The use of stable carbon and oxygen isotopes to examine the fate of dissolved organic matter in two small, oligotrophic Canadian Shield lakes.

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Allochthonous carbon can be a large proportion of the carbon budget in northern temperate and boreal lakes. This thesis uses stable carbon and oxygen isotopes to examine the fate of allochthonous dissolved organic matter (DOM) in northern temperate lakes, and to determine the importance of dissolved organic carbon (DOC) in lake carbon mass balances and in the $\delta^{13}C$ of lake sediments. To use stable isotopes as a tool for studying DOC loss and sedimentation within lakes requires an understanding of processes that affect the $\delta^{13}C$ and $\delta^{18}O$ in aquatic systems. Photolysis is one mechanism that can account for the large allochthonous DOC loss within northern temperate lakes. There is, however, little research examining the effects of photolysis on stable isotopes (e.g. $\delta^{13}C$ and $\delta^{18}O$) in aquatic systems, or how photodegradation of DOM affects the $\delta^{13}C$ of lake sediments.

To study the effects of DOM photodegradation on carbon and oxygen isotopes, stream waters from catchments with varying peatland coverage were incubated in Tedlar bags placed in water baths under natural sunlight. Results from three streams flowing into two oligotrophic headwater lakes (Harp and Dickie Lakes) indicate that O_2 consumption rates and dissolved inorganic carbon (DIC) production rates were an order of magnitude greater in light exposed treatments than in dark treatments, suggesting that light mediated processes control O_2 consumption and DIC production in incubations. The similarity between filtered, inoculated, and sterile treatments, indicate that photolysis was the dominant O_2 consuming and DIC producing process in the incubations, while the contribution of respiration to these processes was not detectable. Differences in both O_2 consumption rates and DIC production rates (normalized to DOC loss) among streams suggest that DOM photolability was an important factor in both O_2 loss and DIC production on a volumetric basis.

A concomitant increase in $\delta^{18}O$-O_2 was observed with O_2 loss indicating that during the photo-oxidation of DOM, the lighter ^{16}O isotopomer was preferentially consumed in the oxidation of DOC to CO_2. Fractionation factors for respiration, photolysis and other abiotic reactions were not a function of O_2 consumption rates and ranged between 0.988 and 0.995, which lies outside the range published for respiration (0.975-0.982). These are the first published photolytic fractionation factors.

The δ^{13}C-DIC produced collectively by photolysis, respiration, and other abiotic reactions in incubations exposed to natural sunlight ranged between –23‰ and –31‰, and were similar in the light incubations for each treatment, but different among streams. Together, the light and dark incubation data suggest that photolysis and other abiotic reactions were largely responsible for the DIC concentration and δ^{13}C-DIC changes observed, while respiration is a relatively minor contributor.

During the incubations, as DOC photodegraded to CO_2, the lighter ^{12}C isotope was preferentially mineralized (or the moieties cleaved were depleted in ^{13}C) leaving the residual δ^{13}C-DOC 1‰ to 4‰ enriched, creating enrichment (ε) values up to ~–3‰. The change in final δ^{13}C-DOC after DOM photodegradation was different for each inflow, ranging from ~1 ‰ to 8.0 ‰, and provides an average enrichment of –2.1‰ (Harp Inflows ε: –1.2‰; Dickie Inflows ε: –3.4‰). These ε values are in agreement with the average ε from previous incubations on 3 of the inflows and 3 published studies based on UV exposed bog water (Osburn et al., 2001), riverine waters (Opsahl and Zepp, 2001), and lyophilized *Juncus* leachate dissolved in lake water (Vähätalo and Wetzel, 2008) (average ε = –2.9‰).

The structure of DOM changed during photolysis. Absorbance data indicated that the aromaticity, colour, UV absorption and the average molecular size of the DOC decreased. Additionally, after exposure to sunlight, C/N ratios of the DOC changed from high values (24-55), indicative of terrestrial inputs, to lower values (4-13) traditionally thought to be representative of algal or microbial inputs. This contradicts the conventional view that terrestrial DOC has C/N ratios >20, and shows that abiotic processes can alter allochthonous carbon structure and the residual allochthonous carbon can have C/N values similar to, or overlapping with, C/N ratios expected from algal or microbial carbon.

With the loss of 61-90% of the DOC, the particulate organic carbon (POC) created accounted for 20-90% of the DOC lost. Values of δ^{13}C-POC ranged from –25.7‰ to –27.7‰, with 80% of the samples within 1‰ of the initial δ^{13}C-DOC indicating that the particulate carbon created from the photodegradation of DOM that settles to the lake sediments could be isotopically similar to the source DOC. Overall, these incubations indicate that the photodegradation of DOM can affect both concentrations and isotopes of O_2, DIC, DOC, and POC of the stream waters flowing into Harp and Dickie Lakes and are important to consider in lake dynamics of high DOC retention lakes.

Two independent methods were used to examine the importance of allochthonous DOC to lake sediments. The first method used a two end-member mixing model to estimate the proportion of allochthonous and autochthonous carbon within the lake sediments. Inflow δ^{13}C-POC data, δ^{13}C-leaf litter measurements, and DOC photodegradation experiments were used to calculate average annual δ^{13}C-POC values for the allochthonous end member. The average annual δ^{13}C-POC values for the autochthonous end member were calculated using estimates of productivity, surface δ^{13}C-CO$_2$ values and estimated average annual fractionation factors. Average annual δ^{13}C-POC values from allochthonous and autochthonous sources for these lakes were distinct. Using the end members to calculate the relative contributions of allochthonous and autochthonous carbon to lake sediments revealed that the δ^{13}C of the lake sediment can be significantly affected by the ratio of autochthonous and allochthonous contributions. Furthermore, peaks in the allochthonous contributions of carbon accompany the δ^{13}C peaks in the sediment records to the lake sediments. This suggests that climate change and/or anthropogenic changes to the landscape, and the concomitant changes in DOC inputs to lakes, can be recorded in the sediment record indicating that sediment records are not just productivity signals, but also mass balance signals in high DOC retention lakes.

In the second method carbon isotope budgets were completed to accompany the carbon mass budgets for Harp and Dickie Lakes. Mass-weighted average annual δ^{13}C-DOC values from the inflows and outflows and δ^{13}C-DIC values from the inflows varied by 0.2‰ to 1.3‰, suggesting the values are well constrained. Conversely, the range of weighted δ^{13}C-DIC values from the outflows were larger (2.2‰) than those of the inflows. Calculated δ^{13}C values of the lake sediment were not equal to the measured δ^{13}C values of the lake sediments for either Harp or Dickie Lakes suggesting a problem lies within the mass balances, or the weighted average annual δ^{13}C values used in the isotope budgets.

To examine the sensitivity of the average annual weighted δ^{13}C values for the carbon entering and exiting the lakes, and the mass of carbon entering the lakes δ^{13}C of the lake sediments, a mass and isotope budget model was created. The model indicated that the δ^{13}C of the lake sediments is sensitive to a number of parameters including the amount of DOC entering the lake, the δ^{13}C-CO$_2$ evaded from the lake, the areal water discharge rate (q_s), the gas exchange coefficient (k), and pH. Many of these parameters required adjustments for the masses of carbon to match those presented in the mass balances suggesting that the mass balances averaged over 8 years have errors associated with them. However, changing the DOC load to the lakes in the model by the variability observed over all the years of the mass balances) indicates that the isotopic signature of the lake sediment could change by up to 2.5‰. This isotope change is large enough to account for the historical δ^{13}C changes observed in the δ^{13}C sediment record, suggesting that allochthonous DOC can drive the sediment record.

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Chapter 1:

Introduction

Dissolved organic matter (DOM) is the predominant form of organic matter entering lakes (Wetzel, 2001), and is responsible for transporting organic carbon, nitrogen, phosphorus and sulphur from terrestrial catchments to aquatic systems (Aitkenhead-Peterson et al., 2003). Transport of dissolved organic carbon (DOC), the dominant organic fraction of DOM in most lake waters, is crucial to aquatic systems as DOC controls the buffering capacity of waters, and is an energy source for productivity (Wetzel, 2001). DOC is not only an integral component of carbon cycling within lakes, but it also affects water quality by mediating the availability of dissolved nutrients and metals (Driscoll et al., 1994), in addition to modifying the optical and thermal properties of water (Schindler, 1971; Schindler and Curtis, 1997; Schindler 2001).

1.1 DOM and the global carbon cycle

Due to the mismatch between the global amount of CO_2 produced (carbon source) and the marine and terrestrial carbon sinks, the global carbon budget cannot be balanced (Smith et al., 1993). There have been suggestions that the missing carbon sink is terrestrial and lies in the Northern Hemisphere (e.g. Tans et al., 1990, Kauppi et al., 1992; Sedjo, 1992; Quay et al, 1992). Sellers et al. (1997) suggest that even with its low productivity, boreal ecosystems could contain an appreciable portion of carbon, serving as an important global carbon sink, since the boreal forest biome can store a significant amount of carbon (Kurz and Apps, 1993;

Sampson et al., 1993) in forest trees, soils, and soils associated with peatlands (Apps et al., 1993). The greatest dissolved component transferred from boreal catchments to oligotrophic lakes is DOC (Schindler et al., 1997). Therefore, streams and lakes can act as conduits for transfer of organic carbon to aquatic systems. By extrapolating their carbon mass balance model to the entire boreal forest biome, Molot and Dillon (1996) estimated that during the export of carbon from the terrestrial catchment to lakes that 30-52 Tg C y^{-1} (of 66 Tg C y^{-1}) is retained in northern surface waters (i.e. either evades or is sedimented). In addition to surface waters, carbon can also be sequestered in lake sediment, however, the transfer of organic carbon to lake sediments is likely very small in terms of the global carbon cycle.

The transport and transition of DOC into other carbon fractions in aquatic systems therefore provides DOC with an important role in lake functioning and the global carbon cycle. Recent increases in atmospheric CO_2 concentrations due to anthropogenic activities, with suggestions of concentrations doubling within a century (Houghton et al., 1995), and the associated climate change predictions resulting from these CO_2 increases, have provided the need for a greater understanding of carbon dynamics and the processes that affect carbon cycling in aquatic systems. With approximately 800,000 boreal lakes in Canada alone, there is great potential for boreal lakes to be significant to the global carbon cycle, which in turn is strongly coupled to the physical climate system (Sellers et al., 1997). Northern temperate and boreal lakes rely on dead or decaying organic matter produced in, and transported from, the terrestrial catchment for sustenance. They are generally considered net heterotrophic ecosystems (del Giorgio and Peters, 1994; Algesten et al., 2003) as allochthonous carbon is mineralized to CO_2 and evades to the atmosphere (Kling et al., 1991; Cole et al., 1994).

Although it was historically assumed that freshwater lakes fixed atmospheric CO_2 and transferred the carbon to the sediments, more recent views suggest that the majority of carbon in boreal and northern temperate lakes has a terrestrial origin, and the lakes sediments actually transfer exported fixed allochthonous carbon to aquatic storage (Molot and Dillon, 1996). Many oligotrophic lakes are supersaturated with CO_2 (Cole et al., 1994) suggesting that terrestrial carbon could be a main carbon contributor to the lakes. Several studies of northern lakes suggest the majority of organic carbon in lakes actually is terrestrial and that is a function of the amount of runoff entering lakes, and the coverage of peatlands within their catchments (Rau, 1978; Kling et al., 1991; Cole et al., 1994; Dillon and Molot, 1997b). Dillon and Molot (1997a) estimated carbon mass balances of seven northern temperate lakes in the Muskoka-Haliburton region and determined that the DOC load into lakes ranged from 6.5 to 39.7 g C m^{-2} y^{-1} while the atmospheric DOC input ranged from 2% to 13% of the DOC load. In most of the lakes, there was net CO_2 evasion to the atmosphere on an annual basis, and the loss was greater than both dissolved inorganic carbon (DIC) loading and precipitation inputs suggesting there is in-lake mineralization of DOC to CO_2 in the lake. The study revealed that the carbon was derived from the terrestrial catchment, and that 38% to 70% of this DOC was retained in lakes, although the transfer mechanisms are unknown.

In boreal lakes, carbon storage was estimated to be a significant carbon sink within lake sediments (Kortelainen et al., 2004). Algesten et al. (2003) examined mass balances of Swedish lakes and found that terrestrial carbon export to freshwaters ranged from 3.0 to 8.4 g C m^{-2} y^{-1} with 30-80% of total organic carbon retained. However, partitioning between the atmosphere and sediment was different than Dillon and Molot (1997a). Algesten et al. (2003) found that the organic carbon burial was eight times less than the carbon loss by CO_2 evasion indicating that mineralization was significant to carbon loss (via CO_2) in these lakes, whereas Dillon and Molot (1997a) found that 50% of the DOC entering some northern temperate lakes is lost to evasion and burial in roughly in equal proportions. Molot and Dillon (1996) applied carbon flux relationships to the global boreal forest biome and estimated that boreal lake evasion and sediment storage range between 12-21 Tg C y^{-1} and 18-31 Tg C y^{-1} respectively, supporting global estimates of 15 Tg C y^{-1} and 36 Tg C y^{-1} stored as DOC and POC in lakes respectively by both Meybeck (1993) and Downing et al. (1993). According to a conservative estimate by Molot and Dillon (1996), lake sediments may contain approximately 120 Pg of carbon after 5000 years of accumulation and, as a consequence, carbon storage within the boreal forest biome may be significantly larger than previously calculated.

Since DOC is the main form of carbon transported into these lakes from the terrestrial catchment, coagulation and/or flocculation into a particulate carbon form is likely integral to carbon sequestration of allochthonous carbon in lake sediments (von Wachenfeldt et al., 2008, von Wachenfeldt and Tranvik, 2008). Alternatively, fixation of inorganic carbon by aquatic organisms can also transform and transport carbon from the surface waters (and the terrestrial catchment) to the lake sediments, and is considered by paleolimnologists as a main source of carbon to sediment organic matter (Meyers and Teranes, 2001). Identifying and understanding the impacts of the mechanisms by which lakes sequester carbon is therefore important to understanding DOM fate, and will help clarify ecological energy flow along the transfer paths from streams to lakes (Mulholland, 1981).

1.2 Carbon transfer mechanisms

To understand the fate of DOM, it is important to understand the in-lake mechanisms that may convert and redistribute the different chemical forms of carbon in lakes, and convert stream DOC to dissolved inorganic carbon

(DIC) and particulate organic carbon (POC). Carbon dynamics within lakes can be affected by a number of processes including the photodegradation, microbial decomposition, and the direct sedimentation of dissolved organic matter (via flocculation/coagulation), in addition to gas exchange with the atmosphere, photosynthesis, respiration (and other redox reactions), and mixing (Figure 1.1).

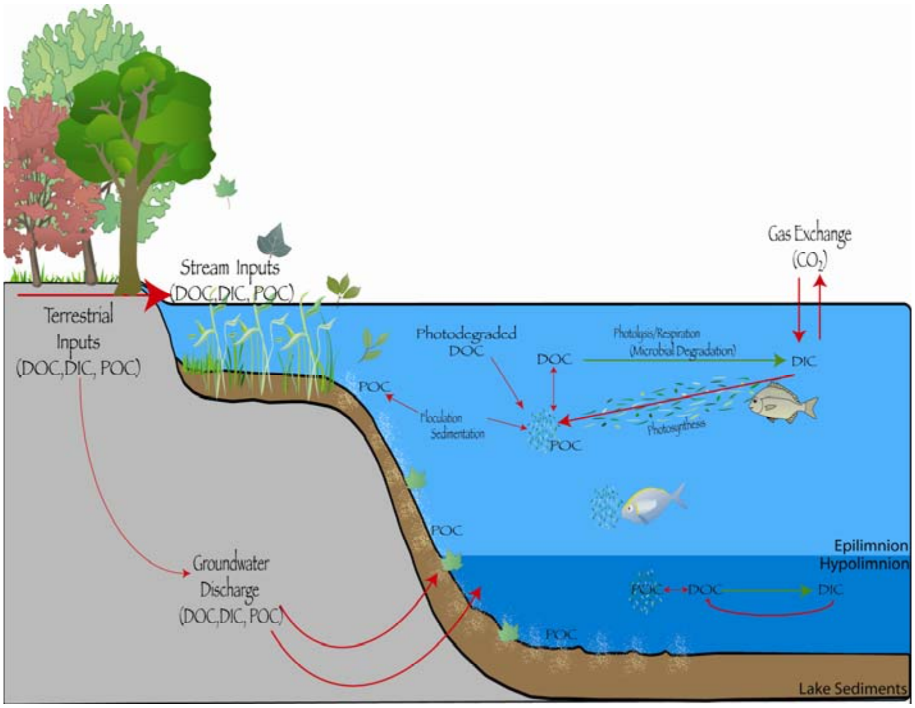

Figure 1.1: A conceptual diagram illustrating carbon cycling in lakes.

1.2.1 Biological processes affecting carbon

In the photic zone, DOM provides metabolic substrates for heterotrophic microorganisms, and influences aquatic microbial communities (Pomeroy, 1974; Azam and Cho, 1987), although allochthonous carbon can also be incorporated into pelagic food webs (e.g. Cole et al., 2002; Pace et al., 2004; Carpenter et al., 2005; Mohamed and Taylor, 2009). Autochthonous DOM can be derived from algae (predominantly phytoplankton) and macrophytes and can be respired by heterotrophic bacteria (Bertilsson and Jones, 2003). Additionally, autochthonous DOM can be released both during herbivore grazing (Lampert, 1978) and during the active growth of cells (Baines and Pace, 1991) and this high quality substrate (Cole et al., 1982) is directly available for uptake by heterotrophs or available to be transformed though enzymatic and abiotic processes to consumable substrates (Bertilsson and Jones, 2003). After cell death, a secondary DOM source is created as the photosynthetically fixed organic substances are released in dissolved or particulate forms to the surrounding waters (Azam and Cho, 1987). Similarly, macrophytes also release photosynthetically produced dissolved and particulate DOM during active growth to the surrounding waters (Bertilsson and Jones, 2003). As with phytoplankton, macrophytes also release a pulse of DOM with death and decay although little information is available regarding this release. In both algal and macrophyte production and release of DOM, predominantly biologically labile and low molecular weight compounds are created for heterotrophic uptake (Bertilsson and Jones, 2003).

1.2.2 Redox Reactions

In natural waters such as lakes, many elemental redox reactions are driven by organic carbon cycling (Morel and Hering, 1993). Photosynthesis is a redox reaction that uses light energy to reduce CO_2 to organic carbon. The organic carbon accumulates at the bottom of lakes, producing steep redox gradients at the sediment water interface (Wehrli, 1990). Organic matter, the most common reducing agent in natural waters, is oxidized to CO_2 during respiration by the reduction of O_2 in aquatic systems (Morel and Hering, 1993). Oxygenated waters have high redox potentials and a low level of chemically reactive electrons as dissolved and adsorbed ions are present in their high oxidation states. However, in lakes, the redox environment can be highly variable between the highly oxygenated surface waters and the sediments at the bottom of the lake due to intermediate zones created by the mixing, diffusion, and various biological activities between the surface and base of a lake (Stumm and Morgan, 1996).

DOM participates in a number of redox reactions and easily complexes with minerals such as iron and manganese oxides that can affect metal transport, water quality and nutrient availability. For example, DOM has a large binding capacity for iron (Koenings and Hooper, 1976; Sojo and de Haan, 1991), and many humic streams in central Ontario transport high loads of DOM (and iron) and create highly coloured and acidic waters (Molot and Dillon, 1997a; Dillon and Molot, 2005). This transport of iron complexed with DOM to lakes can provide an essential micronutrient for phytoplankton growth (Murphy and Yesaki, 1983) and affect carbon dynamics within lakes.

1.2.3 Photodegradation of DOM

Dissolved oxygen is used as an electron acceptor in the photodegradation of DOM and, in conjunction with heterotrophs, can convert otherwise recalcitrant DOM (in addition to fresh DOM) to more labile carboxylic acids, other smaller organic compounds, and DIC such as CO and CO_2. In photolytic reactions, aromatic rings and unsaturated carbon skeletons in DOM absorb UV radiation to break bonds in the presence of a catalyst and a highly reactive oxidant (Sinsabaugh and Findlay, 2003). Since photodegradation reduces the average molecular weight of carbon compounds (Opsahl and Benner, 1998; Zepp et al., 1998) the smaller organic products can enter the microbial food web to be consumed by and stimulate microbial activity (Miller and Moran, 1997; Tranvik et al., 2000).

In addition, the photolytic breakdown of DOM also induces particulate matter formation, especially in the presence of iron as a catalyst (Gao and Zepp, 1998). During photodegradation, DOC is oxidized, low molecular weight organic carbon products are created, and Fe^{3+} is reduced to Fe^{2+}. The ferrous iron is then reoxidized to form new ferric hydrous oxides to which the remaining DOC can bond via ligand exchange. Even though particulate matter can form in both the light and the dark, Gao and

Zepp (1998) suggest that as DOM is oxidized in the light, it complexes iron more readily, converting dissolved iron and carbon to particulate matter.

1.2.4 Mixing

The chemical composition and the amount of DOM and particulate organic matter (POM) entering lakes differ with both season and with the volume of flow (Wetzel, 2001). Once in the lake, both POC and DOC move with the water, with POC settling to the sediment according to Stoke's law (the rate of sedimentation of spherical particles of a certain density is directly proportional to the square of their radii). DOC is subjected to the chemistry of the water layer it is contained within, possibly exposing it to redox reactions, assimilation, photodegradation, etc. As DOC entering lakes can be recalcitrant, it is commonly affected by abiotic processes, which may create more labile forms of carbon. Flocculation of DOC can also occur when particles collide during mixing and adhere due to the attractive van der Waals forces (Wetzel, 2001). Increased collisions and adhesiveness of particles can be affected by physical processes such as Brownian motion, shear from laminar or turbulent flow, the collision of larger particles with smaller particles causing differential settling, capture of smaller particles within the boundary layer of larger particles, surface coagulation at the gas-water interface, small colloids being scavenged as they pass through lake snow, and bacterial collision with colloids (O'Melia and Tiller, 1993; Kepkay, 1994).

1.2.5 Gas Exchange – CO_2 loss to the atmosphere

In aquatic systems, the concentrations of dissolved carbon compounds and the amount of CO_2 invaded to/evaded from the lake are affected by the mineralization of DOM through metabolism or photodegradation. Primary production (see Biological processes) has the ability to decrease CO_2 concentration in the photic zones of lakes, while respiration increases CO_2 concentrations. The balance between the rates of these processes is used to assess if the lakes are heterotrophic, and affects the release or resupply by gas exchange at the atmosphere-water interface. However, DOM photodegradation has also been found to increase concentrations of DIC and CO_2 (e.g. Anesio and Granéli, 2003; Granéli et al., 1998; Bertilsson and Tranvik, 2000) suggesting that the degree of photodegradation could also affect the degree of CO_2 saturation in lakes.

Dillon and Molot (1997a) found that in most of their seven northern temperate study lakes, net CO_2 evasion to the atmosphere occurred and the loss was greater than both DIC loading and precipitation inputs suggesting there was in-lake mineralization of terrestrial DOC to CO_2. Comparing photodecay constants (from DOM photodegradation experiments) to the mass balance rate constants revealed that although photolysis could not account for all DOC losses (to the atmosphere and to the sediments) in lakes with DOC > 4mg/L, it could be responsible for CO_2 evasion and carbon sedimentation in lower DOC lakes (<4 mg/L) (Molot and Dillon 1997b).

1.2.6 Sedimentation

DOC can be lost to sedimentation by a number of processes in aquatic systems (Stumm and Morgan, 1996). Concentration and size distribution of colloids (including or in the presence of natural organic matter) can affect both the coagulation and aggregation rates and the size and sedimentation rates of colloids in all aquatic systems (Filella and Buffle, 1993; Buffle and Leppard, 1995). Other processes such as bubble catalyzed transfer of DOC to POC (e.g. Baylor and Sutcliffe, 1963; Barber, 1966), and the creation of POM through the assembly of DOM polymers to form polymer gels (e.g. Chin et al., 1998) have been documented in marine waters. In riverine systems, turbulence and associated increases in particle contact can affect the creation and size of particulate matter (Droppo and Ongley, 1992, 1994) in addition to the changes cations and pH can have on particulate matter in all aquatic systems. Finally, there can be photochemical and iron induced precipitation where UV reduces Fe^{3+} to Fe^{2+} and transforms H_2O_2 to O_2^*. The O_2^* radical can then react with the reduced iron to create Fe^{3+}, which binds with DOM.

1.3 Use of carbon mass balances to examine allochthonous inputs to lakes

Since the majority (90-95%) of total organic carbon is dissolved organic carbon (DOC) in natural aquatic environments (Wetzel, 2001), aquatic carbon mass balances can be dominated by dissolved organic species in boreal lakes and rivers (Algesten et al., 2003). Carbon cycling in terrestrial and oligotrophic aquatic systems can also be highly dependent on the fate of allochthonous DOC. Carbon mass balances are commonly used to examine the sources and controls of carbon in aquatic systems although, due to the complexity of carbon transfer pathways, studies commonly only concentrate on a portion of the carbon cycle (e.g. the inorganic or organic component; Wetzel et al., 1972, Emerson, 1975; Hesslein et al., 1980). Dillon and Molot (1997a) used carbon DIC and DOC mass balances from 7 oligotrophic and mesotrophic lakes to partition the carbon lost between the atmosphere and the sediments since mass balances bypass the internal carbon transfer pathways. Isotopic balances have also been used to determine the fate of organic matter and isolate sources of carbon in aquatic systems (e.g. Quay et al., 1986; Cifuentes and Eldridge, 1998; Raymond and Bauer, 2001; Jonsson et al., 2001; and Ogrinc et al., 2002) but similar to carbon mass balances alone, only concentrate on a portion of the carbon cycle (i.e. DIC or DOC).

This research explores the use of carbon mass and isotope budgets to examine the fate of DOM and carbon cycling in two northern temperate oligotrophic Shield lakes. In Harp and Dickie Lakes, carbon mass balances suggest that allochthonous carbon controls the carbon budgets in the lakes

(Dillon and Molot, 1997a). Since organic carbon cycling in temperate and boreal lakes can be controlled by terrestrially fixed organic carbon, lakes could be important carbon sinks for organic carbon and zones where terrestrial carbon is mineralized and emitted to the atmosphere (Algesten et al., 2003). Adding complementary isotope budgets to the mass balances estimated by Dillon and Molot, the impact of changing allochthonous inputs to the lakes on organic carbon burial (sedimentation) and mineralization of carbon and CO_2 evasion to the atmosphere can be examined. Furthermore, temporal changes of allochthonous and autochthonous contributions to lake sediments are estimated in this work using the isotope budgets and the $\delta^{13}C$ of lake sediment cores taken from Harp and Dickie Lakes. Paleolimnologists suggest that changes in $\delta^{13}C$ of sediment organic matter reflect changes in past productivity. This thesis will examine whether changes to the allochthonous inputs are also recorded within the $\delta^{13}C$ of lake sediments.

Previously published studies on mass and isotope balances in aquatic systems normally consider respiration, photosynthetic assimilation of carbon, mixing, and gas exchange as the processes affecting the isotopic ratio of carbon (e.g. Quay et al., 1986). These are not, however, the only processes affecting carbon in lacustrine and riverine systems. Approximately 50% of the DOC entering some oligotrophic lakes in the southern Precambrian Shield is lost to the atmosphere and sedimentation (Dillon and Molot, 1997a). Photolysis is one mechanism that produces DIC and that could account for a large DOC loss observed in many boreal lakes with high DOC (Molot and Dillon, 1997b). However, photolysis commonly is not included in carbon mass or isotope balances and the effect of photolysis on carbon isotopes remains understudied. Since photodegradation of DOM can transform DOM and create particulate carbon, it can potentially contribute organic carbon to lake sediments.

Many carbon (and oxygen) stable isotope studies designed to examine photosynthesis to respiration ratios or the importance of allochthonous and autochthonous carbon in food web or sedimenting POC studies do not consider the possible effects that photolysis could have on ^{18}O or ^{13}C of the dissolved and/or particulate compounds in aquatic systems. Carbon cycling in lakes, and incorporation of carbon into food webs, was examined by Cole et al. (2006) using the $\delta^{13}C$ of DIC, DOC, POC and biota (e.g. zooplankton, fish, benthic algae and benthic invertebrates). A series of studies have also been completed on lakes spiked with ^{13}C-DIC to track the uptake and transfer of carbon to POC and the aquatic species within the systems (e.g. Cole et al., 2002; Pace et al., 2004; Carpenter et al., 2005) determining that approximately 50% of the POC in the lakes was terrestrial (Pace et al., 2004). In addition, von Wachenfeldt and Tranvik (2008) used stable carbon isotopes to estimate the importance of allochthonous carbon in sedimenting POC concluding that DOC is a precursor to organic matter that settles in 12 small Swedish boreal lakes. To effectively use stable isotopes as tools to interpret and understand the processes occurring within aquatic systems, it is essential to understand how the processes affect the isotopes. It is therefore imperative to understand the impact DOM photodegradation can have on the carbon (and oxygen) isotopic ratios used in coupled mass and isotope balances and mixing models.

1.4 Thesis Objectives

To examine the fate of DOC and its role in carbon cycling and sedimentation in aquatic systems, an understanding of the processes affecting DOC is needed. Understanding processes such as the photodegradation, microbial decomposition, and the direct sedimentation of DOM is necessary to understand how their carbon isotopes can be used to help understand the fate of DOC and carbon cycling. In this thesis, I first examine how DOM photodegradation affects the $\delta^{18}O$ of dissolved oxygen and the $\delta^{13}C$ of DOC, DIC, and POC. Although the fractionation of $\delta^{18}O$ during DOM photodegradation is not used to explore the role of allochthonous carbon to lake sediments, data were gathered during incubation experiments used to determine the role of photolysis on $\delta^{13}C$. This work (Chapter 2) is the first published study on $\delta^{18}O$ fractionation resulting from DOM photodegradation. Changes to the $\delta^{13}C$ of DOC, DIC and POC were examined concurrently with oxygen fractionation to examine how photodegradation of DOM transforms allochthonous carbon entering lakes. Complementary isotope budgets were then completed for the estimated mass balances of Dillon and Molot (1997a) to examine the importance of allochthonous carbon to the carbon sediment record. The proportion of allochthonous and autochthonous carbon in lake sediments was then estimated by calculating allochthonous and autochthonous $\delta^{13}C$ end-members (using $\delta^{13}C$ values for leaf litter, temporal stream POC, photodegraded DOC, and temporal DIC). These objectives are presented in 5 data chapters with the following objectives:

1. To examine the stable oxygen isotope fractionation during photolytic O_2 consumption in stream waters (Chapter 2);
2. To examine the effects of DOM photodegradation on $\delta^{13}C$-DOC and $\delta^{13}C$-DIC in stream waters (Chapter 3);
3. To examine the effects of DOM photodegradation on $\delta^{13}C$-DOC and $\delta^{13}C$-POC in stream waters (Chapter 4);
4. To examine the influence of allochthonous carbon on the $\delta^{13}C$-lake sediment records in two small oligotrophic lakes using carbon mass and isotope balances (Chapter 5);
5. To examine the relative proportion of allochthonous and autochthonous POC to the carbon isotopic signature of lake sediments (Chapter 6).

Chapter 2:

Stable oxygen isotopic fractionation during photolytic O_2 consumption in stream waters.

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2.1 Overview

Oxygen (O_2) is required for life in higher organisms, however, processes such as respiration, the oxidation of reduced inorganic species, and the photolytic breakdown of dissolved organic matter (DOM) decrease the O_2 concentrations in aquatic systems. Filtered, inoculated, and sterile samples of stream waters from Ontario, Canada, were incubated in natural sunlight to examine the effects of photolysis of DOM, respiration, and abiotic reactions on O_2 consumption and $\delta^{18}O$ of dissolved oxygen ($\delta^{18}O-O_2$). Oxygen consumption rates in the light were up to an order of magnitude greater than in the dark, suggesting light-mediated processes controlled O_2 consumption. Rates of O_2 loss were the same for each treatment (i.e. filtered, inoculated, and sterile) indicating that photolysis was the dominant O_2 consuming process over respiration in these incubations. O_2 consumption rates were different between streams, even when normalized to the change in dissolved organic carbon (DOC), signifying that DOM photolability varied among streams. During DOM breakdown to CO_2, the lighter ^{16}O isotopomer was preferentially consumed. Fractionation factors observed for photolysis, respiration, and abiotic reactions ranged between 0.988 and 0.995, and were similar in both the light and in the dark incubations in all streams. These fractionation factors are not a function of O_2 consumption rates, and are

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outside the range published for respiration (0.975-0.982). In current models of O_2 and $\delta^{18}O$-O_2, photolysis and respiration are not considered separately and the isotopic fractionation during respiration that is measured in the dark is used in the light. In these incubations, DOM degradation and abiotic reactions are important O_2 consuming and $\delta^{18}O$-O_2 fractionating processes. Current models of O_2 and $\delta^{18}O$-O_2 incorporate photolysis of DOM and other abiotic processes into the respiratory component of O_2 consumption, thereby overestimating respiration and underestimating photosynthesis to respiration ratios. Consequently, photolysis and abiotic reactions should be considered separately, particularly in shallow aquatic systems with high DOC.

2.2 Introduction

Oxygen is a fundamental requirement for life in higher organisms (Wetzel, 2001). In aquatic systems, O_2 regulates respiratory metabolism, mediates biogeochemical cycles, and is an integral component of water quality. Oxygen concentration is controlled by the balance between various processes including gas exchange with the atmosphere, photosynthesis, respiration, mixing, photolysis, and other redox reactions.

Oxygen mass balances are commonly used to calculate rates of photosynthesis (P) and respiration (R) and thus ecosystem metabolism (Odum, 1956). More recently, $\delta^{18}O$ of dissolved O_2 – ($\delta^{18}O$-O_2) has been increasingly used to assess ecosystem metabolism and O_2 dynamics in aquatic systems such as lakes, rivers, and ponds. Quay et al. (1995) demonstrated how O_2 and $\delta^{18}O$-O_2 balances could be used simultaneously to directly constrain the P:R in aquatic systems under steady state assumptions. Temporal and spatial variability of trophy was assessed by Russ et al. (2004) in a large oligotrophic lake, and Parker et al. (2005) looked at oxygen isotope changes in rivers with up to 13‰ variation in diel cycles. Since many of the studies using $\delta^{18}O$-O_2 are limited by steady state assumptions and do not consider daily oxygen cycles, Venkiteswaran et al. (2007, 2008) developed a dynamic model (PoRGy) to assess metabolic balance. Using diel O_2 and $\delta^{18}O$-O_2 measurements, the rates and ratios of P:R:G (Photosynthesis: Respiration: Gas Exchange) could be assessed.

Oxygen saturation and $\delta^{18}O$-O_2 can be used in conjunction with each other to calculate P:R and P:R:G ratios. Atmospheric oxygen (23.5‰ vs. SMOW; Kroopnick and Craig, 1972) fractionates in water by 0.7‰ (Benson and Krause, 1984). If gas exchange dominates, O_2 concentrations will be close to saturation, and the $\delta^{18}O$ will remain approximately 24.2‰ (Quay et al., 1993). Aquatic respiration preferentially consumes $^{16}O^{16}O$, decreasing the dissolved O_2 concentration and increasing the $\delta^{18}O$ of the remaining O_2. Fractionation factors for respiration (α_R) in most $\delta^{18}O$-O_2 studies are typically not determined directly but selected from the range of published values for marine and river waters (α_R= 0.975-0.982) (Kiddon et al., 1993; Kroopnick, 1975; Quay et al., 1993; Quay et al., 1995). In contrast, during photosynthesis there is no photosynthetic fractionation (α_p = 1.000; Guy et al., 1993) and the $\delta^{18}O$-O_2 produced will reflect the $\delta^{18}O$-H_2O. Given that the $\delta^{18}O$-H_2O for most aquatic systems is typically less than 0‰, much less than the $\delta^{18}O$ in air (23.5‰), photosynthetic O_2 added to the aquatic system will lower the $\delta^{18}O$-O_2. Therefore, if photosynthesis is the dominant process (over gas exchange and respiration) O_2 will be supersaturated and the $\delta^{18}O$-O_2 value will decrease.

Measured values of O_2 concentrations, $\delta^{18}O$-O_2, and gas exchange rates can be used in two mass balance equations to determine P:R (Quay et al., 1995):

(Equation 2.1)

$$\frac{d(O_2)}{dt} = \frac{G}{Z} \times (O_{2s} - O_2) - R + P$$

(Equation 2.2)

$$\frac{d(^{18}O_2)}{dt} = \frac{G}{Z} \times \alpha_g (O_{2s}\delta^{18}O_a \alpha_s - O_2\delta^{18}O) - R\delta^{18}O\alpha_R + P\delta^{18}O_w\alpha_P$$

where O_2 is the dissolved oxygen concentration, t is the time, Z is the mean depth, G is the gas exchange rate, s is the O_2 value at atmospheric saturation, R is the respiration rate, P is the gross production rate, α_g is the gas exchange fractionation factor (0.9972; Knox et al., 1992), $\delta^{18}O_a$ is the ^{18}O:^{16}O atmospheric value, α_S is the equilibrium air-water fractionation factor, α_R is the respiration fractionation factor, $\delta^{18}O_w$ is the ^{18}O:^{16}O isotopic ratio in water, and α_P is the photosynthetic fractionation factor. If there is an accrual of water from surface or groundwater, an additional term can be added. There is no separate term in these equations for the photolytic or abiotic consumption of oxygen and these processes are thus amalgamated within 'R'. Similarly, α_R includes all fractionations associated with O_2 consumption processes, including respiration, and any other abiotic processes and redox reactions.

Previously published studies on $\delta^{18}O$ in aquatic systems only considered respiration, photosynthesis, and gas exchange as processes affecting the isotopic ratio of O_2 (e.g. Quay et al., 1995; Wang and Veizer, 2000; Russ et al., 2004; Parker et al., 2005, Tobias et al., 2007) although some acknowledge O_2 consumption occurs to a lesser extent by chemical oxidation. However, respiration and chemical oxidation are not the only oxygen consuming processes in lacustrine and riverine systems. Northern temperate and boreal lakes are generally net heterotrophic ecosystems, dependent upon decaying or dead organic matter from the terrestrial catchment for sustenance (del Giorgio and Peters, 1994; Algesten et al., 2003). Approximately 50% of the dissolved organic carbon (DOC) entering some oligotrophic lakes in the southern Precambrian Shield is lost to the atmosphere and sedimentation (Dillon and Molot, 1997a). Photolysis is one mechanism that consumes oxygen and that could account for a large DOC loss observed in many boreal lakes with high DOC (Molot and Dillon, 1997b).

Dissolved oxygen is an electron acceptor in dissolved organic matter (DOM) photodegradation and, in conjunction with heterotrophs, converts recalcitrant DOM to more labile, carboxylic acids, other smaller organic compounds, and dissolved inorganic carbon (DIC) forms such as CO and

CO_2. These smaller organic products can be consumed by and stimulate microbial activity (Miller and Moran, 1997; Tranvik et al., 2000). The breakdown of DOM to CO_2 consumes oxygen and affects the oxygen balance of aquatic ecosystems. It is therefore crucial to understand the photodegradation of DOM, in addition to the other processes controlling oxygen production and consumption, since DOM degradation and O_2 dynamics are linked.

Many studies have looked at DOM photodegradation because of its importance in the carbon cycle (e.g. carbon transport from terrestrial to ocean environments: Miller and Zepp, 1995; supersaturation of CO_2 in lakes: Granéli et al., 1996; and loss of DOM in lake surface layers: Bertilsson and Tranvik, 2000). Other studies have shown that photodegradation of DOM influences water chemistry and transparency (affecting the photic zone depth and the region of photosynthetic activity: Andrews et al., 2000; Anesio and Granéli, 2003), in addition to affecting aquatic organisms (e.g. UV exposure/damage to life and the effects on the food web by altering lability of sustenance sources: Gao and Zepp, 1998). Only a few studies have looked at O_2 consumption in the context of surface water oxygen levels (Amon and Benner, 1996; Miles and Brezonik, 1981), and the relative importance of O_2 consumption during DOM photodegradation due to the combined effects of DOM photodegradation and microbial respiration versus primary production (Lindell and Rai, 1994).

Although photolytic effects on O_2 concentrations have been recognized, changes in $\delta^{18}O\text{-}O_2$ during photolytic O_2 consumption have not been investigated. Photolysis could be an important but neglected component in oxygen isotopic models used to determine P:R ratios in aquatic systems. The goals of this study were to: 1) determine the effects of photolysis, microbial respiration, and other abiotic reactions on $\delta^{18}O\text{-}O_2$ in waters from three different forested streams, and 2) determine the $\delta^{18}O\text{-}O_2$

fractionation factors associated with photolysis, respiration, and abiotic reactions.

2.3 Methods

Incubation experiments were performed on typical small inflows from two headwater oligotrophic lakes. Stream water samples were collected from Harp Lake Inflow 4 (H4), Harp Lake Inflow 5 (H5), and Dickie Lake Inflow 10 (D10). These streams are either major DOC or water contributors to their lakes, and have been the focus of previous studies on DOM consumption by photolysis (e.g. Molot and Dillon, 1997b; Gennings et al., 2001). In these streams, DOC concentration decreases as discharge increases. In addition, the streams have higher DOC concentrations than their lakes due to high rates of in-lake DOC consumption. Inflow waters were collected at weirs just upstream from the lakes. The streams are located in the Muskoka-Haliburton region 200 km north of Toronto, Ontario, Canada. The watersheds lie on the southern tip of the Precambrian Shield, are composed of thin tills (<1m thick), and contain peatlands. A detailed description of the streams and forested catchments can be found in Dillon et al. (1991).

H4 and H5 contribute the majority of the water to Harp Lake, and are surrounded predominantly by deciduous trees. These two streams flow through beaver ponds and swamp valley bottom wetlands, whereas D10 (a major water and carbon contributor to Dickie Lake) flows through a bog. These waters are typically oxic without measurable NH_4^+, but with Fe and Mn complexed to DOC. The extent of peatlands, and general chemical characteristics of each stream are listed in Table 2.1. Stream water samples were filtered to 0.2 μm. One litre of each stream water was filtered through 1 μm Nuclepore membranes leaving suspended bacterioplankton as an inoculant (Sieburth et al., 1978). Once filtered, the waters were divided into three treatments. Filtered treatments contained only the 0.2 μm-filtered water and, accordingly, microbial activity should be absent (Wotton, 1994). Inoculated treatments contained 90% of the 0.2 μm-filtered water, and 10% of the 1 μm filtered and thus contained microbes. The absence of microbial activity was ensured in sterile treatments by spiking the 0.2 μm-filtered water with 1mL of a saturated mercuric chloride ($HgCl_2$) solution per litre of sample.

Table 2.1: Percent peatland and summer stream water characteristics (July 1995) of the three sites.

Site	Catchment % peatland[1]	Total iron (mg/L)[2]	pH[2]	Colour (Hz)[2]	DOC (mg/L)[2]	DOC (mg/L)[3]
Dickie Inflow 10	17.1	1297	4.7	393	28.7	29.4
Harp Inflow 4	5	291	6.5	66.1	7.3	6.8
Harp Inflow 5	13.3	n.d.[4]	n.d.	n.d.	n.d.	15.4

[1] Taken from Dillon and Molot, 1997

[2] Taken from Molot and Dillon, 1997

[3] current study

[4] n.d. = no data

Experiments were performed to ensure that there was no DOM leaching from the bags and that the bags were gas tight. Eight litres of water was pumped into each Tedlar bag that had been previously washed in triplicate with ethanol and rinsed 3 times with nanopure water. The bags were placed in shallow water baths, and exposed to natural sunlight at the University of Waterloo (43° 28' 25.6" N and 80° 33' 27.5" W; elevation ~ 335 m). Each treatment (filtered, inoculated, and sterile) was performed simultaneously in duplicate. The water baths of duplicate treatments were arranged side by side to minimize variation in exposure and temperature. Temperature of duplicate bags was within 0.2°C, however, temperature between treatments on the same day varied according to sampling time. Temperature was not controlled, but water baths moderated daily temperature changes.

A total of 14 bags were incubated in the first experiment (D10) that began on June 17th, 2005 (2 per treatment in the light and in the dark, and two light exposed H5 sterile samples). Treatments incubated in the light were exposed for 4-7 days, while the dark treatments were incubated for 20 days to allow for sufficient O_2 depletion. In the second experiment (H4) 16 bags (2 per treatment in the light and the dark, two H5 light exposed sterile samples, and two D10 light exposed sterile samples) were incubated beginning July 9th, 2005. Light treatments were exposed for 3-8 days, while dark treatments were incubated for 14 days. The concentration data presented is an average of the duplicate bags for each treatment. The isotope data are run in their entirety for one bag, with duplicates run approximately every 5 samples, while samples from the second bag were run every 3-5 samples. Exposure time was dependent on site, treatment (i.e. light vs. dark), and rate of O_2 consumption. Since D10 and H4 waters were incubated on different dates each incubation experiment contains a set of sterile water from H5 and D10 exposed to light to assess the variation of the same samples between the two incubations.

Samples were withdrawn at regular intervals, roughly at increments of 20% dissolved oxygen loss until 80-90% of the oxygen was consumed, to permit the determination of O_2 consumption rates and fractionation factors (α) for $\delta^{18}O$ due to photolysis, respiration, and other abiotic reactions. A three-way valve, tubing and needles were used to collect samples and to minimize O_2 contamination from the atmosphere.

O_2 concentrations were measured in duplicate using the Winkler method. Samples were collected in 20 or 30-mL air-tight glass syringes, instead of BOD/COD bottles, and reagent quantities were adjusted for these volumes. Samples were stored under water and were analyzed within approximately 4 hours. Oxygen concentrations have an associated precision of ±0.2 mg/L. $\delta^{18}O$-O_2 samples were collected in 60mL evacuated Wheaton serum bottles with butyl blue stoppers and 0.3 g of sodium azide. A 5mL helium headspace was added to the $\delta^{18}O$-O_2 samples, and the bottles were shaken for at least 1.5 hours to equilibrate headspace and dissolved oxygen. Gas from the headspace was analyzed on a Micromass Isochrom gas chromatograph isotope ratio mass spectrometer (GC-IRMS) (similar to

Wassenaar and Koehler, 1999) at the Environmental Isotope Laboratory, Waterloo, Ontario. Precision of the $\delta^{18}O\text{-}O_2$ analysis was ± 0.3‰. Duplicates were analyzed periodically, and isotopic ratios of duplicates were always within 0.3‰. Near the end of each experiment, O_2 concentrations were too low to be analyzed for $\delta^{18}O\text{-}O_2$.

DOC samples were filtered to 0.45 μm, acidified to pH 2-3, and sparged to remove DIC. DOC concentrations were analyzed on a total organic carbon analyzer (Dohrmann DC-190) with a precision of ± 0.3 mg/L, although variation among duplicates was often less than this amount. DOC absorbance samples (also filtered to 0.45 μm) were analyzed on duplicate samples on a Beckman DU530 Life Science UV/Vis Spectrophotometer (path length = 1cm) between 200 nm and 700 nm. Absorbance was automatically corrected to the absorbance of nanopure water. The specific UV absorbance ($SUVA_{254}$) was determined using the ratio of UV absorption at $\lambda = 254$ nm (measured in absorbance units m^{-1}) to DOC concentration (mg/L) (Weishaar et al., 2003).

Fractionation of dissolved oxygen due to respiration, photolysis, and other abiotic reactions was calculated from the decrease in O_2 and concomitant increase in $\delta^{18}O\text{-}O_2$ by assuming the processes followed Rayleigh fractionation (Broecker and Oversby, 1971):

(Equation 2.3)

$$\frac{R_t}{R_i} = \left(\frac{O_{2t}}{O_{2i}} \right)^{(\alpha - 1)}$$

where R is the $^{18}O/^{16}O$, and O_2 is the oxygen concentration at initial time (i) and at a time after the starting point (t), and α is the fractionation factor. The α includes all of the oxygen consuming processes occurring within the treatment. The sterile treatments in the light had no biotic activity and therefore the associated fractionation factor would only consist of abiotic processes including photolysis. However, the fractionation factor for inoculated treatments combined biotic respiration and abiotic processes.

2.4 Results and Discussion

2.4.1 Rates of O_2 consumption

Oxygen loss was rapid in all treatments exposed to light, with 80-90% of the O_2 consumed within approximately 4 days (Figure 2.1,Table 2.2). The DOC concentration was reduced by an average of 25% (Table 2.3). Oxygen concentrations in duplicate treatments were generally within 0.2mg/L. As O_2 consumption was similar in the inoculated and sterile treatments from each site, the main mechanism of O_2 loss was not microbial respiration. Although not quantified in this experiment, microscopic examination from samples in a preliminary experiment show bacteria present. Sterile treatments contained no bacteria.

