ± 380	810 ± 210
Ebullition									
Range	0-0.13	0-6.3	0.1-21	0-1.31	0-4.3	0.5-17	0	0-8.7	0.6-17
Mean ± SD	0.03 ± 0.04	1.7 ± 2.5	7.7 ± 8.2	0.4 ± 0.5	1.3 ± 1.9	6.1 ± 5.2	0	2.9 ± 3.6	6.0 ± 5.7
CH_4	High C reservoir (mg CH_4 m^{-2} d^{-1})			Intermediate C reservoir (mg CH_4 m^{-2} d^{-1})			Low C reservoir (mg CH_4 m^{-2} d^{-1})		
Diffusive	1999	2000	2001	1999	2000	2001	1999	2000	2001
Range	–0.07-7.5	0.09-17.4	1.4-15.5	–0.03-3.2	–0.01-6.5	0.9-12.5	–0.07-5.4	–0.03-10.8	4.7-17.3
Mean ± SD	2.8 ± 3.0	7.1 ± 5.4	9.4 ± 4.6	1.1 ± 1.2	3.3 ± 2.3	5.4 ± 4.0	2.1 ± 2.2	5.0 ± 4.0	10.3 ± 4.0
Ebullition									
Range	0-0.67	0-27	0.1-96.8	0-0.96	0-25.3	1.3-78.1	0	0-53.8	0.3-75.7
Mean ± SD	0.01 ± 0.02	7.0 ± 10.0	30.7 ± 34.0	0.1 ± 0.3	5.2 ± 9.5	26.6 ± 23.3	0	17.5 ± 22.1	29.1 ± 28.3

*Diffusive surface CO_2 and CH_4 fluxes were estimated from surface water CO_2 and CH_4 concentrations, which were influenced by water residences times in the reservoirs. Because water residence times varied among reservoirs and slightly with each flooding season (Table 3) direct diffusive flux comparisons between reservoirs and flooding seasons should be done with caution.

Table 3.13: CO_2 and CH_4 fluxes from the surfaces of temperate and tropical reservoirs of different ages and sizes, as well as beaver ponds flooding landscape similar to that flooded by the FLUDEX reservoirs.[+]

Reservoir	Location	Age (years)	Area (km^2)	Flux mg CO_2 m^{-2} d^{-1}	Flux mg CH_4 m^{-2} d^{-1}	Reference
High C	northwestern Ontario	3	0.0074	950 to 1460[=]	2.8 to 9.4	this study
Intermediate C	northwestern Ontario	3	0.0050	580 to 1050[=]	1.1 to 5.4	this study
Low C	northwestern Ontario	3	0.0063	720 to 1340[=]	2.1 to 10.3	this study
ELARP	northwestern Ontario	3	0.2	3700	60	Kelly *et al.*, 1997
Laforge-1	northern Québec	2	960	400 to 9600	0.5 to 202	Duchemin *et al.*, 1995
La Grande-2	northern Québec	17	2835	300 to 6500	0.5 to 53	Duchemin *et al.*, 1995
Revelstoke[§]	British Columbia	8	120	1560 to 3000	———	Schellhase *et al.*, 1997
Kinsbasket[§]	British Columbia	19	430	460 to 600	———	Schellhase *et al.*, 1997
Arrow[§]	British Columbia	22	520	570 to 1770	———	Schellhase *et al.*, 1997
Whatshan[§]	British Columbia	40	15	540 to 790	———	Schellhase *et al.*, 1997
Curua-Una	Brazil	21	72	2900	16	Duchemin *et al.*, 2000
Petit Saut	French Guyana	4	365[॥]	5000[†]	3000[†]	Galy-Lacaux *et al.*, 1997
Beaver pond	Manitoba	———	0.05	6200[‡*]	110[‡*]	Roulet *et al.*, 1997
Beaver pond	Ontario	———	0.04	———	7 to 14[‡]	Weyhenmeyer, 1999

[+] fluxes presented are based on dissolved surface concentrations of CO_2 and CH_4, which are highly dependant on the water residence times of the reservoirs. Differences in water residence times for the following reservoirs are not accounted for; therefore, direct comparison of fluxes from different reservoirs should be done with caution

[=] dissolved gases lost via outflow (representing approximately 70 to 100% of diffusive surface flux) not included

[§] as cited in St. Louis *et al.*, 2000

[॥] includes 105 km^2 of small islands

[†] represents maximum flux values; mean fluxes not given

[‡] calculated from published values

[*] includes ebullition flux

total water losses in all three reservoirs (Table 3.3). Given the high outflow DIC and CH_4 concentrations, inorganic C losses via outflow were important portions of the overall inorganic C loss from the reservoirs (Tables 3.7 to 3.9). Together, total outflow inorganic C losses from the reservoirs were 1 to 2.5 times greater than diffusive surface flux losses. Clearly, in an overall assessment of GHG emissions to the atmosphere from the FLUDEX reservoirs, high C losses in outflow water due to quick flushing rates must be accounted for. In actual reservoirs, water residence times are usually longer than in the FLUDEX reservoirs and GHG loss via outflow and dam seepage likely represents a smaller percentage of diffusive surface GHG fluxes. However, CH_4 losses via water flow through turbines and the spillway of a hydroelectric dam in Brazil were 14 times greater than ebullition and diffusive CH_4 fluxes (Fearnside, 2001).

Ebullition CO_2 and CH_4 fluxes. In 1999 and during the first nine weeks of flooding in 2000, ebullition from all three reservoirs was negligible (Table 3.12, Figure 3.10). From weeks 10 to 14 post-flood in 2000, a sudden increase in ebullition occurred (Figure 3.10). Most of the C (70 to 95%) emitted via ebullition was as CH_4. In 2001, ebullition rates were low during the first six weeks of flooding but increased sharply at around week eight. Except for a sudden drop at around week ten, ebullition rates were high during the remainder of the season until the final week prior to drawdown (Figure 3.10). Ebullition fluxes in 2001 were two to five times greater than in 2000 (Table 3.12).

Ebullition CO_2 fluxes were equivalent to < 1 % of the combined diffusive surface and outflow CO_2 flux during periods of maximum ebullition (Tables 3.7 to 3.9). Other studies have also found ebullition to be insignificant in overall reservoir CO_2 emissions (< 1 % diffusive CO_2 fluxes) (Duchemin *et al.*, 2000; Kelly *et al.*, 1997). However, during periods of high ebullition, CH_4 emitted to the atmosphere via ebullition was greater than CH_4 diffusive surface and outflow fluxes combined (Tables 3.7 to 3.9). During the third season of flooding, ebullition CH_4 fluxes were nearly double diffusive surface and outflow CH_4 fluxes (Tables 3.7 to 3.9).

Mean CH_4 ebullition fluxes in 2000 and 2001 (5 to 30 mg CH_4 m^{-2} d^{-1}) were comparable to CH_4 ebullition fluxes from the ELARP reservoir which flooded a boreal peatland (~20 mg CH_4 m^{-2} d^{-1}; Kelly *et al.*, 1997), a reservoir which flooded tropical forests (up to 65 mg CH_4 m^{-2} d^{-1}; Duchemin *et al.*, 2000), and a beaver pond flooding boreal forest (23 mg CH_4 m^{-2} d^{-1}; Wehenmeyer, 1999). In fact, ebullition rates mid-season in 2001 were

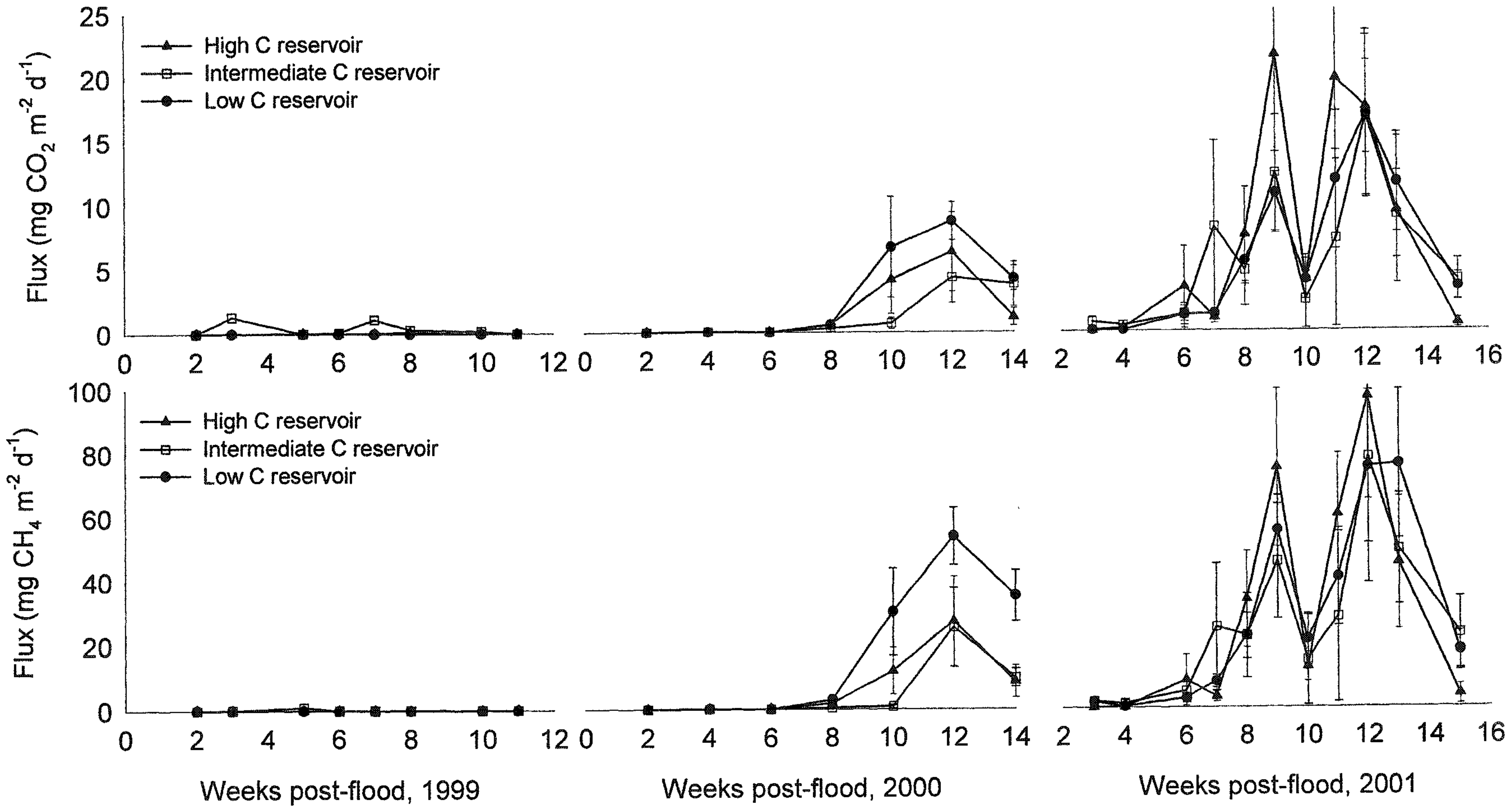

Figure 3.10: Ebullition fluxes of CO_2 (top) and CH_4 (bottom) from the High, Intermediate, and Low C reservoirs during 1999, 2000, and 2001. 1999 data are from Joyce (2001).

higher than the ELARP reservoir and beaver pond, and more closely approximated ebullition fluxes from tropical reservoirs, which typically have much higher mean ebullition rates than temperate reservoirs (St. Louis *et al.*, 2000). For example, in a three year old tropical reservoir, Galy-Lacaux *et al.* (1997) report CH_4 emissions from ebullition of 164 mg CH_4 m^{-2} d^{-1} in 0 to 3 m of water.