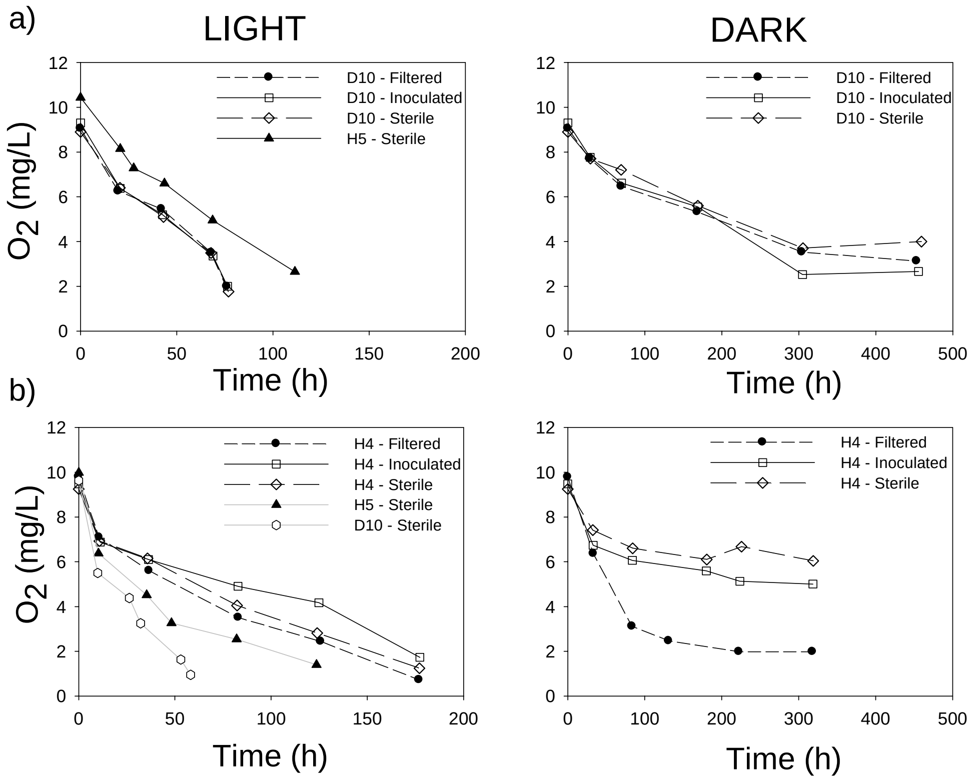

Figure 2.1: O_2 concentrations versus Time of a) D10 and b) H4. Points are the average of two duplicate bags incubated simultaneously. Differences between bags are <0.2 mg/L. D10 inoculated samples in (a) is underneath the filtered and sterile samples. Sterile H5 samples were incubated with both experiments (a and b), and sterile D10 samples were incubated with H4 (b) to assess the effects of differences in light exposure between the two experiments.

Table 2.2: Oxygen consumption rates and O_2 consumption rates normalized for DOC concentration in the water

Site	Treatment		*LIGHT*			*DARK*	
		O_2 consumed (µg/L/hr$_{sunlight}$)	O_2 consumed (µg/L/hr$_{sunlight}$/ mg/L$_{DOC}$)	O_2 consumed (µg/L/hr$_{sunlight}$/ mg/L$_{DOC\ lost}$)	O_2 consumed (µg/L/hr)	O_2 consumed (µg/L/hr/ mg/L$_{DOC}$)	O_2 consumed (µg/L/hr$_{sunlight}$/ mg/L$_{DOC\ lost}$)
Dickie Inflow 10	filtered	122 ± 8	4	13	12 ± 1	0.5	6
	inoculated	127 ± 8	4	15	14 ± 1	0.5	3
	sterile	124 ± 8	4	16	11 ± 1	0.4	3
	Average	*124*			*12*		
	sterile[1]	189 ± 9	7	150	n/s[3]	n/s[3]	n/s[3]
Harp Inflow 4	filtered	68 ± 3	9	62	21 ± 1	3	10
	inoculated	54 ± 3	8	41	11 ± 1	1	6
	sterile	61 ± 3	8	34	8 ± 1	1	7
	Average	*61*			*13*		
Harp Inflow 5	sterile[2]	104 ± 6	7	25	n/s[3]	n/s[3]	n/s[3]
	sterile[1]	90 ± 5	5	32	n/s[3]	n/s[3]	n/s[3]
	Average	*97*					

[1] Incubated with H4 water; [2] Incubated with D10 water; [3] ns = no sample

Values are based on the average of measurements from duplicate bags.

and for DOC lost during the experiment.

Table 2.3: Initial and final DOC concentrations and SUVA$_{254}$ measurements in filtered, inoculated, and sterile incubations.

		LIGHT				DARK			
Site	Treatment	DOC initial (mg/L)[3]	DOC final (mg/L)	SUVA initial	SUVA final	DOC initial (mg/L)	DOC final (mg/L)	SUVA initial	SUVA final
Dickie Inflow 10	filtered	29.1	20.0	5.35	7.09	29.1	26.8	5.35	5.63
	inoculated	29.6	21.1	5.26	6.66	29.6	24.5	5.26	6.09
	sterile	29.5	21.7	5.26	6.44	29.5	25.9	5.26	5.8
	sterile[1]	29.2	27.9	5.29	4.91	n/s[3]	n/s[3]	n/s[3]	n/s[3]
Harp Inflow 4	filtered	7.0	4.3	3.88	2.51	7.0	4.9	3.88	4.95
	inoculated	6.8	5.5	3.95	2.6	6.8	4.9	3.95	4.87
	sterile	6.6	4.4	4.07	3.27	6.6	5.5	4.07	4.34
Harp Inflow 5	sterile[2]	15.6	11.4	5.90	6.03	n/s[4]	n/s	n/s	n/s
	sterile[1]	15.1	12.9	6.10	5.58	n/s	n/s	n/s	n/s

[1] Incubated with H4 water; [2] Incubated with D10 water; [3] DOC precision: ±0.3 mg/L; [4] n/s = no sample.
Values are based on the average of measurements from duplicate bags.

Oxygen was generally consumed more rapidly earlier in the experiment, thus O_2 consumption was not linear with time. The rapid initial loss of O_2 could be consistent with a non-linear process such as light-induced particulate matter formation or with a reaction rate that is first-order with respect to O_2. However, the goodness-of-fit between zero- and first-order fits was not markedly different and there is insufficient evidence to adopt a first-order fit rather than zero-order approach when calculating consumption rates. A linear fit was therefore used to calculate the rates of O_2 consumption in order to compare the rates with other studies using zero-order approaches (e.g. Miles and Brezonik, 1981; Lindell and Rai, 1994).

The O_2 consumption rates in D10 in the light were approximately twice that of H4. However, the original DOC concentration in D10 (29.4 mg/L) was greater than in H4 and H5 (6.8 mg/L and 15.4 mg/L respectively; Table 2.3) a result of higher wetland coverage in the D10 catchment (Table 2.1; Dillon and Molot, 1997b). Normalizing the O_2 loss to the DOC concentration lost reveals that H4 consumed more than twice the O_2 per mg/L of DOC lost from the water than D10 in light and dark treatments. O_2 consumption during the breakdown of DOM from H5 fell between H4 and D10 and illustrates that natural differences exist between streams. Differences in O_2 consumption rates between streams could be due to differences in DOM quality or different degrees of self-shading in waters with higher DOC concentrations (i.e. D10).

The O_2 consumption rates in the dark did not vary among treatments or among streams (Table 2.2), even in inoculated treatments where respiration occurred. Minor variations existed between treatments from each stream with the exception of the dark filtered treatment from H4, which had a higher O_2 consumption rate in both incubation bags for an unknown reason.

Consumption rates in the light treatments were an order of magnitude greater than in the dark treatments of D10 and approximately 3 to 8 times greater in H4. The similarity of the rates in light treatments and large differences between the light and the dark treatments indicates that consumption of O_2 by respiration and redox reactions was very small compared to photolysis in this experiment.

O_2 consumption rates from this study were similar to rates from other streams and other aquatic systems including incubations of sterile highly coloured humic waters of Lake Mize (light: 0.12mg/L/hr; dark: 0.04mg/L/hr; DOC = 38 mg/L), *in situ* rates observed in other coloured Florida lakes with DOC concentrations ranging from 13-60 mg/L (light: 0.02-0.09 mg/L/hr; dark: 0.01-0.04 mg/L/hr; Miles and Brezonik, 1981), and incubations of sterile lake and creek waters with varying humic content from northern Germany (0.02-0.062 mg/L/hr; DOC = 5-37 mg/L; Lindell and Rai, 1994). In contrast, our O_2 consumption rates were much lower than incubations of humic Swedish bog waters with DOC $\geq$70mg/L (Lindell and Rai, 1994).

Others have also noted the importance of photolysis relative to respiration. Amon and Benner (1996) found respiration rates were eight times smaller than O_2 consumption rates due to photochemical processes in incubation experiments of Brazilian Rio Negro (blackwater river; DOC ~10mg/L). Their rates are comparable to those observed by Lindell and Rai (1994) in humic-coloured freshwaters, and in light and dark treatments of this study. Rates in this study normalized for DOC also fall within the range of rates calculated from Amon and Benner (1996).

Although photooxidative O_2 consumption rates appear to be high in incubations, this is often not the case in natural water bodies. In 5 temperate oligotrophic lakes, Granéli et al. (1996) determined that O_2

consumed during photodegradation of DOM was more important than during planktonic community respiration on a volumetric basis in surface waters; however, respiration was greater than photodegradation on an areal basis. Similarly, Anesio and Granéli (2003) found that community respiration was areally greater than photooxidation in mesocosm experiments. In natural systems, respiration may become more important because light is rapidly attenuated with depth whereas respiration occurs throughout the entire water column (Wetzel, 2001). Therefore, the mean depth of the system will, in part, govern the relative importance of photolysis and respiration.

DOC is lost in all the treatments but at a much greater rate in the light indicating the loss is likely a result of the photodegradation of DOM (Table 2.3). However, particulate matter also formed during the incubation in both the light and the dark treatments accounting for a portion of the DOC loss. Although not quantified in this experiment, more particulate matter appeared visually to form in the light treatments. Even though particulate matter can form in both the light and the dark, Gao and Zepp (1998) suggest that as DOM is oxidized in the light, it complexes iron more readily, converting dissolved iron and carbon to particulate phases. During photodegradation, DOC is oxidized and low molecular weight products are created, and Fe^{3+} is reduced to Fe^{2+}. The ferrous iron is then reoxidized to form new ferric hydrous oxides to which the remaining DOC can bond via ligand exchange. Reactions are much slower in the dark where the reduction of Fe^{3+} by organic matter is temperature driven (Faust, 1994). Other O_2 consuming reactions can occur in the dark, including nitrification, methane oxidation, and the oxidation of other reduced inorganic species (e.g. Mn^{2+}, Fe^{2+}; Quay et al., 1995). Sometimes, these reactions can be the result of photochemical products from light-mediated reactions (e.g. iron catalyzed hydrogen peroxide Fenton reactions). Abiotic oxidation could account for particulate matter formation (in the light and in the dark) in this study and could be a direct or indirect mechanism for O_2 loss. Therefore, the calculated O_2 consumption rates are a combination of all O_2 consuming processes.

DOC from different streams may differ in photolability. Changes in $SUVA_{254}$ have been used as an indicator of changes in the chemical character (including % aromaticity) of DOC (e.g. Hood et al., 2006). Initial $SUVA_{254}$ was higher in D10 indicating that its DOC had a different chemical character than H4 with a higher % aromaticity (Table 2.3). Exposure to light alters the DOC character as functional groups are cleaved and particulate matter forms. At the end of the incubation, $SUVA_{254}$ decreased in H4, increased in D10 (Table 2.3) and did not vary greatly in H5. Thus, although DOC was lost in all the stream samples, DOC did not react in the same manner in all streams.

$SUVA_{254}$ increased in all the dark treatments but changes were smaller than in the light (Table 2.3). Particulate matter also formed in the dark treatments. With no photodegradation occurring in the dark treatments, changes in $SUVA_{254}$ likely reflect changes in the DOC character resulting from particulate formation and/or other abiotic processes.

2.4.2 Effects of photolysis and respiration on $\delta^{18}O$-O_2

In these incubations, O_2 consumption caused an increase in the $\delta^{18}O$-O_2 value of both the light and the dark treatments (Figure 2.2). In the light treatments, the $\delta^{18}O$-O_2values increased by approximately 7‰ to 15‰ and changes were similar in filtered, inoculated, and sterile treatments of each inflow. In addition to DOM photochemistry, other photochemical reactions may have occurred (including redox reactions with trace metals, iron, nitrate, etc). Given that photolysis of DOM and other abiotic processes consume O_2 in the light sterile treatments, the increase in $\delta^{18}O$-O_2

shows that photolysis and other abiotic reactions preferentially consume the lighter isotopomer, $^{16}O^{16}O$.

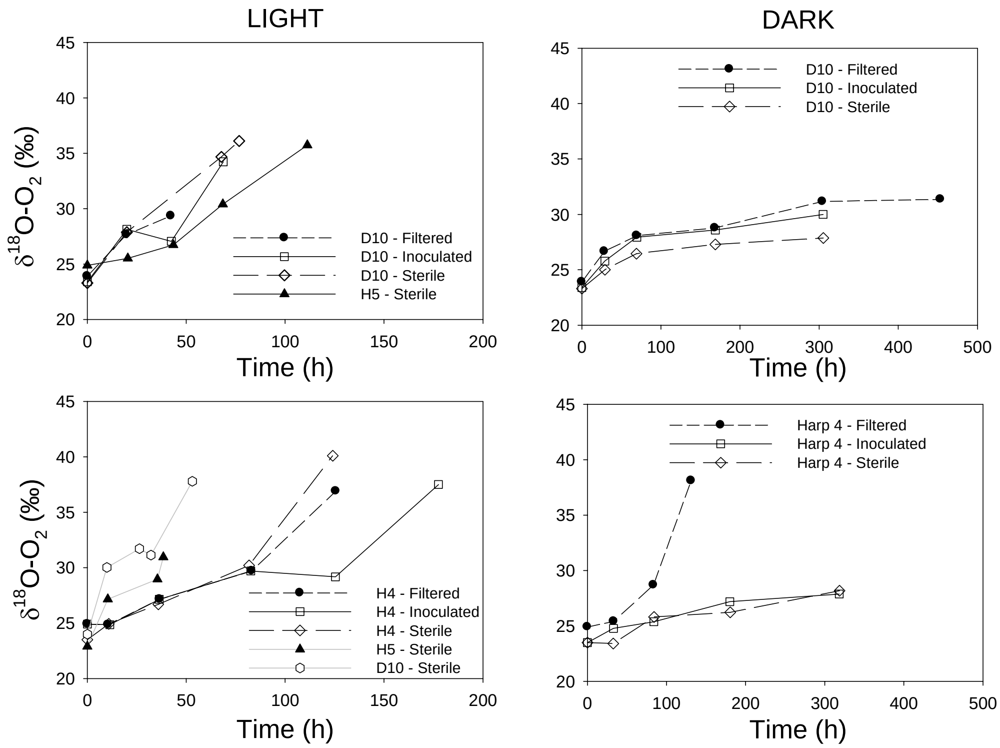

Figure 2.2: $\delta^{18}O-O_2$ versus Time of a) D10 and b) H4. Precision of $\delta^{18}O-O_2$ is 0.3‰. Sterile H5 samples were incubated with both experiments (a and b), and sterile D10 samples were incubated with H4 (b) to assess the differences in light exposure between the two experiments.

Stream water incubated in the dark also exhibited an increase in $\delta^{18}O-O_2$with decreasing O_2 concentration (~4‰ to 7‰ increase) in all treatments including the sterile treatment. Abiotic O_2 consumption mechanisms, are thus also $\delta^{18}O-O_2$ fractionating processes preferentially consuming $^{16}O^{16}O$. Values of α calculated through dark incubation experiments include abiotic O_2 consumption fractionation.

Isotopic fractionation factors in the light treatments ranged between 0.988 and 0.994 (average α = 0.992; Table 2.4). In general, the α ranges were similar for filtered, inoculated, and sterile treatments in D10 and H4. Sterile samples from H5 and D10 incubated on two different dates were also similar. The α values for all the streams were similar even though the DOC from the different streams was of different quality. Isotopic fractionation in the dark incubations (average $\alpha = 0.994$), was similar for the different treatments and for all the streams. In addition, dark and light exposed samples had similar α values. The magnitude of the α values is similar to the O_2 fractionation for pyrite oxidation in mine tailings (0.9957; Taylor et al., 1984). These calculated α values are much closer to 1.000 than the α_R values reported for marine microalgae and bacteria (0.974 – 0.982; Kiddon et al., 1993), and Amazon River water (0.979 – 0.986; Quay et al., 1995) that are usually used in $O_2 – \delta^{18}O\text{-}O_2$ studies.

Table 2.4: Fractionation factors calculated from the incubations using the principles of Rayleigh fractionation.

Site	Treatment	LIGHT	(±)	DARK	(±)
Dickie Inflow 10 (wetland)	filtered	0.991 ± 0.001	0.001	0.993 ± 0.001	0.001
	inoculated	0.990 ± 0.001	0.001	0.995 ± 0.001	0.001
	sterile	0.992 ± 0.001	0.001	0.995 ± 0.001	0.001
	sterile[1]	0.994 ± 0.001	0.001	n/s[3]	
	Average	*0.992*		*0.994*	
Harp Inflow 4 (more upland)	filtered	0.990 ± 0.001	0.001	0.991 ± 0.001	0.001
	inoculated	0.990 ± 0.001	0.001	0.990 ± 0.001	0.001
	sterile	0.985 ± 0.001	0.001	0.985 ± 0.001	0.001
	Average	*0.988*		*0.989*	
Harp Inflow 5 (wetland)	sterile[2]	0.992 ± 0.001	0.001	n/s	
	sterile[1]	0.995 ± 0.001	0.001	n/s	
	Average	*0.994*			

[1] Incubated with H4 water; [2] Incubated with D10 water; [3] n/s = no sample

Isotopic fractionation in these incubations was not dependent on the rate of O_2 loss. There was no relationship between fractionation factors from the incubations and rates of O_2 consumption, similar to the only other published studies of respiration rates and α_R values (Figure 2.3; Kiddon et al., 1993; Quay et al., 1995). Samples generally clustered according to stream and light regime and were separated from the incubations of Kiddon et al. (1993). However, Kiddon et al. (1993) incubated bacteria and microalgae in artificial seawaters where fractionation by the biotic species was enzyme-limited and abiotic redox reactions were likely minimal in comparison to respiration. The dark O_2 consumption incubation rates from this study are similar to the dark incubations performed by Quay et al. (1995) on unfiltered water from the Amazon basin (Figure 2.3) but the α_R values are different. Although the unfiltered Amazon River fractionations also incorporate all abiotic oxidation, nitrification, and bacterial respiration, the similarities to Kiddon et al. (1993) suggest that their fractionation factors could be enzyme-limited and that biotic O_2 consumption could be higher in their waters. Values of α may rely on the relative importance of O_2 consumption by abiotic and biotic processes.

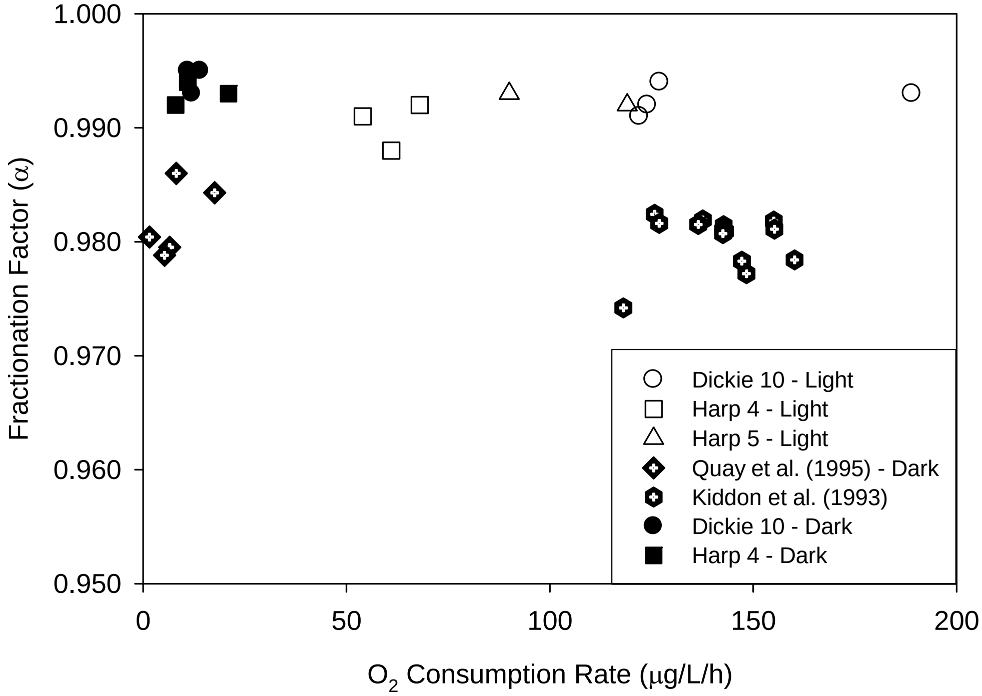

Figure 2.3: Fractionation factor (α) versus O_2 consumption rate for the current incubation study. Filled symbols denote dark incubations, while hollow symbols represent light exposed treatments. Data from Quay et al. (1995) and Kiddon et al. (1993) incubations are included. Kiddon et al. (1993) incubated isolated and mixed bacteria and marine microalgae assemblages in dark syringes with artificial seawater for 4-8 hours at 20°C. Quay et al. (1995) incubated unfiltered Amazon river water in dark bottles for <24hrs for small bottles and 2-7 days for large carboys at 28°C. Respiration rates included all O_2 consuming processes (e.g. bacterial respiration, CH_4 and Mn oxidation, nitrification etc).

Current coupled O_2 – $\delta^{18}O$-O_2 models used to calculate P:R ratios in the Amazon Basin (Quay et al., 1995), Meech Lake (Wang and Veizer., 2000), and Big Hole River (Parker et al., 2005) and P:R:G (Venkiteswaran et al., 2007) do not consider respiration, photolysis, and other abiotic reactions separately. All the O_2 consuming processes in these incubations including the photolytic breakdown of DOM, respiration, particulate matter formation, and other abiotic redox reactions preferentially consume $^{16}O^{16}O$ over $^{18}O^{16}O$. Only two studies have measured α_R values from dark incubations in artificial seawater or river waters, and generally these values are used for both light and dark respiration fractionation in whole ecosystem O_2 – $\delta^{18}O$-O_2 studies (e.g. Wang and Veizer, 2000; Parker et al., 2005). As the α values from this study are different than published α_R values, α_R values measured in dark incubations may not be appropriate for all O_2 consumption in the light when photolysis is an important process, or in either the dark or the light when other abiotic reactions are important. Because photolysis both consumes oxygen and changes the $\delta^{18}O-O_2$, a separate photolytic/abiotic component may need to be incorporated into the models especially in shallow aquatic systems with high DOM where DOM photodegradation may be a significant O_2 consuming process.

2.5 Summary

Oxygen loss occurred in stream water samples incubated in natural sunlight. O_2 consumption rates were similar in incubations of filtered, inoculated, and sterile waters from the same stream under either light or dark conditions. Incubations in the light had substantially higher rates of O_2 consumption than the dark indicating that photolysis was greater than respiration and abiotic processes in the light-exposed treatments. Rates differed in different streams even when normalized for the DOC concentration lost indicating that there were inherent differences in DOM photolability. Consumption of O_2 in photochemical and other abiotic reactions fractionated oxygen isotopes (preferentially consuming the lighter $^{16}O^{16}O$ isotopomer) similar to respiration. Calculated $\delta^{18}O-O_2$ photolysis fractionation factors in the light and the dark regimes were the same for all treatments within a stream, and were confined to a narrow range for the three different streams (α range = 0.988 – 0.995). Furthermore fractionation factors were not dependent on O_2 consumption rates, which differed between streams. The α values calculated from dark incubations were larger than α_R values reported for large rivers and marine systems. As O_2 and $\delta^{18}O-O_2$ applications in aquatic system studies currently do not separately include DOM photodegradation and other abiotic processes, respiration rates in shallow, high DOC aquatic systems, could be overestimated.

2.6 Acknowledgements

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Chapter 3:

The effect of DOM photodegradation on δ^{13}C-DOC and δ^{13}C-DIC in forested stream waters.

3.1 Overview

Carbon is required for sustenance in aquatic systems such as streams and lakes, however, processes such as respiration, the photolytic breakdown of dissolved organic matter (DOM) and the direct sedimentation of DOM also affect carbon concentrations. To examine the effects of respiration, photolysis, and other abiotic reactions on dissolved inorganic and dissolved organic carbon concentrations (DIC, DOC) and isotopes (δ^{13}C-DIC, δ^{13}C-DOC), filtered, inoculated, and sterile samples of stream waters from Ontario, Canada, were incubated in natural sunlight. DIC production rates in the light were up to an order of magnitude greater than in the dark, suggesting that light-mediated processes controlled DIC production. The similarities between DIC production rates for each treatment (i.e. filtered, inoculated, and sterile) indicates that photolysis was the dominant DIC producing process compared to respiration in these incubations and that DIC consumption due to photosynthesis was minimal. DIC production rates were different among streams, even when normalized to the change in DOC concentration, signifying that DOM photolability varied among streams. During DOM breakdown to CO_2, the ^{12}C isotope was preferentially degraded, leaving the residual δ^{13}C-DOC 1‰ to 4‰ enriched in the ^{13}C isotope, creating enrichment (ε) factors down to -3‰. Concurrently, δ^{13}C-DIC was produced by photolysis, respiration, and possibly other abiotic reactions. The δ^{13}C-DIC values of the DIC produced ranged between –23‰ and –31‰, and were similar in the light incubations for each treatment, but different between streams. The δ^{13}C-DIC produced in the dark incubations was inconclusive due to large errors but considering the DIC production rates and the δ^{13}C-DIC values from the light incubations suggests that photolysis and abiotic reactions are mostly responsible for the DIC and δ^{13}C-DIC changes observed, not respiration. In current DIC and δ^{13}C-DIC models, photolysis and respiration are not considered separately and the isotopic fractionation during respiration is either assumed, calculated via models, or measured in the dark and used in the light. In these incubations, DOM photodegradation and abiotic reactions are important DIC producing and δ^{13}C-DIC fractionating processes that can affect the δ^{13}C-CO_2. Current models of DIC and δ^{13}C-DIC or δ^{13}C-CO_2 may incorporate photolysis of DOM and other abiotic processes into the respiratory component of DIC production and DOC mineralization, thereby overestimating respiration. Without incorporating the δ^{13}C-DOC changes from DOM photodegradation, studies examining the ratio of allochthonous to autochthonous carbon contributions could underestimate the importance of allochthonous carbon. Additionally, most models trying to isolate DOC sources using carbon isotopes of DOM assume that photolysis has no effect on δ^{13}C-DOC. However, photolysis and abiotic reactions can both affect δ^{13}C-DIC and δ^{13}C-DOC signatures, particularly in shallow aquatic systems with high DOC.

3.2 Introduction

Carbon is crucial in aquatic systems as it controls the buffering capacity of waters, influences nutrient availability, and is a source for organic productivity. Northern temperate and boreal lakes are generally net heterotrophic ecosystems, partially relying on dead or decaying organic matter produced in the terrestrial catchment for sustenance. Carbon dynamics within these lakes can be affected by a number of processes including the photodegradation, microbial decomposition, and the direct sedimentation of dissolved organic matter (DOM), in addition to gas exchange with the atmosphere, photosynthesis, mixing, and other redox reactions.

Carbon mass balances are commonly used to examine the sources and controls of carbon in aquatic systems. Due to the complex transfer pathways, studies have commonly concentrated on only a portion of the carbon cycle (e.g. the inorganic or organic component; Wetzel et al., 1972; Emerson, 1975a; Hesslein et al., 1980). However, Dillon and Molot (1997a) used dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) mass balances to partition the carbon lost in oligotrophic and mesotrophic lakes between the atmosphere and the sediments. Andersson and Sobek (2006) also used carbon mass budgets and ecosystem models to understand organic matter pathways in lakes, while Sobek et al. (2006)

found a small Swedish boreal lake to be net heterotrophic with respiration acting as the largest organic carbon sink in the lake. Yang et al. (2008) compared mass balances, and gas exchange and carbon burial balances to determine that the eutrophic Lake Donghu acts as carbon sink.

Isotopic balances can also be used to determine the fate of organic matter and isolate sources of carbon in aquatic systems. Estimates of rates of gas exchange and of net organic carbon production were determined using δ^{13}C-DIC mass and isotope balances in Lake Washington by Quay et al. (1986). Cifuentes and Eldridge (1998) used carbon mass and ^{13}C-isotope balances to examine the sources, sinks, and mixing of DOC to estimate the magnitude of the different DOC sources in estuaries. Raymond and Bauer (2001) used DOC and DIC (^{13}C and ^{14}C) isotope balances to examine the sources and fate of DOC in a temperate estuary. Mineralization of DOC in a humic Swedish lake was examined by Jonsson et al. (2001) to reveal the importance of allochthonous and autochthonous carbon as sources of DOC and CO_2 within the lake, and δ^{13}C of DIC and particulate organic carbon (POC) were used to independently trace the organic and inorganic carbon sources. Ogrinc et al. (2002) used carbon isotope balances in addition to other chemical analyses to isolate DIC sources in carbonate rich sediments from a subalpine lake, while Herczeg (1987) completed DIC mass and isotope balances in a softwater lake for a better understanding of lake productivity, assessment and management, and to predict human impacts on lakes. Herczeg et al. (2003) also determined the importance of groundwater to lake water and chemical balances, and changes to the carbon budget using stable carbon and oxygen isotopes of carbonate and the δ^{13}C of organic matter in Blue Lake Australia. However, none of these studies specifically considered photolysis as a separate process affecting the carbon balances.

DIC and DOC concentrations and their isotope ratios can be used in conjunction with each other to isolate carbon sources and cycling in aquatic systems. As terrestrial DOC is respired, the CO_2 produced will have a similar $\delta^{13}C$ to its organic source. Microbial degradation of DOC originating from C3 plants (average foliar $\delta^{13}C = -28‰$; Deines 1980) will increase the DIC concentration, and the $\delta^{13}C$-CO_2 produced will be lower than the atmospheric CO_2 signature of –8‰ (Keeling et al., 1995). Conversely, $\delta^{13}C$-CO_2 derived from carbonate minerals will not necessarily be greater than atmospheric CO_2 (as suggested by Craig, 1953), but will depend on the $\delta^{13}C$ of the carbonate being weathered. Although the $\delta^{13}C$-CO_2 produced may be lower than the atmospheric CO_2 signature, it will be markedly different than DOC originating from C3 plants. Therefore, heterotrophic respiration will decrease $\delta^{13}C$-DIC, while atmospheric inputs of CO_2 and degassing of CO_2 would normally increase the $\delta^{13}C$-DIC. Aquatic photoautotrophs can increase the remaining $\delta^{13}C$-DIC by isotopic fractionation during photosynthesis (McKenzie, 1985).

Previously published studies on $\delta^{13}C$ in aquatic systems consider respiration, photosynthetic assimilation of carbon, mixing, and gas exchange as the processes affecting the $\delta^{13}C$ values of DIC, DOC, and POC (e.g. Quay et al., 1986; Cole et al., 2002; Pace et al., 2004; Carpenter et al., 2005; Cole et al., 2006). These are not, however, the only processes affecting carbon in lacustrine and riverine systems. In a ^{13}C carbon dual isotope flow model developed from a whole-lake ^{13}C addition tracing the pathways of organic carbon utilization, Cole et al. (2002) note that photooxidation could be a significant CO_2 source, but do not include it in their model suggesting that system respiration is much larger than photooxidation. Similarly, Pace et al. (2004) note that allochthonous carbon can aggregate, coagulate, and flocculate upon entering lakes providing a POC source to aquatic consumers such as *Daphnia*, but do not consider the isotopic changes that might accompany these processes in their univariate time-series carbon models. In the multi-variate autoregression model described in Carpenter et al. (2005), although epilimnetic POC turnover is rapid and flocculation of DOC is incorporated into the model (as in Cole et al., 2002), there is no mention of the isotopic effects associated with this process. Cole et al. (2006) further examine the importance of terrestrial POC, DOC, and prey in food web pathways within lakes using the dual isotope flow model, however, they do not examine the isotopic effects of photodegradation on δ^{13}C-DOC. In the same whole lake addition experiments (e.g. Cole et al., 2002; Pace et al., 2004; Carpenter et al., 2005) δ^{13}C-DOC change due to algal carbon contributions was examined by Bade et al. (2007). In their isotope model, Bade et al. (2007) incorporate DOC loss by photooxidation, however they did not use a fractionation factor for this process due to uncertainty in the fractionation over long time frames (Opsahl and Zepp, 2001). Approximately 50% of the DOC entering a suite of 7 oligotrophic lakes in the southern Precambrian Shield is lost to the atmosphere and sedimentation (Dillon and Molot, 1997a). Therefore, a mechanism that could produce DIC could account for the large DOC loss in many boreal lakes with high DOC is photolysis (Molot and Dillon, 1997b). Thus, it is important to understand the impacts that photolysis can have on these systems when conducting isotopic studies.

DOM photodegradation has been extensively studied due to its role in the global carbon cycle (e.g. transport of terrestrial carbon to the ocean: Miller and Zepp, 1995; CO_2 supersaturation in lakes: Granéli et al., 1996; and DOM loss in lake surface layers: Bertilsson and Tranvik, 2000). Photodegradation of DOM also influences water chemistry and transparency affecting both the photic zone depth and the region of photosynthetic activity (Andrews et al., 2000; Anesio and Granéli, 2003). In addition, DOM photodegradation can affect aquatic organisms by altering UV penetration, and the lability of carbon sustenance in the food web (Gao and Zepp, 1998).

During the photodegradation of DOM, dissolved oxygen is used as an electron acceptor in the overall oxidation of DOC into lower molecular weight, more labile carboxylic acids, smaller organic compounds, and DIC which can stimulate microbial activity (Miller and Moran, 1997; Tranvik and Bertilsson, 2001). The breakdown of DOM to CO_2 transforms carbon and affects the carbon balance of aquatic ecosystems. It is therefore crucial to understand the photodegradation of DOM, in addition to the other processes controlling carbon production and consumption, to effectively comprehend and model carbon dynamics in lakes and other aquatic systems with high allochthonous DOC inputs.

Although extensive research has addressed DIC production and DOC degradation during photolysis (e.g. Miller and Zepp, 1995; Granéli et al., 1996; Bertilsson and Tranvik, 2000), only a few studies have examined the changes in the $\delta^{13}C$ of DOC and DIC during photolysis (Opsahl and Zepp, 2001; Osburn et al., 2001; Vähätalo and Wetzel, 2008) and none investigate how the degree of DOM degradation affects these isotopic signatures. This study 1) examines the effects of photolysis, respiration, and other abiotic reactions on $\delta^{13}C$-DIC and $\delta^{13}C$-DOC in waters from three different forested streams; 2) examines the amount of DOC loss necessary before a measurable isotopic shift in $\delta^{13}C$-DOC occurs; and 3) calculates the associated enrichment factor (ε).

3.3 Methods

Bulk water samples were collected for incubation experiments from streams emptying into two oligotrophic headwater lakes (Harp and Dickie Lakes) which are located approximately 200 km north of Toronto, Ontario, Canada, on the southern tip of the Precambrian Shield in the Muskoka-Haliburton region. The lakes' watersheds are composed of tills <1m thick and contain peatlands. Detailed descriptions of these forested catchments and streams can be found in Dillon et al. (1991).

Dickie Inflow 10 (D10), Harp Inflow 4 (H4), and Harp Inflow 5 (H5), are either major carbon or major water contributors to Harp and Dickie Lakes. Stream water was collected at weirs less than 50m upstream from the lakes and their general characteristics can be found in Table 3.1. These inflows have been the focus of other photolytic studies on DOM and O_2 consumption (e.g. Molot and Dillon, 1997b; Gennings et al., 2001; Chomicki and Schiff, 2008: Chapter 2). Generally, DOC concentrations in these streams decrease with increasing discharge. The lakes have lower DOC concentrations than their streams illustrating high rates of in-lake DOC loss.

Table 3.1: Percent peatland and stream water characteristics (taken within one week of the samples from this study) for the three sites.

Site	Catchment % peatland[1]	Total iron (μg/L)[2]	pH[2]	Colour (Hz)[2]	DOC (mg/L)[2]	DOC (mg/L)[3]
Dickie Inflow 10	17.1	1050	4.58	359	31.5	29.4
Harp Inflow 4	5.0	105	6.68	42.8	5.0	6.8
Harp Inflow 5	13.3	778	5.82	175	16.9	15.4

[1] Taken from Dillon and Molot, 1997b

[2] OME unpublished, May 24th, 2005

[3] current study: May 28th, 2005

This study ran concurrently with an experiment tracking the O_2 consumption and $\delta^{18}O$-O_2 fractionation during the photolytic degradation of DOM. The field sites and experimental setup are summarized from Chomicki and Schiff (2008) (Chapter 2). In brief, bulk stream water samples were filtered to 0.2 μm and subjected to three treatments. Filtered treatments contained only the filtered water, and microbial activity should therefore be absent (Wotton, 1994). Inoculated treatments contained a mixture of the 0.2 µm filtered water and the inoculant in a ratio of 9:1, and therefore microbes were present. To create the inoculant, 1 litre of each water was filtered through 1 µm Nuclepore membranes leaving suspended bacterioplankton (Sieburth et al., 1978) (e.g. heterotrophic bacteria and archaea: 0.2-1.2 µm; Legendre and Rivkin, 2009), filtering out most photosynthetic organisms and bacterial grazers such as protists, rotifers, etc. The third treatment was filtered to 0.2 µm and sterilized with 1 mL of a saturated solution of $HgCl_2$ per litre of stream water to ensure the absence of microbial and/or photosynthetic activity.

Preliminary experiments were completed to make certain DOM leaching from Tedlar bags did not occur and to ensure that the bags were gas-tight. The Tedlar bags were washed in triplicate with ethanol and rinsed 3 times with Nanopure water before filling with 8 L of sample water. The bags were exposed to natural sunlight at the University of Waterloo (43° 28' 25.6" N and 80° 33' 27.5" W; elevation ~ 335 masl) in shallow water baths. Each treatment was exposed simultaneously in duplicate such that two bags of each of the filtered, inoculated, and sterile treatments were arranged side by side to minimize variation in solar exposure and temperature. Although duplicate bags were within 0.2°C, the temperature was not controlled. Water baths moderated daily temperature changes, however, temperature between treatments on the same day varied according to sampling time.

In the first experiment (D10: began on June 17th, 2005) 14 bags were incubated (2 replicates of each of 3 treatments in the light and in the dark, and two additional light-exposed H5 sterile samples). Light treatments were exposed for 4-7 days, while the dark treatments were incubated for 20 days. The second experiment (H4) began on July 9th, 2005 and a total of 16 bags were incubated (2 bags for each of 3 treatments in the light and the dark, two H5 light exposed sterile treatments, and two D10 light exposed sterile treatments). Light treatments were exposed for 3-8 days; however, dark treatments were incubated for 14 days.

Phase 1 of the experiment was closed (with no gases entering the bags from the atmosphere or exiting the bags to the atmosphere) and tracked the gas changes in the incubated bags. After the loss of >80% of the oxygen in the light exposed bags (signifying the end of Phase 1), the bags were re-aerated daily and final δ^{13}C-DOC samples were collected once the DOC had declined by $\geq$ 50% (Phase 2). Since the Tedlar bags are gas tight, re-aeration was necessary to reintroduce oxygen into the light exposed bags in order for the remainder of the DOC to be photo-oxidized under aerobic conditions. Bags were well mixed prior to each sampling, and since 3 to 5 L of sample water remained at the end of the incubations, no effects are expected due to the changes in the incubation water volume throughout the experiment.

The concentration data presented is an average of the duplicate bags for each treatment. The isotope data are analyzed in their entirety for one bag, with duplicates analyzed approximately every 5 samples, while only every 2-5 samples from the second (duplicate) bag were run for isotopes. Since D10 and H4 waters were incubated on different dates, each incubation experiment contained a set of sterile water from H5 and D10 exposed to light to assess inter-incubation variation.

Changes in DIC, $p\mathrm{CO}_2$ (partial pressure of CO_2) and DOC concentrations, and δ^{13}C-DIC were tracked over the course of the experiment. DIC concentration and δ^{13}C-DIC samples were taken at regular intervals during Phase 1 (until 80-90% of the oxygen was consumed). A three-way valve, tubing and needles were used to collect samples and to minimize gas contamination from the atmosphere. Samples for δ^{13}C-DOC were collected at the beginning of the experiment, when the bags were first re-aerated (Phase1), and at the final stages of the experiment after ≥ 50% of the DOC was degraded (Phase 2).

DIC samples were collected without headspace in 15 mL Wheaton serum bottles with baked BD Vacutainer stoppers and preserved with 0.02 mL of saturated $HgCl_2$ solution. A 5mL helium headspace was added while removing an equivalent volume of water and samples were acidified with 85% H_3PO_4 to pH < 2 before being shaken on an orbital elliptical shaker for 1.5 hours to equilibrate headspace and liquid phases. Concentrations were measured by equilibrated headspace on a Shimadzu GC-8A Gas Chromatograph fitted with a methanizer (Ni catalyst, He gas carrier, FID detector) with an uncertainty of < 5% (Stainton, 1973).

$p\mathrm{CO}_2$ samples were collected without headspace in evacuated 60 mL Wheaton serum bottles, with baked BD Vacutainer stoppers, containing 3.56 g of KCl as a preservative. A 5 mL helium headspace was added and samples were shaken on an orbital elliptical shaker for 1.5 hours to equilibrate concentrations with the headspace. Concentrations were measured as above.

DOC samples were filtered to 0.45 μm and acidified with 20% HCl to approximately pH 4. Samples were analyzed on a total organic carbon analyzer (Dohrmann DC-190) with a precision of ± 0.3 mg/L after being acidified by the instrument with 85% H_3PO_4 to a pH of 2-3 and sparged to remove DIC. Duplicate DOC absorbance samples (also filtered to 0.45 μm) were analyzed on a Beckman DU530 Life Science UV/Vis Spectrophotometer (path length = 1cm) between 200 nm and 700 nm and automatically corrected to the absorbance of Nanopure water. The ratio of UV absorption at $\lambda = 254$ nm (measured in absorbance units m^{-1}) to DOC concentration (mg/L) was used to determine the specific UV absorbance ($SUVA_{254}$) (Weishaar et al., 2003). The specific absorption coefficient at $\lambda =$

350 nm (SAC_{350}) was calculated by normalizing the absorbance at 350 nm to the DOC concentration (mg/L) (Moran et al., 2000). Other dissolved absorbances (a_d) of interest were a_{d320} and a_{d250}:a_{d365} ratio.

δ^{13}C-DIC samples were collected without headspace in 125 mL Wheaton serum bottles, capped with baked BD Vacutainer stoppers, and preserved with 0.3 mL of a saturated solution of $HgCl_2$. A 5 mL helium headspace was created and samples were acidified with 85% H_3PO_4 to a pH less than 2. Samples were shaken for a minimum of 1.5 hours to equilibrate the gases between the dissolved phase and the headspace. Gas from the headspace was analyzed on a Micromass Isochrom Gas Chromatograph Combustion Isotope Ratio Mass Spectrometer (GC-C-IRMS) at the Environmental Isotope Laboratory, Waterloo, Ontario. Precision of these analyses is within ± 0.3‰. Duplicates were analyzed approximately every 5 samples and results were within 0.3‰ of each other. Results are reported in standard δ notation as $\delta^{13}C = ((R_{sample} / R_{standard}) - 1) \times 10^3$ ‰, where R is ^{13}C:^{12}C.

δ^{13}C-DOC samples were obtained by filtering water through pre-combusted GF/F filters. The filtrate was acidified with 20% HCl to a pH of 4.5, freeze-dried and analyzed with a Carlo Erba 1105 Elemental Analyzer coupled to a Micromass Isochrom IRMS with a precision of ± 0.2‰ by the Environmental Isotope Laboratory, Waterloo, Ontario. Results are reported in standard δ notation as $\delta^{13}C = ((R_{sample} / R_{standard}) - 1) \times 10^3$ ‰, where R is ^{13}C:^{12}C.

Assuming a Rayleigh relationship between the δ^{13}C-DOC and the fraction of DOC remaining after photodegradation, an enrichment factor (ε) was calculated from the fractionation factor using the following relationship: $R = R_o f^{(\alpha-1)}$, where, R = ratio of the DOC isotopes after photodegradation, R_o = initial DOC isotope ratio, f = fraction of DOC remaining, and α = fractionation factor. From the calculated fractionation factor, ε was calculated using: $\varepsilon = (\alpha\text{-}1) \times 1000$ ‰.

3.4 Results and Discussion

3.4.1 Rates of DIC production

In the light-exposed incubation bags, DIC production was rapid during Phase 1 in all treatments, and was accompanied by an 80-90% loss in O_2 and an average DOC loss of 25% in approximately 4 days (Chomicki and Schiff, 2008: Chapter 2). DIC concentrations in duplicate treatments were generally within 5%. DIC production was quasi-linear with time and similar for all three treatments in the light incubation bags (Figure 3.1). O_2 consumption in the inoculated and sterile treatments from each site was similar (Chomicki and Schiff, 2008: Chapter 2) to DIC production, indicating that the main mechanism responsible for DIC production was not microbial respiration. Microscopic examination of samples in a preliminary experiment indicates bacteria were present in unsterilized treatments, although bacterial populations were not quantified in the current experiment.

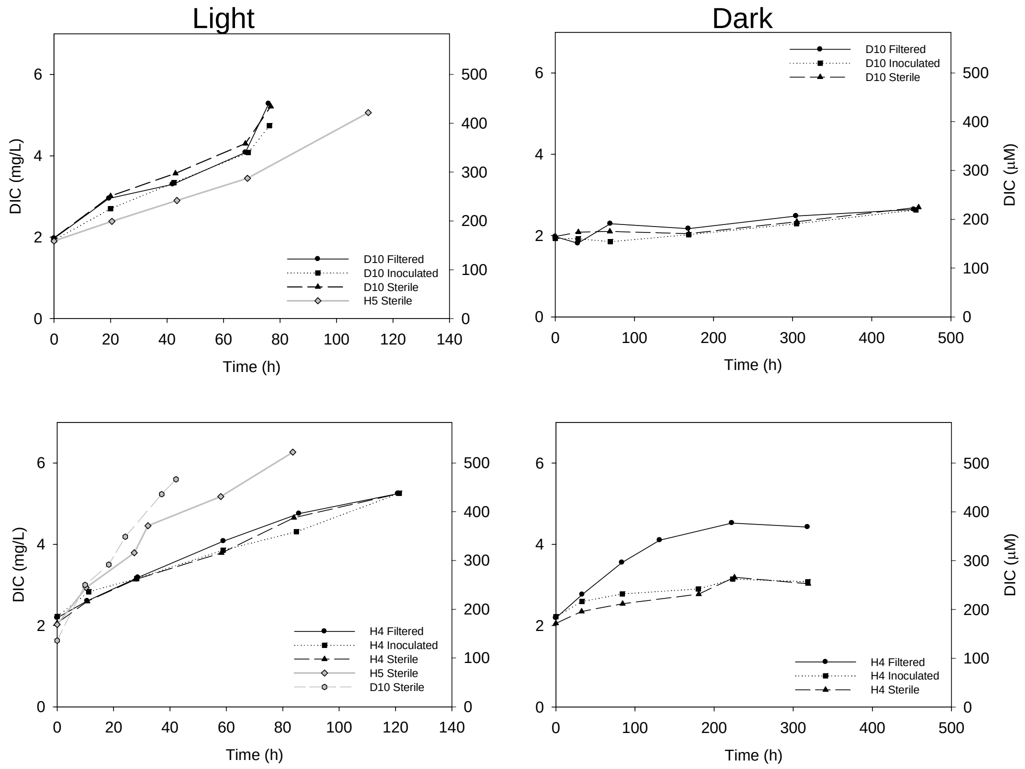


Figure 3.1: DIC concentration versus time of a) D10 and b) H4. Points are the average of two duplicate bags incubated simultaneously. Differences between bags are <0.2 mg/L. Sterile H5 samples were incubated with both experiments (a and b), and sterile D10 samples were incubated with H4 (b) to assess the effects of differences in light exposure between the two experiments.

O_2 loss was similar to the DIC gained, however, they were not equal on a molar basis (Figure 3.2). In the dark incubations, there is greater O_2 consumption than DIC production, and inoculated and sterile treatments were similar, suggesting that abiotic processes increased the O_2 loss in the bags. The light treatments generally produced more DIC than O_2 lost although most of the samples were close to the 1:1 line. The average O_2 consumption:DIC production in the light and dark bags was 0.91 (standard error ± 0.04) and 2.13 (standard error ± 0.41) respectively. In most cases, the average O_2 consumption to DIC production was within error of the 1:1 line, however, the dark bags suggest that some process is occurring within the dark that consumes more O_2 than it produces DIC. By comparing the two sets of incubations, the sterile treatments of H5 and D10 from the second set of incubations produced greater amounts of DIC than in the first set of incubations. For an unknown reason, the dark filtered H4 bag clusters with the light incubations showing a large degree of O_2 loss and DIC gain in comparison to the other dark incubation bags.

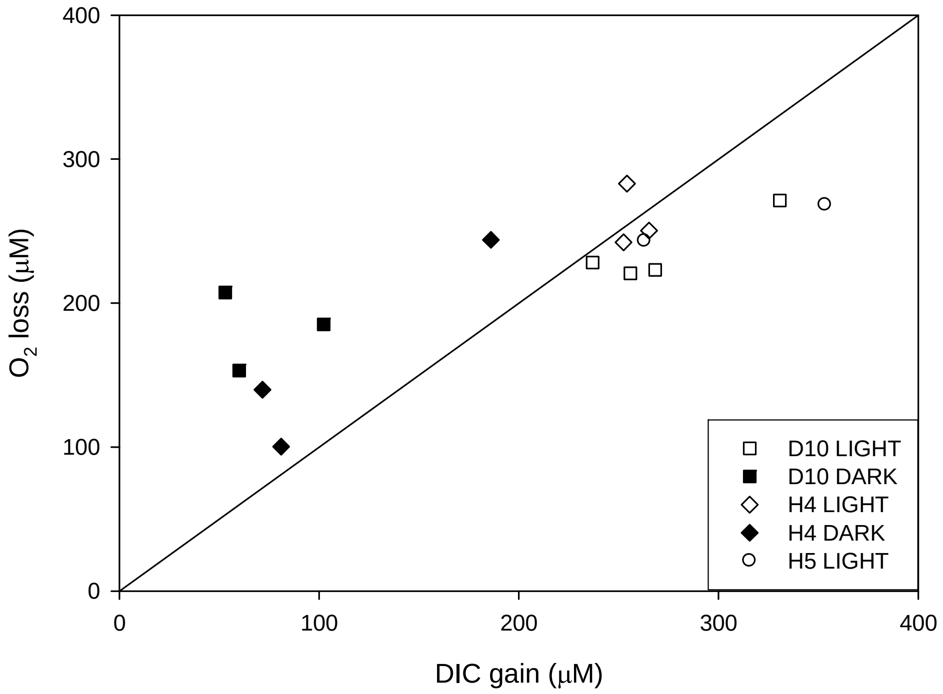


Figure 3.2: The relationship between O_2 loss and DIC gain in the light incubations (open symbols) and the dark incubations (filled symbols). The solid line denotes the 1:1 relationship.

DIC production rates in D10 were approximately twice those in H4 (Table 3.2). As differences exist in the original DOC concentrations in D10, H4, and H5 (29.4mg/L, 6.8 mg/L, and 15.4 mg/L respectively; Table 3.1), the DIC production rates were normalized to the DOC concentration lost. Normalized production rates reveal that in light and dark treatments H4 produced more than twice the DIC per mg/L of DOC lost than D10. It appears that natural differences exist between streams as the DIC production of H5 fell between H4 and D10. These data patterns are similar to the O_2 consumption trends from Chomicki and Schiff (2008: Chapter 2), and were attributed to differences in DOM quality, or degrees of self-shading in highly coloured high DOC concentration waters. However, further studies suggest that these differences could also be attributed to different amounts of particulate carbon formation during the incubations (Chapter 4). Although not quantified, visual inspection of the incubation bags (and the particulate residuals on the filters after sample filtration for δ^{13}C-DOC analysis) suggests that more particulate matter was created in D10 than H4. So, even though D10 produced less DIC per mg DOC lost, there was more visible particulate matter in the final samples and thus more DOC lost than in H4. This is corroborated by greater amounts of DOC lost and particulate matter formed in the photolytic incubations presented in Chapter 4.

There was little variation in DIC production rates in the dark incubations among treatments and among streams (Table 3.2), even in the inoculated treatments where biotic respiration occurred. The dark filtered treatment of H4 produced more DIC than the other dark treatments for unknown reasons.

DIC production rates in the light treatments were approximately 4 to 9 times greater than in the dark treatments of H4, while the rates from the light-exposed D10 treatments were an order of magnitude greater than in the dark treatments. In this experiment, the DIC produced by respiration and other reactions was quite small in comparison to photolysis given the similarity of the production rates in the light treatments and the large differences between the light and dark treatments.

Table 3.2: Dissolved inorganic carbon (DIC) production rates and DIC production rates normalized for DOC concentration in the water and for DOC lost during the experiment.

		LIGHT			*DARK*		
Site	Treatment	DIC produced (μg/L/hr$_{sunlight}$)	DIC produced (μg/L/hr$_{sunlight}$/ mg/L$_{DOC}$)	DIC produced (μg/L/hr$_{sunlight}$/ mg/L$_{DOC\ lost}$)	DIC produced (μg/L/hr)	DIC produced (μg/L/hr/ mg/L$_{DOC}$)	DIC produced (μg/L/hr$_{sunlight}$/ mg/L$_{DOC\ lost}$)
Dickie Inflow 10	filtered	54 ± 7	3.3	5.9	2.6 ± 0.5	0.1	1.1
	inoculated	51 ± 6	2.9	6.0	1.4 ± 0.5	0.1	0.3
	sterile	55 ± 7	3.0	7.1	1.4 ± 0.5	0.1	0.4
	Average	***53***			***2***		
	sterile[1]	92 ± 9	3.3	73	n/s[3]	n/s[3]	n/s[3]
Harp Inflow 4	filtered	26 ± 3	5.1	24	7.0 ± 1	1.7	3.3
	inoculated	23 ± 3	4.8	18	2.5 ± 1	0.6	1.3
	sterile	26 ± 3	6.4	14	3.2 ± 1	0.7	3.1
	Average	***25***			***4***		
Harp Inflow 5	sterile[2]	44 ± 4	4.4	10	n/s[3]	n/s[3]	n/s[3]
	sterile[1]	49 ± 5	4.2	17	n/s[3]	n/s[3]	n/s[3]
	Average	***47***					

[1] Incubated with H4 water; [2] Incubated with D10 water; [3] ns = no sample

Values are based on the average of measurements from duplicate bags.

DIC production rates from these incubations were similar to DIC production rates from photolysis of other streams and aquatic systems including incubations of Lake Skärshulsjön water pumped from 0.5m depth under different pH conditions (18.4 to 31.8 μgC/L/hr; DOC ~ 15 mg/L; Anesio and Granéli, 2003), and in 5 Swedish and 4 Brazilian lakes and the Rio Negro (15 to 283 μgC/L/hr; DOC = 2.9 to 41.8 mg/L; Granéli et al., 1998). Rates also lie within the range observed from light incubations of filter sterilized surface waters from 38 lakes (~1 to 159 μgC/L/hr) with DOC concentrations ranging from 2.0 mg/L to 22.0 mg/L (Bertilsson and Tranvik, 2000) and filter sterilized riverine, near coastal and salt marsh waters incubated under simulated sunlight (~1 to 476 μgC/L/hr; DOC 2.0 to 61.8 mg/L; Miller and Zepp, 1995). In contrast, these DIC production rates were higher than 5 oligotrophic Swedish lakes with DOC ranging between 3.9 to 19 mg/L (3.6 to 17 μg DIC/L/hr; Granéli et al., 1996). In many of the aforementioned studies, dark incubations were performed on unfiltered water or the raw data was not presented preventing direct comparison to the current study (e.g. Granéli et al., 1996; Bertilsson and Tranvik, 2000).

The relative importance of photolysis and respiration has been recognized in terms of O_2 consumption (e.g. Amon and Benner, 1996; Lindell and Rai, 1994), but is often overlooked in carbon mass and $^{13}C/^{12}C$ studies (e.g. Pawellek and Veizer, 1994; Findlay, 2003). However, Raymond and Bauer (2001) suggested photo-oxidation as a potential mechanism to account for lost riverine DOC from their estuarine DOC cycling study. In addition, Jonsson et al. (2001) recognized the importance of photo-oxidative effects on carbon in their whole-lake organic carbon mineralization study based on DIC production rates collected during the photooxidation of waters from the same system (completed by Bertilsson et al., 1999) and estimate that 20% of the DOC mineralization in the epilimnion was due to photo-oxidation. Using 38 lakes of varying organic matter quality, Bertilsson and Tranvik (2000) showed that the majority of temperate lakes will be influenced by photochemical DIC production and it is possible that this could translate to other climate regimes. However, in 5 oligotrophic lake surface waters of different humic content, DIC production from photo-oxidation could exceed community respiration on an areal basis, yet became less important when integrated over the depth of the lakes (Granéli et al., 1996). In the current study, the photodegradation of DOM was examined within incubated stream waters samples from inflow waters flowing into northern temperate lakes. Although DIC production rates were not extrapolated to the lakes (or performed on lake waters), it is important to recognize that the DIC production rates from DOM photodegradation may decrease when considered on a volumetric basis over the depth of the epilimnion.

Absorbances were measured at the beginning of the experiment, and at the end of Phase 1. The chemical character of DOC can be examined by measuring $SUVA_{254}$, an indicator of changes in % aromaticity (e.g. Hood et al., 2006; Weishaar et al., 2003). Initial $SUVA_{254}$ values were generally greater when the incubation waters were from catchments with a higher percentage of peatlands suggesting that the wetland samples had a higher % aromaticity than waters that did not travel through wetlands (Table 3.3). Exposure to UV altered the DOC samples, created particulate matter and cleaved functional groups from the DOC. $SUVA_{254}$ results indicate the DOC did not react the same in all of the incubations (Chomicki and Schiff, 2008: Chapter 2; Table 3.3). Initial $SUVA_{254}$ was higher in D10 indicating that its DOC had a different chemical character than H4 with a higher % aromaticity. By the end of the incubation, $SUVA_{254}$ decreased in H4, and increased in D10 and H5 (Table 3.3). Exposure to light alters the DOC character, and generates photochemical transients (e.g. Haag and Mill, 1990; Zafiriou et al., 1990). High molecular weight DOM can fragment into low molecular weight carbon compounds including (but not limited to) pyruvate, glyoxylate, acetaldehyde and carbon dioxide (Miller, 1994), and particulate matter can form (Gao and Zepp, 1998). Thus, although DOC was lost in all the stream samples, it is possible that it did not react in the same manner in all streams.

Table 3.3: Initial and final DOC concentrations, absorbances, and SUVA$_{254}$ measurements for the three sites under filtered, inoculated, and sterile conditions.

a) Light Treatments

Site	Light Treatment	% peatland in catchment	DOC initial (mg/L)[3]	DOC final (mg/L)	SUVA initial	SUVA final	a_{d250}:a_{d365} initial	a_{d250}:a_{d365} final	SAC$_{350}$ initial	SAC$_{350}$ final	a_{d320} initial	a_{d320} final	a_{d380} initial	a_{d380} final
Dickie Inflow 10 (wetland)	filtered	17.1	29.1	20.0	5.35	7.09	4.03	4.28	3.93	4.90	70.45	60.58	31.90	27.93
	inoculated		29.6	21.1	5.26	6.66	4.06	4.32	3.83	4.55	69.80	59.80	31.60	27.05
	sterile		29.5	21.7	5.26	6.44	4.05	4.34	3.83	4.40	69.90	59.43	31.55	27.05
	sterile[1]		29.2	27.9	5.29	4.91	4.08	4.26	3.83	3.38	69.40	58.68	31.40	26.95
Harp Inflow 4 (more upland)	filtered	8	7.0	4.3	3.88	2.51	4.56	5.73	2.60	1.82	11.90	4.98	4.85	2.13
	inoculated		6.8	5.5	3.95	2.6	4.56	6.00	2.63	1.33	11.85	4.70	4.85	2.08
	sterile		6.6	4.4	4.07	3.27	4.59	5.53	2.72	1.93	11.75	5.50	4.60	2.28
Harp Inflow 5 (wetland)	sterile[2]	13.3	15.6	11.4	5.90	6.03	4.44	4.92	4.02	3.66	40.35	27.25	16.95	11.70
	sterile[1]		15.1	12.9	6.10	5.58	4.47	4.77	4.13	3.53	40.60	29.40	16.80	12.53

[1] Incubated with H4 water; [2] Incubated with D10 water; [3] DOC precision: ±0.3 mg/L; 4 n/s = no sample.

b) Dark Treatments

Site	Dark Treatment	% peatland in catchment	DOC initial (mg/L)	DOC final (mg/L)	SUVA initial	SUVA final	a_{d250}:a_{d365} initial	a_{d250}:a_{d365} final	SAC$_{350}$ initial	SAC$_{350}$ final	a_{d320} initial	a_{d320} final	a_{d380} initial	a_{d380} final
Dickie Inflow 10 (wetland)	filtered	17.1	29.1	26.8	5.35	5.63	4.03	3.97	3.93	4.15	70.45	68.60	31.90	31.65
	inoculated		29.6	24.5	5.26	6.09	4.06	3.99	3.83	4.48	69.80	67.65	31.60	31.00
	sterile		29.5	25.9	5.26	5.8	4.05	4.02	3.83	4.25	69.90	68.15	31.55	30.85
Harp Inflow 4 (more upland)	filtered	8	7.0	4.9	3.88	4.95	4.56	4.81	2.60	3.13	11.90	10.20	4.85	4.10
	inoculated		6.8	4.9	3.95	4.87	4.56	4.77	2.63	3.19	11.85	10.42	4.85	4.05
	sterile		6.6	5.5	4.07	4.34	4.59	4.94	2.72	2.75	11.75	9.98	4.60	4.05

The optical index of molecular weight (a_{d250}:a_{d365}) is indicative of changes in the relative size of the DOM after photodegradation. The increase in the ratio (Morris and Hargreaves, 1997; DeHaan and DeBoer, 1987; Strome and Miller, 1978) indicates that the molecular weight decreased in all of the samples incubated in the light (Table 3.3). The absorption at 350 nm has been used as an index of coloured DOM (CDOM; Moran et al., 2000) and normalization to DOC concentration (SAC_{350}) indicates that the CDOM reacted differently between samples after exposure to light. Decreases in the SAC_{350} of H4 and H5 samples suggest that photobleaching has occurred as CDOM concentrations have decreased, whereas the opposite effect was seen in D10. Furthermore, a_{d380} has also been used as an indicator of CDOM (Buiteveld, 1995) and the decrease in both a_{d380} and a_{d320} suggests that CDOM in the water decreased (and consequently the colour of the water; De Lange, 2000) increasing the UV transparency (Osburn et al., 2001) in all of the light-exposed incubation bags.

In the dark treatments, $SUVA_{254}$ increased but changes were smaller than in the light (Chomicki and Schiff, 2008: Chapter 2). Similar to the light exposed incubations, SAC_{350} increased in the D10 dark incubations, however not in the H4 or H5 samples. The a_{d250}:a_{d365} increased in H4, while there was not much variation in D10, suggesting that the molecular size decreased more in H4 than D10. The absorbances at 320 nm and 380 nm both decreased slightly, indicating CDOM also decreased in the incubations. Additionally, particulate matter formed in the dark treatments. With no photodegradation occurring in the dark treatments, changes in $SUVA_{254}$ and other absorbance parameters reflected changes in the DOC character resulting from particulate matter formation and/or other abiotic processes.

3.4.2 Effects of photolysis and respiration on δ^{13}C-DIC

In these incubations, DIC production caused a decrease in the δ^{13}C-DIC in both the light and dark treatments (Figure 3.3). In the light treatments, the δ^{13}C-DIC values decreased by approximately 3‰ to 7‰ and changes were similar in filtered, inoculated, and sterile treatments of each stream. However, because DOM photolysis and other abiotic processes produced DIC in the light sterile treatments, the decrease in δ^{13}C-DIC could indicate that the source of carbon (or CO_2 produced) has a lower δ^{13}C value than the pre-existing δ^{13}C-DIC. Since the DOC is the source of the new CO_2 produced, the δ^{13}C-DIC should become more similar to the δ^{13}C of the functional groups cleaved (likely carboxylic acids) from the bulk DOC as more DOC is consumed producing more DIC.

Dark incubations also exhibited a decrease in the δ^{13}C-DIC with increasing DIC concentration (~0.5‰ to 5‰ decrease) in all treatments including the sterile treatment. Dark incubation results include abiotic DIC production and, similar to the light incubations, a source (such as DOC) with a lower δ^{13}C value is required to produce δ^{13}C-DIC lower than the initial δ^{13}C-DIC. Abiotic processes that produce DIC are thus also processes that use the lighter δ^{13}C functional groups cleaved from the bulk DOC to create δ^{13}C-DIC.

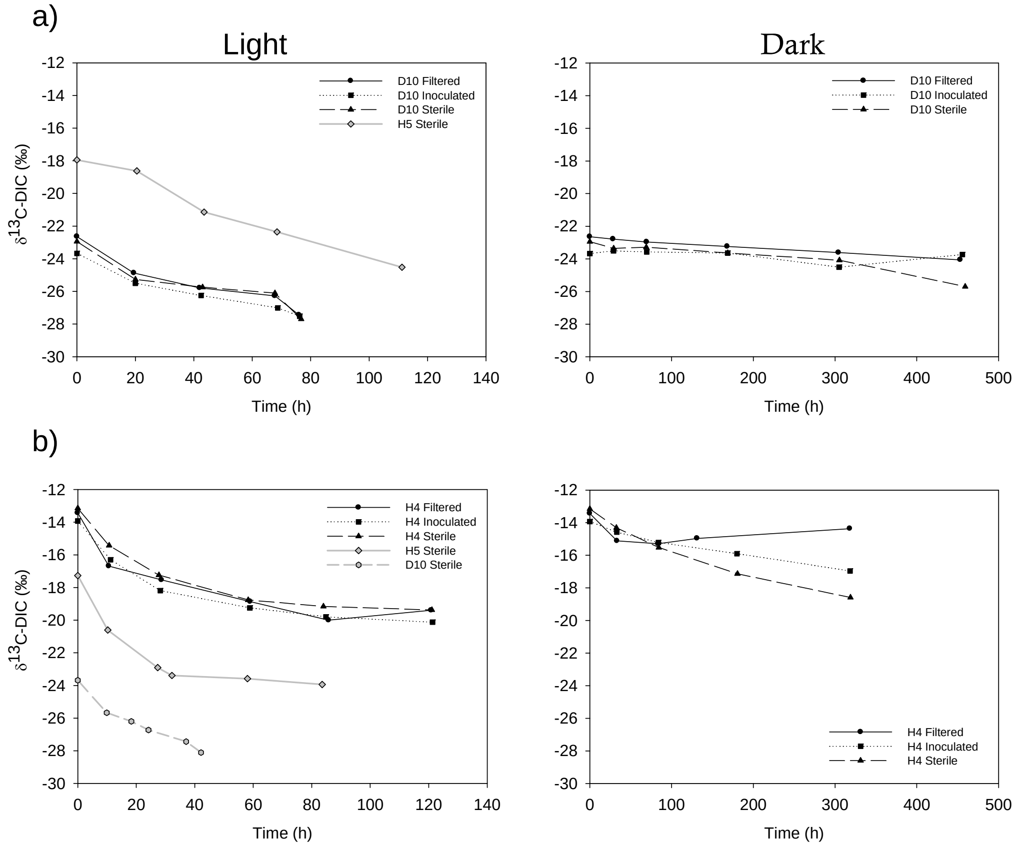


Figure 3.3: δ^{13}C-DIC versus time of a) D10 and b) H4. Precision of δ^{13}C-DIC is 0.3‰. Sterile H5 samples were incubated with both experiments (a and b), and sterile D10 samples were incubated with H4 (b) to assess the effects of differences in light exposure between the two experiments. Note the scale difference between the figures. Initial δ^{13}C-DOC values are: -27.2‰ for H4, -27.0‰ for H5, and –27.5‰ for D10.

The δ^{13}C value of the DIC produced in the light treatments (calculated by mass balance) ranged between –23‰ to –31‰ and was similar between treatments yet different between sites (Table 3.4). The δ^{13}C-DIC produced in the sterile samples from H5 and D10 incubated on two different dates were also similar. In the dark incubations, the δ^{13}C-DIC produced (also calculated using mass balances) was more variable, ranging by approximately 10‰ and 5‰ in D10 and H4 samples, respectively (excluding the H4 dark filtered sample). Since only a small amount of DIC was produced in the dark incubations, a large error is associated with the calculated δ^{13}C-DIC gained. Applying this error to the δ^{13}C values from the individual treatments caused the $\delta^{13}C$ values to overlap, however, the large errors suggest that no conclusive results are available.

Table 3.4: Calculated values for δ^{13}C-DIC and δ^{13}C-CO_2 gained and δ^{13}C-DOC lost during the incubations. The error values listed take into account the maximum error possible on all analyses required to calculate these isotopic signatures. The measured δ^{13}C-DOC remaining at the end of phase 1 (before re-aeration) is also presented and has a precision of 0.2‰. Initial δ^{13}C-DOC values for Dickie 10, Harp 4, and Harp 5 are -27.5‰, -27.2‰, and -27.0‰ respectively**.**

		LIGHT							***DARK***							
Site	Treatment	δ^{13}C-DIC gained	+/- (‰)	δ^{13}C-CO_2 gained	+/- (‰)	δ^{13}C-DOC lost	+/- (‰)	δ^{13}C-DOC remaining	δ^{13}C-DIC gained	+/- (‰)	δ^{13}C-CO_2 gained	+/- (‰)	δ^{13}C-DOC lost	+/- (‰)	δ^{13}C-DOC remaining
Dickie Inflow 10	Filtered	-30.5	-3.6	-30.9	-3.5	-28.8	-0.8	-27.0	-26.3	-5.5	-27.2	-4.9	-33.0	-7.4	-27.2
	Inoculated	-30.1	-3.7	-31.0	-3.9	-28.5	-0.8	-26.9	-23.9	-8.6	-40.5	-42.8	-29.1	-3.2	-27.4
	Sterile	-30.6	-3.6	-33.5	-4.3	-28.5	-0.8	-27.0	-33.2	-9.7	-30.7	-7.7	-29.2	-4.5	-27.2
	Average	***-30.4***		***-31.8***		***-28.6***		***-26.9***	***-27.8***		***-32.8***		***-30.4***		***-27.3***
	Sterile[1]	-29.9	-3.0	-30.3	-3.1	-30.3	-0.9	-27.0	n/s[3]	n/s[3]	n/s[3]	n/s[3]	n/s[3]	n/s[3]	n/s[3]
Harp Inflow 4	Filtered	-23.7	-2.9	-24.2	-2.1	-33.6	-3.1	-22.3	-15.3	-2.4	-18.2	-1.7	-29.8	-5.6	-26.2
	Inoculated	-24.7	-3.0	-25.9	-2.3	-31.0	-2.8	-22.9	-24.8	-6.6	-22.9	-2.5	-26.2	-6.3	-27.7
	Sterile	-23.4	-2.7	-23.7	-2.0	-31.9	-3.2	-21.9	-30.1	-6.6	-25.6	-2.7	-26.1	-11.7	-27.5
	Average	***-23.9***		***-24.6***		***-32.2***		***-22.4***	***-23.4***		***-22.3***		***-27.3***		***-27.1***
Harp Inflow 5	Sterile[2]	-28.5	-3.2	-29.3	-2.9	-28.8	-1.7	-26.6	n/s[3]		n/s[3]		n/s[3]		n/s[3]
	Sterile [1]	-27.1	-2.8	-26.3	-2.3	-28.3	-1.4	-26.8	n/s[3]		n/s[3]		n/s[3]		n/s[3]

[1] Incubated with H4 water. [2] Incubated with D10 water. [3] n/s = no sample

3.4.3 Effects of photolysis and respiration on δ^{13}C-DOC

DOC loss during the light incubations caused an increase in δ^{13}C-DOC values of the light treatments (Figure 3.4) by approximately 1.5‰ to 5‰ after more than 50% of the DOC had been degraded. Changes were similar in filtered, inoculated, and sterile treatments of each stream. There was generally no change in the δ^{13}C-DOC during the dark incubations, except in the H4 filtered incubation, which increased by approximately 1‰. This incubation also exhibited greater DIC production and O_2 consumption rates than the other H4 treatments for unknown reasons (Chomicki and Schiff, 2008: Chapter 2). However, since both photolysis and respiration consumed DOM in the light sterile treatments, and photolysis occurs at a much faster rate than respiration in these incubations (Chomicki and Schiff, 2008: Chapter 2), the increase in δ^{13}C-DOC suggests that photolysis preferentially degraded ^{12}C^{12}C bonds, or cleaved functional groups that were more depleted in ^{13}C than the bulk DOC, leaving the residual DOC enriched in the heavier ^{13}C isotope.

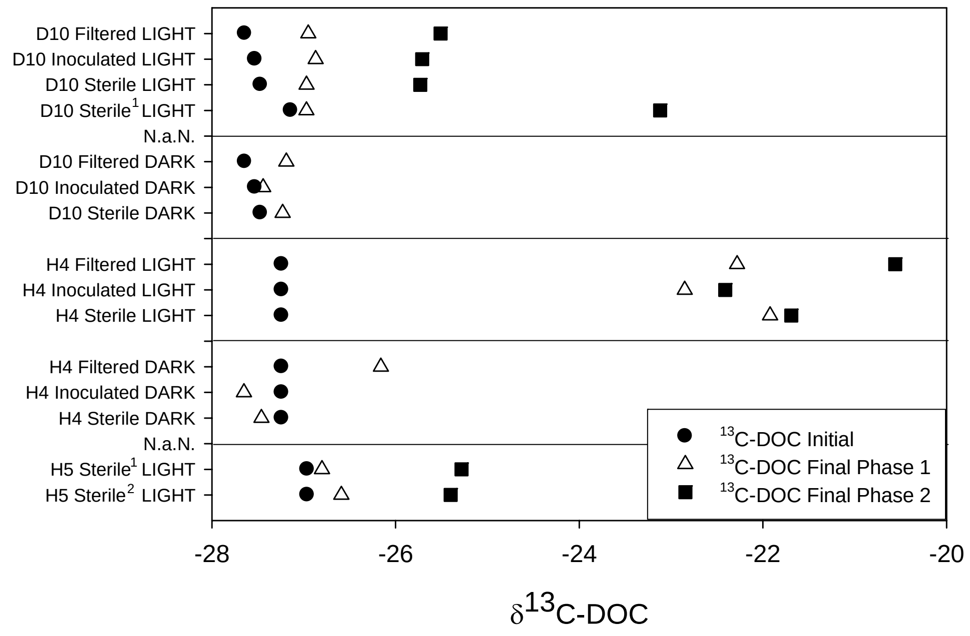


Figure 3.4: δ^{13}C-DOC of D10 and H4. Precision of δ^{13}C-DOC is 0.2‰. Sterile H5 samples were incubated with both experiments (^{1} incubated with H4, ^{2} incubated with D10), and sterile D10 samples were incubated with H4 to assess the differences in light exposure between the two experiments. Phase 1 signifies the end of the closed experiment after which the bags are reaerated. Phase 2 represents the point where ≥ 50% of the DOC was lost after daily reaeration.

The calculated δ^{13}C-DOC lost values are similar (within error) among the three treatments and among the sites (Table 3.4). There was more variability in the δ^{13}C-DOC lost in the dark samples between treatments and the errors are much larger due to the small amount of DOC lost in comparison to the light samples. Similar to this study, Osburn et al. (2001) found a 1.2‰ change in δ^{13}C-DOC after a 16% DOC loss in UV exposed bog DOM samples, which were filtered to 0.2 μm and sterilized with NaN_3. These data also support the 1.6‰ change in riverine waters exposed to natural sunlight (filtered to 0.6 μm, containing microbes, after a 27% DOC loss; Opsahl and Zepp, 2001) and the findings of Vähätalo and Wetzel (2008) who observed a 6‰ increase in photolyzed samples of lyophilized *Juncus*-leachate that was dissolved into lake water samples (0.7 μm autoclaved water) and incubated for 459 days with 72% DOC loss.

Differences existed between the δ^{13}C-DIC produced and the δ^{13}C-DOC lost in all sites and treatments (Table 4). In H4, the average δ^{13}C-DIC gained between treatments was more positive than the δ^{13}C-DOC lost by approximately 8‰ and approximately 2‰ more negative than the residual δ^{13}C-DOC. In contrast, the δ^{13}C-DIC produced in the D10 light treatments had a more negative δ^{13}C value in comparison to the δ^{13}C-DOC lost and the δ^{13}C-DOC remaining by approximately 2‰ and 4‰ respectively. The differences might be attributed to the particulate carbon formed within the incubation bags, however, isotopic fractionation during particulate carbon formation has not been studied and is the focus of Chapter 4. Mass and isotope POC balances would be required to accurately determine its impact.

3.4.4 Photodegradation enrichment factor (ε)

To calculate an enrichment factor (ε) for the DOC loss, the DOM photodegradation process was treated as a Rayleigh-type distillation, assuming that the δ^{13}C-DOC reservoir is finite and well mixed, and that it does not re-react with the product (Clark and Fritz, 1997). Examining the Rayleigh relationship between the δ^{13}C-DOC and the fraction of DOC remaining after photodegradation shows that the light incubated H4 and D10 samples fall along 2 different paths suggesting fractionation is site and possibly DOM dependent (Figure 3.5). Separating the two sites provides an ε for Harp and Dickie as –1.2‰ and –2.3‰ respectively. Previously published photolytic studies of high DOC rivers and bogs fall in along the same path as the D10 samples (Figure 3.5). Incorporating the 5 sample points obtained from 3 previous studies (Osburn et al., 2001; Opsahl and Zepp, 2001; and Vähätalo and Wetzel, 2008) shifts the ε only slightly from –2.3‰ to –3.0‰.

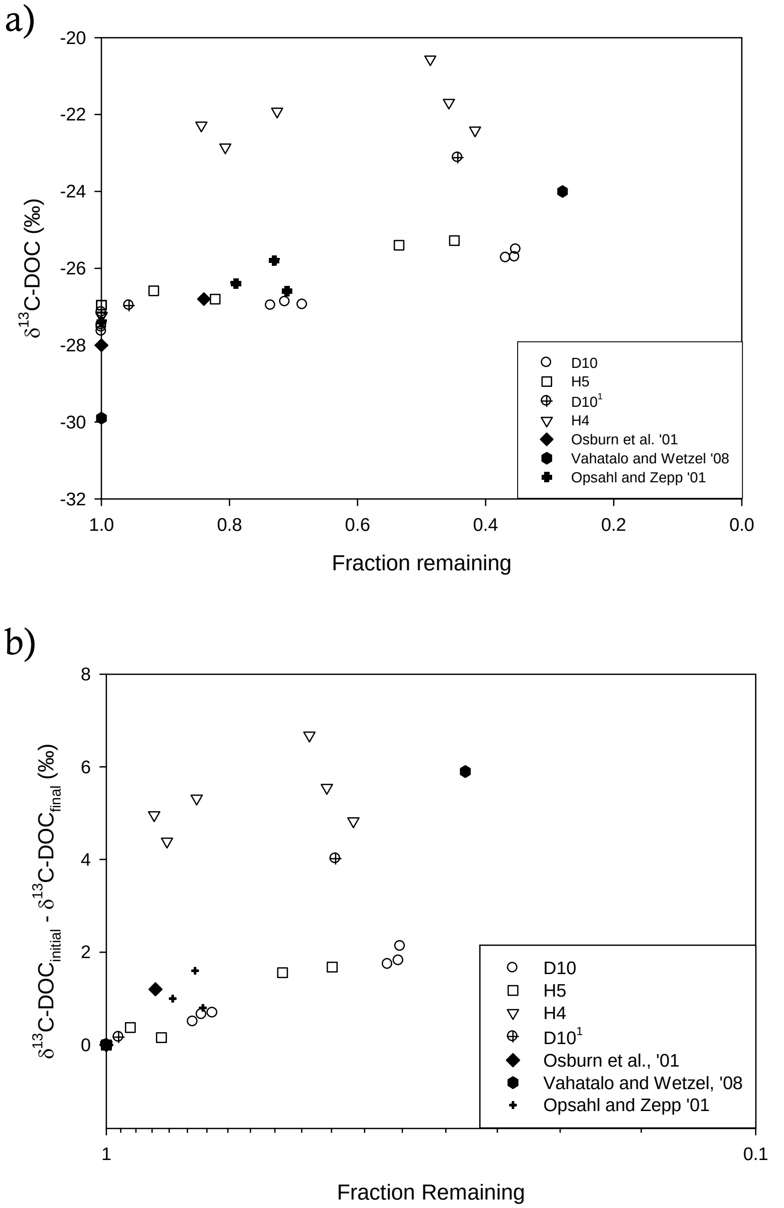


Figure 3.5: The change in δ^{13}C-DOC due to the photodegradation of DOM where a) is a plot of δ^{13}C-DOC as a function of DOC remaining after the photodegradation of DOC, and b) is a Rayleigh plot showing the change in δ^{13}C-DOC with the fraction of DOC remaining. The plots includes Phase 1 and Phase 2 changes from the light incubations (hollow symbols), and data from 3 studies in the literature.

Current coupled carbon and carbon isotope models used to understand carbon cycling in aquatic systems do not consider photolysis (or other abiotic reactions) as processes that are isotopically fractionating, or as processes that will affect the δ^{13}C dynamics within them. Bade et al. (2007)

modeled $\delta^{13}C$ dynamics to examine sources and fates of lacustrine DOC and, although they assumed a removal rate of DOC by photooxidation, the associated fractionation was not included due to uncertainty in fractionation over long time periods (i.e. longer than 3 weeks: Opsahl and Zepp, 2001; and 7 days: Osburn et al., 2001). However, subsequently Vähätalo and Wetzel (2008) observed a 6‰ increase in $\delta^{13}C$-DOC with a 72% DOC loss over 459 days (see above). In other $\delta^{13}C$ balances, it is generally assumed that during respiration and microbial degradation of organic carbon there is no isotopic fractionation (Degens et al., 1968; Smith and Kroopnick, 1981; Quay et al., 1986). The results from the dark incubations in this study show little change in the DOC concentration or the $\delta^{13}C$-DOC indicating that these experiments shed no light on whether there is an isotopic fractionation during the microbial degradation of organic carbon. However, it is apparent that the photolytic degradation of DOM does preferentially mineralize ^{12}C, leaving the remaining DOC more positive with an associated ε value between –1‰ and –3‰. Subsequently, the DIC becomes lighter in the ^{13}C isotope. This process can thereby alter the terrestrial end member $\delta^{13}C$-DOC signal used in food web studies and in studies examining the allochthonous/autochthonous ratios in sedimenting particles (e.g. von Wachenfeldt et al., 2008) and sediments. Therefore, it is likely that most studies that assume a discrete allochthonous end-member value (generally around –27‰ or –28‰) could underestimate the importance of allochthonous carbon in their system. Additionally, DOM photodegradation can also affect the $\delta^{13}C$ in carbon-cycle studies (e.g. Quay et al., 1986), and influence the $\delta^{13}C$-CO_2 in aquatic systems. Because photolysis both produces DIC and changes the $\delta^{13}C$-DIC and $\delta^{13}C$-DOC, a separate photolytic/abiotic component may be needed in models especially in aquatic systems with high DOM where DOM photodegradation may be a significant portion of carbon mineralization.

3.5 Summary

DIC production occurred concurrently with DOC loss (and some POC formation) in stream water samples incubated in natural sunlight. DIC production rates were similar in all treatments (i.e. filtered, inoculated and sterile waters) incubated from the same stream. Light incubations produced considerably higher DIC production rates than the dark, indicating that the DIC source was photolysis of DOM and not the microbial degradation of DOM and/or other abiotic reactions. DIC production rates differed between streams, and differences in DOM photolability were evident after normalizing the production rates to the DOC lost. Degradation of DOM by photochemical oxidation and other abiotic reactions preferentially produced more negative δ^{13}C-DIC values, and ε values that ranged between –1‰ to –3‰. Changes in the δ^{13}C of the terrestrial end-member value when applied to food web studies, or studies examining the proportion of allochthonous to autochthonous carbon could be underestimating the proportion of allochthonous carbon. Since carbon isotopic studies in aquatic systems currently do not consider DOM photodegradation and other abiotic as processes affecting δ^{13}C-DIC and δ^{13}C-DOC values, respiration rates could be overestimated, sources of DOC could be misinterpreted and δ^{13}C studies in shallow, high DOC systems could be missing an important component.

Chapter 4:

Examination of POC formation during DOM photodegradation and the impacts of DOM photodegradation on δ^{13}C-POC and δ^{13}C-DOC in 10 forested streams, southern Ontario

4.1 Overview

The effects of photodegradation on dissolved organic matter (DOM) quality were investigated by examining the isotopic and molar C/N ratios of dissolved organic carbon (DOC), and the particulate organic carbon (POC) created in waters from ten streams within 2 catchments. Stream waters were filtered to 0.2 μm, sterilized, and incubated in natural sunlight. Absorbances ($SUVA_{254}$, SAC_{350}, and a_{d320} and a_{d380}) decreased after the stream waters were exposed to natural sunlight indicating the aromaticity, colour, and UV absorption of the DOC decreased. The optical index of molecular weight (a_{d250}:a_{d365}) increased in most samples indicating that generally the molecular size of the DOC decreased.

During the photodegradation of DOM, 61-90% of the DOC was lost, and 20-90% of the DOC lost was transformed to POC. Initial δ^{13}C-DOC values were within 2‰ in all the inflows. The change in δ^{13}C-DOC was different between inflows, ranging from 2.7 ‰ to 8.0 ‰. Generally, there was a positive relationship between the δ^{13}C-DOC change and the % peatland coverage. Enrichment factors (ε) for DOC photodegradation in the Harp and Dickie inflows are –1.2‰ and –3.4‰ respectively, with an average ε of –2.1‰ for all the 10 inflows. These data are in agreement with previous incubations and other literature data (average ε = –2.9‰). δ^{13}C-POC values ranged from –25.7 ‰ to –27.7 ‰, and were up to 2‰ heavier than the initial δ^{13}C-DOC, with 80% of the samples within 1‰ of the original δ^{13}C-DOC. Since the ε factors are different for DOC loss and POC creation, ignoring stream δ^{13}C-DOC and using lake δ^{13}C-DOC as an indicator of photolyzed DOC is not possible. Also, it is still unknown how the isotopic changes observed from altered stream waters will translate to the lakes.

After exposure to sunlight, C/N ratios of the DOC change from high values (24-55) indicative of terrestrial inputs to lower values (4-13), which are common for algal or microbial inputs. POC C/N ratios ranged from 12 to 26, and were different than the source DOC and the residual DOC after DOM photodegradation. In high DOC aquatic systems, it is possible for photodegradation to alter the δ^{13}C-DOC signature and the structure and C/N of DOC, while creating particulate carbon that in most cases is isotopically similar (i.e. within 1‰) to the DOC from which it is derived.

4.2 Introduction

Carbon budgets within lakes are often dominated by external loading (Caraco and Cole, 2004) and can be controlled by the influx of dissolved organic carbon (DOC) from the terrestrial catchment (Dillon and Molot, 1997a). In aquatic systems, DOC affects water quality by binding to trace metals thereby affecting nutrient availability and trace metal toxicity, in addition to controlling the water transparency, temperature and thermocline depth (Wetzel, 2001). Dead or decaying allochthonous carbon also provides sustenance for northern temperate and boreal lakes which are, generally, net heterotrophic ecosystems (del Giorgio and Peters, 1994; Algesten et al., 2003). With large inputs of terrestrial DOC controlling the mass and the δ^{13}C budgets of high DOC retention lakes (e.g. northern temperate and boreal lakes), it is important to examine the fate and the isotopic effects of processes affecting DOC. Since it is commonly assumed that internal processes do not affect the isotopic signature of DOC, and little work has examined the impact that processes (e.g. photodegradation, direct sedimentation, and microbial alteration) have on the isotopic fate of DOC (Chapter 3; Bade et al., 2007), it is crucial to understand the isotopic effects that DOC undergoes to fully understand what processes control the carbon balance.

Stable carbon isotopes are commonly used to examine carbon cycling and more specifically, the proportion of allochthonous to autochthonous carbon in aquatic systems. Cole et al. (2006) used the δ^{13}C of dissolved inorganic carbon (DIC), DOC, particulate organic carbon (POC) and biota (e.g. zooplankton, fish, benthic algae and benthic invertebrates) to examine the carbon cycling in lakes and including the food web. Pace et al. (2004) used a ^{13}C-DIC spike to track the uptake and transfer of carbon in two lakes and determined that approximately 50% of the POC in the lakes was terrestrial. In addition, von Wachenfeldt and Tranvik (2008) concluded that DOC is a precursor to organic matter that settles in 12 small Swedish boreal lakes. They used stable carbon isotopes to estimate the proportions of allochthonous and autochthonous carbon to the sedimenting POC.

Allochthonous carbon enters streams and lakes as DOC and can be respired or photodegraded into CO_2. Although it has been assumed that there is no isotopic fractionation associated with the respiration of DOM (e.g. Degens et al., 1968; Smith and Kroopnick, 1981; Quay et al., 1986) and little to no carbon isotope fractionation observed during respiration has been subsequently confirmed (e.g. Baril, 2001; Boudreau, 2000; Oelbermann and Schiff, 2008; Venkiteswaran, unpublished data), there is a small fractionation during the photodegradation of DOC (e.g. Osburn et al., 2001; Opsahl and Zepp, 2001; Vähätalo and Wetzel, 2008; Chapter 3) and this creates isotopically light CO_2 (Chapter 3) which may alter the lake δ^{13}C-DIC value. Autochthonous DOC is released by primary producers and is generally assumed to be –20‰ lighter than the source CO_2, although recent work highlights that algal fractionation may be lower than this accepted value (e.g. Cole et al., 2002; Bade et al., 2006; McCallister and del Giorgio, 2008). In addition, allochthonous and autochthonous organic matter deposited in lake sediment is thought to be distinguishable by C/N ratios such that ratios between 4 and 15 are from lacustrine algal sources and C/N ratios greater than 20 are from vascular land plants (Meyers and Teranes, 2001).

Post-burial diagenesis can affect the organic carbon in aquatic sediments until it is buried below the oxic-anoxic interface by decreasing the mass of total organic carbon. For example, the organic matter mass from two sediment cores taken within 6 years of each other from the same location in Lake Ontario decreased by 20% (Hodell and Schelske, 1998). Organic matter C/N ratios can also be affected by early diagenesis. Selective degradation of carbon-rich sugars and lipids is observed by lower C/N ratios observed in buried wood samples in comparison to fresh wood samples (Meyers et al., 1995). However, increases in the C/N ratio of algal derived (autochthonous) organic matter due to degradation of nitrogen-rich proteins can also occur (Meyers and Terranes, 2001). Usually, the observed C/N differences between land plants and algae are not erased by the diagenetic changes to the C/N ratio of sediment organic matter. Post-burial diagenesis can presumably also impact the δ^{13}C of sediment organic matter since different compounds degrade more readily (Herezeg, 1988), but was found to be minimal in the 2 Lake Ontario cores collected from the same location 6 years apart (Hodell and Schelske, 1998).

In aquatic systems, DOC can be lost to sedimentation by a number of processes (Stumm and Morgan, 1996). The size distribution and concentration of colloids (including or in the presence of natural organic matter) affects both aggregation and coagulation rates in addition to the size and sedimentation rates of colloids in all aquatic systems (Filella and Buffle, 1993; Buffle and Leppard, 1995). Bubble catalyzed transfer of DOC to POC (e.g. Baylor and Sutcliffe, 1963; Barber, 1966), and the POM creation via DOM polymer assembly to form polymer gels (e.g. Chin et al., 1998) are other processes that have been documented in marine waters. In riverine systems, the creation and size of particulate matter can be affected by turbulence and associated increases in particle contact (Droppo and Ongley, 1992, 1994) as well as changes in cations and pH (e.g. Maignan, 1983; Abate and Masini, 2003). Lake pH can affect the partitioning of carbon between the sediments and the atmosphere (Dillon and Molot, 1997a; Molot and Dillon, 1996) and although it is conventionally believed that acidified lakes are clear due to the precipitation of DOC-Al complexes (Effler et al., 1985), acidity has also been found to enhance photo-oxidation rates (Gennings et al., 2001; Anesio and Granéli, 2004). Finally, photochemical and iron induced DOC precipitation can also occur to create particulate matter when UV reduces Fe^{3+} to Fe^{2+} and transforms H_2O_2 to O_2*. The O_2 radical reacts with the reduced iron to create Fe^{3+} which binds with DOM.

Dillon and Molot (1997a) determined that in oligotrophic Shield lakes from south central Ontario, carbon is primarily derived from the terrestrial catchment, and that approximately 40% to 70% of the annual input of carbon to lakes is lost to a combination of sedimentation and evasion to the atmosphere. Loss rates of photolyzed total organic carbon measured from some of the streams feeding the Dillon and Molot (1997a) lakes (once corrected for extinction of UVA and UVB in the surface waters with depth, and in situ mixing) are similar to long-term mass balance loss rates in those lakes suggesting that the photo-oxidation of carbon is one mechanism that can account for the loss of carbon to the atmosphere and sediments (Molot and Dillon, 1997b).

DIC production, O_2 consumption, and photo-oxidation rates associated with the photodegradation of DOM have been examined in many studies (e.g. Amon and Benner, 1996; Anesio and Granéli, 2004; Bélanger et al., 2006; Bertilsson and Tranvik, 2000; Ma and Green, 2004; Miller and Zepp, 1995; Granéli et al., 1996; Chomicki and Schiff, 2008: Chapter 2; Chapter 3), however, the effects of DOM photodegradation on δ^{13}C-DIC (Chapter 3), and fractionation of δ^{18}O-O_2 (Chomicki and Schiff, 2008: Chapter 2) and δ^{13}C-DOC (Osburn et al., 2001; Opsahl and Zepp, 2001; Vähätalo and Wetzel, 2008; Chapter 3) remain understudied. Miles and Brezonik (1981) and Gao and Zepp (1998) have recognized the creation of POC during DOM photodegradation, however, minimal work has been completed that examines changes in δ^{13}C-DOC or in the δ^{13}C-POC created from photodegradation of DOM. Commonly, incubation studies on DOM photodegradation are short in duration to avoid any significant particulate matter accumulation. This goals of this study were to: 1) quantify the amount of particulate carbon created due to the photodegradation of DOM in waters from 10 different forested streams, 2) determine the changes and variability in the residual δ^{13}C-DOC and in the δ^{13}C-POC created as a result of photolysis and other abiotic reactions and 3) examine the changes in the C/N ratio of DOC resulting from photodegradation.

4.3 Methods

Water samples were collected from 10 gauged streams in the catchments of 2 oligotrophic headwater lakes, Harp Lake and Dickie Lake. These watersheds are located in the Muskoka-Haliburton region on the southern tip of the Pre-Cambrian Shield approximately 200 km north of Toronto, Ontario, Canada. Dillon et al. (1991) provide detailed descriptions of the watersheds, which contain thin tills (<1m thick) and peatlands. The Ontario Ministry of the Environment (OME) has monitored these streams, and substantial chemistry and hydrology datasets are available. General characteristics of these 10 streams are presented in Table 4.1.

Waters were collected from weirs located less than 100 m upstream from the lakes. Streams with high carbon inputs to the lakes have been the focus of previous carbon and oxygen photolytic DOM studies (e.g. Molot and Dillon, 1997b; Gennings et al., 2001; Chomicki and Schiff, 2008; Chapter 3). Relative to their inflows, Harp and Dickie Lakes have significantly lower DOC concentrations due to in-lake DOC loss.

Table 4.1: General Characteristics of stream water samples taken on the same date as the sample collection for the current study (analyzed by the Ontario Ministry of the Environment; unpublished data).

Inflow	% Peatland[1]	Area (ha)[1]	Stream Length[1] (m)	DOC (mg/L)	True Colour	Fe (µg/L)	Mn (µg/L)	NH_4^+ (µg/L)	Alkalinity (mg/L)	pH	DIC (mg/L)
Dickie 5	25.4	299.8	762	13.4	117	610	29.3	14	0.60	4.65	4.84
Dickie 6	21.8	22.0	488	n/a	263	568	33.3	8	0.15	4.54	1.52
Dickie 8	8.2	67.0	1220	n/a	277	379	20.0	14	2.90	5.10	3.38
Dickie 10	17.1	78.9	975	n/a	302	559	17.0	12	0.55	4.59	2.16
Harp 3	9.3	26.0	1010	11.7	131	339	34.7	6	3.80	5.74	1.50
Harp 3a	2.9	19.7	762	3.1	13	66	8.9	12	4.45	6.08	1.66
Harp 4	8 [2]	119.5	2040	5.2	40	121	7.2	4	5.70	6.50	1.30
Harp 5	13.3	190.5	1830	12.9	135	371	28.1	6	3.70	5.51	2.34
Harp 6	10 [2]	10.0	701	8.6	56	234	33.6	6	7.25	6.38	2.02
Harp 6a	8.5	15.3	610	11.8	115	130	11.0	6	2.25	5.10	2.90

[1] Dillon et al., 1991

[2] Eimers et al., 2008

n/a : not available

Stream waters were filtered to 0.2 μm and sterilized with the addition of 1mL of saturated $HgCl_2$ solution per L of stream water. Three litres of water was pumped into Tedlar bags, which had been triple washed with ethanol and triple rinsed with Nanopure water. Duplicate bags were placed in shallow water baths to minimize temperature and light exposure variations, and placed in natural sunlight at the University of Waterloo (43° 28' 25.6" N and 80° 33' 27.5" W; elevation ~ 335 masl). Since data from a previous experiment indicated little difference between filter-sterilized and $HgCl_2$ sterilized waters (Chomicki and Schiff, 2008; Chapter 3), there was no need for different treatments and thus all waters for these incubations were filtered and sterilized with $HgCl_2$, prior to light exposure.