High ebullition fluxes from the FLUDEX reservoirs were most likely due to rapid decomposition occurring in the first few years of flooding, driven by warm soil temperatures in shallow water and low oxygen concentrations (unpublished data). Wehenmeyer (1999) attributed high ebullition in a boreal beaver pond to increased methanogen activity and decreased CH_4 solubility at high temperatures. Duchemin *et al.* (2000) found a strong correlation between ebullition and water level fluctuation and attributed the correlation to increasing pressure from increasing water column depth. Because the FLUDEX reservoirs were shallow (average depths ranged from 0.9 to 1.1 m), the water column exerted less pressure on the sediments than a deeper reservoir would have.

Estimates of net reservoir GHG production

Net GHG production. Total inorganic C outputs were always greater than total inputs (Tables 3.7 to 3.9), meaning the FLUDEX reservoirs were net GHG producers during the flooding seasons. Net GHG production by all three reservoirs was similar during each of the three flooding seasons (Tables 3.7 to 3.9). During the first flooding season, the Intermediate C reservoir had the highest net GHG production (850 mg C m^{-2} d^{-1}; Table 3.7). The High C reservoir produced the most GHGs in 2000 (595 mg C m^{-2} d^{-1}), while the Intermediate C reservoir produced the least (457 mg C m^{-2} d^{-1}; Table 3.8). In 2001, GHG production from the High and Intermediate C reservoirs was similar (491 and 501 mg C m^{-2} d^{-1}, respectively), but just slightly greater than production in the Low C reservoir (442 mg C m^{-2} d^{-1}; Table 3.9). Although overall OC storage in the three upland forests was different, it appears that litter quality or lability (i.e., susceptibility to decomposition) was more important to decomposition and subsequent flux than subcatchment OC storage.

CO_2 production declined with each successive flooding season (Figure 3.11), decreasing from 724 mg C m^{-2} d^{-1} (1999) to 461 mg C m^{-2} d^{-1} (2001) in the High C reservoir; from 845 mg C m^{-2} d^{-1} (1999) to 469 mg C m^{-2} d^{-1} (2001) in the Intermediate C reservoir; and from 589 mg C m^{-2} d^{-1} (1999) to 442 mg C m^{-2} d^{-1} (2001) in the Low C reservoir (Tables 3.7

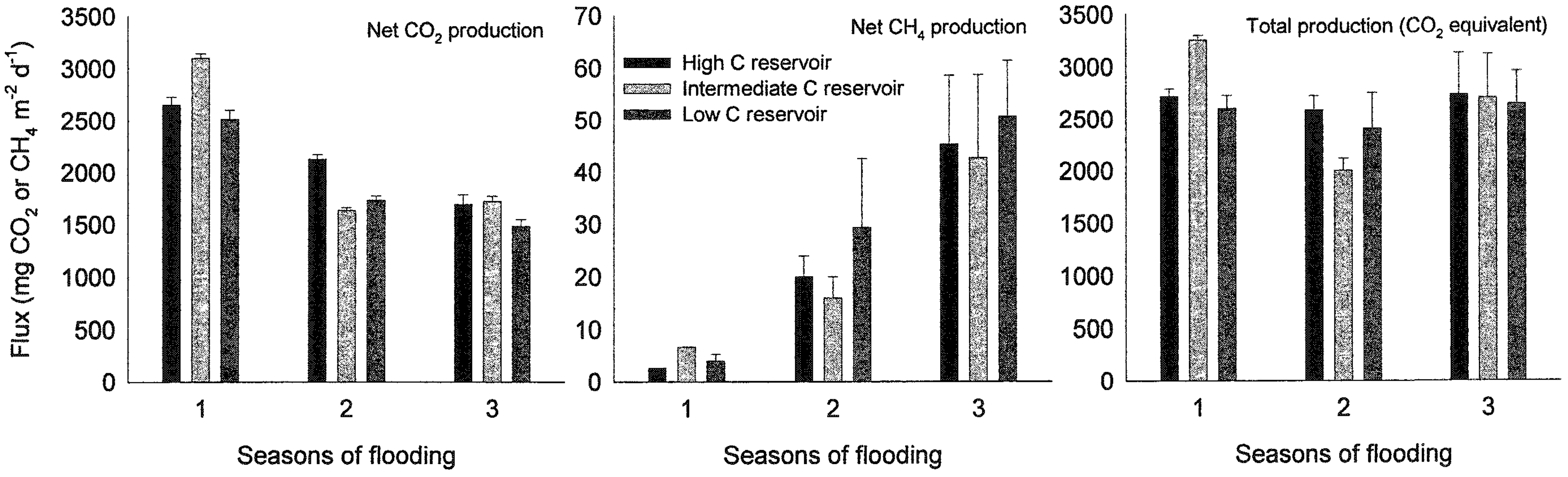

Figure 3.11: Net GHG production of CO_2 and CH_4 from the High, Intermediate, and Low C reservoirs over the first three seasons of flooding. The total GHG production as CO_2 equivalents was determined by adding CO_2 emissions to CH_4 emitted in CO_2 equivalents (calculated by multiplying CH_4 emissions by a GWP of 23 [IPCC, 2001]).

to 3.9). CH_4 production, on the other hand, increased with each flooding season (Figure 3.11), rising from 2 mg C m^{-2} d^{-1} (1999) to 34 mg C m^{-2} d^{-1} (2001) in the High C reservoir; from 5 mg C m^{-2} d^{-1} (1999) to 32 mg C m^{-2} d^{-1} (2001) in the Intermediate C reservoir; and from 3 mg C m^{-2} d^{-1} (1999) to 38 mg C m^{-2} d^{-1} (2001) in the Low C reservoir (Tables 3.7 to 3.9). The relative season to season increase in CH_4 production indicates a progressive increase in anaerobic decomposition (although total decomposition rates [i.e., net production] decreased with each flooding season).