All 20 bags (2 bags of each of 10 streams) were placed outside on August 9th, 2007 and aerated every 1-2 days. Harp and Dickie inflow samples were incubated for 28 and 34 days, respectively until DOC concentrations decreased by more than 50%. These experiments were augmented by data from an experiment run in June and July of 2005 that examined the δ^{13}C-DOC changes associated with photolysis. Details of the first experimental setup are outlined in Chomicki and Schiff (2008: Chapter 2) and in Chapter 3, and only contain samples for Harp Inflow 4, Harp Inflow 5, and Dickie Inflow 10.

DOC samples were periodically taken from the incubation bags to track DOC loss, however, the volume loss for the duration of the experiment was generally less than 100 mL. DOC samples were filtered to 0.45 μm, acidified with 85% H_3PO_4 to a pH of 2-3, sparged to remove DIC, and analyzed on a total organic carbon analyzer (Dohrmann DC-190) with a precision of ± 0.3 mg/L. DOC absorbance samples (also filtered to 0.45 μm) were analyzed in duplicate on a Beckman DU530 Life Science UV/Vis Spectrophotometer (path length = 1cm) between 200 nm and 700 nm and automatically corrected for the absorbance of Nanopure water. The ratio of

UV absorption at $\lambda = 254$ nm (measured in absorbance units m^{-1}) to DOC concentration (mg/L) was used to determine the specific UV absorbance ($SUVA_{254}$) (Weishaar et al., 2003). The specific absorption coefficient at $\lambda =$ 350 nm (SAC_{350}) was calculated normalizing the absorbance at 350 to the DOC concentration (mg/L) (Moran et al., 2000). Other absorbances (a_d) of interest were a_{d320} and the ratio of a_{d250}:a_{d365}.

δ^{13}C-POC and δ^{13}C-DOC samples were collected by filtering incubated waters through QMA (1.2 µm nominal pore size) and GF/F filters respectively. The particulate matter collected on the QMA filter was analyzed on a Carlo Erba 1105 Elemental Analyzer coupled to a Micromass Isochrom IRMS with a precision of ± 0.2‰. The mass of particulate carbon created was calculated by multiplying the fraction of carbon in the sample (as measured on the Elemental Analyzer) with the weight of the POC created. Because initial samples were filtered to 0.2 µm, they contained (by definition) no POC. The water which passed through the GF/F was acidified with 20% HCl to a pH of 4.5, freeze-dried and analyzed on the same instrument by the Environmental Isotope Laboratory, at the University of Waterloo, Ontario also with a precision of ± 0.2‰. Results are reported in standard δ notation as $\delta^{13}C = ((R_{sample} / R_{standard}) - 1) \times 10^3$ ‰, where R is ^{13}C:^{12}C.

An enrichment factor (ε) was calculated from the fractionation factor determined by assuming a Rayleigh relationship between the δ^{13}C-DOC and the fraction of DOC remaining after photodegradation, using the following relationship: $R = R_o f^{(\alpha-1)}$, where, R = ratio of the DOC isotopes after photodegradation, R_o = initial DOC isotope ratio, f = fraction of DOC remaining, and α = fractionation factor. From the calculated fractionation factor, ε was calculated using: $\varepsilon = (\alpha-1) \times 1000$ ‰.

4.4 Results and Discussion

4.4.1 Effects of DOM photodegradation on DOC loss and POC production

In the Harp Lake watershed, allochthonous DOC entering the streams and lake is generally expected to be from a young labile DOC pool and not an older DOC pool recalcitrant to decomposition (Schiff et al., 1997). The Harp and Dickie inflow samples lost an average of 75% (± 11%) of their DOC after exposure to natural sunlight, and 0.4 mg C/L to 13.6 mg C/L of particulate carbon was created (Table 4.2). On average, slightly higher concentrations of POC were produced in the Dickie Inflows (Table 4.2) reflecting higher initial DOC concentrations and the proportion of wetlands in the catchments. However, on average, 53% ± 21% of the DOC lost during exposure to UV transformed to particulate carbon in both the Harp and Dickie Lakes inflows (Table 4.2), and the remainder likely transformed to DIC. Previous experiments designed to examine gas production during photolysis indicate that DIC is produced during photodegradation and production rates were similar in filtered, inoculated, and sterile treatments (Chapter 3) indicating that DIC is being produced in addition to POC in the current incubations.

Table 4.2: Changes in DOC concentration, and particulate carbon created during the August 2007 incubations. Data are an average of the two incubation bags and standard deviations between the two bags are in mg/L.

Inflow	Initial DOC (mg C/L)	Final DOC (mg C/L)	Std Dev ±	Change in DOC (mg C/L)	Final POC concentration (mg C/L)	Std Dev ±	POC as a % of DOC lost	POC as a % of original DOC
Dickie 5	13.1	2.2	0.5	10.9	4.3	0.6	39	33
Dickie 6	20.9	0.8	0.2	20.1	4.7	2.8	23	22
Dickie 8	24.7	9.7	0.5	15.0	13.6	0.8	91	55
Dickie 10	24.5	9.3	1.1	15.2	9.2	2.9	61	38
Harp 3	12.4	2.9	0.1	9.5	6.2	1.3	66	50
Harp 3a	3.2	1.2	0.1	1.9	0.4	0.0	20	12
Harp 4	5.7	1.4	0.1	4.3	2.1	0.1	49	36
Harp 5	13.1	2.2	0.1	10.9	5.3	0.6	49	40
Harp 6	9.4	2.2	0.2	7.3	4.5	0.5	62	48
Harp 6a	12.3	3.5	0.5	8.8	6.0	0.4	67	48

Miles and Brezonik (1981) incubated humic coloured waters to examine photolytic O_2 consumption and the ferrous-ferric catalytic cycle and found that O_2 consumption increased linearly with increasing Fe^{3+}, and that humic matter precipitated within 6 hours in samples with iron concentrations that were greater than 10 mg/L. Gao and Zepp (1998) noted that DOM photooxidation converted iron to particulate matter (likely via polymeric iron oxides) and caused DOC transformation to particulate matter in their incubations of water from the Satilla River, Georgia (iron concentration 12 ± 2 μg/L) after 72 h of irradiation. As DOM photodegraded, carboxylate moieties oxidized (evident from the DIC produced) and Fe^{3+} formed polymeric iron oxides as the Fe^{3+} hydrolyzed to hydroxy complexes. These oxides then induced the flocculation of DOM creating particulate matter. Although iron concentrations and speciation were not monitored during these incubations, concentrations measured on unfiltered water by the Ontario Ministry of the Environment (Table 4.1) show iron ranging between 66 and 610 μg/L (presumably oxidized or complexed to DOC) creating conditions for the flocculation of DOM to form polymeric iron oxides.

While approximately half of the DOC lost was transformed into particulate carbon, the particulate carbon formed was between 12 to 55% (38% ± 13%) of the original DOC. This is similar to the results of Dillon and Molot (1997a), that carbon sedimentation is 13% to 60% of the annual DOC inputs of their 7 study lakes (Harp: 22%; Dickie: 32%), however, it is possible that the same photolytic transformations may not occur in the lakes as in the incubation bags. von Wachenfeldt and Tranvik (2008) found a positive relationship between sedimentation rates of allochthonous matter per m^2 in lakes and DOC concentration in the water, in addition to a positive relationship between DOC concentrations and % wetlands surrounding their catchments. Similarly, the amount of POC created in the incubations from this experiment increases with increasing DOC concentrations. However, normalizing the POC created to the original DOC indicates that as the percentage of peatlands increases, the amount of POC created decreases with the exception of H3a (Figure 4.1; $R^2 = 0.61$ without H3a) once the original DOC concentration is accounted for. H3a has a lower iron concentration than the other stream samples (Table 4.1), and it is possible that the flocculation of DOM is inhibited since there is little iron in comparison to the other streams to form polymeric iron oxides.

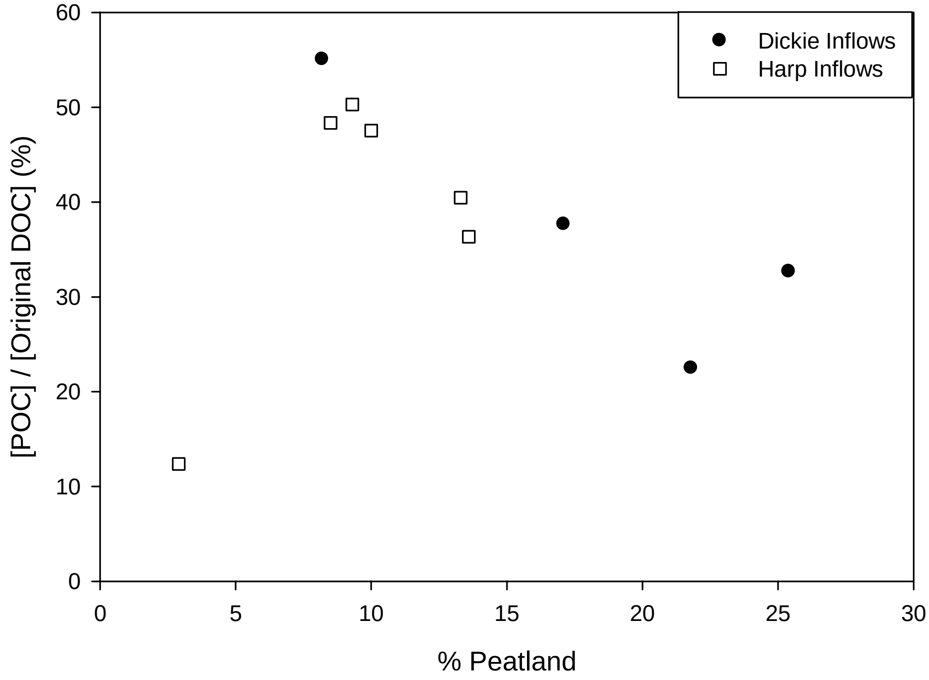


Figure 4.1: Relationship between the POC concentration normalized to the original DOC concentration and the % peatland coverage in the associated catchments.

The initial iron concentration may be an overestimate since a portion of the iron may have been removed by filtering the initial samples. Comparing the POC created to the initial total iron concentration shows no relationship ($R^2 = 0.18$; data not shown) suggesting that iron is not the only parameter influencing particulate matter formation. Separating the Harp and Dickie samples indicates that while Harp shows a weak positive relationship ($R^2 = 0.51$; data not shown) between the concentrations of POC created and iron, Dickie shows a strong negative relationship ($R^2 = 0.84$; data not shown) suggesting that the importance of iron in particle formation might be different between the two catchments. Molot et al. (2005) found that as pH increases, the importance of iron to DOC loss decreases, however, this is based on only one stream (Dickie 5) and there is no mention of particulate matter created. The initial pH of the Dickie stream waters ranges between 4.5 and 5.1, whereas the Harp streams range between 5.1 and 6.5. Generally, there is no relationship ($R^2 = 0.40$; data not shown) between the particulate carbon created and pH in Harp streams samples and a positive relationship between the POC created and pH ($R^2 = 0.70$; data not shown) in the Dickie streams samples. Since iron concentrations and pH were not tracked during this experiment, it is difficult to determine whether iron was acting as a catalyst for particulate carbon formation (Gao and Zepp, 1998), or whether it is co-precipitating with the DOC.

$SUVA_{254}$ changes have been used as indicators of changes in % aromaticity and thus changes in the chemical character of DOC (e.g. Hood et al., 2006; Weishaar et al., 2003). $SUVA_{254}$ of initial stream samples were generally greater in streams from catchments with a higher fraction of peatlands suggesting that those samples had a higher % aromaticity than samples from catchments with a lower fraction of peatlands (Table 4.3). Exposure to UV altered DOC, created particulate carbon and altered the DOC structure in all of the incubations. These changes caused the $SUVA_{254}$ to decrease by at least 5-fold after light exposure in each of the 10 streams (Table 4.3) indicating the aromaticity of the remaining DOC decreased.

Table 4.3: Changes in absorption after exposure to light. Values are the average changes in the duplicate bags in m^{-1}. All a_d values are multiplied by 100, and n.d. denotes non detectable.

Inflow	Initial $SUVA_{254}$	Final $SUVA_{254}$	Initial $SAC_{\lambda 350}$	Final $SAC_{\lambda 350}$	Initial $a_{d250}:a_{d365}$	Final $a_{d250}:a_{d365}$	Initial a_{d320}	Final a_{d320}	Initial a_{d380}	Final a_{d380}
Dickie 5	5.24	0.23	3.31	0.09	4.84	4.25	27.25	0.30	12.30	0.93
Dickie 6	5.21	0.21	3.41	0.21	4.54	1.11	43.70	0.13	20.45	0.55
Dickie 8	5.39	1.24	3.38	0.40	4.86	7.84	51.80	2.90	23.10	2.00
Dickie 10	5.49	1.76	3.44	0.78	4.75	6.82	51.60	5.20	24.05	2.70
Harp 3	5.19	0.59	3.23	0.21	4.94	9.75	25.50	0.33	11.05	0.13
Harp 3a	3.82	0.88	2.03	0.45	6.00	7.54	4.05	0.30	1.95	0.20
Harp 4	4.38	0.85	2.59	0.34	5.16	10.00	9.25	0.15	4.60	0.15
Harp 5	5.36	0.55	3.27	0.19	5.00	19.40	27.25	0.15	12.00	0.15
Harp 6	4.22	0.64	2.10	0.33	6.47	15.00	13.90	0.18	4.80	0.03
Harp 6a	3.02	0.50	3.10	0.15	2.71	16.13	18.40	0.33	13.30	n.d.

The optical index of molecular weight (a_{d250}:a_{d365}) increased in the majority of the streams (except Dickie 5 and Dickie 6; Table 4.3) suggesting a reduction in the relative size of the DOM after photodegradation (Morris and Hargreaves, 1997; DeHaan and DeBoer, 1987; Strome and Miller, 1978). Absorption at 350 nm has been used as an index of coloured DOM (CDOM; Moran et al., 2000) and normalization to DOC concentration (SAC_{350}) indicates that photobleaching had occurred and CDOM concentrations decreased in all streams after exposure to light. In addition, a_{d380} has also been used as an indicator of CDOM (Buiteveld, 1995) and the decrease in both a_{d380} and a_{d320} (Table 4.3) also suggests that CDOM has decreased (and consequently the colour of the water; De Lange, 2000) and UV transparency has increased (Osburn et al., 2001). Photodegradation of DOC in the stream waters thus alters the chemical structure of DOC. The aromaticity and size of the residual DOC decreased, possibly making it more bioavailable in the natural environment (Sulzberger and Durisch-Kaiser, 2009). Additionally, the penetration depth of UV-B radiation would increase exposure of enhancing aquatic organisms to UV radiation.

4.4.2 Effects of DOM photodegradation on $\delta\,^{13}$C-DOC and $\delta\,^{13}$C-POC

The initial δ^{13}C-DOC of the 10 streams ranged between –28.6‰ and -26.7‰. After more than 50% of the DOC had degraded in the incubations, the δ^{13}C-DOC increased by 2.7‰ to 8.0‰ (Figure 4.2). In general, larger changes in δ^{13}C were observed in samples with higher initial DOC concentrations, peatland coverage (Table 4.1, Table 4.2, Table 4.3), and normalized DOC loss (Figure 4.3). The magnitudes of δ^{13}C-DOC changes observed in the 2005 incubations on light exposed Harp 4, Harp 5, and Dickie 10 streams (Chapter 3) were similar to those observed here (Figure 4.2, Figure 4.3). DOM photodegradation, respiration, and abiotic redox reactions can all affect DOM concentrations in the light, however, since these samples were sterilized with $HgCl_2$ and abiotic reactions did not alter DOM in dark incubations (Chapter 3) the isotopic changes can be attributed to photodegradation. These incubations thus could support that photolysis preferentially degrades the lighter $^{12}C^{12}C$ bonds leaving a residual DOC more enriched. Additionally, since the ^{12}C and ^{13}C atoms are not evenly distributed within DOC molecules, it is possible that the functional groups cleaved from the molecule during DOM photodegradation (i.e. -COOH moieties) contain an abundance of ^{12}C atoms leaving the residual DOC molecule with the heavier ^{13}C atoms. The increases in $\delta^{13}C$-DOC due to photodegradation from this experiment agree with the 1.2‰ increase in $\delta^{13}C$-DOC of UV-exposed bog DOM samples (0.2 μm filtered water sterilized with NaN_3; Osburn et al., 2001), the 1.6‰ increase in $\delta^{13}C$-DOC of riverine waters exposed to natural sunlight (0.6 μm filtered water – microbes present; Opsahl and Zepp, 2001), and the 6‰ increase in $\delta^{13}C$-DOC of Vähätalo and Wetzel (2008) who incubated lyophilized *Juncus*-leachate dissolved in lake water samples for 459 days (0.7 μm filtered and autoclaved water).

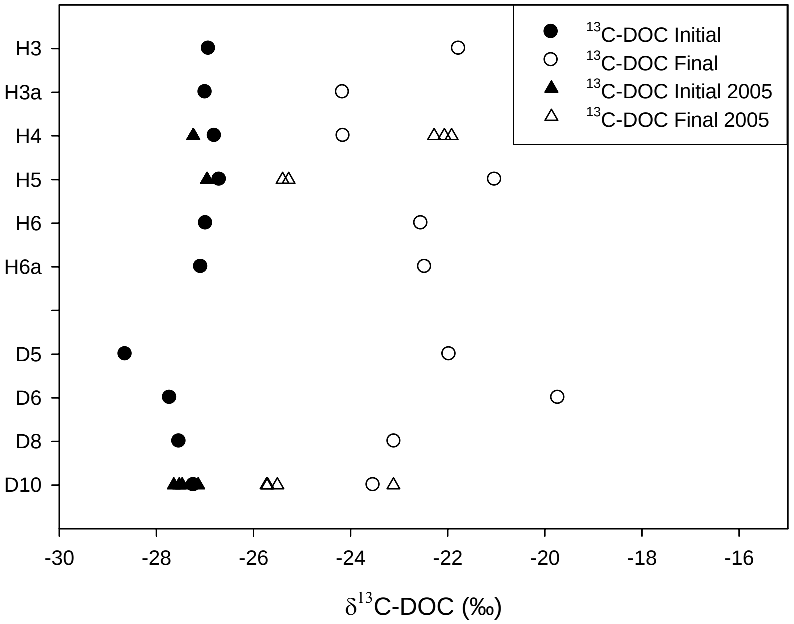


Figure 4.2: The change in δ^{13}C-DOC in the current (circles) and 2005 (triangles) incubations after exposure to natural sunlight. Filled symbols denote initial conditions, while hollow symbols represent photodegraded samples.

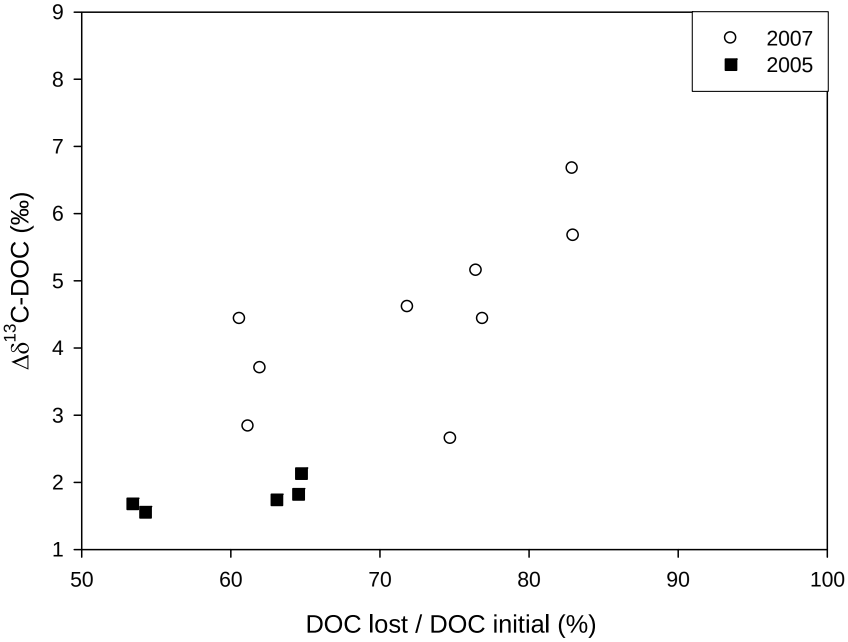


Figure 4.3: The change in δ^{13}C-DOC after exposure to natural sunlight vs. the DOC lost normalized to initial DOC concentrations.

Assuming a Rayleigh relationship between the δ^{13}C-DOC and the fraction of DOC remaining after photodegradation, a fractionation factor was calculated using the following relationship: $R = R_o f^{(\alpha - 1)}$, where, R = ratio of the DOC isotopes after photodegradation, R_o = initial DOC isotope ratio, f = fraction of DOC remaining, and α = fractionation factor. From the calculated fractionation factor, an enrichment factor (ε) was calculated using: $\varepsilon = (\alpha-1) \times 1000‰$. The incubated Harp and Dickie inflow samples plot along a similar line (Figure 4.3, Figure 4.4) suggesting fractionation is similar between the sites with an average enrichment factor (ε) of –2.1‰ (Figure 4.4). Separating the two sites provides an ε for Dickie and Harp as –3.4‰ and –1.7‰ respectively. These ε values are relatively similar to the 2005 experiments (Harp 4: –1.2‰; Dickie 10: –2.3‰; Chapter 3) suggesting that fractionation may be dependent on individual sites or DOM quality. The data from these incubations are similar to previously published photolytic studies of high DOC rivers and bogs fall and the D10 samples from the 2005 incubations discussed in Chapter 3 (Figure 4.4). However, the H4 samples from the 2005 incubations (Figure 4.4) plot in a different region compared to the 2007 incubations suggesting that they are fractionating differently. Recalculating the ε to include the current incubation samples with the 2005 incubations and previously published studies provides an ε of –2.6‰ ($R^2 = 0.44$). Considering that, in 2005, H4 does not follow the same trend and possibly fractionated differently than the other incubations, excluding it provides an enrichment factor of –2.9‰ ($R^2 = 0.78$), which is nearly identical to the ε of –3.0‰ calculated in Chapter 3. Photodegradation of DOM is therefore an isotopically fractionating process and could be dependent on site or initial DOM quality.

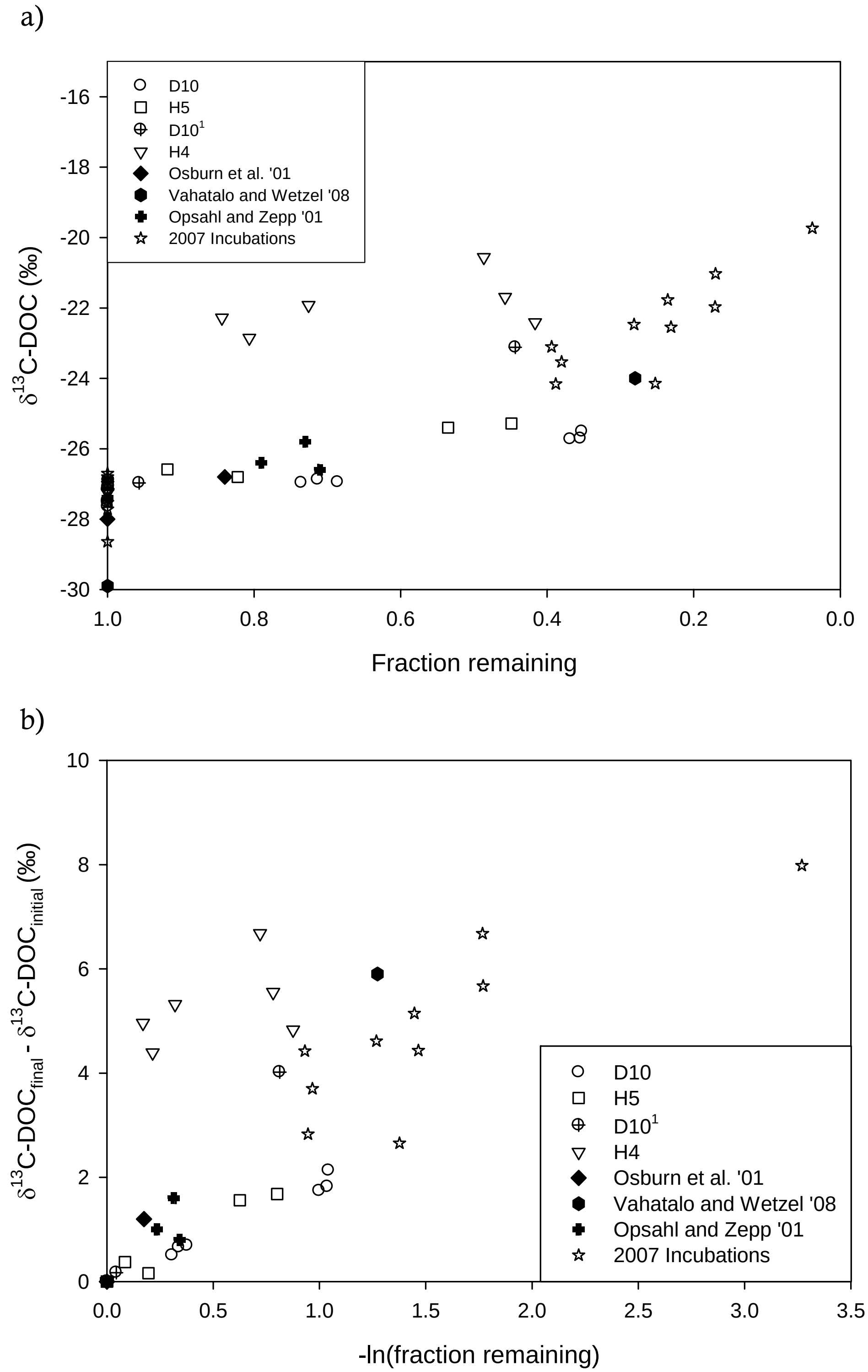


Figure 4.4: The relationship between δ^{13}C-DOC and the fraction of DOC remaining (a) and (b) the Rayleigh relationship between the δ^{13}C-DOC of the photodegraded DOC and the fraction of DOC remaining after photodegradation for the current 2007 incubations, the 2005 incubations, and other available literature data. Error bars for the current study are contained within the size of the symbols.

The δ^{13}C-DOC$_{\text{lost}}$ from the 10 inflows ranged between –30.4‰ and -27.7‰ (Table 4.4). Given the involved errors, the δ^{13}C-DOC$_{\text{lost}}$ from the 10 inflows are similar and support the data from the 2005 incubations, in which different treatments (filtered, inoculated, and sterile) among three sites (H4, H5, and D10) also found that the δ^{13}C-DOC$_{\text{lost}}$ are similar when errors are considered (–28.5‰ ± 1.6‰ to –32.2‰ ± 3.0‰; Chapter 3).

Table 4.4: Comparison of the δ^{13}C-DOC lost, the δ^{13}C-POC created, and the δ^{13}C-DIC gained (estimated by mass balance) in the 2007 incubations. Data are the averages of the 2 incubation bags.

Inflow	Initial DOC (mg/L)	Final DOC (mg/L)	δ^{13}C-DOC initial (‰)	δ^{13}C-DOC final (‰)	δ^{13}C-DOC lost (‰)	± (‰)	δ^{13}C-POC (‰)	Calculated δ^{13}C-DIC gained (‰)	± (‰)
Dickie 5	13.1	2.2	-28.6	-22.0	-30.0	-1.1	-26.8	-32.1	-3.3
Dickie 6	20.9	0.8	-27.7	-19.7	-28.0	-0.8	-26.8	-28.4	-5.1
Dickie 8	24.7	9.7	-27.5	-23.1	-30.4	-0.8	-26.5	-68.9	-17.8
Dickie 10	24.5	9.3	-27.2	-23.5	-29.5	-0.8	-27.7	-32.3	-13.7
Harp 3	12.4	2.9	-26.9	-21.8	-28.5	-1.2	-26.4	-32.6	-11.3
Harp 3a	3.2	1.2	-27.0	-24.2	-28.8	-6.8	-25.7	-29.6	-7.2
Harp 4	5.7	1.4	-26.8	-24.1	-27.7	-2.9	-26.3	-29.0	-5.4
Harp 5	13.1	2.2	-26.7	-21.0	-27.9	-1.0	-26.5	-29.2	-3.6
Harp 6	9.4	2.2	-27.0	-22.5	-28.3	-1.6	-26.6	-31.1	-6.5
Harp 6a	12.3	3.5	-27.1	-22.5	-28.9	-1.3	-26.7	-33.4	-5.8

Values of δ^{13}C-POC created after DOM exposure to natural sunlight ranged between and –27.8‰ and –25.7‰ (Table 4.4). Although the average δ^{13}C-POC for the 10 streams is –26.6‰, it is similar to the average calculated δ^{13}C-DOC$_{\text{lost}}$ (–28.8‰) once errors are applied to each parameter (Table 4.4). In 80% of the samples, the POC created is within 1‰ of the initial δ^{13}C-DOC but can be up to 2‰ heavier than the initial δ^{13}C-DOC (range: –0.4‰ to +1.9‰; Table 4.4; Figure 4.5). Since the ε for the DOC lost does not equal the difference in δ^{13}C-POC from the source DOC, lake DOC cannot be used as a proxy for photolyzed DOC. Although isotopic changes are observed for DOC loss during photodegradation in the stream water incubations, it is currently unknown how much DOC loss in the lakes is attributed to photodegradation. Therefore, it is difficult to know how the isotopic changes observed in the incubations will translate to the lakes.

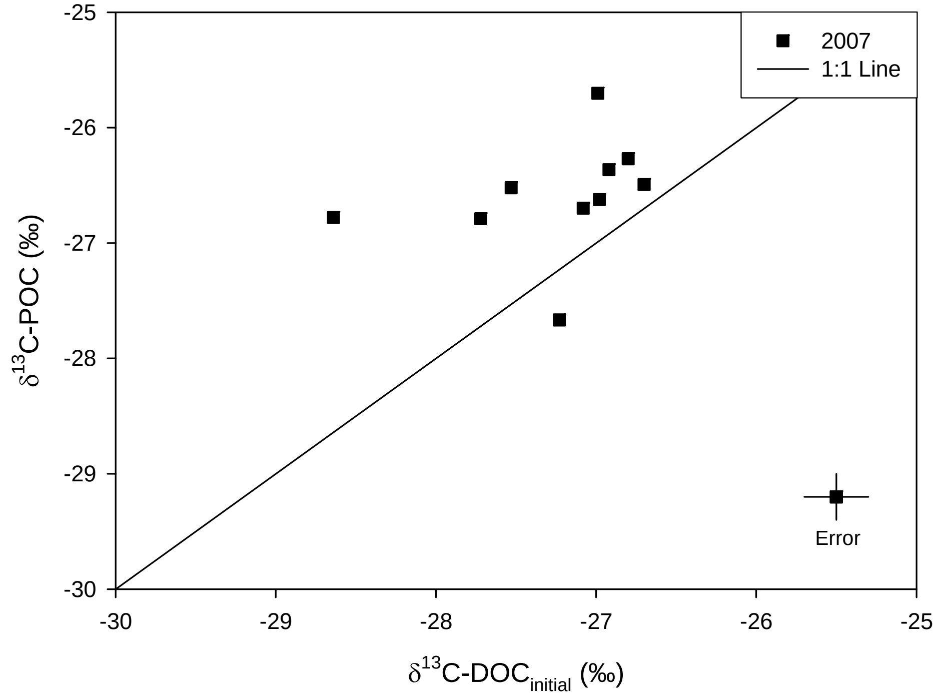


Figure 4.5: The similarity of δ^{13}C-POC created after exposure to natural sunlight and the initial δ^{13}C-DOC from which it was created. Precision is 0.2‰ on isotopic measurements.

The 2005 and the 2007 incubations were different because the initial phase of the 2005 experiments was closed to allow monitoring of changes in O_2 and DIC concentrations, δ^{18}O-O_2 (δ^{18}O of dissolved oxygen; Chapter 2) and δ^{13}C-CO_2 (Chapter 3). These experiments indicated the DIC photoproducts (such as CO_2) have δ^{13}C values lower than their original δ^{13}C-DIC (Chapter 3). The remaining pathways for carbon removal in the current incubations can be estimated using the isotopic signature and concentration of the DOC$_{lost}$, and the isotopic signature and concentration of the particulate carbon created under the assumption that the remaining carbon from the degraded DOC that is not POC, would be DIC. Although δ^{13}C-DIC and DIC concentrations were not measured, by assuming that the initial DIC concentration is negligible (in comparison to the DOC), the δ^{13}C-DIC produced in 9 out of the 10 stream samples ranged between –28.4‰ and –33.4‰ (Table 4.4). Although the error associated with the

δ^{13}C-DIC$_{gained}$ is relatively large (as the POC created in the bags had standard deviations up to 2.9 mg/L), these values are comparable to the D10 and H5 samples in the 2005 incubations, with isotopic signatures of δ^{13}C-DIC gained ranging from –27.1‰ to –30.6‰ (Chapter 3).

The data required to calculate enrichment factors for the transformation of DOC to DIC is not available because the experiment was not designed to track the temporal changes in DIC or POC. To calculate an ε with the existing data would require the assumption that the ratio of DIC produced to POC produced was constant throughout the incubations, and there is no evidence to support this. An ε can be calculated at a single point, by assuming that there is an open system between the DOC lost (source) and the DIC and POC produced (products) such that DOC is constantly lost and always lost only to DIC and POC. In this case, the ε values would range between ~–5‰ to 0‰ in 9 out of 10 cases with an average ε of –2.3‰. By applying the same assumptions to the 2005 incubation data, the ε would range between –2‰ and ~0‰ for the D10 samples, ~0‰ to –1‰ in the H5 samples, and ~–6‰ to –10‰ in the H4 samples. The 2005 incubations were incubated for less time than the 2007 incubations, and only exhibited a DOC loss of 4% to 34% (compared to ~60% to 95% in 2007). This suggests that partitioning between DIC and POC as well as isotopic fractionation during DIC and POC production during DOC photodegradation may be a function of (or partly related to) DOC quality and amount of DOC loss.

4.4.3 Effects of DOM photodegradation on C/N ratios of DOC

Organic matter derived from vascular (e.g. land grasses, shrubs, trees and aquatic macrophytes) and non-vascular (e.g. phytoplankton) plants maintains its geochemical source distinctiveness and resulting organic matter accumulation in lake sediments can reflect the amount and type in addition to the extent of alteration and/or degradation of the original material (Meyers and Teranes, 2001). Initial molar C/N ratios of the DOC ranged between 24 and 55, however, it is unknown whether the POC derived from this DOC would retain similar C/N ratios to the allochthonous DOC source. Low N content is common in the lignaeceous material of higher plants while higher relative N content (and lower C/N ratios) is expected in algal derived DOC (McKnight et al., 1994). In the surface waters of Loch Vale, McKnight et al. (1997) found that fulvic acids and some large particulates clustered in the range of plant derived carbon, while smaller particulates and colloids had greater $\delta^{13}C$ values (and lower C/N ratios) suggesting possible algal sources. With the photodegradation of more than 50% of the DOC in the current incubations, the C/N ratios of the residual DOC decreased to 4 to 14 in 9 out of 10 of the 2007 incubation samples (and increased by approximately 3‰ to 8‰ in $\delta^{13}C$), to become more similar to what is expected for algal sources (Figure 4.6). The low DOC C/N ratios from samples after photodegradation were not treated to remove NO_3^{2-} or NH_4^+, which could affect the C/N ratios. However, by assuming all of the nitrogen is retained, the importance of not treating the samples can be assessed by applying the DOC loss to 1) the measured initial DOC concentrations and OME total nitrogen measurements, and to 2) the initial DOC C/N ratios. The calculated C/N values (assuming all the nitrogen is retained) range from ~1 to 20 (with 90% of the samples below 16.5), and are within the ranges measured for the final DOC (C/N = ~1 to 14) suggesting that treating the samples for NO_3^{2-} or NH_4^+ was not important.

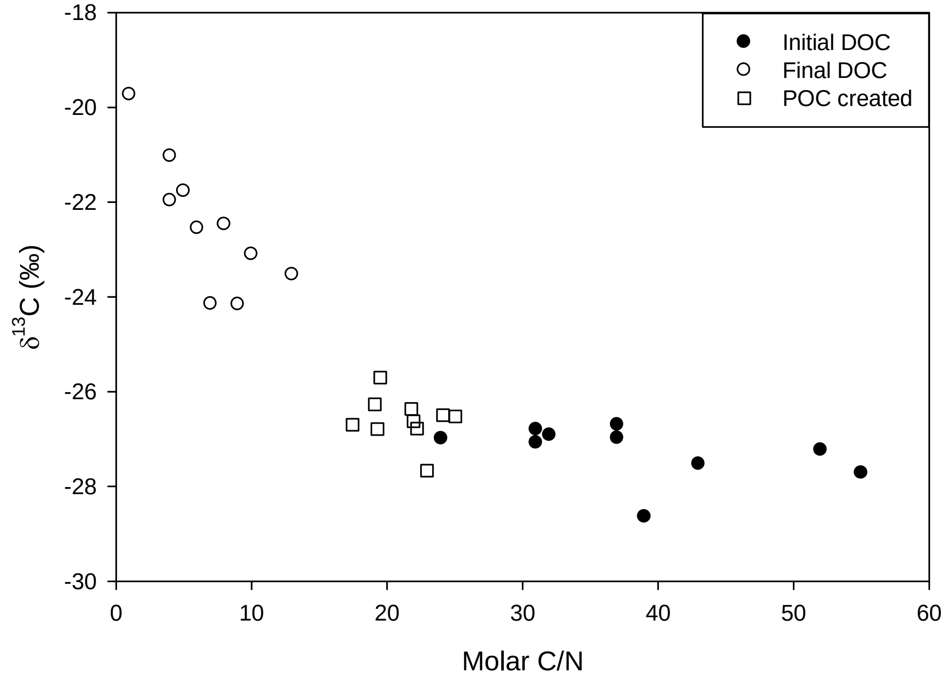


Figure 4.6: The differences between the δ^{13}C-DOC and C/N ratio of DOC of the initial DOC and final incubation samples after exposure to natural sunlight. Values are the averages of duplicate bags.

In aquatic systems, photochemical release of NH_4^+ has been observed (e.g. Bushaw et al., 1996; Gao and Zepp, 1998; Gardner et al., 1998; Bushaw-Newton and Moran, 1999; Buffam and McGlathery, 2003; Vähätalo et al., 2003; Kitidis et al., 2006) and can affect inorganic nutrient budgets (Bushaw et al., 1996). However, Kitidis et al. (2006) suggest that the potential impact of NH_4^+ photoproduction is largest in shelf waters and marginal seas. Nitrite and low molecular weight organic nitrogen compounds (e.g. primary amines and dissolved free amino acids) are also observed photoproducts (as cited in Kitidis et al., 2006), but photoproduction rates are generally one order of magnitude less than NH_4^+ production. Photoammonification is not always detected in lake and river waters (e.g. clear water lake, Sweden: Jørgensen et al., 1998; humic surface waters in boreal watersheds: Bertilsson et al., 1999; agricultural and forest runoff into rivers: Wiegner and Seitzinger, 2001), and therefore the importance of NH_4^+ must be considered in a regional context (Kitidis et al., 2006). Detection of NH_4^+ from photolysis could depend on the reactivity of DOM and other environmental controls that are not well understood (Kitidis et al., 2006) including the presence of dissolved iron (Gao and Zepp, 1998), the intrinsic properties of DOM, levels of O_2, and the degree of prior exposure to radiation (Koopmans and Bronk, 2002; Buffam and McGlathery, 2003).

Although the C/N ratios were not treated to remove NH_4^+ or NO_3^{2-}, it is possible that it is not necessary as these photoproducts may be absent after photodegradation or the photoproducts may not be produced in large enough quantities to impact the C/N ratios. Perhaps more important than the degree of C/N alteration, is merely the idea that photodegradation of DOM can alter the C/N ratio of DOC, possibly obscuring the origins of or the proportion of autochthonous DOC in aquatic systems with high proportions of allochthonous DOC inputs. In addition, the POC C/N ratios ranged between 12 and 26, and were different than the residual DOC C/N ratios. Thus C/N ratios of DOC that has been subjected to photolysis cannot be used to ascertain sources of DOC.

4.5 Summary

Photodegradation of DOC altered the DOC and created POC in waters from 10 streams flowing into 2 oligotrophic lakes on the Canadian Shield. After exposure to natural sunlight for 28 to 34 days (Harp and Dickie Lake Inflow samples respectively), 61% to 90% of the DOC was degraded. According to the optical index of molecular weight (a_{d250}:a_{d365}) and SUV_{254} absorbance data, the molecular weight and the aromaticity of the residual DOC decreased in the most of the samples. Decreases in SAC_{350}, a_{d380} and a_{d320} values confirmed that photobleaching occurred, decreasing CDOM concentrations, the colour of the water and increasing UV transparency.

Loss of DOC to photodegradation was accompanied by the creation of 0.4 mg C /L to 13.6 mg C /L of particulate carbon, which accounts for 20% to 90% of the DOC loss. Higher POC concentrations were generally produced in the inflows with high initial DOC concentrations and a high proportion of wetlands in the catchments. Although approximately half of the DOC lost was transformed to POC, POC was 12-55% of the original DOC concentration.

After exposure to natural sunlight, δ^{13}C-DOC values increased by 2.7‰ to 8‰ after, on average, 75% of DOC was degraded; large changes were generally observed in samples with high initial DOC concentrations and peatland coverage. Data from 2005 incubations, and other literature data (e.g. Osburn et al., 2001; Opsahl and Zepp, 2001; Vähätalo and Wetzel) show increases in δ^{13}C-DOC similar to the current incubations, further supporting the suggestion that photodegradation of DOM either preferentially degrades the lighter ^{12}C^{12}C bonds, and/or that the ^{12}C and ^{13}C atoms are not equally distributed within DOC and the moieties cleaved from the DOC have more ^{12}C atoms than average with an average enrichment factor of –2.9‰ (ε range: –1.2‰ to –3.4‰).

The δ^{13}C-DOC$_{lost}$ from the 10 streams was similar across inflows. The average δ^{13}C-POC created value of the 10 inflows was –26.6‰ (range: –25.7‰ to –27.7‰) and was similar to the average calculated δ^{13}C-DOC$_{lost}$ (–28.8‰) once errors are applied, and to the initial average δ^{13}C-DOC (-27.3‰) suggesting that the isotopic signature of POC created during photodegradation is generally within 1‰ of the DOC it is created from. The remaining carbon loss pathway resulting from the photodegradation of DOM is likely DIC production and, assuming the initial DIC concentrations are negligible, the average δ^{13}C-DIC produced (of 9 samples) was –30.9‰.

$\delta^{13}C$ studies in aquatic systems currently do not consider DOM photodegradation as a process affecting isotopic values. The $\delta^{13}C$ changes could become important to isolating and interpreting DOC sources. Since DOM photodegradation can create POC ranging from –0.4‰ lighter than to 2 ‰ heavier than the initial DOC, it can affect the $\delta^{13}C$ value of lake sediments depending on the proportion of POC in the sediments derived from photodegraded DOM. In lakes, this could become important to the interpretation of the ratio of autochthonous to allochthonous carbon in both the POC in the water column and the lake sediments. Additionally C/N ratios of DOC can be altered to resemble microbial sources. Furthermore, $\delta^{13}C$ carbon cycling studies in shallow, high DOC systems could be missing an important component.

Chapter 5:

The use of carbon mass and isotope balances to examine the influence of allochthonous carbon on the δ^{13}C-lake sediment records in two small Ontario lakes.

5.1 Overview

Carbon mass and stable isotope balances were completed for Harp and Dickie Lakes in the Muskoka-Haliburton region of Ontario, Canada based on stream inflows, and outflows, precipitation, lake surface, and sediment measurements. Mass-weighted average annual δ^{13}C-DOC and δ^{13}C-DIC values from the inflows varied by 0.2‰ and 1.3‰ respectively from year to year suggesting that these values are well confined. The ranges of the mass-weighted average annual δ^{13}C-DOC values of the outflows were similar to the inflows for δ^{13}C-DOC (0.2‰); however, the ranges of the outflow mass-weighted average annual δ^{13}C-DIC were larger (range: 2.2‰) than the inflow range. Precipitation was found to be a small part of the mass and isotopic balances of these lakes. Calculated δ^{13}C values of the lake sediment were less than measured δ^{13}C values of the lake sediments for Dickie Lake by approximately 2‰; however, they were approximately 5‰ greater in Harp Lake. A dynamic model, created to examine the effects of mass change on the δ^{13}C of the lake sediments, revealed that changing the DOC mass entering lakes by 5% (a small annual variation, or the bias in measuring the mass balances) does not appear to significantly alter the δ^{13}C of the lake sediment. However, altering the mass of DOC entering the lakes by the long-term annual variability of DOC entering the lakes from the years of the mass balances (e.g. 40%) can change the isotopic signature of the lake sediment by up to 2.5‰. Examining the input parameters to the model suggests that the value calculated for δ^{13}C-CO_2 evaded to the atmosphere is key for completing the isotope balances, and calculating the δ^{13}C of the sediments. Flux calculations suggest that detailed lake surface measurements must be collected at the onset of and times surrounding the fall turnover for accurate calculation of δ^{13}C-CO_2 lost to the atmosphere.

According to the model, the $\delta^{13}C$ of lake sediments is sensitive to the long-term changes in the mass of DOC entering and the areal water discharge in both lakes. The $\delta^{13}C$ of the sediments in Harp Lake is also sensitive to pH and the gas exchange coefficient whereas Dickie Lake is not as sensitive to these inputs due to the size, depth, and carbon content differences between the lakes.

5.2 Introduction

The fate of organic carbon and carbon cycling within lakes impacts the health of aquatic systems, global carbon budgets, and emissions of greenhouse gases (e.g. CO_2) to the atmosphere. Allochthonous dissolved organic carbon (DOC) exported from terrestrial systems through streams and into lakes can affect water transparency (e.g. Schindler, 1971; Schindler and Curtis, 1997) and thermocline depth (Perez-Fuentetaja et al., 1999; Schindler, 2001), nutrient availability due to binding of metals (Wetzel, 2001), lake metabolism (e.g. Cole et al., 2006), and food web energy sources (Pace et al., 2004). DOC can also be mineralized releasing CO_2 to the atmosphere (Algesten et al., 2003) or sequestered sediment (Dillon and Molot, 1997a; Molot and Dillon, 1996; Molot and Dillon, 1997b).

Carbon mass budgets are often used in aquatic systems to examine carbon controls and sources. Commonly, only one component of the carbon cycle is examined (e.g. dissolved inorganic carbon (DIC) or DOC; Wetzel et al., 1972; Emerson, 1975; Hesslein et al., 1980) but more recent studies use the complete carbon budgets (DOC and DIC) to examine pathways and sinks of organic matter (Andersson and Sobek, 2006; Sobek et al., 2006; Yang et al., 2008) to assess the potential of lakes as carbon sinks. Using carbon mass balances in high DOC retention lakes can potentially reveal the relative importance of terrestrial and atmospheric derived CO_2 as well as the importance of in-lake mineralization of DOC (e.g. Dillon and Molot, 1997a). In addition, the estimated carbon mass balances from 7 unproductive central Ontario lakes have illustrated the impact of DOC on sedimentation and carbon evasion/invasion (Dillon and Molot, 1997a).

Quay et al. (1986) used mass and isotope balances of DIC to estimate gas exchange and the production rates of organic carbon in Lake Washington, U.S.A.. Raymond and Bauer (2001) looked at the mass balance of both stable and radioactive carbon isotopes ($^{13}C/^{12}C$ and $^{14}C/^{12}C$) to investigate DOC sources and fate in an estuarine environment. The importance of autochthonous and allochthonous carbon to DOC and CO_2 production in lakes has also been examined through mass and isotope balances by Jonsson et al. (2001). Using whole-lake ^{13}C additions, Cole et al. (2002) evaluated the importance of allochthonous and autochthonous carbon within East Long Lake, Wisconsin by constructing a process-based carbon flow mass balance model using ambient and manipulated ^{13}C values for 12 carbon pools. Similarly, Carpenter et al. (2005) used 3 different dynamic models including the same process rich, dual-isotope dynamic flow model as Cole et al. (2002) to estimate allochthony within two ^{13}C enriched unproductive lakes. However, carbon isotope balance studies rarely examine both the organic and inorganic forms of carbon, and have not been used to investigate their role as drivers controlling the $\delta^{13}C$ values of the sediment record in lakes.

According to Dillon and Molot (1997a), long-term mass balance studies using DOC and DIC measurements from stream and precipitation inputs and outflows can be useful in examining the relative importance of atmospheric and terrestrial carbon sources. By calculating annual flux measurements of DIC and DOC in inflows, outflows, and sediments of unproductive lakes, the invasion/evasion of carbon from/to the atmosphere can be examined. Particulate organic carbon (POC) was not measured separately in Dillon and Molot (1997a) as POC in screened water samples was found to be an insignificant compared to DOC concentration (<10%). Thus these mass balances include some unknown part of the POC since DOC samples were not filtered. Accordingly, the following equation can be used to describe the annual mass balances:

(Equation 5.1)

$$DOC_{in} + DIC_{in} = DOC_{out} + DIC_{out} + Sed + Atm$$

where DOC_{in} and DIC_{in} are the mass of carbon transported from the inflows in the form of DOC and DIC (including atmospheric deposition), DOC_{out} and DIC_{out} are the mass of carbon transported from the outflows in the form of DOC and DIC, *Sed* is the mass of carbon lost to sedimentation, and *Atm* is the mass of carbon lost to the atmosphere. Should the *Atm* parameter be negative, DIC would be invading the lake.

Similarly, the complementary annual isotopic budget requires weighted average annual δ^{13}C values for each of the parameters. To calculate a weighted average annual δ^{13}C value, the δ^{13}C and the mass of the carbon entering the lakes through each individual inflow must be considered on a monthly basis, and then weighted annually. The isotope budget was determined using the following equation:

(Equation 5.2)

$$\begin{aligned}&\delta^{13}C{-}DOC_{in}(DOC_{in}) + \delta^{13}C{-}DIC_{in}(DIC_{in}) = \\ &\quad \delta^{13}C{-}DOC_{out}(DOC_{out}) + \delta^{13}C{-}DIC_{out}(DIC_{out}) + \delta^{13}C{-}Sed(Sed) + \delta^{13}C{-}CO_2(Atm)\end{aligned}$$

This study will 1) calculate the isotope mass balance by determining the weighted average annual δ^{13}C signatures of the inflows, outflows, and gas invaded/evaded to the atmosphere, 2) use the completed isotope mass balance and the carbon mass balances presented by Dillon and Molot (1997a) to calculate the expected δ^{13}C of the sediment (δ^{13}C-Sed), 3) examine the sensitivity of the input parameters examined (weighted δ^{13}C values, DOC_{in}, DIC_{in}, q_s (areal water load), v (apparent settling coefficient), pH, and k (gas exchange coefficient)) to the δ^{13}C-Sed, 4) compare the measured δ^{13}C of the sediment to the expected δ^{13}C of the sediment to test the method of Dillon and Molot (1997a) for determining lake carbon mass balances, and 5) assess whether changes in the $\delta^{13}C$ of lake sediments can be driven by changes in the carbon mass balance.

5.3 Methods

Harp and Dickie Lakes are relatively clear oligotrophic headwater lakes located approximately 200 km north of Toronto in the Muskoka-Haliburton region on the southern tip of the Precambrian Shield. Their watersheds generally contain tills (<1m), forested primarily by deciduous trees. Inflow streams also travel through beaverponds, wetlands, and bogs en route to the lakes. Lake catchments are divided into a series of sub-catchments based on surface drainage patterns (Figure 5.1). More detailed physical and chemical descriptions can be found in Dillon et al. (1991) and Dillon and Molot (1997a) for the inflows and lakes respectively (Table 5.1).

To determine the mass weighted average annual $\delta^{13}C$ values of the inflows, outflows, and gas evaded to the atmosphere between 2004 and 2005, samples for DIC, DOC, partial pressure of CO_2 (pCO_2), $\delta^{13}C$-DIC, and $\delta^{13}C$-DOC were collected bimonthly to monthly from the lakes and associated inflows between April (immediately after ice-off) and the end of November prior to ice cover on the lakes. Additional samples for DIC, pCO_2, and $\delta^{13}C$-DIC were collected in the spring of 2007. Winter lake sampling was completed twice, generally in the middle of March, and weekly sampling was performed immediately after ice-off. Additional winter sampling and ice-off samples were collected from the inflows between March to the end of May in 2007 and from the lake (from the end of April to the end of May) to capture the high CO_2 evasion period from the lake.

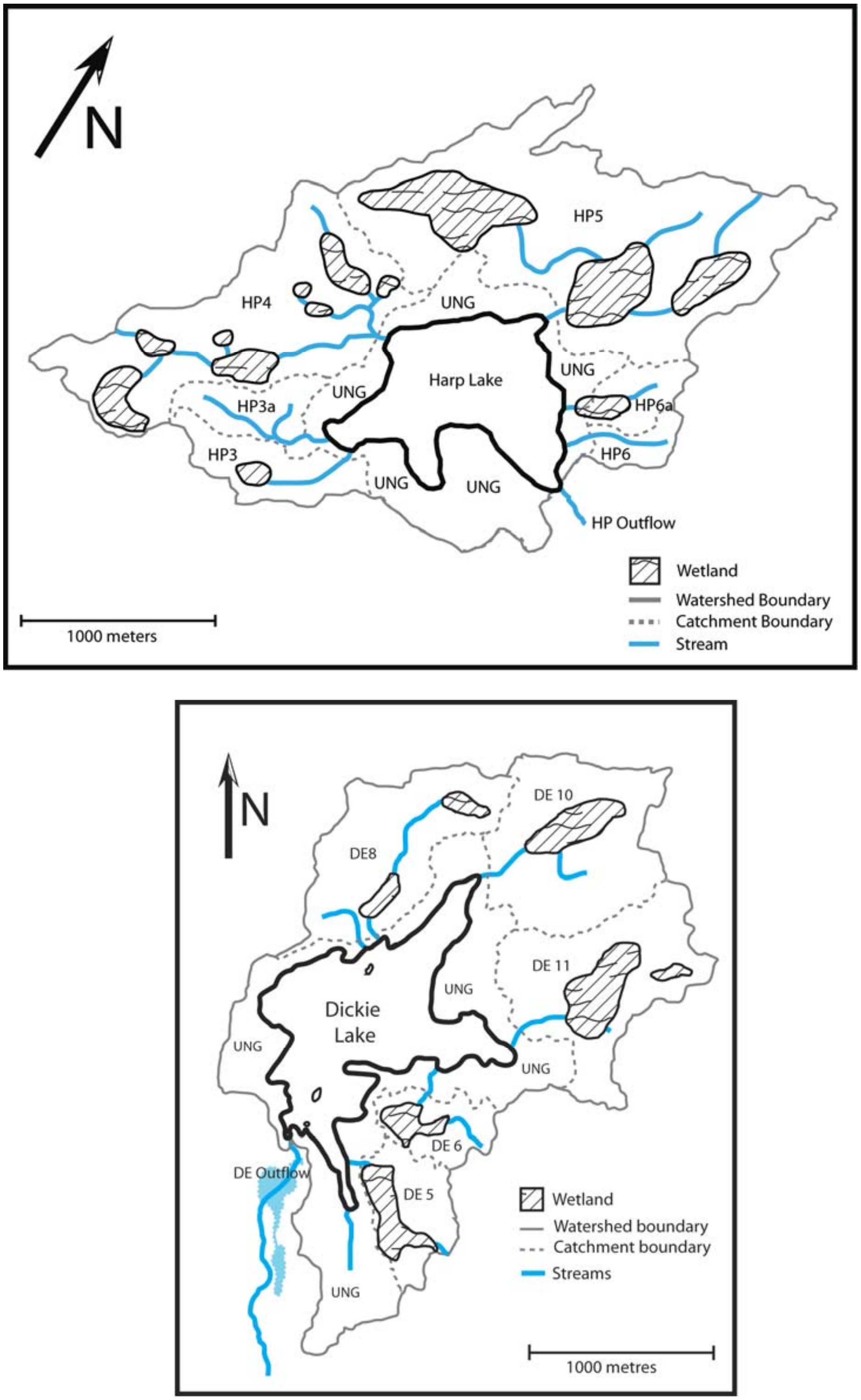


Figure 5.1: Maps of Harp and Dickie Lakes illustrating the watershed boundary, the sub-catchment boundaries, ungauged areas (UNG), inflow streams, and wetlands.

Table 5.1: Physical and chemical characteristics of Harp and Dickie Lake inflows.

	Length[1] (m)	Catchment Area (ha)	Lake Area (ha)	Peat (%)	DIC[2] (mg C /L)	DOC[2] (mg C /L)
Harp Inflow 3	1010	25.99		9.3	1.9	12.0
Harp Inflow 3a	762	19.65		2.9	2.7	3.1
Harp Inflow 4	2040	119.50		8 [4]	1.7	6.7
Harp Inflow 5	1830	190.50		13.3	3.8	16.0
Harp Inflow 6	701	9.97		10 [4]	3.1	8.8
Harp Inflow 6a	610	15.28		8.5	3.8	12.3
Harp Outflow	n/a			n/a	1.6	4.6
Harp Lake	n/a	470.70	71.38	n/a	1.5[3]	3.9
Dickie Inflow 5	762	29.98		25.4	6.3	16.2
Dickie Inflow 6	488	21.80		22.0	3.0	21.5
Dickie Inflow 8	1220	66.96		8.2	4.7	22.4
Dickie Inflow 10	975	78.89		17.1	2.7	21.7
Dickie Outflow	n/a			n/a	1.0	6.2
Dickie Lake	n/a	406.40	93.60	n/a	0.9[3]	5.1

[1] Dillon et al., (1991)

[2] Average DIC and DOC values of weekly measurements from 2004-2007 (n = 127-179; OME unpublished)

[3] Annual weighted concentrations (OME, unpublished)

[4] Eimers et al., (2008)

DIC samples were collected in 15 mL Wheaton bottles, capped with baked BD vacutainer stoppers without headspace, and preserved with 0.02 mL of a saturated $HgCl_2$ solution. Samples were acidified with 85% H_3PO_4 to a pH < 2 after a 5 mL helium headspace was added. To equilibrate headspace and liquid concentrations, acidified samples were shaken on an orbital elliptical shaker for 1.5 hours. Concentrations were measured by equilibrated headspace on a Shimadzu GC-8A Gas Chromatograph fitted with a methanizer (Ni catalyst, He gas carrier, FID detector) with an uncertainty of < 5% (Stainton, 1973).

DOC samples were filtered to 0.45 μm, and acidified with 20% HCl to approximately pH 4 after collection. Samples were analyzed on a total organic carbon analyzer (Dohrmann DC-190) with a maximum error of ± 0.3 mg/L after being acidified by the instrument with 85% H_3PO_4 to a pH of 2-3 and sparged to remove DIC.

δ^{13}C-DIC samples were collected in 125 mL Wheaton serum bottles without headspace, capped with baked BD Vacutainer stoppers, and preserved with 0.3 mL of a saturated solution of $HgCl_2$. A helium headspace was created (5 mL He: 155 mL water) and samples were acidified with 85% H_3PO_4 to a pH less than 2. Samples were shaken for a minimum of 1.5 hours to equilibrate the gases between dissolved and headspace phases. Headspace gas was analyzed on a Micromass Isochrom gas chromatograph combustion isotope ratio mass spectrometer (GC-C-IRMS) at the Environmental Isotope Laboratory (EIL), Waterloo, Ontario. Precision of this analysis is less than ± 0.3‰. Periodically, duplicate samples were analyzed and results were within 0.3‰ of each other. Low-concentration samples were either extracted offline (Heemskerk and Diebolt, 2006) and analyzed on a Prism 903 dual inlet mass spectrometer or on a Carlo Erba 1110 EA coupled to a Delta Plus XP CF-IRMS, also at EIL.

δ^{13}C-DOC samples were collected by filtering water through GF/F filters (nominal pore size of 0.7μm). The filtrate was acidified with 20% HCl to a pH of 4.5, freeze-dried, and run on a Carlo Erba 1105 Elemental Analyzer coupled to a Micromass Isochrom IRMS with a precision of ± 0.2‰ at EIL, Waterloo, Ontario.

To supplement these data, weekly to monthly DIC, DOC, $p\text{CO}_2$, δ^{13}C-DIC and δ^{13}C-DOC samples from 1990-1992 in the Harp Lake watershed (Schiff and Aravena, unpublished) were also used to construct the isotope budget. These supplementary Harp and Dickie Lake inflow data were either used to augment the measurements from this study or provide data where no data were available. These DIC concentration samples were analyzed by the Ontario Ministry of the Environment (OME) colourmetrically using an autoanalyzer with a phenolphthalein indicator (Dillon and Molot, 1997a) while DOC concentrations were analyzed using the persulfate oxidation method (OME, 1983). Samples for δ^{13}C-DIC were acidified and the CO_2 was collected and analyzed at EIL (Aravena et al., 1992). δ^{13}C-DOC was sampled, and analyzed using the methods reported by Schiff et al. (1990). Additionally, supplementary δ^{13}C-DOC data from the inflows to Dickie Lake were obtained from Humphries (2003) and Sentance (2006).

Cores from the middle of Harp and Dickie Lakes had previously been ^{210}Pb-dated (Paterson, unpublished). The Harp core was previously analyzed for δ^{13}C (Schiff, unpublished), and the Dickie core required δ^{13}C analysis (Table 5.2). Analyses were performed as above with a precision of ± 0.2‰ at EIL.

The OME collected DOC and DIC samples from the inflows and the outflows of Harp and Dickie Lakes every 1 to 4 weeks (Dillon and Molot, 1997a) as part of their ongoing monitoring of these catchments over the last 30 years. Concurrently, they also continuously monitored stream stage at stream weirs or flumes and constructed stage-discharge relationships. The OME compiled monthly DOC and DIC data to complete monthly DOC and DIC mass balances used by Dillon and Molot (1997a). More details on the collection methods and analysis of the DOC and DIC concentration samples and construction of the mass balances can be found in Dillon and Molot (1997a). Although Dillon and Molot (1997a) used mass balances from 1981-1989 in their study, to examine the inter-annual variability over a longer time scale, mass budget data from 1978 to 1998 are used in this study.

Table 5.2: Range of ^{13}C isotope data from inflows, outflows, and surface waters, and the calculated mass weighted average, minimum, and maximum annual ^{13}C values using measured ^{13}C values and the carbon budgets from 1978-1998. Mass weighted annual ^{13}C signatures were calculated for each year of the balance to provide a range of ^{13}C mass weighted annual signatures. The calculated ^{13}C sedimented is determined using the mass balances and solving for the ^{13}C-Sed parameter. Measured sedimentation is actual ^{13}C analyses on the sediments of the lakes. Note that the ^{13}C-precipitation is not included in the minimum and maximum ranges of the inflows, however, it was included in calculations.

	Harp Lake						**Dickie Lake**					
	Loading Rate[1] (gC/m^2/yr)	***Measured δ^{13}C***		***Mass Weighted Annual δ^{13}C***			Loading Rate (gC/m^2/yr)	***δ^{13}C range (‰)***		***Mass Weighted Annual δ^{13}C***		
		Min	Max	Min	Max	AVG		Min	Max	Min	Max	AVG
DOC$_{IN}$	28.9	-27.7	-26.2	-26.9	-26.7	-26.8	31.2	-28.8	-26.6	-27.3	-26.8	-27.1
DIC$_{IN}$	7.85	-24.4	-11.7	-20.5	-19.2	-19.9	7.35	-23.7	-15.8	-21.9	-20.7	-21.3
DOC$_{OUT}$	16.9	-27.3	-26.3	-26.9	-26.7	-26.9	14.2	-27.1	-26.6	-26.9	-26.9	-26.9
DIC$_{OUT}$	6.35	-17.4	-7.4	-17.1	-14.9	-16.0	2.53	-18.9	-6.1	-16.2	-13.7	-15.1
Gas Exchange*	7.17	n/a	n/a			-21.9	11.7	n/a	n/a			-25.7
Sedimentation (calculated)	6.26	n/a	n/a			-34.7	10.1	n/a	n/a			-27.7
Sedimentation (measured)		n/a	n/a			-29.9		n/a	n/a			-30.0

[1] from Dillon and Molot (1997a)

* calculated using ^{13}C-DIC and CO_2 saturation data; interpolated between sampling dates

Since the OME mass balances were calculated on a monthly basis, samples for DIC, DOC, pCO$_2$, δ^{13}C-DIC, and δ^{13}C-DOC were collected weekly to monthly to complete the complementary isotope balance. To determine the weighted average annual δ^{13}C values for DIC and DOC entering and exiting the lakes, monthly δ^{13}C values were calculated as the arithmetic average of 1 to 8 samples per month. For months with no data, the δ^{13}C values were interpolated between months with existing data. To determine the weighted annual δ^{13}C value, average monthly δ^{13}C values were weighted by the mass of carbon entering the lakes each month. This was done for the 20 years of monthly mass balance data to determine the variability in the weighted average annual δ^{13}C value.

The net δ^{13}C-CO$_2$ lost to the atmosphere through gas exchange was calculated from ice off to ice cover using lake surface δ^{13}C-DIC values, pCO$_2$, and DIC concentrations. Weekly measurements were used in the month proceeding ice off because of the expected high fluxes of CO$_2$ with low δ^{13}C values from the ice-cover season, and monthly measurements were used for the remainder of the ice-free season. Due to preservational and/or analytical issues, complete data sets of the required parameters were not available to calculate the net δ^{13}C-CO$_2$ evaded from the lake in all years. In 2005, CO$_2$ concentrations from Harp Lake were calculated using measured DIC concentrations and pH collected and measured by the OME (on the same day as DIC). Surface water saturation CO$_2$ concentration was calculated (based on temperature), and since the lakes were almost always supersaturated, CO$_2$ evasion to the atmosphere occurred. The net annual CO$_2$ ((Equation 5.3) and δ^{13}C-CO$_2$ ((Equation 5.4) fluxes were calculated for each day according to the following equations:

(Equation 5.3)

$$CO_2\ Flux = k(CO_{2sat} - CO_{2\,in\,situ})$$

(Equation 5.4)

$${}^{13}C/{}^{12}C{-}CO_2\,Flux = k\alpha_{GK}\left[\left({}^{13}C/{}^{12}C{-}CO_{2atm}\right)\left(CO_{2sat}\right)\left(\alpha_{G_{Eq}}\right) - \left({}^{13}C/{}^{12}C{-}CO_{2insitu}\right)\left(CO_{2insitu}\right)\right]$$

where k is the gas exchange coefficient, $CO_{2\ sat}$ and $CO_{2\ in\ situ}$ are the concentrations of CO_2 at saturation, and in the lake water respectively, ${}^{13}C/{}^{12}C\text{-}CO_{2\ atm}$ is the atmospheric ${}^{13}C/{}^{12}C\text{-}CO_2$ (where $\delta^{13}C\text{-}CO_2$ is –8‰; e.g. Quay et al., 1986; Levin et al., 1987), ${}^{13}C/{}^{12}C\text{-}CO_{2\ in\ situ}$ is the measured $\delta^{13}C\text{-}CO_2$ at the lake surface converted from ‰ to ratio, α_{GK} is the kinetic fractionation factor associated with gas exchange (0.9987; Clark and Fritz, 1997), and α_{GEq} is the equilibrium fractionation factor for gas exchange (0.9989; Mook et al., 1974). These values were summed to determine the net annual flux and used to calculate the average annual weighted ${}^{13}C/{}^{12}C\text{-}CO_2$ ratio, which was converted to a $\delta^{13}C\text{-}CO_2$ value. Concentration and temperature data required for the calculations were linearly interpolated between sampling points. Since the calculated values are net flux and net $\delta^{13}C\text{-}CO_2$ values evaded from the lakes, they incorporate the influx of atmospheric CO_2 (with a $\delta^{13}C\text{-}CO_2$ of -8‰) into the lakes.

To investigate the sensitivity of the isotope mass balance (and carbon inputs) to the lake sediment $\delta^{13}C$ value, a dynamic mass and isotope budget model was constructed for Harp and Dickie Lakes using Stella v9.0. The model used the carbon inputs from Dillon and Molot (1997a), and the weighted average annual $\delta^{13}C$ values for the inflows, outflows, and CO_2 lost to the atmosphere to calculate the expected $\delta^{13}C$ of the lake sediments. Rearranging Equation 5.2, the $\delta^{13}C$ of the lake sediments can be calculated:

(Equation 5.5)

$$\delta^{13}C{-}Sed = \frac{\left[\left(\delta^{13}C{-}DOC_{in}(DOC_{in}) + \delta^{13}C{-}DIC_{in}(DIC_{in})\right) - \left(\delta^{13}C{-}DOC_{out}(DOC_{out}) + \delta^{13}C{-}DIC_{out}(DIC_{out}) + \delta^{13}C{-}CO_2(Atm)\right)\right]}{Sed}$$

DOC_{in} and DIC_{in} input parameters are taken from Dillon and Molot (1997a).

The DOC_{out} and DIC_{out} parameters are calculated based on the mass of DOC and DIC in the lakes according to:

(Equation 5.6)

$$DOC_{out} = \frac{DOC_{in\ lake} \times q_s \times A}{V}$$

(Equation 5.7)

$$DIC_{out} = \frac{DIC_{in\ lake} \times q_s \times A}{V}$$

where, $DOC_{in\ lake}$ is the mass of DOC within the lake, q_s is the areal water load, A is lake area, and V is lake volume. The mass of CO_2 evaded to the atmosphere (*Atm*) was also calculated within this model:

(Equation 5.8)

$$Atm = \frac{k\left(CO_{2\ in\, situ} - CO_{2\ sat}\right) \times A}{V}$$

In this model, the CO_2 mass in the lake was calculated from DIC in the lake ($DIC_{in\ lake}$), pH and the acid dissociation equations (Wetzel, 2001).

The mass of carbon lost to the sediment was calculated via a sediment partition (sed partition) coefficient based on the DOC removed from the lake:

(Equation 5.9)

$$Sed = DOC_{removed} \times \ sed\ partition$$

The $DOC_{removed}$ and the sed partition were calculated using:

(Equation 5.10)

$$DOC_{removed} = \frac{DOC_{in\ lake} \times v \times A}{V}$$

(Equation 5.11)

$$sed\ \ partition = \frac{Sed_{D\&M}}{DOC_{in} - DOC_{out}}$$

where v is the apparent settling coefficient, and $Sed_{D\&M}$ is the average carbon sedimentation calculated by Dillon and Molot (1997a).

Most of the model input parameters were either provided by Dillon and Molot (1997a) or calculated from field measurements (Table 5.3). It was necessary to adjust the pH in Harp and Dickie Lakes, and q_s and v in Harp Lake for the masses of DOC_{out}, DIC_{out}, *Sed*, and *Atm* in the model to equal the average masses calculated by Dillon and Molot (1997a) from the mass balances suggesting that there might be errors associated with the mass balances and/or these measured/calculated input parameters.

Table 5.3: Input parameters to the model.

Parameter	Source of Data
δ^{13}C-DOC_{IN}	Calculated from monthly measurements
δ^{13}C-DIC_{IN}	Calculated from monthly measurements
δ^{13}C-DOC_{OUT}	Calculated from monthly measurements
δ^{13}C-DIC_{OUT}	Calculated from monthly measurements
δ^{13}C-CO_2 (GE)	Calculated from monthly measurements
$DOC_{IN\ LAKE}$	Calculated from data in Dillon and Molot (1997a)
$DIC_{IN\ LAKE}$	Calculated from data in Dillon and Molot (1997a)
DOC_{IN}	Calculated by Dillon and Molot (1997a)
DIC_{IN}	Calculated by Dillon and Molot (1997a)
pH	Annual Ice off average measured by OME[1,2]
qs	Calculated by Dillon and Molot (1997a)[1]
v	Calculated by Dillon and Molot (1997a)[1]
k	Calculated from wind speed measurements
sediment partition coefficient	Calculated from Dillon and Molot (1997a)

[1] Adjusted slightly to improve fit in Harp Lake to carbon mass balances of Dillon and Molot (1997a)

[2] Adjusted slightly to improve fit in Dickie Lake to carbon mass balances of Dillon and Molot (1997a)

5.4 Results and Discussion

To calculate the isotope mass balance, the following must be determined:

1) the weighted average annual δ^{13}C-DIC and δ^{13}C -DOC of the inflows,
2) the importance of precipitation on the weighted average annual δ^{13}C-DIC and δ^{13}C-DOC values of the inputs,
3) the weighted average annual δ^{13}C-DOC and δ^{13}C-DIC of the outflows, and
4) the weighted average annual δ^{13}C-CO_2 evaded to the atmosphere.

5.4.1 δ^{13}C-DIC of the Inflows (δ^{13}C-DIC$_{in}$)

Average monthly DIC concentrations for the Harp and Dickie inflows ranged between approximately 1 mg C/L and 9 mg C/L (Figure 5.2). Concentrations were elevated in the winter, peaking around February to March, and then declined to a minimum in April; after winter, DIC concentrations increased throughout the spring and summer, peaking between June and September, then concentrations steadily declined in the fall.

The ranges of the δ^{13}C-DIC measurements of the inflows between the early 1990's and 2004-2005 differed; however, average values in the two time periods were similar. Seasonally, δ^{13}C-DIC in streams generally increased from ice-off to a maximum in July or August, after which values declined. The δ^{13}C-DIC of the inflows ranged between –23.7‰ to –15.8‰ in Dickie Lake and –24.4‰ to –11.7‰ in Harp Lake (Figure 5.3). The overall range of δ^{13}C-DIC over all of the inflows to each lake was up to ~13‰ (e.g. ~–25‰ to –12‰). However, the annual variations observed within each individual stream (~7‰: Figure 5.3) and the range in mass weighted annual δ^{13}C signatures (1.3‰: Table 5.2) are both smaller than the ranges observed over all the inflows (~13‰).

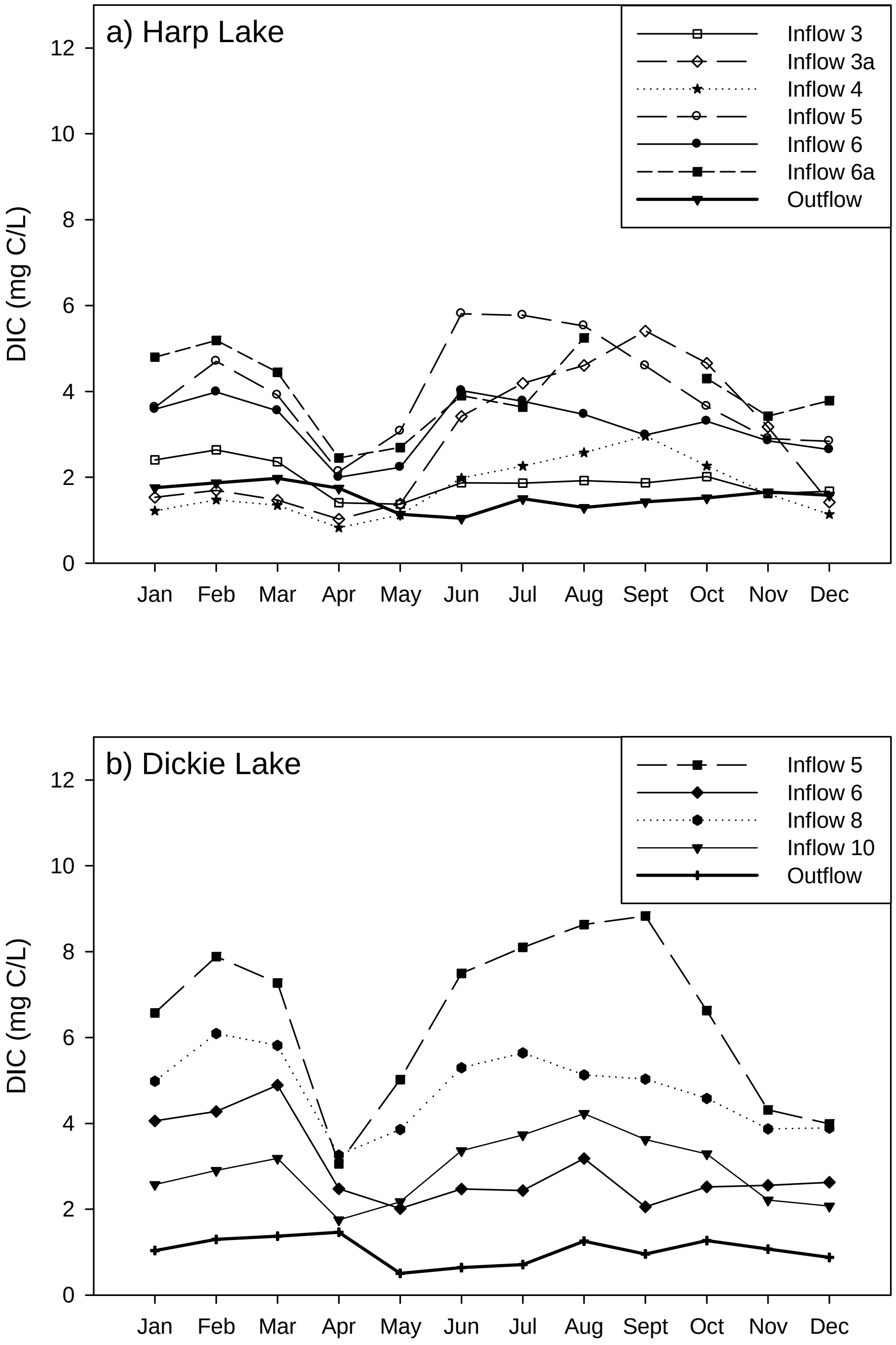
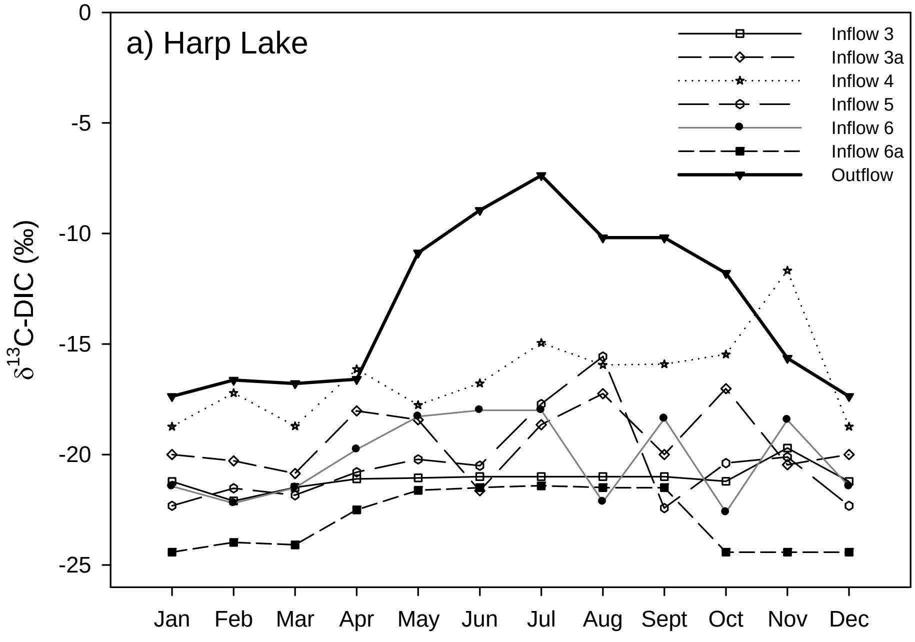


Figure 5.2: Annual variability in DIC concentrations for a) Harp Lake and b) Dickie Lake. DIC concentrations were based on monthly averaged values of weekly DIC collected from 2004-2007 (OME, unpublished).



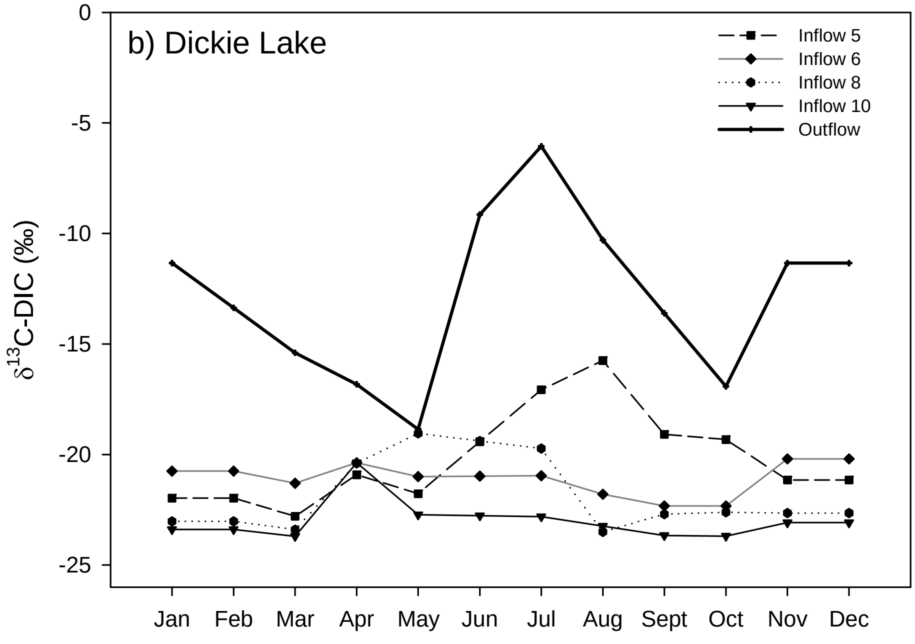
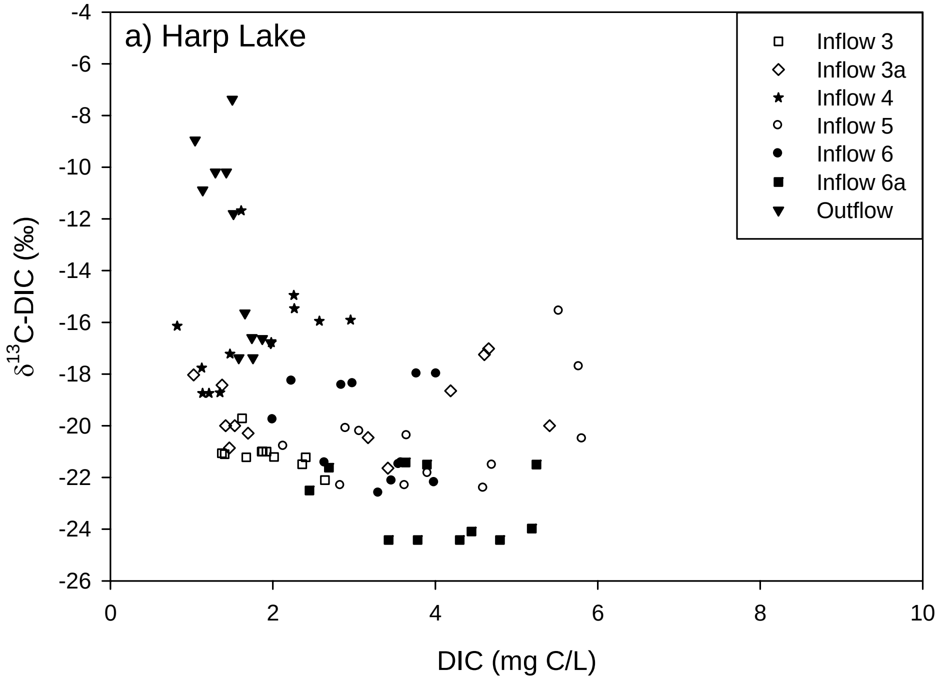


Figure 5.3: Annual variability in monthly averages of δ^{13}C-DIC values for a) Harp Lake and b) Dickie Lake. During months with extremely low flow or no flow at the time of sampling, δ^{13}C-DIC values were linearly interpolated using existing δ^{13}C-DIC measurements. Precision is 0.3 ‰.

In Harp Lake Inflow 3, generally as DIC concentrations increased, the δ^{13}C-DIC values decreased (Figure 5.4) suggesting that the stream was degassing increasing the δ^{13}C-DIC, or the source of DIC changes slightly as the water table level changes affecting diffusion of CO_2 out of the soil. Doctor et al. (2008) found increased outgassing with increases in δ^{13}C-DIC values along a forested stream during the growing season, since there was likely an increase in soil CO_2 production (creating a larger pCO_2 gradient between the soil and atmosphere), with more pronounced stream CO_2 outgassing expected in the warmer months. Outgassing changes the δ^{13}C-CO_2 due to isotopic fractionation (i.e. between $CO_{2\ (aq)}$ and $CO_{2\ (g)}$, HCO_3^- and CO_2 etc.). DIC is partitioned into HCO_3^- and $CO_{2\ (aq)}$ based on pH, and there is a large equilibrium fractionation between HCO_3^- to CO_2 (Mook et al., 1974), with an isotopic difference of ~9‰. The CO_2 lost to the atmosphere is ~1‰ different than the $CO_{2\ (aq)}$ (Zhang et al., 1995), thus the δ^{13}C-DIC increases as more CO_2 is lost to the atmosphere. Similarly, a small kinetic fractionation has been observed during dissolution of CO_2 in water (Usdowski and Hoefs, 1990). However, there is no evidence to suggest that the changes in δ^{13}C-DIC in the remainder of the Harp and Dickie Lake inflows were due to outgassing.



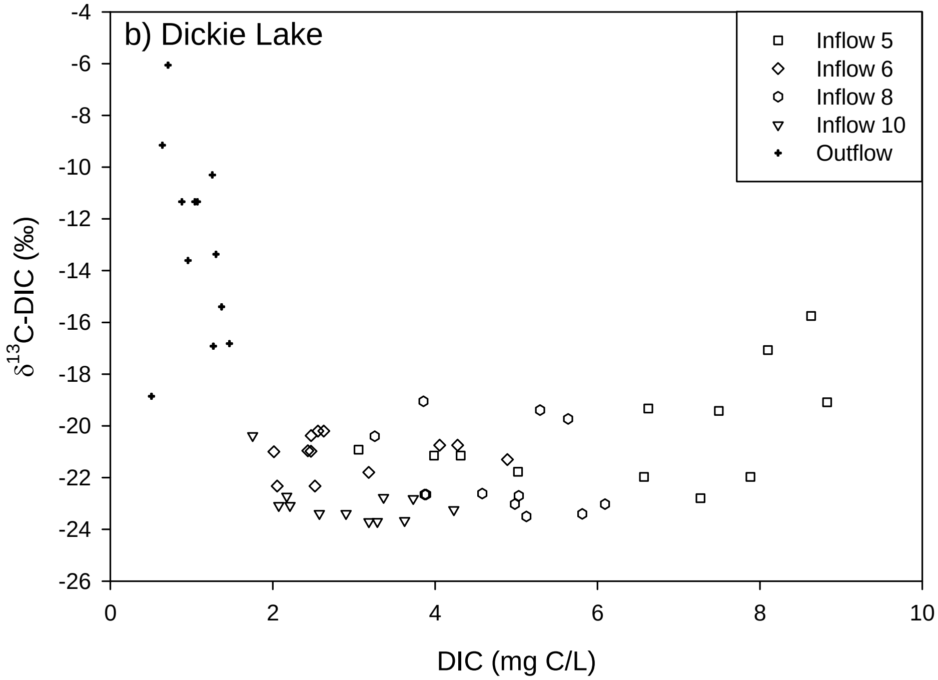


Figure 5.4: Annual variability in DIC versus δ^{13}C-DIC for a) Harp Lake and b) Dickie Lake. DIC concentrations are based on average values of weekly DIC collected from 2004-2007 (OME, unpublished).

In Harp Lake Inflows 4, and 5, and Dickie Lake Inflow 5, generally there is a positive relationship between in δ^{13}C-DIC and DIC although the trend is not strong in all cases (Figure 5.4). This suggests that degassing is not prevalent in these stream waters, and that the source of DIC has changed and caused the variation in δ^{13}C-DIC; however, there is not enough evidence to support this since it is unknown how production has affected the δ^{13}C-DIC. Also, this trend could be observed if the DIC concentration was changing in the system with no change to the δ^{13}C-DIC. The DIC concentrations increase in the remainder of the inflows, yet the δ^{13}C-DIC remains relatively similar on an annual basis also suggesting that the balance of processes affecting the δ^{13}C-DIC may be changing, although conclusive results cannot be made due to lack of evidence.

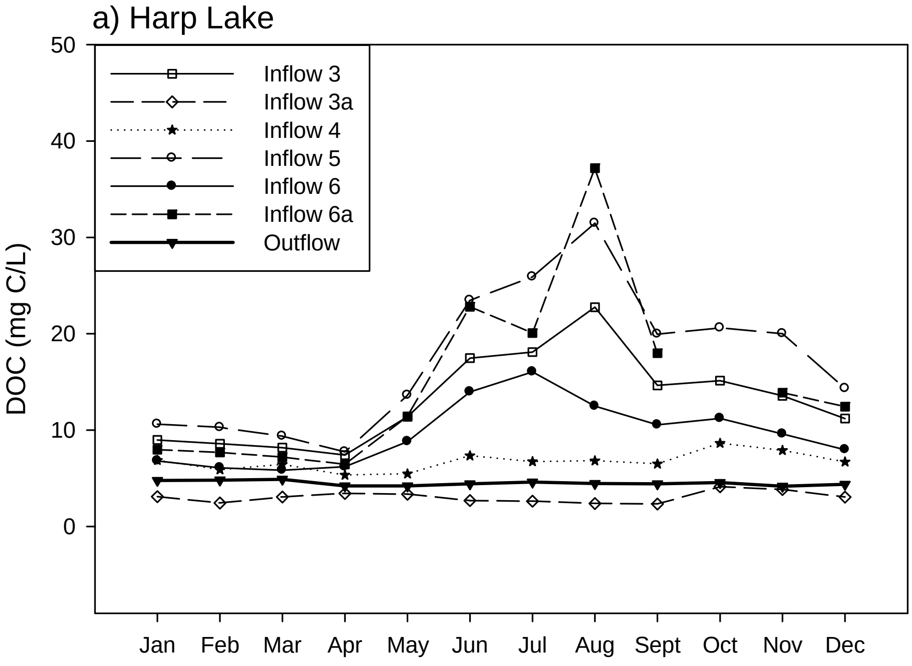
Lower δ^{13}C-DIC values in the late summer suggest that there was less water flow than in spring and the more negative δ^{13}C-DIC values could be due to greater production of soil CO_2. Although not measured in the current study, Aravena et al. (1992) report δ^{13}C values between –21‰ and –25‰ for soil CO_2. However, low δ^{13}C-DIC values in the autumn and winter suggest increased drainage from the catchment during times of high flow affected the δ^{13}C-DIC. Increases in aquatic photosynthesis could increase the stream δ^{13}C-DIC values during the growing season, however, in the early spring during snowmelt, stream temperatures are low, and as the growing season proceeds light becomes limited in the forested catchments (although not in the wetland ponds and streams) and could affect productivity.

The δ^{13}C-DIC inflow values observed in this study were lower than many of the previously reported δ^{13}C-DIC stream data. Findlay (2003) observed a minimum δ^{13}C-DIC of –17.7‰ during summer baseflow of small streams from a temperate forested watershed in northern California and found increases to –6.4‰ with increasing stream size. Many other streams from temperate watersheds have been found to range between –9‰ and –13‰ in summer months (cited in Finlay, 2001) while springs and groundwater ranged between –15‰ to –18‰ and –15‰ to –19‰, respectively (cited in Finlay, 2003). The variations observed could be a result of the DIC sources in the region as the main DIC sources in river water are soil CO_2, carbonate mineral dissolution, and exchange of atmospheric CO_2 at the air water interface (Yang et al., 1996). If carbonate dissolution prevailed in the Harp Lake catchment, it would produce δ^{13}C-DIC signatures around –11‰ in closed systems (assuming soil CO_2 = -22‰; carbonate = 0‰; Aravena et al., 1992) and between –19‰ to –13‰ in open systems (Deines et al., 1974; Wigley, 1975; Aravena et al., 1992). However, there is no carbonate in the Harp catchment and the δ^{13}C-DIC of the groundwater from wells close to recharge and discharge areas, in addition to the middle of the basin at Harp Lake, lies within the range of -22‰ to -24‰, typical isotope values for CO_2 in soils without $CaCO_3$. In conjunction with ^{14}C and soil CO_2 data, these data have been shown to reflect silicate weathering of underlying geology in the catchment (Aravena et al., 1992). The isotopic composition of DIC, in the case of silicate weathering, will reflect the soil CO_2 produced from root respiration and soil organic matter decomposition, which in turn is related to the type of vegetation cover (Amiotte-Suchet et al., 1999). Low variability in the δ^{13}C-DIC values from November to May can be explained by the loss of vegetation in autumn and subsequent snow cover throughout the winter. During this time the snow and ice cover provides a "cap" creating a closed system where diffusive CO_2 losses are low (compared to summer) and the water in the streams (and under the ice) are reflective of the soil CO_2, even though there is reduced soil respiration. As spring melt causes the snow pack and ice to recede, diffusive losses increased and the soil CO_2 increases, causing increased outgassing and a change in δ^{13}C-DIC further illustrating that DIC is controlled by silicate weathering (and soil CO_2).

Using the monthly average $\delta^{13}C$ values, the mass weighted average annual inflow $\delta^{13}C$-DIC values of Dickie and Harp Lake inflows are -21.3‰ and -19.9‰ respectively (Table 5.2).

5.4.2 $\delta^{13}C$-DOC of the Inflows ($\delta^{13}C$-DOC$_{in}$)

Average monthly inflow DOC concentrations ranged between approximately 3 mg C/L and 50 mg C/L (Figure 5.5; OME, unpublished). Concentrations were low in April, and steadily increased in all Dickie inflows. The majority of the Harp inflows peak between June and September. After the peak concentration, the DOC concentrations steadily declined in the fall until they reached a minimum in April. DOC concentrations in Harp Inflows 3a and 4 did not show a lot of annual variability.



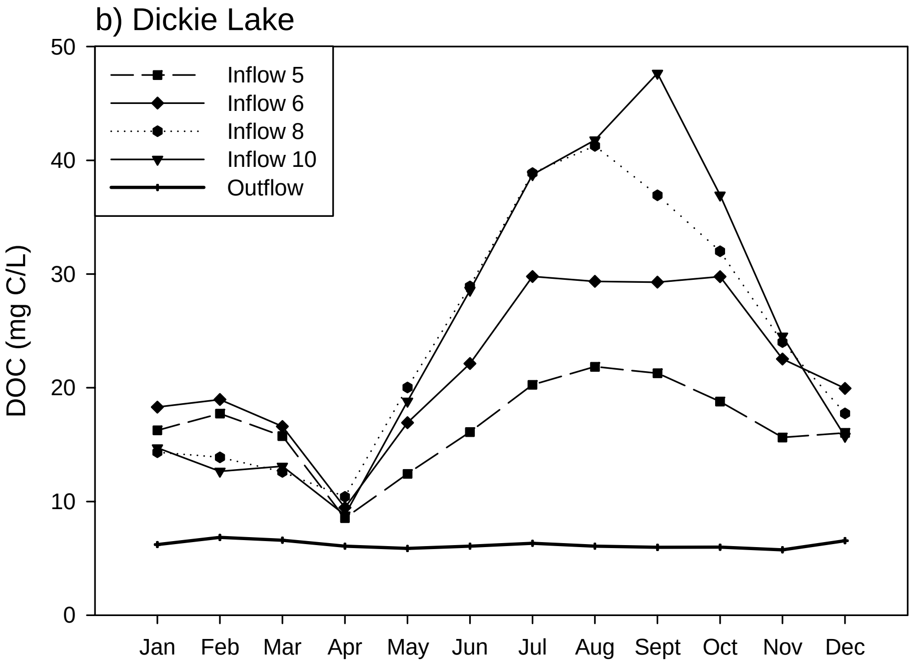


Figure 5.5: Annual variability in DOC concentrations for a) Harp Lake and b) Dickie Lake. DOC concentrations were based on monthly averaged values of weekly DOC collected from 2004-2007 (OME, unpublished).

In contrast to the isotopic composition of the stream δ^{13}C-DIC values, there was little inter-annual variation in δ^{13}C-DOC values of the inflows. Additionally, inflow and outflow δ^{13}C-DOC values generally did not vary greatly between similar months in the early 1990's and 2004-5 and thus the data were used in conjunction with each other to augment existing data, or provide values where data was unavailable. Dickie and Harp Lake inflows ranged between –28.8‰ to –26.6‰ (mass weighted average annual δ^{13}C = –27.1‰) and –27.7‰ to –26.2‰ (mass weighted average annual δ^{13}C = –26.8‰) respectively (Figure 5.6). The similarities between annual δ^{13}C-DOC values of inflows, and between the sub-catchments within the watersheds (with the exception of Dickie Lake inflow 5) indicated that DOC sources in the streams did not change annually. Since the δ^{13}C-DOC values were similar to shallow soil percolates from the LFH horizon (-27.9‰; Schiff et al., 1990) and the DOC content for streams, lysimeter and groundwaters (–27‰ to –28‰; Trumbore et al., 1992), suggests that the DOC source was from the terrestrial catchment. Similar conclusions on the origin of DOC in streams have also been drawn by Duan et al. (2007), who noted that dissolved organic matter (DOM) parameters including δ^{13}C-DOM for Pearl River, a small blackwater river, are likely controlled by hydrologic conditions affecting organic matter transport from local or deep soils and not in-situ processing as in larger rivers such as the Mississippi. The δ^{13}C-DOC from Dickie Lake inflow 5 was approximately 1‰ to 1.5‰ lower than the other inflows in the Dickie Lake catchment and it noticeably declined to a minimum in the summer months. This catchment contains a wetland comprised of a floating peat layer underlain by a water pocket. Since the δ^{13}C of *Sphagnum* in the Dickie 5 catchment is lower and lays between –26.6‰ and –27.1‰, and the peat ranges between –25.3‰ and -27.7‰ with depth (Schiff, unpublished data), it is likely that peat is a more important carbon source than shallow soil percolates to the stream water during the winter and spring months when flow was high and DOC was being flushed from the wetlands. In the summer, the floating peat mat compressed and sometimes did not float resulting in a disconnection between the upland and wetland systems. δ^{13}C-DOC values in the pocket water under the peat were –28.5‰ to –29.1‰ (Schiff, unpublished) indicating this water could be draining to the streams suggesting its importance to the stream in the summer months. Although local vegetation and wetland vegetation (e.g. *Sphagnum*, tamarack, fern, labrador tea and leatherleaf) have δ^{13}C values between –30.6‰ and –28.0‰ (Schiff, unpublished), they were above the water table and likely did not contribute to the observed minimum during the summer months.