Photosynthesis, and methane oxidation in the reservoirs. Net reservoir GHG production (Tables 3.7 to 3.9) is essentially an estimate of 1) the diffusive soil CO_2 and CH_4 flux minus water column consumption of the two gases via photosynthesis and CH_4 oxidation and 2) ebullition CO_2 and CH_4 fluxes from the soil directly to the atmosphere. In the FLUDEX reservoirs, photosynthetic uptake of CO_2 and CH_4 oxidation were important processes in reducing both CO_2 and CH_4 concentrations in the water column, and therefore, diffusive fluxes to the atmosphere and losses via outflow.

Algal assemblages on submerged tree surfaces (periphyton) were the dominant photoautotrophs in the reservoirs. Photosynthetic uptake by periphyton was equivalent to 102, 178, and 56 mg C m^{-2} d^{-1} in the High, Intermediate, and Low C reservoirs, respectively in 2000 and 27, 11, and 8 mg C m^{-2} d^{-1} in 2001 (D. Findlay and M. Patterson, Freshwater Institute, Winnipeg; unpublished data). Photosynthetic uptake rates were important compared to the net reservoir CO_2 production (10 to 40% and 2 to 5% in 2000 and 2001, respectively), especially because the considerable quantities of CO_2 produced by the reservoirs and eventually sequestered in algal material was likely emitted to the atmosphere upon decomposition of the algae after reservoir drawdown. This GHG source was not accounted for in the net CO_2 production estimates.

CH_4 oxidation by methanotrophic bacteria at the soil water interface consumed approximately 43, 53, and 56% of the flooded soil diffusive CH_4 flux in the High, Intermediate, and Low C reservoirs, respectively (Venkiteswaran, 2002). Methane oxidation was therefore important in lowering the overall GHG impact of the FLUDEX reservoirs through consumption of CH_4, which has a higher GWP compared to CO_2 (including direct and indirect effects, CH_4 is 23 times more effective as a GHG than CO_2 over a 100 year period [Dentener *et al.*, 2001]).

Net GHG production: the influences of organic carbon storage and time

Organic carbon storage and carbon degradability

While organic C input from streams and watershed run-off is believed to provide an important substrate for decomposition and subsequent GHG emissions from reservoirs (Duchemin *et al.*, 2000) and beaver ponds (Yavitt and Fahey, 1994), organic C inputs from inflow water and direct run-off were low (inflow water was from an oligotrophic lake and none of the three FLUDEX reservoirs received a substantial volume of water from the surrounding landscape [Table 3.3]). Therefore, water column increases in CO_2 and CH_4 after flooding were due to flooded soil fluxes resulting from decomposition of OC stored in the subcatchments. Roulet *et al.* (1997) attributed nearly all of the CO_2 and CH_4 flux from a beaver pond flooding boreal peatland to sediment decomposition, and found that both DOC inputs from adjacent ecosystems and organic matter introduced by beaver activity were negligible sources of the large surface GHG flux.

However, GHG production in the FLUDEX reservoirs was not related to the amount of OC stored in the flooded subcatchments. The observed similarity in net GHG production from the three reservoirs likely reflects the influence of substrate quality, rather than overall OC storage, on decomposition rates. Joyce (2001) attributed CO_2 soil emissions during the first year of flooding to the rapid decomposition of high amounts of labile carbon present in leaf litter and to root respiration by the flooded, stressed trees. Decomposition rates determined from litter bags containing vegetation characteristic of the sites showed leaf litter typical of the Intermediate and Low C reservoirs to decompose quite rapidly after the first season of flooding (70% mass loss in birch leaves, 60% mass loss in blueberry leaves, and 50% mass loss in alder leaves; unpublished data). Conversely, decomposition of leaf litter and ground vegetation characteristic of the High C reservoir was slow (10% and 20% mass loss of *Sphagnum* spp. and *Polytrichum* spp. and 30% mass loss in Labrador tea leaves; unpublished data). Therefore, although the High C reservoir had the highest amount of stored OC, carbon compounds in the litter of the Intermediate and Low C reservoirs were more quickly decomposed and production from all reservoirs was similar. Jack pine needles, which were an important litter component in all three reservoirs, lost only 15 to 20% of their mass during the first year of flooding (unpublished data).

There was only slight mass loss of all vegetation types in litterbags during the second and third flooding seasons in all three reservoirs (unpublished data), explaining the decrease in GHG production with each successive flooding season. High decomposition of labile carbon during the first season of flooding may have left more recalcitrant carbon to be more slowly broken down during subsequent flooding seasons. The decrease in production from the first to second flooding season was greater than that from the second to third flooding season. Labile C supplied in litterfall from dead trees near the end of the second season of flooding (2200 to 2500 kg C ha^{-1} in 2000; B. Hall, University of Alberta, Edmonton; unpublished data) may have helped sustain reservoir GHG production during the third flooding season.

Time scale of reservoir GHG emissions studies

To best understand the relationship between OC storage and GHG fluxes from flooded landscapes, carbon cycling in reservoirs needs to be studied over the long term. GHG emissions from reservoirs are assumed to decrease with time as decomposition depletes OC stores. St. Louis *et al.* (2000) found a significant negative exponential decline in CO_2 fluxes with age from 21 temperate reservoirs. However, St. Louis *et al.* (2000) note that using data from several reservoirs to determine flux-age relationships introduces biases that affect emissions over time, such as differences in the quantity or quality of flooded OC between reservoirs.