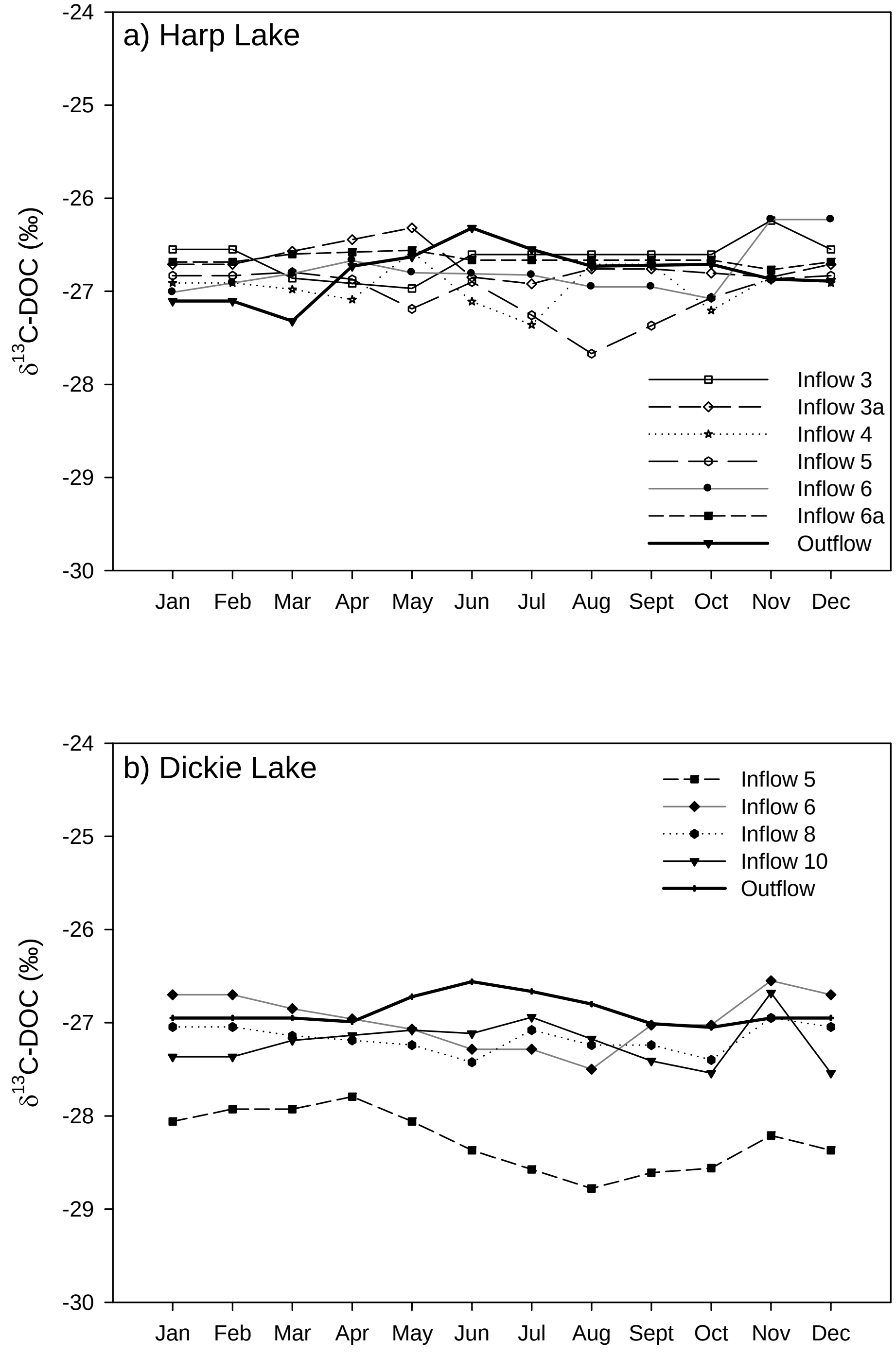


Figure 5.6: Annual variability in δ^{13}C-DOC values for a) Harp Lake and b) Dickie Lake. During months with no data, δ^{13}C-DOC values were linearly interpolated. Precision is 0.2 ‰.

Fresh plant material and relatively undecomposed litter in the Harp catchment was more depleted (–28‰ to –30‰) than the stream δ^{13}C values (Aravena et al., 1992; Trumbore et al., 1992) and their δ^{13}C values lie within the range observed for C3 plants (–24‰ to –29‰; Deines, 1980). The narrow ranges of the 2004-2007 δ^{13}C-DOC data were similar to the data from Schiff et al. (1997) where the δ^{13}C-DOC of Harp inflows ranged between –28.6‰ to –25.5‰ with more than 80% of the data within 0.5‰ of –27.0‰. Averages of monthly δ^{13}C-DOC data from both sets of data were used to calculate the mass weighted average annual δ^{13}C-DOC. δ^{13}C-DOC values were similar to those from summer stream water and water table well samples, which ranged from –27.3‰ to –28.3‰, in a region of the Allequash Creek catchment, Wisconsin, where the local hydrology influenced the δ^{13}C-DOC in small streams entering Lake Allequash (Elder et al., 2000). Similar to the Dickie watershed, the Allequash catchment contains extensive peatlands upstream of the lake and δ^{13}C-DOC values reflected this carbon source, in addition to local vegetation.

5.4.3 δ^{13}C of Atmospheric Deposition

From the mass budgets between 1978 to 1998, precipitation was calculated to be, on average, approximately 2.6% and 3.3% of the total DIC and total DOC inputs, respectively, to both Dickie and Harp Lakes. These averages fell at the lower end of the ranges observed for the contribution of atmospheric deposition to carbon budgets of the lakes included in the study by Dillon and Molot (1997a). In general, DOC inputs via precipitation were highest in the late 1970s then decreased by approximately 50% by 1980, and generally fluctuated between 2% and 4% of the total annual DOC inputs (Figure 5.7). DIC inputs via precipitation were also higher in the late 1970s after which DIC inputs from precipitation decreased around 1980 and fluctuated around 1.5% to 2.5% of the total annual DIC inputs to the lake. An increase in DIC inputs in the mid 1990s was accompanied with lower

DOC inputs (Figure 5.7). No data are available for DIC inputs in precipitation for the last 3 years of the budget, therefore, these years were not used to determine the mean weighted δ^{13}C-DIC values. The atmospheric δ^{13}C-CO_2 and δ^{13}C-DOC of precipitation has been reported as -11.3‰ (Aravena et al., 1992) and -23.9‰ (Schiff et al., 1990). However, since precipitation contributes such a small component of the total DIC and DOC, adjusting these values does not greatly affect the calculation of the average annual mass weighted δ^{13}C-DIC or δ^{13}C-DOC values.

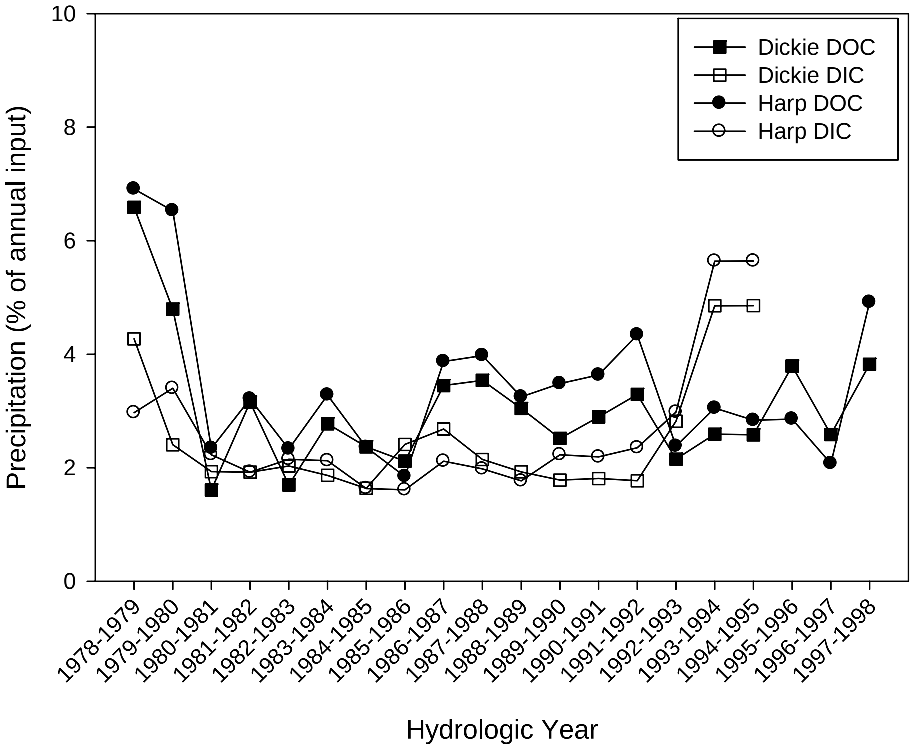


Figure 5.7: DOC and DIC inputs through precipitation as a function of the total annual DOC or DIC inputs. Hydrologic years frun from June 1st to May 31st.

5.4.4 δ^{13}C-DIC of the lake surface water and Outflows (δ^{13}C-DIC_{out})

Average monthly outflow DIC concentrations for Harp and Dickie Lakes ranged between approximately 0.5 mg C/L and 2 mg C/L (Figure 5.2). Concentrations were elevated in the winter, and declined to a minimum in May after ice-off. DIC concentrations slowly increased throughout the spring, summer, and fall, however on an inter-annual basis, there was not much variability in the DIC concentrations exiting the lakes.

The δ^{13}C-DIC leaving Harp and Dickie Lakes via the outflows was annually variable with the δ^{13}C-DIC ranging from –18.9‰ to –6.1‰ for Dickie Lake and–17.4‰ to –7.4‰ from Harp Lake (Figure 5.3). The mass weighted average annual δ^{13}C-DIC values of the outflows were –15.1‰ and –16.0‰ for Dickie and Harp Lake outflows respectively. The δ^{13}C-DIC values of the outflows were greater than the inflows, show more variability than the inflows, and were similar to the surface waters within the lakes (Figure 5.3, Figure 5.8, and Figure 5.9).

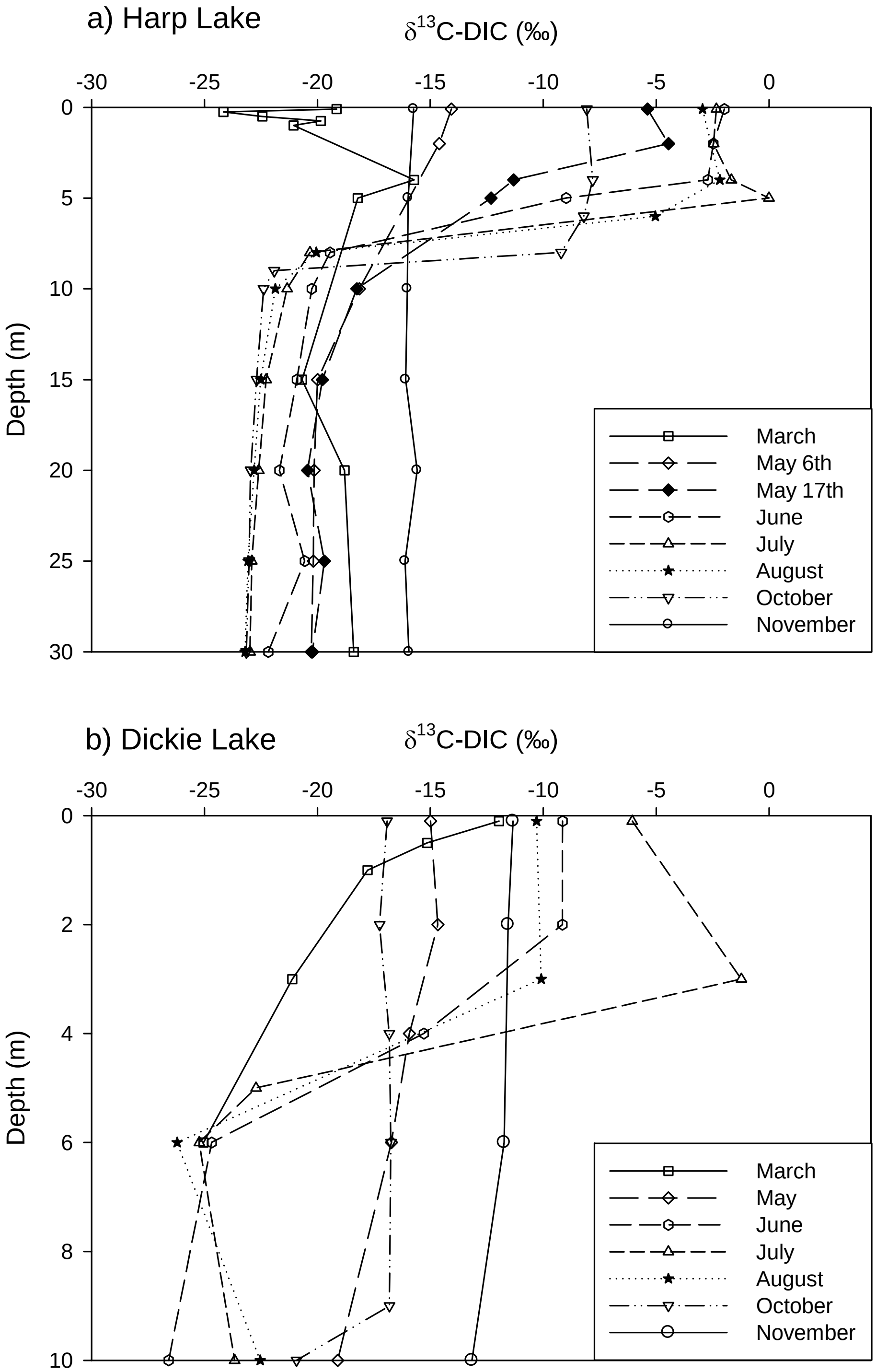


Figure 5.8: Annual variability in δ^{13}C-DIC profiles in a) Harp Lake and b) Dickie Lake. Profiles are from 2004, and measurements have a precision of 0.3‰.

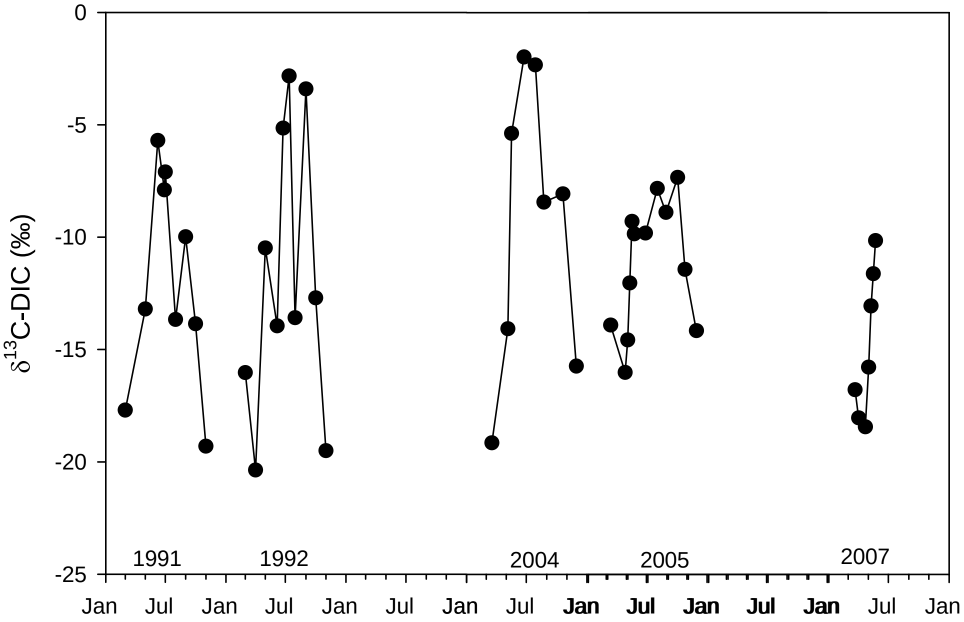


Figure 5.9: Variation in the annual δ^{13}C-DIC of the surface waters of Harp Lake.

The lake surface water δ^{13}C-DIC values increase after ice off, peaking in mid-summer after which they declined until the lakes turned over in the fall. δ^{13}C-DIC values decreased during the winter in Dickie Lake, while they were about constant in Harp Lake (Figure 5.3). The difference in δ^{13}C-DIC between the inflows and the surface waters, and outflows of the lakes suggest that CO_2 was lost from the lake, and/or in-lake processing of the DIC was dominated by preferential uptake of ^{12}C during photosynthesis, both of which would increase δ^{13}C-DIC values during the summer. Photodegradation creates DIC with δ^{13}C-DIC values lower than the ambient δ^{13}C-DIC values, and/or lower than the original δ^{13}C-DOC thus shifting the δ^{13}C-DIC to more depleted values (Chapter 3). In fall, winter, and early spring when temperatures were low and the lakes were ice covered, δ^{13}C-DIC values either remained uniform or they decreased. Since there is little to no carbon isotope fractionation during respiration (e.g. Baril, 2001; Boudreau, 2000; Oelbermann and Schiff, 2008; Venkiteswaran, unpublished data), the decrease in δ^{13}C-DIC during the colder and ice covered months could have been due to oxidation of organic carbon to DIC (Striegel et al., 2001). Also, since gas exchange is limited after ice formation (after the fall turnover), initial mixing of the colder bottom waters after turnover will increase CO_2 concentration and decrease δ^{13}C-DIC by mixing in water with low δ^{13}C-DIC values, characteristic of decomposition/respiration, into the whole lake (Figure 5.8). Therefore, the low hypolimnetic δ^{13}C-DIC values will be recorded in the outflows. However, as winter progresses, the lakes stratify under the ice at which point respiration in the epilimnion and the sediments could have become important to the outflow δ^{13}C-DIC values in the winter and when the lake mixes vertically after ice-off; these processes also occur during the summer and will likely become important at the fall turnover as well. Although winter respiration is slow due to the cold, it could have a greater effect than the rate suggests due to the lack of gas exchange across the ice. Furthermore, the negative relationship between δ^{13}C-DIC and DIC in the outflows (Figure 5.4) suggests that degassing (and/or primary production) heavily influences the δ^{13}C-DIC values of the lake surface waters.

These δ^{13}C-DIC outflow data fit within the range of values measured in the surface waters of lakes (Bade et al., 2004), which show that the large δ^{13}C-DIC variation among lakes was much greater than the temporal changes observed within individual lakes. Using 395 measurements in the literature from 72 freshwater lakes, δ^{13}C-DIC values ranged between -29.6‰ and +2.6‰, and data from Bade et al.'s 32 lakes (2004) exhibited a similar δ^{13}C-DIC range of –31‰ to –2.1‰. These data were used to develop a process-based lake model, which suggested that for most lakes in their data set, low GPP:R (Gross Primary Production to Respiration) ratios were associated with more negative δ^{13}C-DIC values suggesting that it was likely respiration within the surface of the lake controlled the δ^{13}C-DIC of the outflows from fall to early spring. However, as noted above, increased lake mixing will bring hypolimnetic water in which respiration, but no gas exchange and little primary production, have occurred to the surface.

5.4.5 δ^{13}C-DOC of the lake surface waters and Outflows (δ^{13}C-DOC$_{out}$)

Average monthly DOC concentrations for the Harp outflow range between approximately 4 mg C/L and 5 mg C/L, while Dickie outflow DOC concentrations were generally between 6 mg C/L to 7 mg C/L (Figure 5.5; averages from 2004-2007: OME, unpublished). Concentrations showed little annual variability and the intra-annual variability was generally small.

Outflow δ^{13}C-DOC values were not as variable as δ^{13}C-DIC and the average annual δ^{13}C-DOC value of Dickie and Harp Lake outflows was -26.9‰ (Dickie range: -27.1‰ to -26.6‰; Harp range: -27.3‰ to -26.3‰). The range for Harp Lake was similar to published δ^{13}C-DOC values from 20 years earlier (–25.7‰ August 1988; –27.9‰ May 1989; Schiff et al., 1990). Small temporal ranges of δ^{13}C-DOC are common in the literature (e.g. 15 Swedish Lakes: -29.9‰ to –27.6‰, Karlsson et al., 2003; 8 Québec Lakes: –28.8‰ ± 0.6‰, McCallister and del Giorgio, 2008) suggesting that on a temporal basis similar DOC sources or similar processes are controlling δ^{13}C values within the lakes. The δ^{13}C-DOC outflow values were fairly uniform from September through April, but showed a slight increase peaking around June (Figure 5.6). These temporal changes were close to the reported precision of the measurements in Dickie Lake, however, there was a 1‰ variation in Harp Lake δ^{13}C-DOC values. Unlike the δ^{13}C-DOC of the inflows, outflow δ^{13}C-DOC values reached a maximum in the summer suggesting that photodegradation of DOC could be occurring (Ch 3 and 4), or that the relative importance of DOC sources has changed, or that the δ^{13}C value of the source has changed. Overall, the similarily between the δ^{13}C-DOC of the inflows and outflow are likely due to the continuous replenishment of unprocessed or minimally processed DOC from the terrestrial catchment. Elder et al. (2000) observed higher $\delta^{13}C$-DOC values (–24.5‰ to –25‰) in lake outflow samples of Allequash Lake compared to the peat-influenced inflow values (Allequash Creek: –28.3‰) and concluded that outflow values were affected by a combination of sources, whereas the inflows mainly reflected the $\delta^{13}C$ of the peat.

5.4.6 $\delta^{13}C$-CO_2 lost to Gas Exchange ($\delta^{13}C$-CO_2)

In small lakes, the rate of gas exchange between the lake and the atmosphere is calculated from CO_2 saturation in the lake (relative to the atmosphere) and the gas exchange coefficient, k. If wind speed is known, then empirical relationships have been used to estimate k, however, these estimates can span over 2 orders of magnitude (Wanninkhof, 1992). Wind speeds are often low around small sheltered lakes. Below wind speeds of ~2 to 3 m/s (at 10 m height), k cannot reliably be predicted using empirical equations (Crill et al., 1988; Clark et al., 1995; MacIntyre et al., 1995; Ho et al., 1997). Cole and Caraco (1998) estimated a mean k_{600} value of 2.69 cm/h (normalized to a Schmidt number of 600, the Schmidt number of CO_2 at 20ºC) in Mirror Lake, New Hampshire by tracking the mass loss of SF_6 in the lake during a SF_6 tracer experiment. Similarly, a k_{600} of 2.65 cm/h was estimated using the surface water SF_6 data. Crusius and Wanninkhof (2003) measured an average k_{600} of ~4 cm/h in a small oligotrophic lake on the Canadian Shield at the Experimental Lakes Area (ELA).

Cole and Caraco (1998) noted that at low wind speeds (1-2 m/s) k_{600} values were underestimated using the common wind speed to gas exchange relationships of Liss and Merlivat (1986) and Wanninkhof (1992). By combining data from various ecosystems, they created a power function which indicated that at low wind speeds, k_{600} is approximately 2 cm/h. Wind speed and tracer experiments were not performed to determine k in this study, however, wind data from meteorological towers at Harp Lake (from 2003-2007) and near Dickie Lake (from 1991-2007) were used to estimate k. Wind speeds were converted to wind speeds at 10 m height (U_{10}) assuming neutral stability using the wind profile power law relationship, since U_{10} is a common way of parameterizing the k to U relationship. Because Harp and Dickie Lakes are reasonably sheltered small lakes, the U_{10} speeds were used in the relationship derived by Cole and Caraco (1998) to estimate k_{600} values of 2.3 cm/h and 2.5 cm/h respectively. These values were within the above range for small sheltered lakes.

Harp and Dickie Lakes were almost always supersaturated with CO_2 with the highest saturations at the end of April after ice melt, and in fall prior to ice cover (Figure 5.10). Generally, there is a negative relationship between CO_2 concentrations and $\delta^{13}C\text{-}CO_2$ values (Figure 5.11) suggesting isotopic fractionation or mixing was occurring.

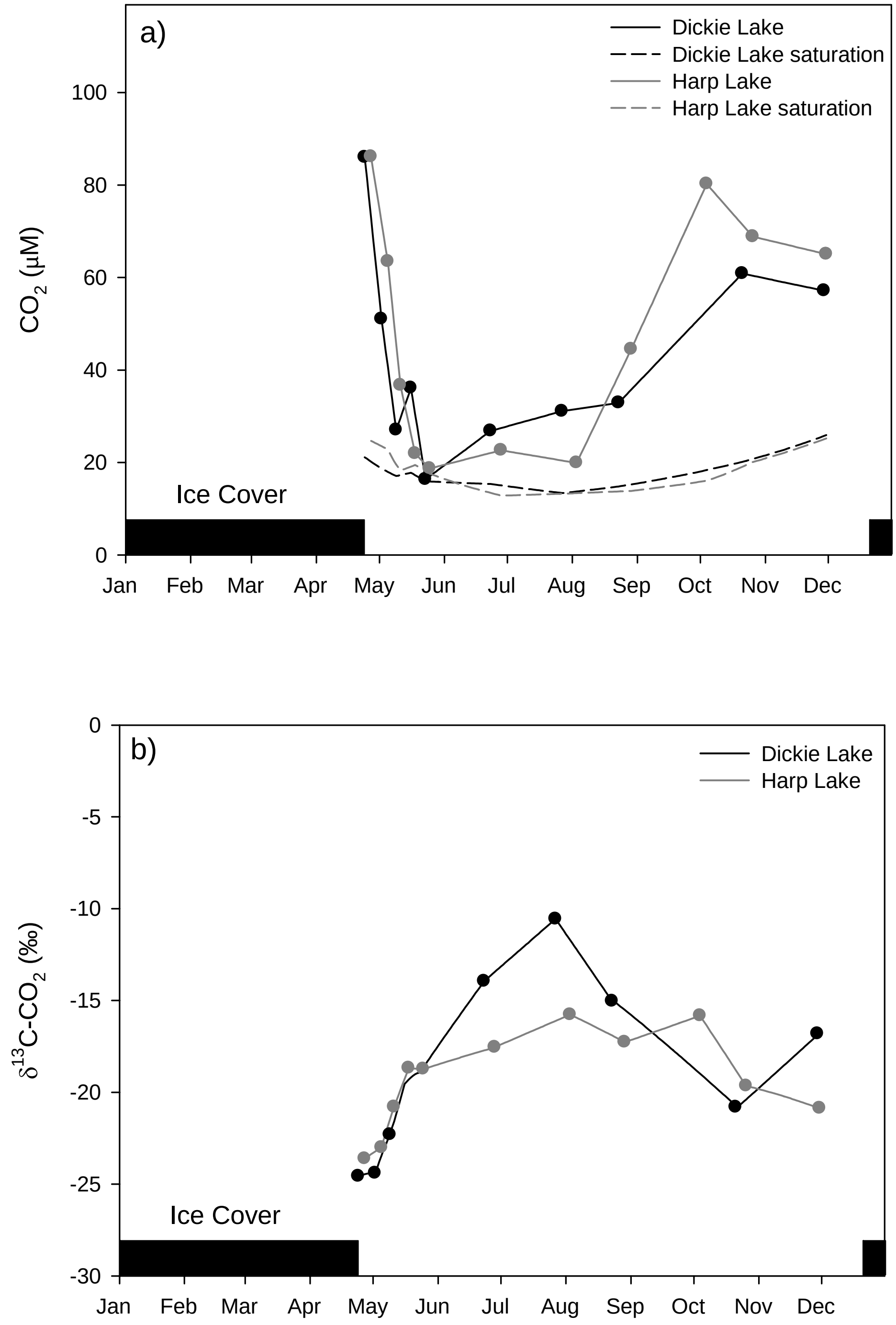


Figure 5.10: Annual variability in the a) CO_2 concentrations and b) $\delta^{13}C$-CO_2 in the surface waters of Harp and Dickie Lakes. Dickie Lake spring melt data is based on data from 2007 and combined with 2004 surface water data. Additional sampling at spring melt provides 5 data points to capture the rapid loss of CO_2 and changes in $\delta^{13}C$-DIC within the lakes. $\delta^{13}C$-CO_2 values were calculated from measured $\delta^{13}C$-DIC values and pH. Precision of the CO_2 measurements is 5%, and the $\delta^{13}C$-DIC is 0.3‰.

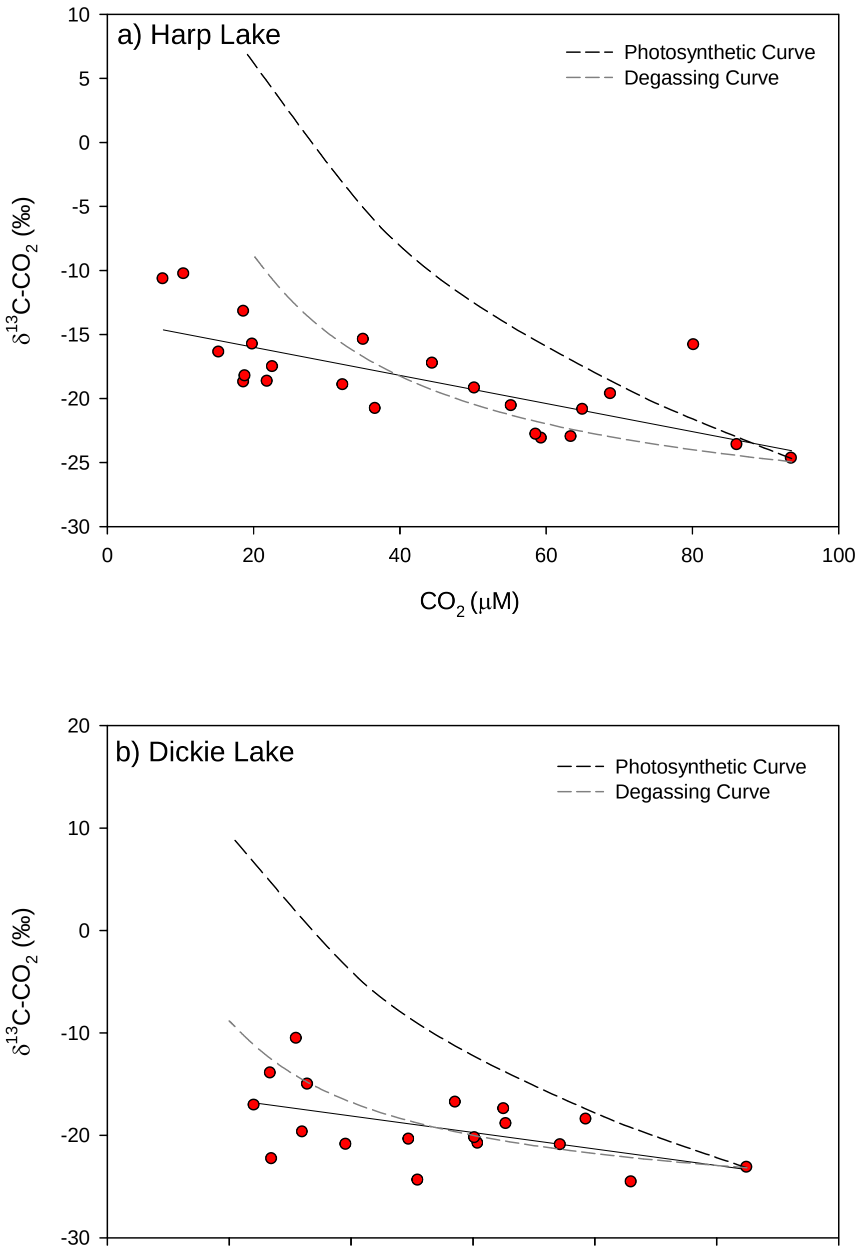


Figure 5.11: $\delta^{13}C-CO_2$ versus CO_2 concentrations of surface samples in Harp and Dickie Lakes. Hatched lines represent hypothetical pathways the highest CO_2 concentration sample would follow if CO_2 was either being taken up for photosynthesis assuming a Rayleigh relationship (enrichment factor -20‰; black hatched line) or if CO_2 was being lost by degassing (enrichment factor -1‰; grey hatched line) with no other inputs or outputs.

The net $\delta^{13}C$-CO_2 lost to the atmosphere from Harp Lake during the month after ice melt, calculated using weekly measurements of CO_2 and $\delta^{13}C$-CO_2 in the lake surface waters, was –30.3‰. The net annual flux weighted $\delta^{13}C$-CO_2 value of Harp Lake in 2005 was –21.9‰. In Dickie Lake, 2004 and 2007 data were used together since detailed 2004 ice melt samples were not collected. The net average flux weighted $\delta^{13}C$-CO_2 lost to the atmosphere during ice melt was –33.4‰ and the net annual flux weighted $\delta^{13}C$-CO_2 value lost to the atmosphere was –25.7‰. The annual weighted values may be different between the 2 lakes because the Dickie Lake data did not capture the CO_2 loss as well as the Harp data since Dickie datasets from 2 different years have been combined to calculate the $\delta^{13}C$ value. Or, the values could be different because the balance of processes affecting the $\delta^{13}C$ are different between the lakes, thereby affecting the $\delta^{13}C$ of the CO_2 evaded from the lakes (i.e. Figure 5.12). The calculated monthly $\delta^{13}C$-CO_2 fluxes were lower than the measured surface water $\delta^{13}C$-CO_2 values since the equilibrium $\delta^{13}C$-CO_2 value of the atmosphere was always greater than the measured $\delta^{13}C$-CO_2 of the epilimnion and net monthly fluxes were almost always from the lake to the atmosphere. At low net flux rates, there can be a large difference between the $\delta^{13}C$-CO_2 and the net $\delta^{13}C$-CO_2 fluxed to the atmosphere. For example, to degas an ecosystem from 70 μM CO_2 and $\delta^{13}C$-CO_2 of –27‰ to the equilibrium values of 20 μM and –8.9‰ requires a net flux out of 50 μM at –34.3‰. However, to degas an ecosystem from 25 μM CO_2 and $\delta^{13}C$-CO_2 of –27‰ to the equilibrium values of 20 μM and –8.9‰ requires a net flux out of 5 μM at ~–90‰. Calculating the evaded $\delta^{13}C$-CO_2 when CO_2 values are close to saturation yields net $\delta^{13}C$-CO_2 values much lower than expected suggesting that there may be a problem with calculating net flux when the lakes are close to atmospheric saturation.

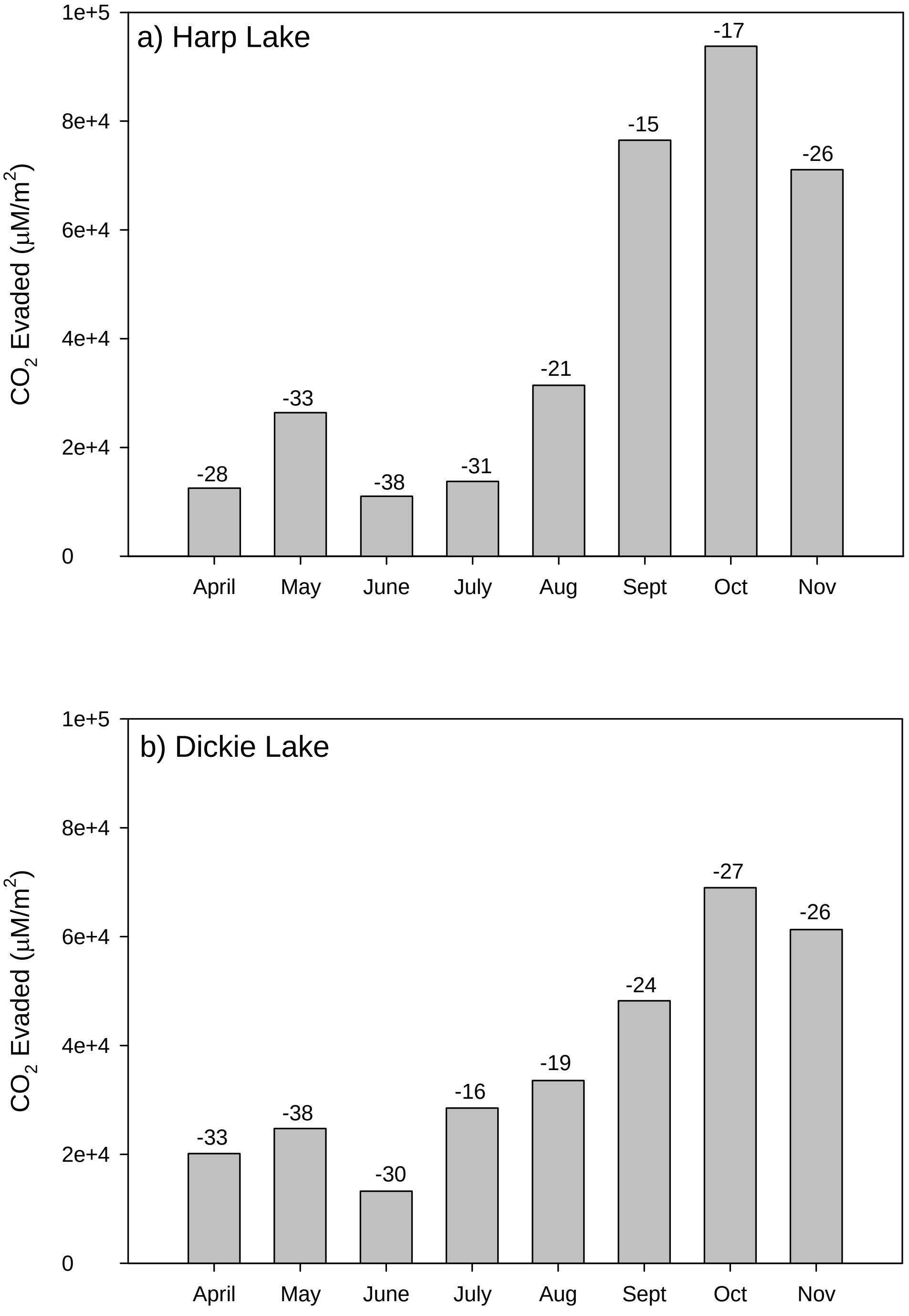


Figure 5.12: Annual variability in CO_2 flux evaded from a) Harp Lake and b) Dickie Lake. Numbers above the fluxes are the calculated $\delta^{13}C$-CO_2 values (‰) of the CO_2 evading the lake. Fluxes and $\delta^{13}C$-CO_2 values were interpolated between sampling dates.

The $\delta^{13}C$-CO_2 of the surface water in Harp Lake is generally lower than Dickie Lake in the summer and fall except for October (Figure 5.10). The net $\delta^{13}C$-CO_2 evaded from Harp Lake is ~9-10‰ greater than from Dickie Lake for September and October. The Harp fall peak in $\delta^{13}C$-CO_2 could be due to a fall algal bloom in the lake, which would decrease the CO_2 concentration and increase the $\delta^{13}C$-CO_2 at a period when the gas flux is high. Using chlorophyll *a* as a proxy for productivity in the lakes suggests that the fall bloom hypothesis is a possible explanation for the data trends since a peak in chlorophyll *a* in Harp Lake was observed in the fall (OME, unpublished).

Figure 5.12 indicates that the CO_2 flux in the fall, as the lakes are beginning to turnover, comprises a large part of the annual CO_2 flux. Since there was no sampling in September when the thermocline was beginning to deepen, it was possible that a crucial sampling time was omitted. Therefore, it is apparent that the fall CO_2 flux from the lake was an important CO_2 flux to capture and should have been sampled with greater frequency. Additionally, according to historical chlorophyll *a* data (OME, unpublished), fall blooms do not always occur in Harp Lake therefore perhaps the surface water $\delta^{13}C$-CO_2 values are not representative of the lake surface waters on a long-term basis.

The annual weighted $\delta^{13}C$-CO_2 values evaded to the atmosphere from Harp and Dickie Lakes were different. This could reflect that Dickie Lake loses mass at a faster rate than Harp Lake since it has a greater lake surface area and a smaller mean depth. Figure 5.8 indicates that in the surface waters of Dickie Lake, the $\delta^{13}C$-DIC decreased by approximately 8‰ between August and October. During this time, the lake was almost completely mixed (with the exception of the bottom metre of the lake) suggesting that sampling in September could have provided a different CO_2 flux or a different $\delta^{13}C$ value than the interpolated value used to calculate the net $\delta^{13}C-CO_2$ value evaded to the atmosphere depending on when the majority of mixing occurred. Additionally, given that Harp Lake has a larger mean depth and a smaller surface area than Dickie Lake, the fall CO_2 fluxes and $\delta^{13}C-CO_2$ changes were likely better captured as complete turnover did not occur until late fall.

5.4.7 δ^{13}C lost to Sedimentation (δ^{13}C-Sed)

The δ^{13}C-Sed (δ^{13}C of the organic matter lost to the sediments in the lake) was calculated from the carbon isotope budgets (Equation 5.5). The calculated δ^{13}C-Sed did not equal the measured sediment value from the Harp and Dickie Lake sediment cores (Table 5.2). The calculated δ^{13}C-Sed values were greater than the measured δ^{13}C-Sed values by approximately 2‰ in Dickie Lake and approximately 5‰ less than the measured δ^{13}C-Sed values in Harp Lake.

Digenetic effects and other lake processes that could have affected the δ^{13}C values used to calculate the δ^{13}C-Sed value (e.g. photosynthesis, respiration, etc) are incorporated into the mass balance model as changes to other parameters (e.g. gas exchange, load exiting through the outflows, etc.) and therefore included in the calculated δ^{13}C-Sed. For example, photosynthetic fractionation causes the δ^{13}C of POC to be less than the δ^{13}C-DIC and the remaining δ^{13}C-DIC would increase. This increase would be reflected in surface and outflow δ^{13}C-DIC values, and the weighted average annual δ^{13}C evaded to the atmosphere, illustrating that changes in productivity would become incorporated into the measured values. Since the calculated δ^{13}C-Sed did not equal the measured δ^{13}C-Sed in either Harp or Dickie Lakes, there is either an error in the δ^{13}C value of the parameters, and/or an error in the carbon mass balance, and/or an input or output of the mass balance is not adequately characterized. For example, the difference between the expected and the measured δ^{13}C-Sed could be attributed to POC entering the lakes from the inflows, or $\delta^{13}C$ is not a good tool to test the carbon budgets created by Dillon and Molot (1997a) since it is difficult to calculate the flux of $\delta^{13}C$-CO_2 evading the lake when the lakes are near atmospheric saturation.

5.4.8 Carbon Mass and Isotope Budget Model

To examine the discrepancy between the calculated and measured $\delta^{13}C$-Sed values, and the importance of each of the parameters involved in the mass balance, a dynamic mass and isotope budget model was created. This model was based on the mass balances of Dillon and Molot (1997a) and the calculated weighted average annual $\delta^{13}C$ values above. The model assumed that:

1) The DIC evaded from the lake was a function of DOC lost within the lake that did not go to the sediments and the DIC entering and exiting the lake. The lakes remained supersaturated in CO_2 so that there is a net flux to the atmosphere. Microbial and phytoplankton biomass, and vegetation were assumed to be small and at steady state on an annual basis (such that changes in carbon storage were unimportant except in the sediments).

2) The DOC removed in the lake (Equation 5.10) was first order with respect to the DOC in the lakes and the apparent settling coefficient (v) was a constant.

3) The DOC lost to the sediments (Equation 5.9 and 5.11) was a constant fraction of the DOC removed in the lake. Humic aggregation may be regulated by pH (Maignan, 1983; Abate and Masini, 2003). However, inter-annual pH did not fluctuate drastically annually (standard deviation < 0.1 pH units; OME, unpublished), so the DOC removal rate and sediment partitioning (Equation 5.11) were assumed constant.

4) The DOC and DIC exiting the lake through the outflows were a function of the DOC and DIC within the lake respectively and the areal water load (q_s) of the lake (i.e. average annual evaporation is constant).
5) The lake is at annual steady state with respect to carbon and water (i.e. constant lake volume).

Model inputs included two types of input parameters (Table 5.3): constants calculated from field measurements in the current study, and constants calculated from OME data or by Dillon and Molot (1997a). Constants calculated in the current study include all of the weighted average annual δ^{13}C values (i.e. DOC_{in}, DIC_{in}, DOC_{out}, DIC_{out}, and CO_2 lost to the atmosphere through gas exchange). The constants calculated from OME data or by Dillon and Molot (1997a) include the initial mass of carbon within the lakes ($DOC_{in\ lake}$, $DIC_{in\ lake}$), the gas exchange coefficient (k), and the mass of DOC and DIC entering the lakes (DOC_{in} and DIC_{in}). Additionally, as DOC and DIC loads change, the areal water load (q_s), the apparent settling coefficient (v), and pH could be affected, therefore, their relationships with load were determined using historical OME data. Although most of the input parameters used in the model were provided by Dillon and Molot (1997a), or calculated from OME measurements (Table 5.3), it was necessary to adjust the pH in Harp and Dickie Lakes, and q_s and v in Harp Lake, in order to cause the masses of DOC_{out}, DIC_{out}, Sed, and Atm in the model to equal the masses measured by Dillon and Molot (1997a). The necessary adjustments, and the sensitivity of each of the parameters, are examined below.

5.4.8.1 Sensitivity of δ^{13}C-Sed to weighted average annual δ^{13}C values

Changing the weighted average annual δ^{13}C-DIC and δ^{13}C-DOC values by 0.5‰ did not change the δ^{13}C-Sed appreciably with the exception of changing the δ^{13}C-DOC of the inflows (Table 5.4). The δ^{13}C-Sed was most sensitive to δ^{13}C-DOC because DOC was the largest carbon mass entering or exiting the lakes (Table 5.5). However, of all δ^{13}C values measured, the δ^{13}C-DOC of the lake inflows and outflows was the least annually-variable parameter. The intra-annual difference between the δ^{13}C-DOC measurements from the 1990s and 2004-2005 was generally within analytical error, and in conjunction with low annual variability (Figure 5.6, Table 5.2), the weighted annual average δ^{13}C-DOC calculated from the field data likely will not change appreciably annually. Since the data range was minimal within the individual inflows (Figure 5.6), this suggested that sources of DOC to the inflows were not changing over time, and/or sources have similar δ^{13}C values; therefore, it is unlikely that the weighted annual average values will be offset by more than 0.5‰. Thus, although an offset of only 1‰ in δ^{13}C-DOC$_{in}$ is required for the Harp Lake calculated and measured δ^{13}C-Sed to match, it is improbable that the δ^{13}C-DOC$_{in}$ value can be the main source of this difference.

Table 5.4: Sensitivity of the sediment δ^{13}C value to increases in a) the average annual isotopic values by 0.5‰ and b) the input parameters of the model.

a)

	Harp	Dickie
Increase average annual δ^{13}C by 0.5 ‰	Sediment changes by	
	(‰)	(‰)
DOC$_{IN}$	2.3	1.5
DIC$_{IN}$	0.4	0.4
DOC$_{OUT}$	-1.4	-0.7
DIC$_{OUT}$	-0.5	-0.1
DIC$_{GE}$	-0.6	-0.6

b)

Parameter	Increase by	Harp Sediment changes by (‰)	Dickie (‰)
DOC$_{IN}$	5%	0.11	0.06
DIC$_{IN}$	5%	0.35	-0.04
k	0.1	0.17	0.03
qs	0.1	-0.15	-0.11
v	0.1	-0.01	-0.04
pH	0.1	-0.95	-0.11

Table 5.5: Model parameters used, and comparison of masses from the Dillon and Molot (1997) mass balances and the mass outputs from the model. Retention of DOC and DIC (RDOC and RDIC respectively) is calculated as ($Load_{in}$-$Load_{out}$)/($Load_{in}$) and q_s is the areal water load. Standard deviations are reported for q_s and v.

	Harp		***Dickie***	
Parameter	D&M (1997)	Model from this study	D&M (1997)	Model from this study
DOC_{IN} (g C $m^{-2}y^{-1}$)	28.9	28.9	31.2	31.2
DIC_{IN} (g C $m^{-2}y^{-1}$)	7.85	7.85	7.35	7.35
DOC_{OUT} (g C $m^{-2}y^{-1}$)	16.9	16.9	14.2	14.1
DIC_{OUT} (g C $m^{-2}y^{-1}$)	6.35	6.36	2.53	2.54
DIC_{GE} (g C $m^{-2}y^{-1}$)	7.17	7.18	11.7	11.7
SED (g C $m^{-2}y^{-1}$)	6.26	6.26	10.1	10.1
Lake Volume (m^3)	82.6 x 10^5		46.4 x 10^5	
Residence Time (y)	3.16		1.71	
RDOC	0.42		0.55	
RDIC	0.19		0.66	
Mean depth (m)	13.3		5.0	
pH	6.22	6.44	5.85	5.75
qs (my^{-1})	4.16 ± 0.75	4.26	2.66 ± 0.59	2.66
v (my^{-1})	2.9 ± 0.4	3.00	3.2 ± 0.4	3.21
k (cmh^{-1})		2.26		2.46
sediment partition coefficient	0.52*	0.52	0.6*	0.60

* Calculated from Dillon and Molot, 1997a

5.4.8.2 *Sensitivity of δ^{13}C-Sed to δ^{13}C-CO_2 lost to the atmosphere*

To further examine the 2‰ to 5‰ difference between calculated and measured δ^{13}C-Sed values, the sensitivity of the model to the net δ^{13}C-CO_2 lost to the atmosphere was re-examined by adjusting the net δ^{13}C-CO_2 value to close the 2‰ to 5‰ gap. This requires changing the annual weighted values from –21.9‰ to –25.9‰ for Harp Lake, and from –25.7‰ to –24.0‰ for Dickie Lake. These net δ^{13}C-CO_2 evasion values yield a calculated δ^{13}C-Sed of –30.1‰ and –29.7‰ for Harp and Dickie Lakes respectively, within 0.3‰ of the measured δ^{13}C-Sed values. Inaccuracies in estimating the net δ^{13}C-CO_2 evaded from the lake may be the cause of the difference between the calculated and measured δ^{13}C-CO_2 values, since it is the least well known parameter.

CO_2 concentrations in the lakes were supersaturated surrounding and preceeding the onset of autumn turnover (Figure 5.10a). CO_2 flux rates from the lakes were highest in the autumn and $\delta^{13}C$-CO_2 values of emitted CO_2 were lower than those of the summer in Harp and Dickie Lakes (Figure 5.12). High autumn flux rates suggest that turnover was important for estimating total CO_2 fluxes from the lakes and their $\delta^{13}C$-CO_2 values.

According to Eimers et al. (2006), Dickie Lake usually mixes and turns over in September. As Dickie Lake is darker and shallower (~11 m) than Harp Lake (~34 m), autumn turnover begins much sooner than in Harp Lake (late October to early November). Rapid changes to surface $\delta^{13}C$-CO_2 values were observed (Figure 5.10b and Figure 5.12). There was also a gap in the data during this time frame. Since summer surface $\delta^{13}C$-CO_2 values of Dickie Lake were greater than for Harp Lake, there was a much larger change during the fall evasion. It was therefore possible that using data from a different year to fill in a missing monthly data point or using incomplete annual data would result in different average annual $\delta^{13}C$-CO_2 values. High net $\delta^{13}C$-CO_2 values evaded from the Harp Lake in September and October may be due to a fall bloom and thus not characteristic of the entire month or every fall. The loss of CO_2 and the net $\delta^{13}C$-CO_2 flux estimated using mass balance calculations in the lake between August and November are different than the monthly net $\delta^{13}C$-CO_2 flux calculated from the interpolated data in Figure 5.12, suggesting that other factors besides degassing are influencing the $\delta^{13}C$-CO_2. Accurate determination of the net $\delta^{13}C$-CO_2 evaded from the lakes requires more detailed surface water data from the onset of autumn turnover until ice cover.

5.4.8.3 Initial C mass within Lakes ($DOC_{in\ lake}$, $DIC_{in\ lake}$)

A steady state model of chemical flux (Equation 5.12; Vollenweider, 1976) requiring data available from the mass balances of Dillon and Molot (1997a) was used to determine the initial mass of carbon as DIC and as DOC within the lakes by multiplying the calculated concentration with the volume of the lake.

(Equation 5.12)

$$Concentration = \frac{LR_T(1-R)}{z}$$

The steady state model of chemical flux required the load entering the system (L: g/m^2/y), the water residence time (R_T: y), the retention of the load (R: m/y), and the mean depth of the lake (z: m). Subsequently, weighted annual DIC and DOC concentrations within the lakes became available (OME, unpublished) and can be compared to the results of (Equation 5.12. Using Vollenweider's equations (1976), the calculated annual DIC and DOC concentrations were within 0.01 to 0.03 mg/L of the annual weighted ice-free concentrations (OME, unpublished), with the exception of the Harp average annual weighted DOC concentration, which was 0.2 mg/L different. Therefore, both methods (Vollenweider's equations or weighted annual measured concentrations) give similar results for the initial mass of carbon within the lakes.

5.4.8.4 Sensitivity of δ^{13}C-Sed to DOC_{in} and DIC_{in}

The DOC and DIC entering the lakes had previously been determined from 8 years of mass balances averaged by Dillon and Molot (1997a). The DOC and DIC loading rates to Harp Lake were 28.9 g C m^{-2} y^{-1} and 7.85 g C m^{-2} y^{-1} respectively (Table 5.5). Relative to Harp Lake, Dickie Lake had a greater DOC loading rate (31.2 g C m^{-2} y^{-1}) and a lower DIC loading rate (7.35 g C m^{-2} y^{-1}) (Table 5.5).

More than 20 years of carbon mass balance data for Harp and Dickie Lakes indicate that a 5% annual difference in DOC or DIC loading entering the lakes was not uncommon. Inter-annual variability of DOC entering the lakes ranged between 25-40% depending on the lake (OME, unpublished). Schindler et al. (1997) note that, in reference lakes at the ELA, DOC concentrations decreased 15-25% in the 1980s indicating that climate-induced DOC changes can significantly affect the carbon budgets of boreal lakes as climate affects annual stream flow and DOC loading, and thus lake residence time (and in-lake processing). Similarly, Dillon and Molot (1997a) found that declining DOC concentrations in Dickie Lake could be attributed to stream flow since DOC loading was a predictable function of water loading. Other controls on DOC concentrations in a suite of 9 boreal lakes (including Harp and Dickie Lakes) based on 21 years of data include mean solar radiation and winter precipitation (Hudson et al., 2003).

Before using the model to determine the effects that DOC and DIC mass changes would have on the δ^{13}C-Sed value, it was necessary to consider that as carbon loading rates change, the CO_2 flux to the atmosphere may change. This may change the δ^{13}C-CO_2 evaded value, which can affect the δ^{13}C-Sed. To account for changes in δ^{13}C-CO_2 values that coincide with changes in CO_2 flux to the atmosphere, the relationship between surface δ^{13}C-CO_2 values and CO_2 concentrations from the lakes (Figure 5.11) was used. A stronger relationship exists for Harp Lake ($R^2 = 0.69$) than for Dickie Lake ($R^2 = 0.26$). This may reflect problems calculating CO_2 concentrations in the Dickie Lake waters with higher DOC concentrations and lower pH, differences in mixing within the lakes, or variable photosynthetic fractionation with time.

To understand the controls on the negative relationship between CO_2 and δ^{13}C-CO_2, it is important to consider that different processes affect CO_2 and δ^{13}C-CO_2 differently. Two of these are photosynthesis and degassing.

Assuming a single starting point for illustrative purposes, the theoretical photosynthetic and degassing pathways that a high concentration CO_2 sample would follow are shown in Figure 5.11. If the high CO_2 sample was only affected by photosynthesis, the $\delta^{13}C\text{-}CO_2$ value would increase as CO_2 declines as a result of photosynthetic isotopic fractionation (e.g. black hatched line in Figure 5.11). For degassing, the point would follow the hatched grey line (Figure 5.11) since the fractionation associated with gas exchange is much smaller than photosynthetic fractionation. CO_2 concentrations and $\delta^{13}C\text{-}CO_2$ values can also be affected by the photodegradation of DOM, respiration, or inputs of high DIC stream waters. That surface waters of Harp and Dickie Lakes are affected by degassing is evident from decreasing DIC concentrations and concomitant increases in $\delta^{13}C$-DIC (Figure 5.4, Figure 5.11). Since the lake surface samples lie above and below the degassing curve (Figure 5.11), the surface waters are also likely affected by other CO_2 consuming processes (e.g. photosynthesis) and CO_2 producing processes (e.g. photodegradation and/or respiration) and mixing. Temperature changes and pH also affect CO_2 concentrations within the lakes by changing the equilibrium between CO_2 and DIC.

Since DOC and DIC loading rates will change with hydrological changes to the ecosystem (OME, unpublished), the relationship between q_s and load was determined to account for how the q_s in the two lakes would change when the mass of DOC or DIC changed by 5%. The linear relationship between q_s and carbon loading rates from the OME mass balances was stronger in Harp Lake than in Dickie Lake (i.e., q_s versus DOC loading, not shown; Dickie: $R^2 = 0.47$, Harp: $R^2 = 0.83$).

Increasing the mass of the DOC and DIC entering the lakes by 5%, causes only small changes in the $\delta^{13}C$-Sed (Table 5.4). Increasing the DOC loading rate of Harp Lake by 5% changed the $\delta^{13}C$-Sed by less than the precision of the δ^{13}C-Sed measurement (0.2‰). This mass change in Dickie Lake also had little effect on the δ^{13}C-Sed, which may be due to the weaker relationships between CO_2 concentration and δ^{13}C-CO_2 and the weaker relationship between the carbon inputs and q_s than in Harp Lake.

A positive relationship exists between q_s and total carbon (DOC + DIC) load rates (Harp: $R^2 = 0.87$; Dickie: $R^2 = 0.61$). Changing q_s affects carbon retention and DOC concentrations in the lakes since $R = v/(v+q_s)$, where R is retention ($R = (DOC_{in} - DOC_{out})/DOC_{in}$), and v is the apparent settling velocity (Dillon and Molot, 1997a). If q_s is not altered with carbon loading rates, the observed changes in the Dickie Lake δ^{13}C-Sed value are much greater than the Harp Lake δ^{13}C-Sed value. Dickie Lake loses a greater fraction of carbon to the atmosphere and sediments than Harp Lake since it has a greater DOC and DIC retention and lower pH.

Changing the carbon loading rates by 5% has a smaller effect on δ^{13}C-Sed than altering the weighted δ^{13}C values of the mass balance parameters by 0.5‰ does. The 5% change represents the lower range of typical inter-annual variability in DOC loading rates. Long-term DOC load variability increases to 25% to 40% if the 8 years of the mass balances are used instead of year-to-year changes. This long-term variability can change the δ^{13}C-Sed value by 0.5‰ to 2.5‰. Since lake sediment slices are typically multi-year, they would record the range in carbon loading rate variability.

In the δ^{13}C sediment record of Harp and Dickie Lakes, δ^{13}C peaks in the mid-1950s. To reproduce these peaks within the model, (–27.6‰ in 1957, Harp Lake; –28.7‰ in 1955, Dickie Lake), the DOC loading rates had to be decreased by ~40% in Harp Lake and ~42% in Dickie Lake, assuming that average annual δ^{13}C values were the same then as in this study with the exception of the δ^{13}C-CO_2 evaded to the atmosphere.

Although the model suggests that the peaks in δ^{13}C-Sed are coincident with a large reduction in DOC entering the systems, it indicates nothing about the proportions of allochthonous and autochthonous carbon in the lake sediments (Chapter 6). Peak δ^{13}C values are very similar to δ^{13}C-DOC values entering the system suggesting that although the model indicates a 40% to 42% reduction in DOC loading rates (allochthonous carbon) from present day rates, it was possible that in the 1950s the allochthonous carbon was more important to the sediment record than autochthonous carbon. However, this hypothesis needs to be tested.

5.4.8.5 Sensitivity of δ^{13}C-Sed to pH

The model also required adjustment of the average annual pH in the lakes in order to reproduce the carbon loss rates of Dillon and Molot (1997a). Weighted average annual ice-free pH measurements (and their standard deviations) from Harp and Dickie Lakes from the years of Dillon and Molot's (1997a) study are 6.22 ± 0.06 and 5.85 ± 0.09 respectively (OME, unpublished). However, the model required pH inputs of 6.44 and 5.75 for Harp and Dickie Lakes respectively for the carbon loss rates to match (which changes the H^+ concentrations for Harp and Dickie Lakes by -0.26 μmol and +0.37 μmol, respectively). Since these lakes are poorly buffered, and have low surface DIC concentrations, accurately measuring pH in the system is difficult (Herczeg and Hesslein, 1984; Herczeg et al., 1985).

The δ^{13}C-Sed in Harp Lake is sensitive to lake pH, decreasing by almost 1‰ with a 0.1 increase in pH. However, Dickie Lake δ^{13}C-Sed was less sensitive, with only a 0.1‰ decrease from a 0.1 increase in pH. This may be due to the difference in DIC concentrations between the two lakes. Ice-free annual DIC concentrations during the study periods used by Dillon and Molot (1997a) are 1.50 mg C/L in Harp Lake and 0.86 mg C/L in Dickie Lake. The mass of carbon as DIC in Harp Lake is an order of magnitude greater than in Dickie Lake, and the mean depth of Harp Lake is approximately 2.7 times that of Dickie Lake. Therefore, an equivalent change in pH in both lakes would represent a larger change in the total amount of CO_2 in Harp Lake than in Dickie Lake.

5.4.8.6 Sensitivity of δ^{13}C-Sed to Areal water load (q_s)

Dillon and Molot (1997a) published average areal water loads (q_s) of 2.66 ± 0.59 my^{-1} and 4.16 ± 0.75 my^{-1} for Dickie and Harp Lakes respectively, however, the dynamic model required an adjusted q_s of 4.26 my^{-1} for Harp Lake to produce results most similar to the mass balances of Dillon and Molot (1997a; Table 5.5). This optimized q_s value is within the reported standard deviations and is within the 5% error in measuring the annual water balances of lakes (Winter, 1981). Changing the q_s by 0.1 my^{-1} can change the δ^{13}C-Sed by at least the same magnitude as changing the DOC loading rate by 5% (Table 5.4). Over the range of the standard deviation of q_s, the δ^{13}C-Sed value could decrease by up to 1‰ in Harp Lake indicating that q_s could change the δ^{13}C-Sed value by affecting DOC retention.

5.4.8.7 Sensitivity of δ^{13}C-Sed to Apparent settling coefficient (v)

The apparent settling coefficient is a first order rate constant for DOC loss (by sedimentation and mineralization) from the lake, was calculated using $R=v/(v+q_s)$, [rearranged to $v = Rq_s/(1-R)$], where R is the DOC retention in the lake (Dillon and Molot, 1997a). In Harp and Dickie Lakes, the v (averaged over 8 years) was 2.9 ± 0.4 my^{-1} and 3.2 ± 0.4 my^{-1} respectively (Table 5.5). However, to match the DOC loss rates in the model with those of Dillon and Molot (1997a), Harp Lake required a v of 3.01. Changing v by 0.1 my^{-1} did not change the δ^{13}C-Sed value. Increasing v by the standard deviation decreased the δ^{13}C-Sed value up to 0.16‰, therefore v does not have an appreciable effect on δ^{13}C-Sed. This is a result of the model assumption that a constant fraction of DOC lost within the lakes via the apparent settling coefficient is lost to the sediments.

5.4.8.8 Sensitivity of δ^{13}C-Sed to the Gas Exchange Coefficient (k)

The gas exchange coefficient was estimated to be 2.3 cm/h and 2.5 cm/h for Harp and Dickie Lakes respectively using 5 years of daily wind speed data. The gas exchange coefficient controls the rate at which CO_2 is evaded from the lake and has been estimated by nearby wind speeds in this study therefore there could be additional error associated with calculating k. Changing these values by 0.1 cm/h did not change the δ^{13}C-Sed value in Dickie Lake, but changed the Harp δ^{13}C-Sed by almost 0.2‰ (Table 5.4). Since k is calculated using wind speed relationships, including the intra-annual variability of wind speed is very important. The precision of the assumed average annual k is likely more than 0.1 cm/h, therefore if a larger range of k values were considered, it would be possible for greater changes to the δ^{13}C-Sed value to occur.

Since the optimization of pH, v, and q_s is required for the masses in the carbon model to match the masses from the mass balances published by Dillon and Molot (1997a), it is possible that there could be some error associated with the mass balances estimated by Dillon and Molot (1997a), or that the model is not adequately representing the carbon loss rates.

Changes to the weighted average annual δ^{13}C values for the different carbon loading and loss rates, q_s, v, and pH can affect the δ^{13}C-Sed, thus changing the δ^{13}C-CO_2 might not be the only way to make the model and Dillon and Molot (1997a) loading rates match. There might be other combinations of changes to the input values (Table 5.3) to alter the δ^{13}C-Sed, however, changing pH, qs, and/or v would also change the carbon loss rates and thus the mass balances. Additionally, although the δ^{13}C-Sed value appears to be most sensitive to q_s and pH, the changes observed are relatively small and would require large shifts to account for a 5‰ difference between the calculated and the measured $\delta^{13}C$ of the sediments. Since $\delta^{13}C$-DOC is well defined to a narrow range of 0.2 ‰, the difference between the calculated and measured $\delta^{13}C$-Sed values is due to the $\delta^{13}C$-CO_2, which will also affect the $\delta^{13}C$-DIC exiting the lakes. Therefore, the $\delta^{13}C$ and mass balances can be used as tools to explore how carbon balances affect the $\delta^{13}C$ of lake sediments, however, a more accurate technique is required to characterize of the $\delta^{13}C$-CO_2 flux from lakes near atmospheric saturation.

5.5 Summary and Implications

Calculated mass weighted average annual $\delta^{13}C$-DOC and $\delta^{13}C$-DIC values of the inflows to Harp and Dickie Lakes appear to be well constrained and vary by only 0.2‰ and 1.3‰ respectively. The range in the mass-weighted average annual $\delta^{13}C$-DOC of the outflows was similar to the inflows (0.2‰), however, the range of the mass-weighted average annual $\delta^{13}C$-DIC of the outflows was larger (2.2‰). Isotope mass balances for the two lakes indicate that calculated $\delta^{13}C$-Sed values were greater by 5‰ for Harp Lake and less by 2‰ for Dickie Lake than the measured $\delta^{13}C$-Sed values.

That calculated and measured $\delta^{13}C$-Sed values of both lakes do not match suggests there may be error associated with the mass budgets and/or isotope budget. Possible error within the mass balances may be indicated by the need to adjust input parameters in order for the carbon loading rates from the mass balance model (Dillon and Molot, 1997a) to match the dynamic carbon model. There may be other error associated with input parameters to the mass and isotope model, such as pH dependent calculations and the $\delta^{13}C$-CO_2 values of the gas flux.

Sensitivity analyses on the input parameters to the carbon mass and δ^{13}C budgets revealed that δ^{13}C-DIC entering the lakes can affect the δ^{13}C-Sed values in Harp Lake, but little in Dickie Lake. This could be due to the larger range in measured δ^{13}C-DIC values. Changes in DOC loading rates to the lakes by 40% could change the δ^{13}C-Sed by up to 2.5‰. This alone can account for the observed changes in the δ^{13}C-Sed record.

Since approximately 50% of the DOC entering the lakes was lost in roughly equal amounts to the atmosphere and sediment, understanding the gas exchange from these lakes is also crucial to accurately complete the δ^{13}C and mass balances. The model does not appear to be extremely sensitive to the net δ^{13}C-CO_2 lost to the atmosphere relative to the δ^{13}C-DOC (Table 4). However, the net δ^{13}C-CO_2 value is the least well known parameter. Autumn was a crucial period where most of the CO_2 was evaded from the lakes. The net δ^{13}C-CO_2 changes associated with autumn turnover were not well captured. The calculated and measured δ^{13}C-Sed values would match if the δ^{13}C-CO_2 value was increased by 1.7‰ in Dickie Lake and decreased by 4‰ in Harp Lake.

The sensitivity analysis reveals that Harp Lake is more sensitive to k than Dickie Lake. However, k values, estimated from daily averages of measured windspeeds, fell within the range of other published k values from small sheltered lakes. The areal discharge rate (q_s) has control over the retention of DOC in the lakes and therefore affects the δ^{13}C-Sed value. However, q_s was calculated from measured hydrology budgets. The model was also sensitive to pH in Harp Lake, but almost an order of magnitude less sensitive in Dickie Lake. The sensitivity to variability in input parameters to the mass and δ^{13}C model suggests that DOC loading rates and q_s are important controls of δ^{13}C-Sed values. There is a positive relationship between q_s and retention, suggesting that they are linked. Depending on the lake, other factors such as k and pH can become important because of their effects on CO_2 flux and it's $\delta^{13}C$-CO_2 value. That DOC loading rates and q_s are important controls on lake $\delta^{13}C$-Sed values in high DOC retention lakes has implications for paleolimnology since productivity records are inferred from the $\delta^{13}C$-Sed values. DOC loading and q_s can therefore confound the often-reconstructed primary production record from $\delta^{13}C$-Sed records.

Chapter 6:

The importance of allochthonous and autochthonous POC to lake sediment $\delta^{13}C$ records.

6.1 Overview

To calculate the $\delta^{13}C$ of particulate organic carbon (POC) reaching lake sediments, allochthonous and autochthonous end member values within two small, oligotrophic, high dissolved organic carbon (DOC) retention, Shield lakes, were determined by calculating average annual $\delta^{13}C$-POC values for terrestrially derived and aquatic derived POC. The allochthonous $\delta^{13}C$ end member value was calculated using $\delta^{13}C$-POC data from inflows, from POC production during DOC photodegradation experiments, and from litter and vegetation. To determine the autochthonous end member, monthly $\delta^{13}C$-DIC (dissolved inorganic carbon), POC, DIC, and zooplankton measurements from lake surface waters were used to calculate the average annual autochthonous $\delta^{13}C$-POC contribution. These end member values suggest that the average annual $\delta^{13}C$-POC values from allochthonous and autochthonous sources are distinct. Estimates of POC mass balances in Harp and Dickie Lakes suggest that between 1.2 to 3.1 g C/m^2 of POC enters the lakes from streams, while 1.4 to 3.0 g C/m^2 of litter is deposited on the lakes compared to average sedimentation rates of 23.9 g C/m^2 in Harp Lake and 41.1 g C/m^2 in Dickie Lake. Incubations of the inflow waters tracking DOC loss and POC creation suggest that on average 56% of the DOC lost is converted to POC potentially adding 7.7 to 9.1 g POC/m^2 to the lakes. Sediment accumulation rates from estimated mass balances in Harp and Dickie Lakes (6.3 g C/m^2 and 10.1 g C/m^2; Dillon and Molot, 1997a) are smaller than the sum of the estimated allochthonous POC mass contributions in the current study, however, a portion of the POC will exit through the outflows and a portion could be lost to diagenesis. The relative proportion of stream POC, litter, and photolyzed DOC remains important and is used to calculate the $\delta^{13}C$ of the allochthonous end member.

The allochthonous to autochthonous ratio in the $\delta^{13}C$ of the lake sediments was calculated using the isotopically distinct $\delta^{13}C$ end members of allochthonous and autochthonous carbon in a 2 end-member mixing model. Results from the mixing models indicate that the isotopic signature of sediment organic matter can be affected by the ratio of autochthonous and allochthonous contributions, suggesting that climate change and/or anthropogenic changes to the landscape, and the concomitant changes in DOC inputs to lakes can be preserved in the sediment record. A short sediment core from both lakes suggests that the allochthonous contributions to the lake sediments have varied historically between 66% and 97%. The importance of allochthonous POC contradicts Molot and Dillon (1997b) who suggest that the DOC loss in lakes (< 4 mg C/L) can be entirely explained through photodecay constants (or the decay of allochthonous contributions) of DOC to DIC, which then is used in photosynthesis to produce POC. The $\delta^{13}C$ of lake sediments can thus be affected by the amount of particulate carbon created through the photodegradation of DOC, POC entering lakes, and litter fall onto lakes, suggesting that sediment records are not just a productivity signal, but a mass balance signal in high DOC retention lakes. Furthermore, applying allochthonous and autochthonous carbon contributions to sedimentation rates indicates that the autochthonous contributions in Harp Lake were relatively constant from the early 1800s until ~1960 even though the $\delta^{13}C$ of the lake sediments were changing. This indicates that the $\delta^{13}C$ of lake sediments cannot always be used to infer past productivity in aquatic systems with high DOC retention.

6.2 Introduction

The relative importance of allochthonous and autochthonous carbon inputs to lakes has recently gained attention due to their importance to carbon cycling in and greenhouse gas fluxes to the atmosphere from aquatic systems. Eutrophic lakes tend to produce large amounts of autochthonous carbon and are net carbon sinks if carbon fixation is greater than respiratory losses. However, oligotrophic lakes can have high allochthonous inputs from their catchments which can support net CO_2 evasion to the atmosphere if respiration is larger than carbon fixation (del Giorgio et al., 1999; Pace et al., 2004) and can be net carbon sinks on the landscape.

In boreal lakes, carbon storage within lake sediments is estimated to be a significant carbon sink (Kortelainen et al., 2004). Up to 80% of the total organic carbon (TOC) entering lakes can be mineralized or stored within lake sediment according to carbon mass budgets from Swedish lakes (Algesten et al., 2003). Similarly according to Dillon and Molot (1997a), approximately 50% of the dissolved organic carbon (DOC) entering a suite of northern temperate lakes is lost to a combination of the atmosphere and the sediment roughly in equal proportions (i.e. ~25% evaded and ~25% sedimented). Typically, particulate organic carbon (POC) in the inflows to the lakes is neither measured nor included in carbon mass balances (e.g. Dillon and Molot, 1997a) as POC concentrations are typically less than 10% of the DOC concentrations entering the lakes (Wetzel, 2001). However, during the photodegradation of dissolved organic matter (DOM) from streams flowing into some of the lakes studied by Dillon and Molot (1997a), 20% to 90% of the DOC lost can be transformed to POC (Chapter 4).

In aquatic systems with large allochthonous inputs, the balance between allochthonous and autochthonous carbon also becomes important when interpreting the $\delta^{13}C$ record of the lake sediments ($\delta^{13}C$-Seds). Traditionally, examining the organic content and the $\delta^{13}C$ of lake sediments has been used as an indicator for changes in productivity and surface water nutrient levels, to aid in the reconstruction of lake and watershed paleoenvironments, and to infer regional climate change (Meyers and Teranes, 2001). During photosynthesis, phytoplankton create organic matter that is isotopically lighter than the dissolved inorganic carbon (DIC) source through the preferential consumption of ^{12}C, due to a fractionation of ~20‰ between the carbon source and the organic product (O'Leary, 1988). However, this fractionation value can be variable (e.g. Hecky and Hesslein, 1995; Bade et al., 2006; Mohamed and Taylor, 2009).

Productivity is not the only process that affects the $\delta^{13}C$-Seds in aquatic systems. Photodegradation of DOM uses O_2 as an electron acceptor in the breakdown of DOC to DIC. During this process, POC is created and the δ^{13}C- of the remaining DOC is altered (Chapters 3 and 4). In stream waters from 10 Ontario inflows, the δ^{13}C of the majority of POC samples created through DOM photodegradation were similar to, or greater than, the initial δ^{13}C-DOC, and always greater than the δ^{13}C of the DOC lost (Chapter 4). This indicates that in lakes with high DOC, photodegradation can alter the δ^{13}C-DOC and the POC created is generally within 1‰ of the δ^{13}C-DOC from which it formed. Similarly, von Wachenfeldt and Tranvik (2008) have shown that trapped sedimenting materials in 12 boreal lakes were dominated by allochthonous matter resembling the source δ^{13}C-DOC (as suggested by fluorescence index data and δ^{13}C values, by assuming an estimated allochthonous δ^{13}C end-member of –27‰).

The organic carbon in aquatic sediments can be composed of a combination of: i) litter falling onto the lake from the surrounding shoreline; ii) POC entering the lake through the inflows; iii) the flocculation of photodegraded allochthonous DOC; iv) allochthonous and/or autochthonous DOC flocculating within the lake; and v) autochthonous POC. In the carbon balances calculated by Dillon and Molot (1997a), if 25% of the DOC entering lakes is ultimately sedimented, and POC is 10% of the DOC entering, then stream POC and the POC formed from the degradation of allochthonous DOM could become important components of the lake sediments. However, organic carbon in aquatic sediments can be affected by post-burial diagenesis decreasing the mass of total organic carbon until it is buried below the oxic-anoxic interface (Meyers and Teranes, 2001). For example, two sediment cores taken from the same location in Lake Ontario 6 years apart indicate that microbial processing decreased the organic matter mass by 20% during that time (Hodell and Schelske, 1998). Early diagenesis can also affect the C/N ratios of organic matter. For example, buried wood samples have lower C/N ratios than fresh wood samples indicating selective degradation of carbon-rich sugars and lipids (Meyers et al., 1995). The C/N ratio of algal derived (autochthonous) organic matter, however, can increase due to degradation of nitrogen-rich compounds. Diagenetic changes to the C/N ratio of sediment organic matter are not often large enough to erase the observed C/N differences between land plants and lake algae (Meyers and Terranes, 2001). The δ^{13}C-Seds can also be impacted by post-burial diagenesis since different compounds degrade more readily (Herezeg, 1988), but this was found to be minimal in the 2 Lake Ontario cores collected from the same location 6 years apart (Hodell and Schelske, 1998). Although sediment diagenesis is included in the whole lake mass balances of Dillon and Molot (1997a), based on organic measurements in the lake sediments it is expected to be minimal (Ontario Ministry of the Environment, unpublished data).

Methanogenesis can also occur in unconsolidated lake sediments and soils under anaerobic conditions, and methanotrophs do fractionate carbon. Fractionation will depend on whether the source carbon is CO_2 or preformed reduced carbon substrates however, even when the soils/sediments are CH_4 saturated methane only accounts for approximately 1% of the total organic carbon present in organic rich shallow sediments. (Whitcar, 1999), therefore it is unlikely that methanogenesis will affect the δ^{13}C-Seds.

Since incoming POC from streams and POC that formed by allochthonous DOM degradation can be important contributors to lake sediments, their role in the δ^{13}C of lake sediments should be assessed. This paper will 1) estimate the proportions and the δ^{13}C values of litter, POC entering through streams, and POC created through photodegradation to calculate the δ^{13}C of the allochthonous sediment input end-member, 2) estimate a δ^{13}C value for the autochthonous end-member to determine if the allochthonous and autochthonous end-members are isotopically distinct, and 3) examine whether the δ^{13}C of lake sediments can be used to discern the relative proportions of allochthonous and autochthonous carbon within them for two northern temperate lakes.

6.3 Methods

Harp and Dickie Lakes are oligotrophic headwater lakes that are part of a long-term monitoring program carried out by the Ontario Ministry of the Environment (OME). The 25-year chemistry and hydrology datasets indicate that stream DOC concentrations decrease with increasing discharge, and generally that discharge has a 7 or 10 year cycle. The watersheds lie on the southern tip of the Precambrian shield approximately 200 km north of Toronto, Ontario, Canada in the Muskoka-Haliburton region. Descriptions of these inflows and catchments are summarized in Dillon et al. (1991) and the location and general characteristics are located in Figure 5.1 (Chapter 5) and Table 6.1 (current chapter).

Table 6.1: General Stream Characteristics for the Inflows of Harp and Dickie Lakes.

Stream/Lake	% Peatland[1]	Area (ha)[1]	Stream Length[1] (m)
Harp Inflow 3	9.3	26.0	1010
Harp Inflow 3a	2.9	19.7	762
Harp Inflow 4	8 [3]	119.5	2040
Harp Inflow 5	13.3	190.5	1830
Harp Inflow 6	10 [3]	10.0	701
Harp Inflow 6a	8.5	15.3	610
Harp Lake		71.38 [2]	
Dickie Inflow 5	25.4	299.8	762
Dickie Inflow 6	21.8	22.0	488
Dickie Inflow 8	8.2	67.0	1220
Dickie Inflow 10	17.1	78.9	975
Dickie Lake		93.6 [2]	

[1] Dillon et al., (1991)
[2] Dillon and Molot, (1997a)
[3] Eimers et al., 2008

Stream waters are generally oxic with low NO_3^{2-} and NH_4^+ concentrations (e.g. Dickie Inflows maximum NH_4^+ = 0.36 mg/L, maximum NO_3^{2-} + NO_2^- = 0.18 mg/L; OME, 2004-2007 unpublished data). Additionally, although annual-weighted ice-free concentrations of iron have fluctuated (between ~190 μg/L and 380 μg/L) and concentrations of manganese have increased slightly (~40 μg/L to 95 μg/L) in Dickie Lake, both iron and manganese are decreasing in Harp Lake (Fe: ~170 μg/L to ~35 μg/L, Mn: ~76 μg/L to 7 μg/L; OME, unpublished). These lakes have an appreciable amount in-lake DOC consumption, evident by the lower lake and outflow DOC concentrations in comparison to their inflows. The inflows travel through peatlands ranging between 0% and 25.4% of their sub-catchment area (Dillon et al., 1991).

The inflows and outflows of Harp and Dickie Lakes were sampled between March and the end of November in 2004 to 2005 and in the spring of 2007. Additional samples were collected from the Harp inflows between 1990-1992 (Schiff, unpublished). Inflow and outflow water was collected from weirs located approximately 50 m upstream and downstream from the lakes. Many of these streams have been the focus of photolytic DOM and carbon balance studies (e.g. Dillon and Molot, 1997a; Molot and Dillon, 1997b; Gennings et al., 2001; Kelton et al., 2007; Chomicki and Schiff, 2008; Chapters 2 through 4).

Inflow and outflow samples were analyzed for δ^{13}C-POC and δ^{13}C-DOC. Samples for δ^{13}C-POC and δ^{13}C-DOC were obtained by filtering stream water sequentially through Whatman QMA and pre-combusted GF/F filters. The particulate carbon collected on the QMA filter was analyzed on a Carlo Erba 1105 Elemental Analyzer coupled to a Micromass Isochrom (EA-IRMS) at the Environmental Isotope Laboratory, Waterloo, Ontario, with a precision of ± 0.2‰, and with duplicate samples measuring within 0.2‰ of each other. The filtrate passed through a GF/F was acidified with 20% HCl to a pH of 4.5, freeze-dried and run on the same instrument used for analysis of δ^{13}C-POC to obtain δ^{13}C-DOC values, also with a precision of ± 0.2‰. Molar C/N ratios were calculated using the %C and %N results from the elemental analyzer.

To examine the δ^{13}C of POC created from the degradation of stream DOM, incubation experiments were performed on inflow waters to Harp and Dickie Lakes. Details of the experimental setups are outlined in Chapter 4. Briefly, large samples of inflow waters were filtered to 0.2 µm. Further microbial growth was inhibited by adding 1mL/L of a saturated solution of $HgCl_2$ to the 0.2 µm filtrate. Initial experiments indicated little difference between concentration and isotope analysis in filter-sterilized and $HgCl_2$ sterilized samples (Chapters 2 and 3). In the current photolytic experiment, Harp and Dickie inflow samples were incubated under natural sunlight at the University of Waterloo (43° 28' 25.6" N and 80° 33' 27.5" W; elevation ~ 335 m) for 28 and 34 days respectively. Duplicate samples were placed in Tedlar bags and incubated together in shallow water baths to minimize temperature and light exposure variations. After more than 50% of the DOC degraded, the POC created was collected and analyzed as above.

Samples for DIC, CO_2, and δ^{13}C-DIC were collected weekly to monthly from the mid-epilimnion of Harp and Dickie Lakes between 2003-2005 and 2007. Samples for DIC were collected without headspace in 15 mL Wheaton serum bottles, capped with baked BD Vacutainer stoppers (heated to remove residual CO_2), and preserved with 0.02 mL of a saturated $HgCl_2$ solution. For analysis, the samples were acidified with 85% H_3PO_4 to a pH < 2 after a 5 mL helium headspace was added. To equilibrate headspace and liquid concentrations, the acidified samples were shaken on an orbital elliptical shaker for 1.5 hours. DIC concentrations were measured by equilibrated headspace on a Shimadzu 8A Gas

Chromatograph fitted with a methanizer (Ni catalyst, He gas carrier, FID detector) with an uncertainty of < 5% (Stainton, 1973).

Water was slowly pumped from the mid-epilimnion via peristaltic pump into evacuated 60 mL Wheaton serum bottles capped with baked BD Vacutainer stoppers without headspace for CO_2 concentrations. Each bottle contained 3.56 mg of KCl as a preservative. Helium was introduced into the samples (5 mL He: 55 mL water) and the CO_2 in the water was equilibrated with the headspace by shaking the samples for a minimum of 1.5 hours on an orbital shaker. CO_2 concentrations were measured on the same gas chromatograph described above (Davies et al., 2003).

Samples for δ^{13}C-DIC were collected in 125 mL Wheaton serum bottles without headspace, capped with baked BD Vacutainer stoppers, and preserved with 0.3 mL of a saturated solution of $HgCl_2$. A helium headspace was created (5 mL He: 155 mL water) and samples were acidified with 85% H_3PO_4 to a pH less than 2. Samples were shaken for a minimum of 1.5 hours to equilibrate the gases between the dissolved phase and the headspace. Gas from the headspace was analyzed on a Micromass Isochrom isotope ratio mass spectrometer interfaced to a gas chromatograph combustion unit (GC-C-IRMS) at the Environmental Isotope Laboratory, Waterloo, Ontario. Precision of these samples is better than ± 0.3‰. Periodically, duplicate samples were analyzed and were within 0.3‰ of the first sample.

Sediment cores were extracted from the centre of Harp and Dickie Lakes in 1999 using a KB-type gravity corer (Glew, 1989). A detailed description of the coring and sediment processing is described in Eimers et al. (2006) and Faulkenham et al. (2003). Briefly, a minimum of fifteen 0.5-cm sediment slices were ^{210}Pb dated at Queen's University (A. Paterson, unpublished data) following the sample preparation and the core chronology establishment of Schelske et al. (1994). The constant rate of supply model (Binford, 1990) was used to calculate ages of the sediment samples after the ^{210}Pb activities were corrected for isotopic decay. Sediment δ^{13}C signatures were also measured from the ^{210}Pb dated short cores taken. Carbon and nitrogen stable isotopes of the sediment organic matter from Dickie Lake was analyzed on EA-IRMS as above, with a precision of ± 0.2‰.

6.4 Results and Discussion

To determine the ratio of allochthonous to autochthonous carbon in lake sediments using δ^{13}C, the δ^{13}C values of the allochthonous and autochthonous end-members are required for each lake. Additionally, the importance of different sources that comprise allochthonous POC must be determined. For the allochthonous end-member the δ^{13}C was calculated using the following equation:

(Equation 6.1)

$$\delta^{13}C_{alloch} = \frac{(m_{litter}\delta^{13}C_{litter}) + (m_{stream}\delta^{13}C_{stream}) + (m_{DOCphoto\deg raded}\delta^{13}C_{DOCphoto\deg raded})}{(m_{litter} + m_{stream} + m_{DOCphoto\deg raded})}$$

where m_{litter} is the mass of the litter entering the lakes, m_{stream} is the mass of POC entering through the inflows, $m_{DOCphotodegraded}$ is the mass of POC created through the photodegradation of DOC, $\delta^{13}C_{litter}$ is the δ^{13}C of litter and vegetation in the lake catchments, $\delta^{13}C_{stream}$ is the weighted average annual δ^{13}C of the POC entering through the inflows, and $\delta^{13}C_{DOCphotodegraded}$ is the δ^{13}C of the POC created during DOC photodegradation.

The autochthonous δ^{13}C end member value was calculated using:

(Equation 6.2)

$$\delta^{13}C_{auto} = \sum_{month=1}^{12}(relative\ production_{month} \times (\delta^{13}C{-}CO_{2month} + \varepsilon))$$

where month is the month of the year, relative production is the relative annual production of each month, δ^{13}C-CO_{2month} is the δ^{13}C of the surface water CO_2 for each month, and ε is the average annual photosynthetic fractionation. The values used to calculate these allochthonous ($\delta^{13}C_{alloch}$) and autochthonous ($\delta^{13}C_{auto}$) end-member values will be discussed in the following sections.

6.4.1 δ^{13}C-Allochthonous POC ($\delta^{13}C_{alloch}$)

There are many difficulties associated with quantifying the $\delta^{13}C_{alloch}$ end member. Commonly, the isotopic signature of the allochthonous source is considered to be equal to the terrestrial δ^{13}C-DOC signal, which usually falls within the range of –26‰ to –29‰ (commonly –28‰ in boreal regions; Junger and Planas, 1994). However, the allochthonous end-member can be composed of leaf litter and other vegetation falling onto lakes, and POC from streams, in addition to the DOC entering from streams that is photodegraded to POC in lakes. In order to calculate an allochthonous end-member, the importance of each of these components needs to be assessed. The following allochthonous POC section will be organized into three subsections (Litter, Stream POC, and Photodegraded DOC) and will explore i) the potential mass contribution of the allochthonous component, ii) measured ranges in the C/N ratios, iii) the δ^{13}C values associated with each component, and iv) a summary of the values used to calculate the average annual δ^{13}C value for each component.

6.4.2 Litterfall

6.4.2.1 Estimate of mass contribution (m_{litter})

The mass of leaves and other litter transported into Harp and Dickie Lakes through the inflows or falling on the lakes has not been quantified. Due to the complexity and the potential number of carbon transfer pathways, often complete carbon mass balances are scarce (Quay et al., 1986). Since 90-95% of total organic carbon in streams is DOC (Wetzel, 2001), mass balance calculations are controlled by the dissolved components (Algesten et al., 2003). Dillon and Molot (1997a) completed DOC and DIC mass balances for Harp and Dickie Lakes but did not separately measure allochthonous POC inputs. TOC samples were screened through a 70-µm mesh (Dillon and Molot, 1997a), which would exclude a large portion of the litterfall coming in through the streams from the measured TOC. Additionally, litter falling onto the lake was not included. It was therefore necessary to estimate the litter falling onto Harp and Dickie Lakes to determine its importance to the $\delta^{13}C$ allochthonous end-member value.

The studies that have estimated or measured shoreline litter in addition to DOC and DIC entering lakes have shown variable results, with litterfall ranging from 0% to 50% of the total carbon inputs and between 0.4% and 88% of the allochthonous inputs (e.g. Wetzel and Rich, 1973; Wetzel et al., 1972; Gasith, 1975; Gasith and Hasler, 1976; Wissmar et al., 1977; Hall and Hyatt, 1974; Hargrave, 1969; Jordan et al., 1985). However, the high allochthonous and high total inputs are from Lake Findley and Mirror Lake, while litter from the remaining lakes cited above is less than approximately 3% of the allochthonous and total inputs. The carbon budgets of Lake Findley lack any data for macrophytes, algae, CO_2 uptake by bacteria, or precipitation, suggesting that some important carbon contributions could be missing. If included, the actual proportion of litter in comparison to the other carbon inputs may be different. Additionally, Lake Findley has a very rapid flushing time (0.14 years) which influences carbon cycling. Lakes that flush rapidly have much higher inputs of allochthonous to autochthonous carbon (Jordan et al., 1985).

Mirror Lake, the other lake with high litter input (~25% of allochthonous inputs; ~7% of total inputs), has a longer flushing time (1.0 years) than Lake Findley, but is a good comparison to Dickie Lake in terms of its depth, flushing time, and landuse (recreational/forest). However, it is located near the mouth of Hubbard Brook Valley, and its basin is characterized by steep land slopes, and high knobs and ridges (Winter, 1985) perhaps transporting additional litter to the lake. Litter at Mirror Lake has been estimated as 354 g C m^{-1} shoreline falling onto the lake (as twigs, branches, leaves, flowers, pollen, seeds, *etc.*), which is similar to Polish lakes (Szczepanski, 1965) and Lake Wingra (Gasith and Hasler, 1976). Using this estimate as a maximum, Harp and Dickie Lakes could have an additional 2.3 g C $m^{-2}y^{-1}$ and 3.0 g C $m^{-2}y^{-1}$ falling onto the lakes respectively (on an areal basis). Incorporating these litter values into the inputs of the budgets suggests litter could contribute a maximum of 6% and 7% of the total carbon inputs to Harp and Dickie Lakes respectively and approximately 7% to 9% of the TOC inputs to the lake.

However, the shores of Harp and Dickie Lakes are covered with cottages that are seasonally and permanently occupied (e.g. 140 homes on Dickie Lake of which 36 are fulltime homes; Dickie Lake Association, 2007) suggesting that estimates for litterfall into the lakes can be treated as maxima since many trees surrounding the lake near the shore have been cleared for cottage development. At Mirror Lake, leaves contributed 62% of the total litterfall (e.g. reducing 354 g C m^{-1} to 219 g C m^{-1} shoreline). Using only the Mirror Lake leaf contribution, 3.7% and 4.5% of the total carbon inputs (and approximately 4.5% to 5.5% of the total organic carbon inputs) to the Harp and Dickie Lakes respectively are from leaves. To calculate the allochthonous $\delta^{13}C$ end-member value, and assess the sensitivity of this value to the amount of litter, a range of 219 g C m^{-1} shoreline to 354 g C m^{-1} shoreline will be used to estimate the m_{litter} contribution (Table 6.2).

Table 6.2: Scenarios used to calculate the possible ^{13}C range of the allochthonous end-member in a) Harp Lake, and b) Dickie Lake. Mass is normalized to area and displayed in g C m^{-2}y^{-1}, and δ^{13}C values are in ‰. The photolytic component (Photo) indicates that 56% of the DOC is converted to POC. The contribution of each of the three allochthonous sources to the allochthonous endmember are listed in % such that the litter, stream POC and photolyzed DOC contributions sum to 100%.

a) Harp Lake

Conditions	Litter			Stream POC			Photolyzed DOC			Allochthous endmember	
	Mass/ Area	%	^{13}C	Mass/ Area	%	^{13}C	Mass/ Area	%	^{13}C	Mass/ Area	^{13}C
Litter: 354g/m POC: 4% of DOC Photo: 56% DOC to POC	2.3	19	-28.9	1.2	10	-28.6	8.2	71	-26.4	11.6	-27.1
Litter: 354g/m POC: 10% of DOC Photo: 56% DOC to POC	2.3	18	-28.9	2.9	22	-28.6	7.7	60	-26.4	12.9	-27.3
Litter: 219g/m POC: 4% of DOC Photo: 56% DOC to POC	1.4	13	-28.9	1.2	11	-28.6	8.2	76	-26.4	10.8	-26.9
Litter: 219g/m POC: 10% of DOC Photo: 56% DOC to POC	1.4	12	-28.9	2.9	24	-28.6	7.7	64	-26.4	12.0	-27.2

b) Dickie Lake

Conditions	Litter			Stream POC			Photolyzed DOC			Allochthous endmember	
	Mass/ Area	%	^{13}C	Mass/ Area	%	^{13}C	Mass/ Area	%	^{13}C	Mass/ Area	^{13}C
Litter: 354g/m POC: 4% of DOC Photo: 56% DOC to POC	3.0	22	-29.5	1.2	9	-31.0	9.1	68	-26.6	13.3	-27.7
Litter: 354g/m POC: 10% of DOC Photo: 56% DOC to POC	3.0	20	-29.5	3.1	21	-31.0	8.5	58	-26.6	14.6	-28.2
Litter: 219g/m POC: 4% of DOC Photo: 56% DOC to POC	1.8	15	-29.5	1.2	10	-31.0	9.1	75	-26.6	12.1	-27.5
Litter: 219g/m POC: 10% of DOC Photo: 56% DOC to POC	1.8	14	-29.5	3.1	23	-31.0	8.5	63	-26.6	13.4	-28.0

6.4.2.2 C/N ratios

In the Harp and Dickie watersheds, the unweighted average C/N ratios of a variety of leaves and vegetation are 62 and 117 respectively (Schiff, unpublished). Similarly, *Sphagnum* and other vegetation from the region also had high C/N ratios ranging between 73 and 162 (Sentance, 2006). High C/N ratios in litter are expected since vascular land plants are protein poor and contain fibrous tissues such as cellulose and lignin, which have C/N ratios greater than 20 (Meyers and Teranes, 2001). Temporal C/N ratios are not available for the litter surrounding Harp and Dickie Lakes, but the ratios likely vary on a seasonal basis and are higher at litterfall time.

6.4.2.3 δ^{13}C values ($\delta^{13}C_{litter}$)

The average δ^{13}C values of leaves and vegetation was –28.9‰ and –29.5‰ in Harp and Dickie catchments respectively (Schiff et al., 1997; Schiff, unpublished; Sentance, 2006) which is similar to the –28‰ to –30‰ measured by Aravena et al. (1992) and Trumbore et al. (1992).

6.4.2.4 Average annual δ^{13}C value

The mean δ^{13}C values of leaves and vegetation at Harp and Dickie Lakes were used in combination with the range of litter fall estimates (219 g C m^{-1} shoreline to 354 g C m^{-1} shoreline) to calculate the litter component to the δ^{13}C allochthonous end-member, and to assess the sensitivity of litter on the δ^{13}C allochthonous end-member value.