Few studies have monitored GHG emissions from one reservoir over a period of time, but changes in patterns of CO_2 and CH_4 production with reservoir age is an important consideration in the evaluation of GHG emissions from reservoirs (Kelly *et al.*, 1994; Fearnside, 1995, 1997; Rosa *et al.*, 1996; Galy-Lacaux *et al.*, 1999; St. Louis *et al.*, 2000). Galy-Lacaux *et al.* (1997, 1999) showed dissolved CO_2 and CH_4 concentrations in surface waters and CH_4 fluxes (both diffusive and ebullition) from the Petit Saut reservoir in French Guyana to reach maximum levels one year after impoundment, but to rapidly decrease by the third year of flooding. Fearnside (1995, 1997) *simulated* carbon emissions from Brazilian reservoirs and predicted CO_2 emissions to be concentrated in a tremendous pulse in the first ten years of flooding. CO_2 and CH_4 surface concentrations and fluxes monitored from the ELARP experimental reservoir has been ongoing since impoundment in 1993, and dissolved CO_2 and CH_4 surface concentrations remain elevated seven years after impoundment (St. Louis *et al.*, unpublished data).

After three years of flooding the FLUDEX reservoirs, two temporal GHG production trends became apparent: 1) total net production and net CO_2 production decreased with each flooding season, while 2) net CH_4 production increased with each flooding season (Tables 3.7 to 3.9, Figures 3.5 and 3.10). Temporal changes in GHG emissions are important to consider in an overall evaluation of the effects of reservoir GHG emissions to the atmosphere. For example, the relative year-to-year increase in CH_4 emissions in the FLUDEX reservoirs is important because the GWP) of CH_4 is 23 times greater than that of CO_2 (Dentener *et al.*, 2001). Over three season in the FLUDEX reservoirs, relatively small increases in CH_4 production offset larger decreases in CO_2 production from a GWP perspective (Figure 3.11).

Kelly *et al.* (1997) predicted decomposition of peat in the ELARP could sustain post-flood GHG emissions for approximately 2000 years. For comparison, the FLUDEX reservoirs have enough stored OC (in soils, litter, and vegetation) to support current rates of decomposition (~60 g C m^{-2} yr^{-1}) for approximately 60 to 100 years. However, decomposition of wood is minimal in northern reservoirs, especially if they are in cold or anoxic waters (Smith, 1991). Litter bag results showed essentially no decomposition of wood over the first three years of flooding in the FLUDEX reservoirs (unpublished data), despite the reservoirs being shallow and relatively warm (wood decomposition is important in warmer tropical reservoirs [Campo and Sancholuz, 1998]). With nearly one third to half of the total OC flooded by the FLUDEX reservoirs contained in wood (Table 3.1), the extend of wood decomposition in the FLUDEX reservoirs will be important in long term reservoir GHG emissions. Furthermore, long term flux patterns in these reservoirs may differ from those observed in the first three years of flooding as decomposition rates in each reservoir reflect the relative amounts of labile vs. recalcitrant OC remaining for decomposition. For example, some of the OC available for decomposition in the High C reservoir is present in slowly degraded plant material like *Sphagnum* spp. (unpublished data; Heyes *et al.*, 1998).

The net effect of reservoir creation

To approximate the *net effect* of the creation of the FLUDEX reservoirs on CO_2 fluxes between the biosphere and atmosphere, the NEE of CO_2 prior to flooding needs to be accounted for in addition to reservoir GHG emissions. At the time of flooding, all subcatchments were fire-regenerating forests, and therefore assumed to be assimilating carbon *at maximum rates* through accumulation of organic soils and plant biomass. Daily (daytime and nighttime) NEE of CO_2 has been determined in growing boreal forests to be around –1000 to –2000 mg C m^{-2} d^{-1} (McCaughey *et al.*, 1997; Jarvis *et al.*, 1997). The average total CO_2 production by the FLUDEX reservoirs over the first three years of flooding was approximately 550 mg C m^{-2} d^{-1}. Using published values of CO_2 NEE for boreal forests, the net change in CO_2 flux between the undisturbed subcatchments and the flooded reservoirs was approximately 1550 to 2550 mg C m^{-2} d^{-1}. Over the three seasons of flooding (~315 days), the net effect of reservoir creation on CO_2 cycling in the FLUDEX subcatchments was about 490 to 800 g C m^{-2} emitted to the atmosphere. This estimate should be treated as a maximum because the NEE rates were determined during the growing season in young forests accumulating carbon at high rates.

Long-term carbon accumulation in upland boreal soils since the last glaciation is small (~1 to 12 g C m^{-2} yr^{-1}, or 3 to 33 mg C m^{-2} d^{-1}) (Schlesinger, 1990) because frequent fires in the boreal ecoregion cause much of the carbon stored in vegetation and soils to be returned to the atmosphere as CO_2 every 50 to 100 years. The net effect of reservoir creation on CO_2 dynamics in the landscape would result only from the loss of long-term CO_2 storage for the length of time the reservoir existed because, upon removal of the reservoir, the landscape could begin to accumulate carbon again through reforestation. Using the long-term C accumulation rate in boreal forests (Schlesinger, 1990), the net change in carbon fluxes upon flooding would have been 3 to 33 mg C m^{-2} d^{-1} and the net effect over the three seasons of flooding would have been only about 1 to 10 g C m^{-2} (compared to 490 to 800 g C m^{-2} in a forest rapidly accumulating C).

The FLUDEX reservoirs had an important impact on CH_4 cycling in upland boreal forests. Prior to flooding, all subcatchments consumed CH_4 at rates of 0.7 to 1.1 mg C m^{-2} d^{-1}. Total average CH_4 fluxes to the atmosphere over the first three seasons of flooding were about 19 mg C m^{-2} d^{-1}, representing a net change of about 20 mg C m^{-2} d^{-1}. Over the three seasons of flooding (~315 days), the reservoirs were a CH_4 source of 6.3 g C m^{-2} d^{-1}. Factoring in the GWP of CH_4, CH_4 emissions were equivalent to about *53 g C m^{-2} emitted in CO_2 equivalents*. Therefore, despite the much lower emissions of CH_4 compared to CO_2 over the three seasons of flooding, the GHG effect of CH_4 emissions was 5 to 50 times greater than that of CO_2 when the net CO_2 effect is calculated using long-term rates of CO_2 uptake in the boreal ecosystem.

To estimate long-term net effects of reservoir creation in the boreal upland ecosystem on CH_4 dynamics based on this study would be difficult. Long-term CH_4 fluxes may be lower than the three-year average because decomposition should slow with depletion of OC stores. However, CH_4 emissions from actual reservoirs may remain constant over time; Fearnside (1995, 1997) projected CH_4 emissions from Brazilian reservoirs would be constant over a 50 to 100 year period, fuelled in part by decomposition of organic matter entering the reservoir via river flow. On the other hand, Galy-Lacaux *et al.* (1999) projected CH_4 emissions from a reservoir in French Guyana to decrease to negligible levels within just 20 years after flooding.

Furthermore, the estimate of the long-term net effect on CO_2 fluxes is likely low, because the calculation was made assuming that upon removal of reservoir, the landscape begins accumulating C again through reforestation (so that the only net effect on CO_2 cycling was the loss of the terrestrial CO_2 sink for the duration of flooding). However, while individual reservoirs are not permanent structures, if the total area they occupy remains the same or continues to increase, the total area flooded would represent a permanent landscape change in which original ecosystem C storage would not be recovered. Currently, removal or decommissioning of major dams globally, even those no longer in use, is rare (McCully, 1996).

Finally, the above estimates were calculated based on reservoir inorganic C fluxes during the flooded seasons. However, the FLUDEX reservoirs likely have important effects on GHG cycling during drawdown periods as well. While fluxes in May 1998 showed CO_2 soil fluxes to be similar to pre-flood ecosystem fluxes, NEE of CO_2 was altered because most of the flooded vegetation was dead and no longer assimilating CO_2. Furthermore, while both the Intermediate and Low C subcatchments consumed CH_4 at rates similar to pre-flood rates, the High C reservoir, likely because of moist conditions, continued to be a CH_4 source after drawdown. Winter emissions of both gases from the subcatchments are likely lower than in late spring because of cooler conditions (Winston *et al.*, 1997), but both CO_2 and CH_4 emissions through the snowpack can be important in forest ecosystems (Sommerfeld *et al.*, 1993).

General conclusions

After three flooding seasons, GHG production in FLUDEX reservoirs was not related to OC stores in subcatchment soils and vegetation. Inorganic C mass budgets showed all reservoirs to produce similar amounts of both CO_2 and CH_4, with the Intermediate C reservoir having the highest GHG production during two of the three flooding seasons. Soil fluxes measured using submerged chambers also indicated fluxes from individual sites within the reservoirs to be independent of OC storage. A vegetation decomposition study using litterbags showed vegetation characteristic of both the Intermediate and Low C reservoirs to decompose faster than typical vegetation in the High C reservoir, suggesting that in the early stages of flooding, fast decomposition of labile carbon compounds is important in determining overall GHG production in flooded upland forests. These findings suggest that the amount of OC stored in landscapes may not be a good indication of subsequent GHG production upon reservoir creation, at least over a short time period.

Total net GHG production (both CO_2 and CH_4 combined) declined with each flooding season. Large decreases in CO_2 production were indicative of decreased decomposition rates with each successive flooding season. However, increases in CH_4 production with each season implied a relative increase in anaerobic decomposition rates. Despite decreased decomposition rates with each flooding season, the overall GHG effect of the FLUDEX reservoirs remained constant because greater production of CH_4, a stronger GHG than CO_2, offset the larger decreases in CO_2 production. This has important implications for long-term emissions scenarios from reservoirs, and in evaluating the atmospheric effects of reservoir GHG production. At this point, it is unclear whether or not CH_4 production will continue to increase, stabilize, or decrease as organic carbon stores are depleted. The FLUDEX is one of the few studies to have monitored GHG production in reservoirs over a period of time, and initial findings indicate GHG dynamics in newly flooded landscapes change dramatically during the first few years following impoundment.

The FLUDEX is rare among studies of GHG production in reservoirs because the net impact of reservoir creation on terrestrial landscapes was determined by examining GHG dynamics in both the undisturbed and post-flood ecosystem. Static chamber measurements prior to flooding showed CO_2 respiration rates and CH_4 oxidation rates to be typical of boreal forests. The FLUDEX subcatchments, characterized by an 18-yr-old fire regenerating forest, were estimated, on an ecosystem level, to be assimilating CO_2 at rates similar to published values for other boreal forest sites. Upon flooding, the subcatchments, which were sinks for atmospheric CO_2 and CH_4 in their undisturbed state, became sources of both gases to the atmosphere. The net effect of reservoir creation on CO_2 cycling in the FLUDEX subcatchments was pronounced, because flooding occurred during the primary growing months in a newly re-establishing forest. When long-term CO_2 accumulation rates in boreal ecosystems are used to calculate the change between pre- and post-flood CO_2 cycling in the upland boreal forest, CH_4 becomes largely responsible for the overall effect of reservoir creation on GHG emissions to the atmosphere.

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Chapter 4: The FLUDEX, the ELARP, and other reservoir studies

General discussion

The FLooded Uplands Dynamics EXperiment was a whole ecosystem manipulation designed to address the issue of landscape OC storage and subsequent GHG (CO_2 and CH_4) emissions from reservoirs. Due to the various difficulties associated with attempting to replicate whole ecosystem experiments (Schindler, 1998; Carpenter *et al.*, 1998; Hurlbert, 1984), experimental units (i.e., High, Intermediate, and Low C reservoirs) were not replicated in the FLUDEX. However, the location, temperatures, average depths, volumes, pH, nutrient levels, water supply, and flushing rates of the FLUDEX reservoirs were similar and justify direct comparisons of GHG production in the three reservoirs (Chapter 3). A more difficult task, but an important consideration, is the extrapolation of FLUDEX findings to those of other reservoir studies (notably the ELARP, which flooded a boreal wetland at the ELA [Kelly *et al.*, 1997]) to clarify the potential relationship between OC stores and subsequent changes in CO_2 and CH_4 cycling between landscapes that vary greatly in OC storage, and to examine how the FLUDEX findings may be related to larger hydroelectric complexes.

The FLUDEX, the ELARP, and landscape OC storage

The main initiative of the GHG portion of the FLUDEX was to determine whether CO_2 and CH_4 production from reservoirs is related to the amount of OC stored in vegetation and soils of flooded landscapes, and to ultimately help hydroelectric companies consider potential GHG effects when deciding on the locations of future reservoir projects. With this ultimate goal in mind, it is important to compare GHG production in the FLUDEX reservoirs to GHG production in the ELARP reservoir.

While the FLUDEX reservoirs varied in the amount of OC flooded (41 100 to 66 000 kg C ha^{-1}), the flooded ELARP wetland, with OC stores of ~1 000 000 kg C ha^{-1}, represented an extremely high OC storage relative to the FLUDEX reservoirs. Net GHG production in the FLUDEX reservoirs was not related to landscape OC storage, most likely because within the small range of OC storage in the three boreal subcatchments, the lability of carbon compounds was more influential on decomposition rates in the early years of flooding. However, if a relationship between landscape OC storage and subsequent GHG production exists, it should emerge upon comparison of the FLUDEX and ELARP data due to the substantial difference between OC storage in boreal forest uplands and wetlands. The similarity in GHG production among the FLUDEX reservoirs provides justification for grouping them together to represent low end OC storage relative to the ELARP wetland.

To compare the FLUDEX findings to the ELARP findings, we have to assume that the reservoirs were similar enough that factors other than OC storage did not greatly influence net GHG production in the systems. While the FLUDEX reservoirs were more similar to each other than to the ELARP reservoir, important characteristics between the FLUDEX and ELARP reservoirs were also comparable Primarily, the reservoirs 1) were flooded during the same time interval (June to September); 2) were located in the same vicinity (approximately 1 km apart); and 3) had similar average depths (ELARP reservoir, 1.3 m; FLUDEX reservoirs, 0.9 to 1.1 m). However, a major difference between the FLUDEX and ELARP reservoirs related to their water inputs and residence times. Water input to the FLUDEX reservoirs was highly controlled and watershed run-off was minimal. Water input to the ELARP reservoir, on the other hand, was from watershed run-off and upstream lake outflow and considerable. Therefore, water residence times in the ELARP reservoir were not controlled, and were dictated by storm events and precipitation volumes. The ELARP reservoir had water residence times ranging from a couple of days to months (K. Beaty, Freshwater Institute, Winnipeg, personal communication).

Therefore, the same issue of water residence times that confounded direct comparisons between the FLUDEX reservoirs for certain variables such as diffusive surface fluxes also poses a problem when comparing the FLUDEX and ELARP reservoirs. While surface diffusive fluxes of both CO_2 and CH_4 from the pond surface of the ELARP during the first three years of flooding were approximately 3 and 12 times greater, respectively, than emissions from the FLUDEX upland reservoirs on an areal basis, this could be due largely to differences in water residence times. As in the FLUDEX, surface diffusive fluxes of both CO_2 and CH_4 were calculated from surface concentrations of CO_2 and CH_4, which were heavily dependent on flushing rates. Unfortunately, an inorganic C mass budget does not currently exist for the ELARP reservoir, so net GHG production rates comparable to the FLUDEX reservoirs are not available. Nevertheless, some comparisons between the FLUDEX and ELARP reservoirs can be made.

Unlike surface concentrations and fluxes of CO_2 and CH_4, ebullition fluxes of CO_2 and CH_4 can be directly compared between the FLUDEX and ELARP reservoirs. Mean FLUDEX CH_4 ebullition fluxes in 2000 and 2001 (5 to 30 mg CH_4 m^{-2} d^{-1}) were comparable to CH_4 ebullition fluxes from the ELARP reservoir (~20 mg CH_4 m^{-2} d^{-1}; Kelly *et al.*, 1997). However, lower ELARP ebullition fluxes relative to FLUDEX ebullition fluxes are misleading because ebullition fluxes were measured only over deeper water in the center of the original wetland pond of the ELARP reservoir. Bubble production in the flooded peatland portion of the ELARP reservoir caused large mats of peat to become dislodged and float on the water surface around the shallow margins of the flooded wetland (Scott *et al.*, 1999). CH_4 fluxes from peat increased from approximately 64 mg CH_4 m^{-2} d^{-1} when submerged to 440 mg CH_4 m^{-2} d^{-1} when floating (Scott *et al.*, 1999), about 4 to 10 times greater than ebullition fluxes from the FLUDEX reservoirs. This increase occurred primarily because floating peat lies at the surface of the water column so that CH_4 produced within the peat islands fluxes directly to the atmosphere with minimal oxidization by methanotrophic bacteria (Scott *et al.*, 1999).

Long term soil carbon accumulation rates in northern peatland ecosystems of 10 to 80 g C m^{-2} yr^{-1} (Schlesinger, 1997) are much greater than accumulation rates in upland boreal forest ecosystems (~1 to 12 g C m^{-2} yr^{-1}; Schlesinger, 1997), meaning that if both types of landscapes were flooded for an equivalent amount of time, wetland flooding would have a greater impact on atmospheric CO_2 concentrations due to the loss of the larger CO_2 sink. Long term CH_4 flux dynamics also make the ELARP reservoir more influential on atmospheric CH_4 concentrations than the FLUDEX reservoirs. While both the pond and peatland part of the ELARP wetland emitted CH_4 prior to flooding (the FLUDEX subcatchments consumed CH_4), the net difference between pre- and post-flood CH_4 fluxes from the ELARP reservoir was greater. Prior to flooding the ELARP wetland, the pond and peatland emitted approximately 17 and 1 mg CH_4-C m^{-2} d^{-1}, respectively (Kelly *et al.*, 1997) The FLUDEX subcatchments consumed approximately 1 mg CH_4-C m^{-2} d^{-1}. After flooding the ELARP wetland, the pond and peatland together emitted approximately 40 and 44 mg CH_4-C m^{-2} d^{-1}, respresenting net changes of ~ 23 and 43 mg CH_4-C m^{-2} d^{-1} with most of this change occurring over the flooded peatland area (Kelly *et al.*, 1997). For comparison, the net change in CH_4 fluxes in the FLUDEX subcatchments prior to and after flooding was about 20 mg CH_4-C m^{-2} d^{-1} (Chapter 3).

Finally, other trends indicate that the ELARP reservoir may produce GHGs for a longer period of time than the boreal upland FLUDEX reservoirs. While net GHG production in the FLUDEX reservoirs is already noticeably declining with each flooded season, dissolved concentrations of both CO_2 and CH_4 in the ELARP reservoir remain as high 10 years post-flood as during the first few seasons after flooding (V. St. Louis, University of Alberta, Edmonton, personal communication). Furthermore, the amount of stored carbon in the ELARP wetland is predicted to sustain current fluxes for approximately 2000 years, while current GHG production rates in the FLUDEX reservoirs cannot last more than 60 to 100 years if fuelled only by soil and vegetation decomposition.

When FLUDEX and ELARP are considered to represent low and very high extremes of landscape OC storage, there appears to be a relationship between OC storage and subsequent reservoir GHG production. Quantifying GHG production from reservoirs flooding landscapes with extremely low OC stores, such as desert ecoregions in the southwestern United States, would be valuable input to completing the picture of GHG production and reservoir OC storage (St. Louis *et al.*, 2000). Lower GHG production in the FLUDEX reservoirs compared to the ELARP reservoir is especially important considering that more and more reservoirs are flooding large expanses of low-lying peatlands because favourable sites for construction of canyon-style reservoirs are becoming rarer (Kelly *et al.*, 1997). While overall OC storage may not be useful in predicting GHG production in similar flooded ecosystems (such as the boreal uplands of FLUDEX; Chapter 3), long-term GHG fluxes from reservoirs flooding ecosystems with vastly different OC storage (e.g., boreal wetlands vs. boreal uplands) may be loosely predicted based on OC storage. Future research involving more detailed pre- and post-flood data collection from a variety of reservoirs could ultimately be used to develop more accurate predictive models.

Comparison to other reservoirs and predictive capabilities of the FLUDEX data

Schindler (1998) provides strong support for whole ecosystem manipulations, and discusses the issue of scale and extrapolation of results from small ecosystem manipulations to the larger ecosystems they represent. Clearly, any relation of FLUDEX results to other reservoir studies, and to reservoir GHG issues in general, must take into account the small scale on which the experiment was based.

Aspects of the FLUDEX reservoirs are comparable to larger hydroelectric complexes flooding northern landscapes. The FLUDEX reservoirs, with average depths of about 1 m, are comparable to shoreline margins of larger reservoirs, characterized by dead trees protruding from the water surface. The winter drawdown of the FLUDEX reservoirs mimicked the seasonal drawdown of many northern hydroelectric reservoirs, as winter demands for electricity dictate increased turbine flow, and subsequent seasonal fluctuations in reservoir depth. Like the FLUDEX reservoirs, many hydroelectric reservoirs flood large areas of boreal ecosystems in northern Canada (Duchemin *et al.*, 1995; Kelly *et al.*, 1994; St. Louis *et al.*, 2000; ICOLD, 1998).

However, there are various characteristics of actual reservoirs that make direct comparisons between the FLUDEX reservoirs unreasonable. Large differences in area flooded and average volume and depth exist between the FLUDEX and actual hydroelectric reservoirs. For example, La Grande reservoir in northern Québec has an average depth of 22 m and an area of 2840 km^2 (Duchemin *et al.*, 1995). Cold temperatures in deep reservoirs likely slow decomposition rates at the soil water interface, and development of stable thermoclines may allow anoxic conditions to develop quicker in larger reservoirs. Large reservoirs are likely to receive much greater allochthonous OC via watershed inputs and depending on river supply to the reservoirs, sedimentation rates will vary and influence decomposition rates in larger reservoirs. Atmospheric effects of GHG production in the flooded soils of margins of larger reservoirs (which the FLUDEX reservoirs are supposed to mimic) may vary depending on the mixing of the produced gases in the rest of the reservoir volume. Finally, all studies of reservoir emissions to the atmosphere have used one or more of several techniques to estimate surface diffusive CO_2 and CH_4 fluxes, which, depending on the environment in which they are used, may result in highly variable flux estimates (Chapter 2), making inter-comparison of reservoir GHG emissions or net production complicated.

In short, the FLUDEX reservoirs are likely too different from large hydroelectric reservoirs to make direct comparisons of FLUDEX findings to those of other studies feasible. Nevertheless, despite the above differences and their inevitable influences on decomposition rates and GHG dynamics in large reservoirs, surface diffusive and ebullition fluxes from the FLUDEX reservoirs are quite similar to those of large hydroelectric complexes (Table 3.13). In the end, though, the contribution of the FLUDEX results to understanding GHG emissions from larger reservoirs (in addition to comparison with the ELARP results) may ultimately lie in the development of models. While the direct comparison of FLUDEX data to other reservoirs is questionable, the original focus of the FLUDEX, to compare GHG cycling in three systems that differed little from each other (except in OC storage), is valid. The conclusions and detailed information (both spatially and temporally) drawn from the FLUDEX reservoirs is unmatched by other reservoir studies, and may eventually be incorporated into models of carbon processes occurring in the margins of larger hydroelectric complexes. For example, measures of carbon lost during the drawdown of the FLUDEX reservoirs and the draining of C rich soil porewaters may help determine processes related to winter drawdown of larger reservoirs.

General discussion

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