6.4.3 Stream POC

6.4.3.1 Estimated mass contribution (m_{stream})

The mass of stream POC entering Harp and Dickie Lakes is also unknown, therefore a range of masses for stream POC must be estimated. On a subset of samples, Dillon and Molot (1997a) measured both filtered and unfiltered DOC samples in the data accumulated for their mass budgets and found that POC was insignificant compared to DOC. In addition, Molot and Dillon (1997b) performed incubation experiments on some of the same streams and lakes of the current study, and cite unpublished data by Dillon (1991), indicating POC was less than 5% of total organic carbon (TOC). Since POC is a small proportion (< 5%) of the total organic carbon inputs in

Harp and Dickie Lakes (Dillon, unpublished data, 1991 as cited in Molot and Dillon 1997b) it is not measured separately from DOC by the OME. However, many studies infer or measure POC concentrations. Some of these studies will be examined to isolate a range of POC values to use in the determination of the m_{stream} value.

Generally, POC is 3% to 10% of the total carbon entering the lakes (Wetzel, 2001). Baker et al. (2008) show that a comparison between filtered DOC and DIC to the total organic and inorganic carbon in the River Tern, which is surrounded by wetlands, yields a linear slope of 0.97 with an intercept of zero illustrating that the majority of carbon is dissolved (not particulate carbon). Sand-Jensen and Pedersen (2005) found DOC concentrations to be 2 to 18 times higher than POC among 4 streams with highest POC concentrations in open streams downstream of plankton rich lakes and low concentrations in a groundwater-fed forest spring. The most similar stream to streams in this study contained high DOC concentrations (18.3 mg/L) with POC concentrations 18 times lower than the DOC (POC = 0.9 mg/L; POC ~5% of DOC).

Similarly, historical inflow data from Lake 239 at the Experimental Lakes Area (ELA) near Kenora, Ontario indicate that on average, the POC load was approximately 4% of the DOC load (Kasian, ELA Database, DFO unpublished). In unproductive forest lakes, with high allochthonous carbon inputs, DOC is the dominant organic carbon input (Kortelainen et al., 2006). This is seen in a boreal Finnish humic river where POC concentrations were on average approximately 12% of the DOC concentrations, and peatlands accounted for 50%-60% of the land area surrounding the river (Heikkinen, 1994). This is approximately 2 to 5 times the peatland coverage in the current study (Harp subcatchments 0%-13%; Dickie subcatchments 8%–25% peatland coverage). The carbon budgets of Mirror and Marion Lakes indicate that POC is approximately 10% of DOC

(Jordan et al., 1985). However, Lakes Lawrence and Wingra are less similar than the lakes from this study (e.g. influenced by an agricultural marsh or lie within an urban forested region) and have higher POC inputs into the lakes (~20% and ~149% of the DOC inputs respectively; Jordan et al., 1985) likely on account of increased soil erosion (Jonsson and Jansson, 1997).

Considering the literature, the amount of POC entering the study lakes is likely between 4% to 10% of the DOC load, and is likely more similar to ELA, and the forested stream (POC ~5% of DOC) in Sand-Jensen and Pedersen (2005) than the regions influenced by agricultural marshes and urban development. Although Dillon (unpublished data, 1991) suggest that POC is less than 5%, a POC range of 4 to 10% of DOC will be used to assess the sensitivity of stream POC on the allochthonous $\delta^{13}C$ end-member value, and the $\delta^{13}C$ of the lake sediments.

If the amount of POC entering the lakes is between 4% and 10% of the DOC load, then stream POC can account for 5% to 13% of the TOC loss through sedimentation and via the outflows in Harp and Dickie Lakes. Similarly, applying the same POC range to the aquatic carbon fluxes from 21 northern and central Sweden catchments in Algesten et al. (2003) indicates that the "estimated POC" from terrestrial export ranges from 5% to 35% of the total carbon lost to sedimentation and the outflows (i.e. if POC = 4% of TOC, then the range is 5% to 13%; if POC = 10% of TOC, then the range is 14% to 35%). It is therefore understandable that since POC is usually a small influence on lake budgets, TOC is often measured instead, accounting for the POC (e.g. Algesten et al., 2003; Dillon and Molot, 1997a).

Although the majority of allochthonous carbon transported to boreal aquatic systems is DOC, carbon accumulation within lakes is presumably dominated by POC (Kortelainen et al., 2004), which is primarily transported at high stream flow periods (i.e. spring and autumn) when terrestrially derived POC inputs are high (Jonsson and Jansson, 1997). Although POC may only be 4% to 10% of the carbon entering the lakes, if all the POC settled to the lake sediments they could contribute 12% to 31% and 18% to 46% of the total carbon accumulation in the lake sediments of Dickie and Harp Lakes respectively. However, although stream POC will likely have a much higher settling velocity, these are overestimations since a combination of stream POC and within lake POC could exit the lakes through their outflows.

6.4.3.2 C/N ratios

Stream POC has C/N ratios ranging between 8.6 and 16.5 with 62% of the samples below 12 and 90% of the samples below 15 (Figure 6.1a). These stream POC C/N ratios are similar to C/N ratios in northern temperate lakes (8.3 to 17.9) and streams (10.4 to 14.2) from ELA (Hecky et al., 1993). While land plants have C/N ratios greater than 20 (Meyers and Teranes, 2001), phytoplankton, with little to no cellulose and lignin, contain more N and commonly have C/N values between 4 and 10. Different phytoplankton groups have C/N ratios ranging between 6.6 (Goldman et al., 1979; Morris, 1981, Biddanda and Benner, 1997), similar to the Redfield ratio, and 12 (Legendre and Rivkin, 2009), but Goldman and Dennett (2000) indicate that growth conditions may cause variations in the C/N ratio. C/N ratios less than the Redfield ratio have been found in both bacteria and protozooplankton (Legendre and Rivkin, 2009), while filamentous periphyton samples composed of mostly algae can have higher average C/N ratios (e.g. C/N = 20, n=21, 2000; C/N = 31, n=13, 2001; Venkiteswaran, 2008). Although the C/N range of the inflows suggests that POC from the streams reflects a mixture of algal and vascular plants, the majority of samples reflect an algal source.

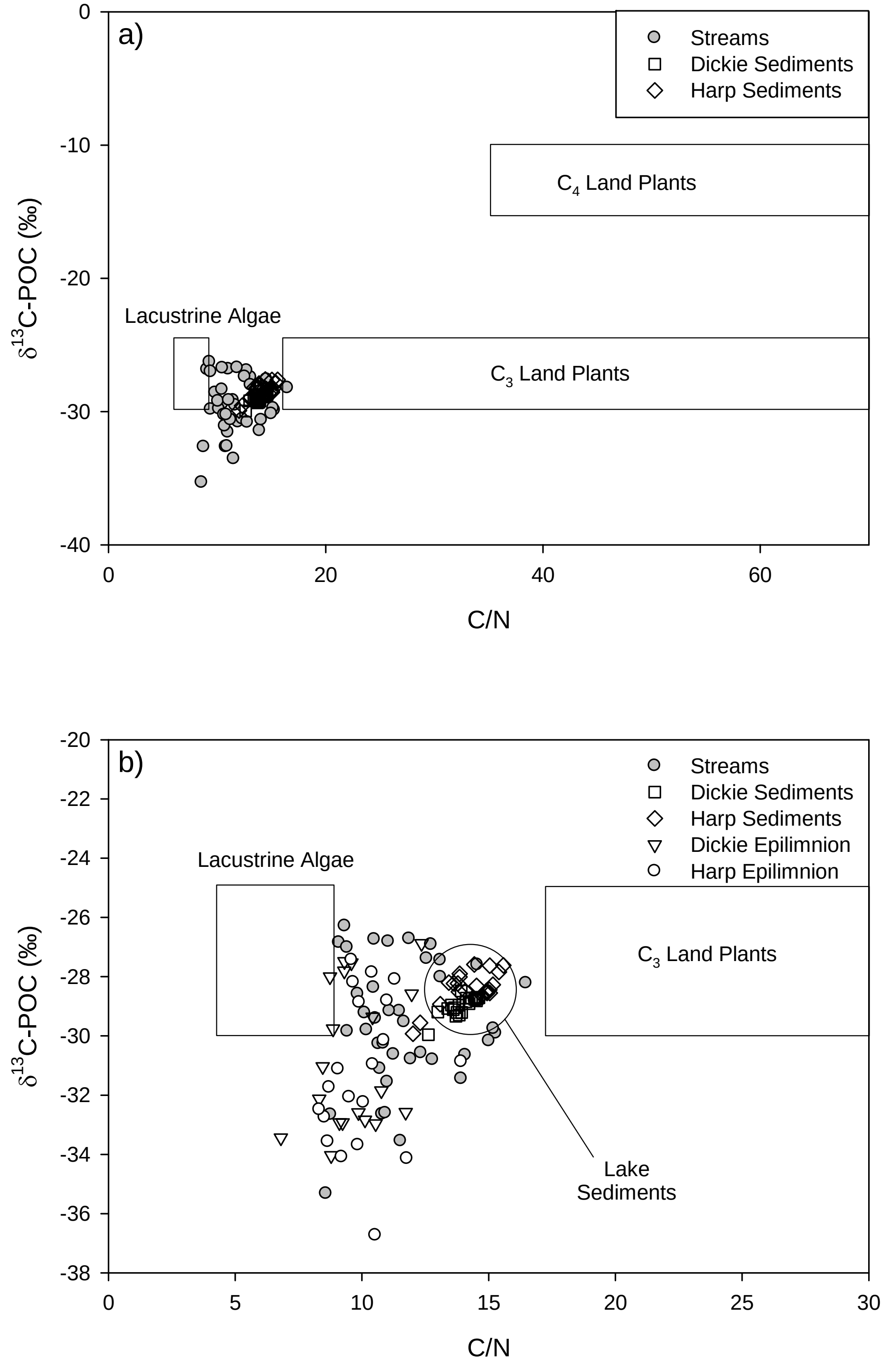


Figure 6.1: δ^{13}C-POC vs. C/N in a) the inflows and the sediment of Harp and Dickie Lakes; and b) the inflows, lake sediments and epilimnion POC samples from Harp and Dickie Lakes. Boxes are constructed after Meyers and Terranes (2001), however, algae can be less than –30‰.

Cross et al. (2005) note that in freshwater benthic systems there are substantially higher C/N and C/P ratios in leaf, litter, and green leaves than in terrestrial and other aquatic environments. The C/N ratios of leaves and other vegetation (62 to 117) are much larger than the C/N range observed in the POC of the inflows, lakes, and sediments (Figure 6.1) suggesting that litter transported to lakes may not be a large carbon source to the lake sediments (C/N range: 12.6 to 14.6) or that litter is heavily processed within the lake. The C/N range observed for the POC in the Harp and Dickie Lake inflows is similar to the C/N ratios in the lake sediments (Figure 6.1b) suggesting that if there were an appreciable amount of POC from the inflows which is not heavily processed within the lakes, it could influence or become incorporated into the sediment record.

6.4.3.3 *δ^{13}C values ($\delta^{13}C_{stream}$)*

The δ^{13}C-DIC of the groundwater from wells close to recharge and discharge areas, and from wells near the middle of the basin at Harp Lake were within the range of –22‰ to –24‰, typical isotope values for CO_2 in soils without $CaCO_3$ (Aravena et al., 1992). These data (in conjunction with ^{14}C and soil CO_2 data) reflect the silicate weathering of underlying geology in the catchment (Aravena et al., 1992). The isotopic composition of stream DIC, in the case of silicate weathering, reflects the soil CO_2 produced from root respiration and soil organic matter decomposition.

It is possible that some of the changes in the δ^{13}C-DIC values in the streams over the course of the year are due to changes in the diffusive gas losses. As diffusive gas losses increase and the soil CO_2 increases, outgassing increases and changes the δ^{13}C-DIC, further illustrating that the DIC is controlled by soil CO_2 and the silicate weathering of the underlying geology. This suggests that in stream production or consumption was not the dominant process affecting the δ^{13}C-DIC signatures.

The δ^{13}C-POC of the inflows ranged between –26.3‰ and –35.3‰ for Harp Lake and –27.4‰ and –39.1‰ for Dickie Lake (Figure 6.2 and Figure 6.3). Using the DOC mass balances, and assuming that POC was 4% to 10% of the DOC, the monthly POC was estimated in each inflow and used to calculate an weighted average annual δ^{13}C-POC inflow value of -28.6‰ and -30.9‰ for Harp and Dickie inflows respectively. Seasonally, in the Harp Lake inflows, δ^{13}C-POC signatures were at a maximum in the spring, becoming more depleted as the snow melts reaching a minimum in May. As summer progressed, the δ^{13}C-POC increased and, in most cases, reached a maximum (similar to the spring maximum) in the late fall (Figure 6.3a).

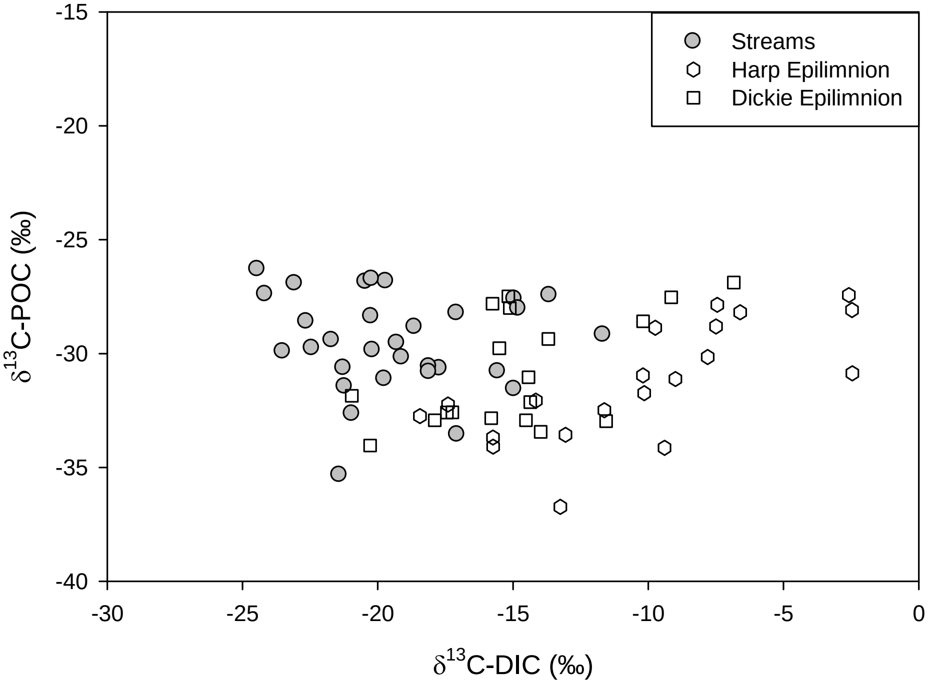


Figure 6.2: δ^{13}C-POC vs. δ^{13}C-DIC in stream waters and in the epilimnion of Harp and Dickie Lakes. δ ^{13}C-POC and δ ^{13}C-DIC have a precision of 0.2‰ and 0.3‰ respectively.

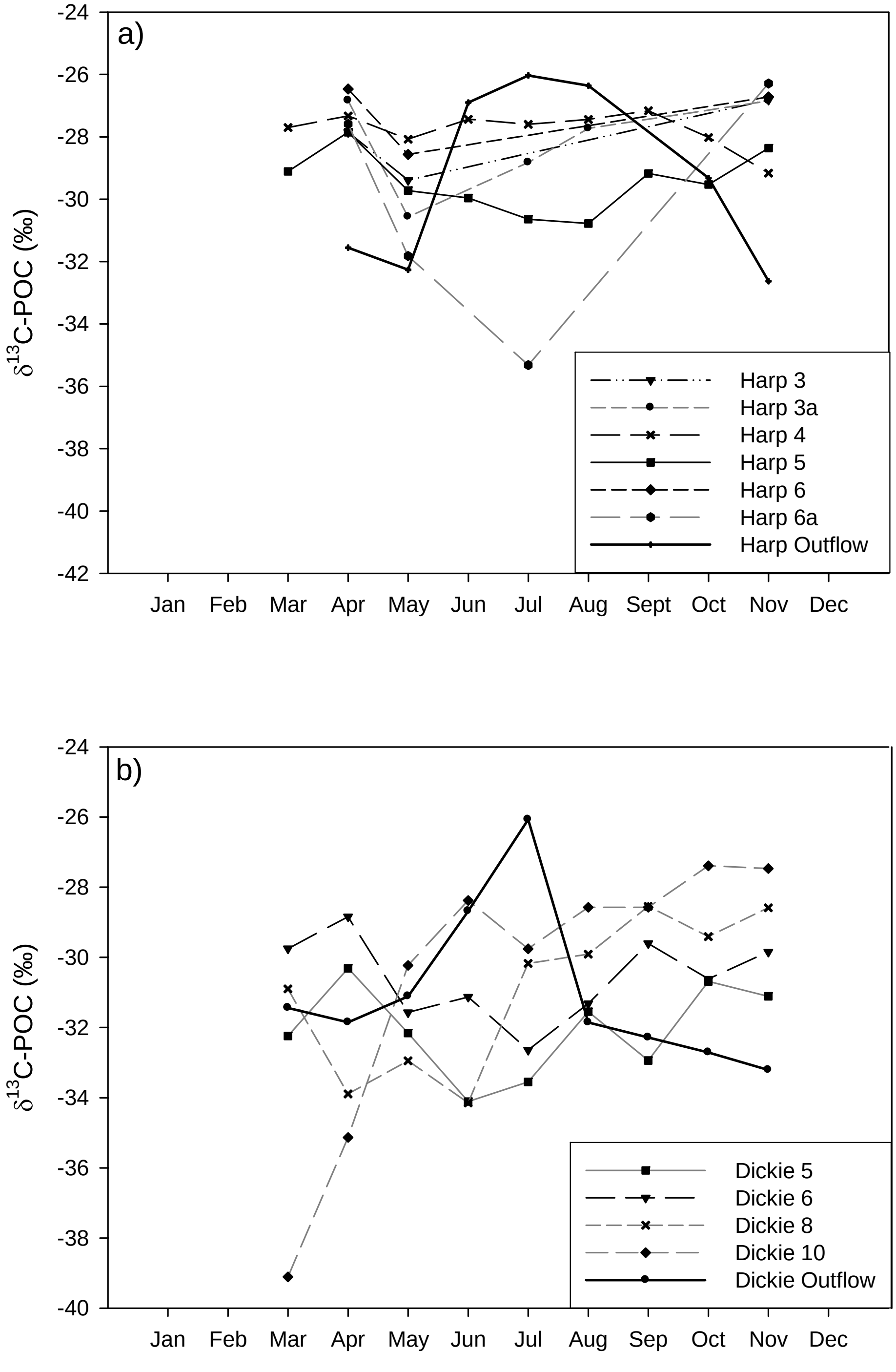


Figure 6.3: Annual variation in the δ^{13}C-POC of the inflows and outflows of a) Harp Lake and b) Dickie Lake. Precision is 0.2‰.

In general, the range of stream δ^{13}C-POC (–25‰ and –35‰) overlaps with the range observed for C3 plants (–24‰ to –29‰; Deines, 1980), fresh plant material, and relatively undecomposed litter in the Harp catchment (–28‰ to –30‰; Aravena et al., 1992; Trumbore et al., 1992). The upper range of the δ^{13}C-POC values overlaps soil δ^{13}C values (–26.4‰ and –25.6‰ in the A1 and B2 soil horizons respectively; Trumbore et al., 1992). However, the δ^{13}C-POC values were generally less than the δ^{13}C-DIC in both the streams and epilimnion of the lakes but the slope for the two lakes does not equal 1 (Figure 6.2), suggesting that POC is not entirely autochthonous, or that photosynthetic fractionation is changing.

The depleted δ^{13}C-POC values reaching –35‰, suggest that stream δ^{13}C-POC appears to be influenced by algal sources (Figure 6.1 and Figure 6.2) suggesting that aquatic cellulose is transported into the lakes and possibly to the lake sediments. Low C/N ratios also suggest that algae are an important source of POC within the streams (Figure 6.1). Therefore, the δ^{13}C and C/N ratios both suggest that stream POC is a mix of terrestrial and algal carbon. The range in δ^{13}C values suggests that the source of POC either changes or the importance of different sources (i.e. terrestrial vs. algal) changes over the year. In the early spring, prior to shading from forest cover, δ^{13}C-POC and δ^{13}C-DIC values were generally lower than in the summer months and the POC could be created via in-stream primary productivity. The δ^{13}C-POC became enriched in the summer, suggesting the role of terrestrial carbon in POC development becomes more important. D10 is an anomaly with extremely depleted δ^{13}C signatures (DIC and POC) and higher C/N ratios (i.e. 18 to 33) in the winter months through early spring suggesting that a different POC source exists.

In the Dickie Lake inflows, there was more month-to-month variability in δ^{13}C-POC than in Harp Lake inflows and, while Dickie

Inflows 5 and 6 generally follow the same trends as Harp Lake inflows, Dickie Inflows 8 and 10 do not (Figure 6.3b). Dickie Inflow 8 reached a minimum earlier in the spring months than the other inflows, reaching a maximum in summer. In the fall, Dickie Inflow 8 δ^{13}C-POC values generally stayed close to -29‰. Dickie Inflow 10 was initially very depleted during March and April, increasing until June after which the observed δ^{13}C-POC trend is similar to the Harp Lake Inflows.

Annual changes in δ^{13}C-POC values were 2‰ to 13‰, while within month changes between the inflows were 1.4‰ to 7.7‰ and 1.6 to 10.3‰ for Harp and Dickie inflows respectively. The greatest variation and lowest δ^{13}C values were observed in streams with a higher percentage of peatlands in their catchments, suggesting that with increasing peatland coverage there is an increasing deviation from a terrestrial δ^{13}C value (or δ^{13}C-DOC) and more of an algal influence likely due to ponded water.

The δ^{13}C-POC range observed in the Harp and Dickie Inflows are larger than δ^{13}C-POC ranges from other studies. δ^{13}C-POC values during peak spring runoff from 14 streams within forested and agricultural regions of the Hudson-Mohawk watershed had a much smaller inter-stream δ^{13}C-POC range (2.5‰) with an average δ^{13}C-POC of –27.3‰ (Longworth et al., 2007). However, temporal data from six of these streams with minimal wetland area show similar variability (~1 to 6‰ within April to September) to the range observed in the Harp and Dickie streams (~1 to 8‰ from April to September). Small temporal δ^{13}C-POC ranges were observed within the main river inflows to Loch Ness, ranging between –25.0‰ and –27.1‰ in September and November (Jones et al., 1997). Townsend-Small et al. (2007) measured δ^{13}C-POC between –23‰ and –28‰ in 3 small Amazon headwater rivers during July and August. These rivers are much larger than the inflows in this study, and have more of an allochthonous contribution. It is important to recognize in the rivers listed above, algal POC will depend on the δ^{13}C-DIC of the individual systems. Temporal δ^{13}C-POC data on streams of similar size to the Harp and Dickie streams was scarce since these streams are shorter and shallower than streams reported in the literature.

6.4.3.4 Average annual δ^{13}C value

Overall, the weighted-average annual δ^{13}C value of POC entering the lakes was –28.6‰ and –31.0‰ for the Harp and Dickie inflows respectively. Generally, the lower δ^{13}C-POC values measured in the summer do not have much effect in the shaded streams since the carbon load is highest during non-summer periods. To assess the sensitivity of stream POC on the allochthonous δ^{13}C end-member value (and the δ^{13}C of the lake sediments) a POC range of 4 to 10% of DOC will be used to calculate the allochthonous end-member (Table 6.2).

6.4.4 POC created by DOC photodegradation

6.4.4.1 Estimated mass contribution ($m_{DOCphotodegraded}$)

Using the relationship between the DOC lost and the POC created during the incubations tracking the photodegradation of DOC and creation of POC (Chapter 4), on average, approximately 56% of the DOC lost is transformed to POC (Figure 6.4). Two statistical outliers were identified by Systat and were removed for regression analysis. The regression line is forced through the origin since there will be no POC formation if DOC is not lost. Although the relationship between the POC created and the DOC lost is good within the incubations of the Harp inflows, the relationship is not clear in the Dickie inflow incubations as the POC created compared to the DOC lost is more variable between the streams. Additionally the two statistical outliers were the incubations from Dickie Inflows 6 and 8. The reasons for this variability are unknown. However, Gao and Zepp (1998) note the formation of particulate matter is influenced by the presence of iron during

DOM photooxidation. As DOM photodegrades, carboxylate moieties oxidize (evident from the DIC produced) and Fe^{3+} forms polymeric iron oxides as the Fe^{3+} hydrolyzes to hydroxy complexes. These oxides then induce the flocculation of DOM creating particulate matter. It is possible that differences in iron concentrations (or other precursors to particulate matter formation such as manganese) could affect the amount of POC created and explain the scatter. However, iron and other metal concentrations were not measured in these incubations, therefore it is difficult to determine whether any differences in the concentrations of metals within the inflows controlled the variability in particulate matter formation. Consequently, the average POC created of all the incubations of both lakes will be used to estimate the importance of photodegraded DOC to the allochthonous ^{13}C end-member. Assuming that 1) POC is 4% -10% of the DOC entering the lake and 2) DOC will be converted to POC by photodegradation only during ice free months (e.g. May to November), then the mass of POC created by DOC photodegradation was calculated by:

(Equation 6.3)

$$m_{DOCphoto\deg raded} = \sum_{month=5}^{11} ((TOC_{stream})_{month} - (POC_{stream})_{month}) \times 0.56$$

where $m_{DOCphotodegraded}$ is the mass of POC created by the photodegradation of DOC, TOC_{stream} is the mass of total organic carbon (TOC) in the stream for each month m, POC_{stream} is the mass of POC in the streams assuming that stream POC is 4% to 10% of the TOC, and 0.56 is the slope of the line in Figure 6.4 once the two statistical outliers are removed. Using this equation, the $m_{DOCphotodegraded}$ is 7.7 to 8.2 g C m^{-2} and 8.5 to 9.1 g C m^{-2} of POC in Harp and Dickie Lakes respectively.

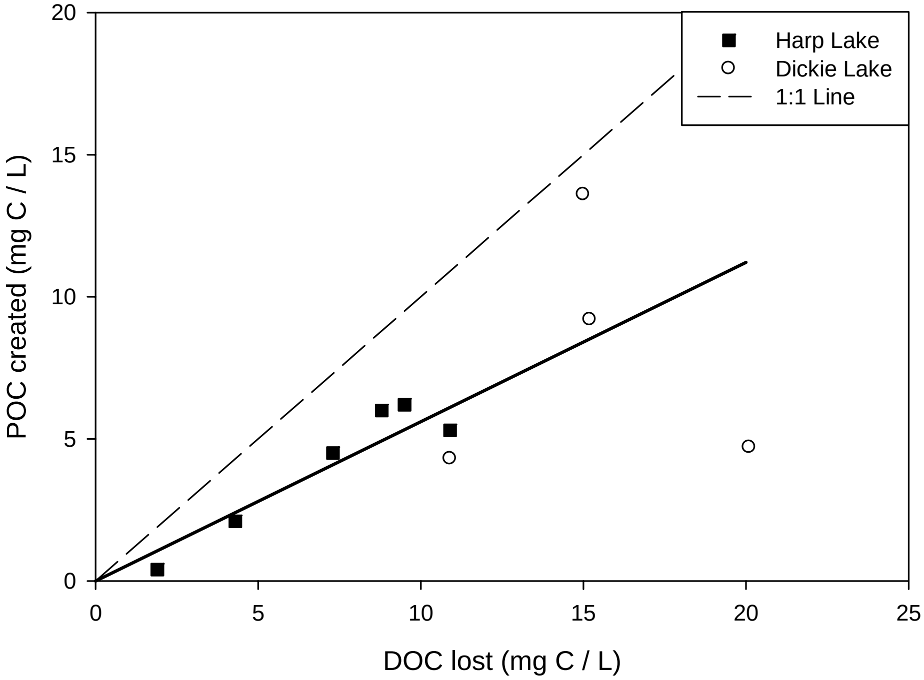


Figure 6.4: The relationship between the DOC lost and POC created during the photodegradation of DOC in incubation waters from the 10 inflows to Harp and Dickie Lakes. With the two statistical outliers (identified by Systat) removed for the regression analysis, the equation of the line is $y = 0.5603x$, and has an R^2 of 0.86. The statistical outliers remain on the plot.

6.4.4.2 C/N ratios

If the amount of POC created from the photodegradation of DOC is significant to the POC mass balances in aquatic systems, then determining the effects of DOM degradation on C/N ratios and $\delta^{13}C$ becomes important if this POC is incorporated into lake sediments. DOC can be lost to the sediment through coagulation and flocculation of DOC (Molot and Dillon, 1997b; von Wachenfeldt and Tranvik, 2008) or assimilation and sedimentation. The incubation experiments from Chapter 4 indicate that during the photodegradation of DOC in waters from the inflows to Harp and Dickie Lakes (with DOC original concentrations ranging between 3.2 mg C/L and 24.7 mg C/L, and C/N ratios ranging between 24 and 55) between 20% and 90% of the DOC lost was transformed to POC (Chapter 4) with C/N ratios ranging between 12 and 26. Photodegradation of DOM therefore creates POC with C/N ratios different from the source DOC and different from the residual DOC (C/N range: 1 to 13). Furthermore, the C/N ratios of POC created during DOM photodegradation overlap the C/N ratios of the lake sediments in Harp and Dickie Lakes (C/N range: 12 to 16).

6.4.4.3 δ^{13}C values

The incubations in Chapter 4 show that, in all cases except one, the δ^{13}C of the POC created was more enriched than the DOC it was created from (by 0.2‰ to 1.9‰) and ranged from -25.7‰ to -26.7‰ and -26.5‰ to -27.7‰ in the Harp and Dickie inflows respectively. The average δ^{13}C-POC from the 10 inflows was –26.6‰ and, although the POC was up to 2‰ greater than the original DOC, generally it was within 1‰ of the δ^{13}C-DOC it was created from (Chapter 4). This could become important to the δ^{13}C of the allochthonous end-member calculation if the amount of DOC that transforms to particulate carbon during DOM photodegradation is appreciably higher than the other allochthonous ^{13}C sources. If there is a large contribution of POC created by the photodegradation of DOC then, since the δ^{13}C-POC created is appreciably lower than the δ^{13}C of the inflows and the δ^{13}C of the litter, it could draw the $\delta^{13}C_{alloch}$ end member value close to the commonly assumed range (–27‰ to –28‰) for the terrestrial end member making the errors associated with assuming that terrestrial DOC is the allochthonous end member smaller.

Few studies have considered the POC created during DOC photodegradation, and even fewer have examined the isotopic impacts. Vähätalo and Wetzel (2008) had little particulate matter accumulation after their 459-day incubation of lyophilized *Juncus effusus* leachate dissolved in lake water. Consequently, there were no measurements to quantify or determine the δ^{13}C value of the POC created. However, von Wachenfeldt and Tranvik (2008) suggest that light stimulates allochthonous DOC flocculation in lakes and, using isotopic signatures for an end-member mixing model and the fluorescence index of settling organic carbon from sediment collection traps, suggest that allochthonous DOC was the dominant form of organic carbon flocculating and settling in 12 Swedish lakes. Although von Wachenfeldt and Tranvik (2008) mention unpublished flocculation experiments regarding the dependence of DOC flocculation on light and temperature, they did not measure the δ^{13}C of the flocculated POC. Similarly, other studies examining optical, chemical, structural and/or isotopic changes in DOC (or DIC) resulting from the photochemical alteration of DOM do not mention POC formation (e.g. Osburn et al., 2001; Opsahl and Zepp, 2001; Vähätalo and Wetzel). The formation of POC due to flocculation and coagulation of DOC is thus understudied and the δ^{13}C is assumed to be identical to the source DOC. The current study shows that the source δ^{13}C changes as it is photodegraded, and the POC created is on average 0.7‰ heavier than the source DOC.

6.4.4.4 Average annual δ^{13}C value

To determine the annual average δ^{13}C signature for the photolytic component of the allochthonous δ^{13}C signal, the contribution of organic carbon from each inflow was calculated for ice-free months using (Equation 6.3. It was assumed that 56% of the DOC available for photodegradation would form particulate carbon and that the δ^{13}C-POC created will deviate from the DOC by +0.7‰.

6.4.5 Calculating the δ^{13}C of the Allochthonous end member

Combinations of different scenarios were used to estimate the δ^{13}C of the allochthonous end-member (Table 6.2). The ranges of estimates of litterfall (219 g C/m shoreline to 354 g C/m shoreline) and stream POC (4% to 10%

of the DOC load entering the lakes) were used, with estimates of photolyzed DOC (56% of the DOC load during the ice free months).

The mass estimates suggest that litter and stream POC could account for roughly equal proportions of the allochthonous carbon entering lakes (12% to 22% and 9% to 24% respectively), while the POC created through DOC photodegradation could contribute 58% to 76% of the allochthonous carbon to the lakes (Table 6.2). This suggests that stream inputs to the lake could be incorporated into lake sediments. Since POC C/N ratios are low (< 16.5 with 90% of the samples below 12) and δ^{13}C-values range between -25‰ and -35‰, it is likely that stream POC is a combination of productivity and terrestrial inputs indicating that in stream (or wetland) productivity can be incorporated into the lake sediments. In addition, the lake sediment C/N ratios (~12 to 16) fall within the ranges observed for POC created by photodegraded DOC and stream POC, further suggesting that they could be important to lake sediments in addition to autochthonous POC C/N ratios (which are expected to be < 20). This goes against the conventional view that the organic matter within lake sediments originates from organics produced by organisms living in or around the lake with the detritus of single-celled phytoplankton as the source of primary organic matter (e.g. Meyers, 1997; Rullkötter, 2000), although it has been suggested that in lakes and marine sediments close to river mouths land plant detritus could also become important (Meyers, 1997). The high degree of POC created by the photodegradation of DOC corroborates von Wachenfeldt et al. (2008) who suggest that DOC photoflocculation could account for up to 60% of the DOC loss in lake and mire waters and that photoflocculation could lead to allochthonous carbon sequestration in lake sediments (von Wachenfeldt and Tranvik, 2008; von Wachenfeldt et al., 2008). However, the amount of particulate carbon made will likely be system dependent and depend on DOC concentration, previous light exposure (von Wachenfeldt et al., 2008), and possibly residence time in the photic zone.

The $\delta^{13}C$ of litter, the weighted annual $\delta^{13}C$ value of stream POC entering the lakes, and the $\delta^{13}C$ of POC created by photodegrading DOC were used in combination with the POC mass estimates to calculate the $\delta^{13}C_{alloch}$ end member (Table 6.2). In Harp Lake, these scenarios yielded similar final $\delta^{13}C$ signatures for the allochthonous end-member (mean: -27.1‰; range: -26.9‰ to -27.3‰; Table 6.2). In Dickie Lake the scenarios yielded a slightly larger range (mean: –27.8‰; range: –27.5‰ to –28.2‰; Table 6.2) than Harp Lake, however, the range is still small. The allochthonous end-member $\delta^{13}C$ value is influenced by a combination of litter, stream POC, and POC created from photodegraded DOC, and ~55% to 75% of it's signature is derived from the DOC entering lakes and photodegrading to POC (Table 6.2). Since the POC created through photolysis ($\delta^{13}C$ > –28‰) is heavier than the other allochthonous end-member components, the stream POC and litter ($\delta^{13}C$ < –28‰) draw the end-member value back towards a commonly assumed allochthonous DOC range ($\delta^{13}C$ ~ –27‰ to –28‰) making the errors associated with assuming that terrestrial DOC is the allochthonous end-member smaller.

Although the allochthonous $\delta^{13}C$-POC range is small, there is a small difference between the two lakes (2 tailed t-test, $p = 0.005$) suggesting that the between lake differences $\delta^{13}C$-POC are likely driven by the stream $\delta^{13}C$-POC values. Since one goal of this study is to try to put bounds on the relative proportion of allochthonous and autochthonous carbon in lake sediments, the entire range of $\delta^{13}C_{alloch}$ end member values (Table 6.2) will be used in an attempt to include the errors associated with the estimates such that the Harp and Dickie Lake allochthonous end members are likely between -26.9‰ to -27.3‰ for Harp Lake and -27.5‰ to -28.2‰ for Dickie Lake. Changing the litter and stream $\delta^{13}C$ values by 0.5‰ only changes the allochthonous end member $\delta^{13}C$ value by a maximum of 0.1‰, while changing the POC created from photodegraded DOC by 0.5‰ changes the

$\delta^{13}C_{alloch}$ by a maximum of 0.4‰. Assuming that the optimal parameters are that litter contributes 219 g C/m shoreline, and stream POC is 4% of stream DOC, then the allochthonous $\delta^{13}C$ signature is likely at the higher end of the calculated range at –26.9‰ and –27.5‰ for Harp and Dickie Lakes respectively.

6.4.6 $\delta^{13}C$-Autochthonous POC

To calculate a $\delta^{13}C$ autochthonous end member value, it is necessary to determine the $\delta^{13}C$ value of POC created each month, and to weight the $\delta^{13}C$-POC value accordingly ((Equation 6.2). Therefore, primary production curves with the relative monthly production are required for Harp and Dickie Lakes. Detailed productivity curves have not been completed for these lakes; therefore it was necessary to estimate the relative production in each month. This section is set up to i) estimate the relative monthly production (relative production$_m$, (Equation 6.2), ii) estimate the average annual photosynthetic enrichment factor (ε, (Equation 6.2), iii) calculate the $\delta^{13}C$ value of POC created by production each month ($\delta^{13}C$-CO_2 + ε, from (Equation 6.2), and iv) provide a summary of the values used to calculate the autochthonous $\delta^{13}C$ end member.

6.4.6.1 Estimated relative production (relative production$_m$)

The monthly proportion of the total annual primary was estimated using a variety of scenarios. Scenario 1 used an annual productivity curve from Lake Erken, Sweden (59°50’24” N, 18°34’48” E; Figure 6.5a) - a mesotrophic clearwater lake with a maximum depth of 21m, total phosphorus 27ug/L, ice cover and stratified periods similar to the study lakes (Kalff, 2002). For the second scenario, productivity curves from Lakes 239 and 442 at ELA from periods with no ice cover were used (Figure 6.5b and c; Kasian: ELA, unpublished, pers. comm.). Lake 239 is an oligotrophic first order lake that is approximately 30m deep, and Lake

442 is a coloured shallow (maximum depth: 17m) first order oligotrophic lake that becomes anoxic in the bottom waters during summer (similar to Dickie Lake). Although no annual ice cover production was completed from 1973 to 2004 in Lake 239 or from 1987 to 1998 in Lake 442, historical ice cover production data from 1969 to 1972 suggests that in the winter production in Lake 239 contributed only 1% to 5% of the total annual production (Reid et al., 1975). These winter production fractions were used in conjunction with the ice-free production curves of Lakes 239 and 442 to create an estimate of annual production. Scenario 3 assumed equal productivity over the entire year (Figure 6.5d).

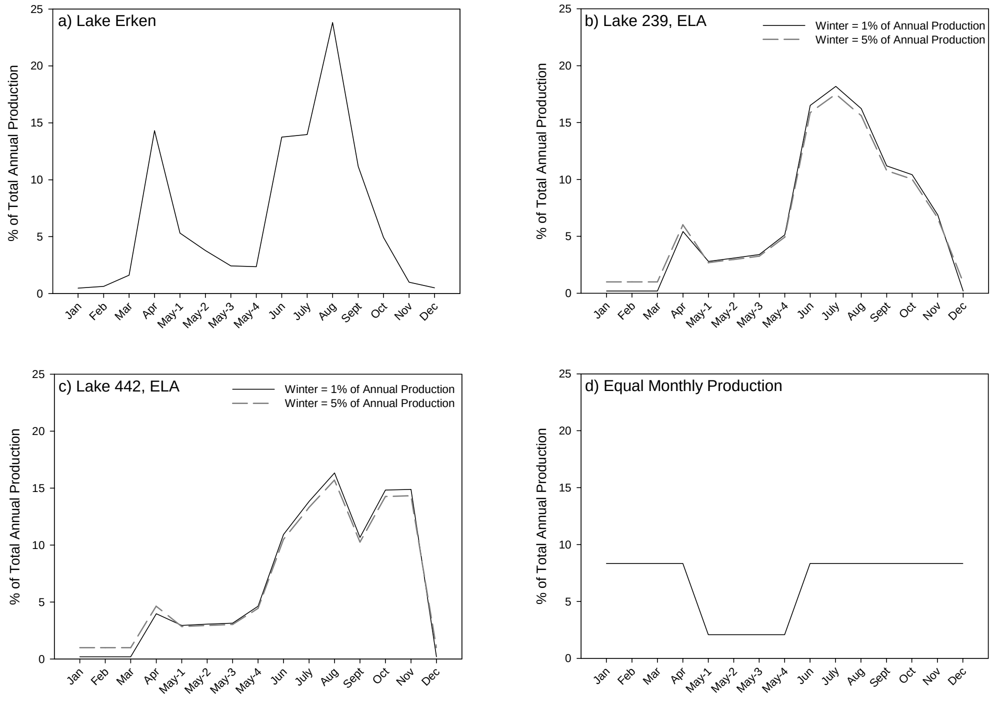


Figure 6.5: The total percent of annual production for each month for a) Lake Erken, b) Lake 239, c) Lake 442, and d) assuming equal monthly production. May has been split into 4 weeks to characterize the rapid changes in surface water $\delta^{13}C\text{-}CO_2$ occurring after ice melt.

6.4.6.2 Estimating a mean annual photosynthetic enrichment factor (ε)

Since POC within lakes will be from a combination of allochthonous and autochthonous carbon that can be created by a variety of processes, it is difficult to determine the δ^{13}C autochthonous end-member directly. Because separation of the autotrophic portion of POC is difficult, Mohamed and Taylor (2009) mention that measuring the autochthonous δ^{13}C signature at the base of the planktonic food web is problematic. Presumably, if measuring phytoplankton was easy, then the δ^{13}C of phytoplankton could be used as the autochthonous end member. It is difficult to physically separate phytoplankton, and when it is done, it is often done on one type of phytoplankton, which might not be representative of the lake. In 10 out of 12 Finnish lakes, phytoplankton were impossible to separate from POM since they were dominated by small flagellates, however, in two lakes the dominant species (*Gonyostomum semen*) was measured between ~ –36‰ to –40‰ (Jones et al., 1999), and diatoms collected by repeated sedimentation measured between ~ –29‰ and –33‰ in the deep oligotrophic Loch Ness (Jones et al., 2001). In a suite of 11 UK lakes with a range of trophic states, the separation of phytoplankton into pure isolates was attempted by repeated sedimentation or by the natural buoyancy of different species, and measured between –16.4‰ and –35.2‰ with the oligotrophic samples around –32‰ (Grey et al., 2000). Weekly measurements from Pel et al. (2003) provide phytoplankton δ^{13}C biomass values (from fatty acids) between approximately –34‰ to –45‰ in the shallow eutrophic Lake Loosdrecht using flow cyclometric retrieval and a cell sorter. It is therefore difficult to use the literature ranges of δ^{13}C-phytoplankton to estimate the δ^{13}C autochthonous end member in lakes, since the measured ranges are variable, and the dominant species could be lake dependent. Additionally, the autochthonous end member likely varies across systems since the δ^{13}C-DIC (and δ^{13}C-CO_2) varies across systems.

To estimate the $\delta^{13}C$ of the autochthonous end-member, $\delta^{13}C$-CO_2 values and a photosynthetic enrichment factor are required along with the percent of annual production occurring each month determined above. Mohamed and Taylor (2009) found $\delta^{13}C$-CO_2 values to be a good predictor of $\delta^{13}C$-zooplankton (and presumably algae) in their suite of northern temperate lakes in the Muskoka-Haliburton region (including the two lakes from this study), suggesting that CO_2 is a good indicator of autochthonously produced POC in lakes with no CO_2 limitation or bicarbonate use. Similar to Mohamed and Taylor (2009), temporal $\delta^{13}C$ values of zooplankton from this study also show a positive relationship with $\delta^{13}C$-CO_2 values (Harp $r^2 = 0.80$, Dickie $r^2 = 0.52$; Figure 6.6). The relationship between $\delta^{13}C$-zooplankton and $\delta^{13}C$-CO_2 improves if the outlier is removed ($r^2 = 0.76$). Presumably, since 76% to 80% of the variation in $\delta^{13}C$-zooplankton can be explained by $\delta^{13}C$-CO_2, temporal $\delta^{13}C$-CO_2 values can be used to calculate an average annual photosynthetic enrichment factor.

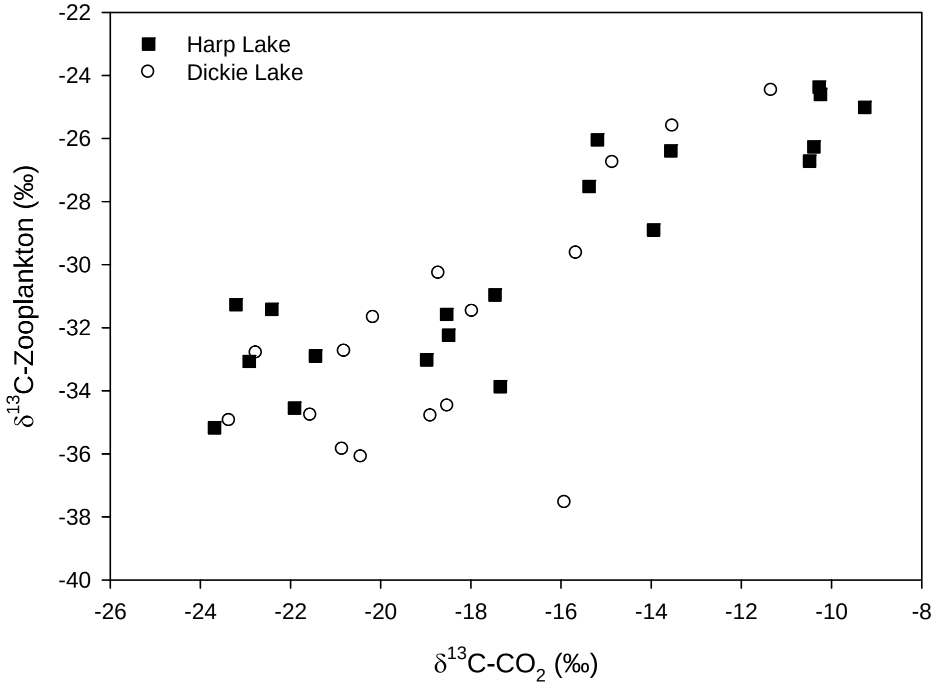


Figure 6.6: The relationship between δ^{13}C-Zooplankton and δ^{13}C-CO_2 in Harp and Dickie Lakes.

Estimating the $\delta^{13}C_{auto}$ end-member requires monthly surface δ^{13}C-CO_2 values calculated from epilimnion δ^{13}C-DIC samples (using CO_2 and DIC concentrations), and an average photosynthetic enrichment factor estimated for each of the lakes. Mohamed and Taylor (2009) used epilimnetic δ^{13}C-CO_2 values and δ^{13}C-POC to derive an estimate of the average photosynthetic enrichment factor (–15.9‰) in a suite of 27 Lakes (including Harp and Dickie Lakes) during late summer. They reasoned that POC or zooplankton should vary with CO_2 if CO_2 was a primary inorganic carbon source to phototrophs, such that a slope of 1 (on a $\delta^{13}CO_2$ vs. δ^{13}POC or δ^{13}C-zooplankton plot; e.g. dashed line on Figure 6.7) would indicate that the POC or zooplankton were entirely autochthonous (since they would only be influenced by the δ^{13}C-CO_2 value). If POC were entirely allochthonous, there would be no relationship (slope = 0) and the δ^{13}C-POC data points would fall along the allochthonous δ^{13}C (e.g. grey line on Figure

6.7). However, it is likely that POC is a combination of allochthonous and autochthonous sources indicating that δ^{13}C-POC data should fall between these two extremes (Figure 6.7). The point where the δ^{13}POC or δ^{13}C-zooplankton relationship intersects the allochthonous ^{13}C value represents a point where the allochthonous contribution to the POC or zooplankton will not influence the δ^{13}C-POC or δ^{13}C-zooplankton signature. Therefore, if there is any autochthonous contribution, the δ^{13}C-CO_2 value when the δ^{13}C-POC intersects the allochthonous signal can provide an estimate of the mean enrichment. They used a simple mixing model:

(Equation 6.4)

$$\delta^{13}C{-}POC = C_{auto}(\delta^{13}C - CO_2 + \varepsilon) + (1 - C_{auto})\delta^{13}C_{alloch}$$

where C_{auto} and C_{alloch} are the autochthonous and allochthonous contributions of carbon). At the point where the POC relationship intersects the terrestrial δ^{13}C value, this equation simplified to:

(Equation 6.5)

$$\begin{aligned} \delta^{13}C{-}POC &= \delta^{13}Calloch \\ &= \delta^{13}C - CO_2 + \varepsilon \end{aligned}$$

and can be used to estimate ε, the mean photosynthetic enrichment factor. A more thorough explanation can be found to in Mohamed and Taylor (2009).

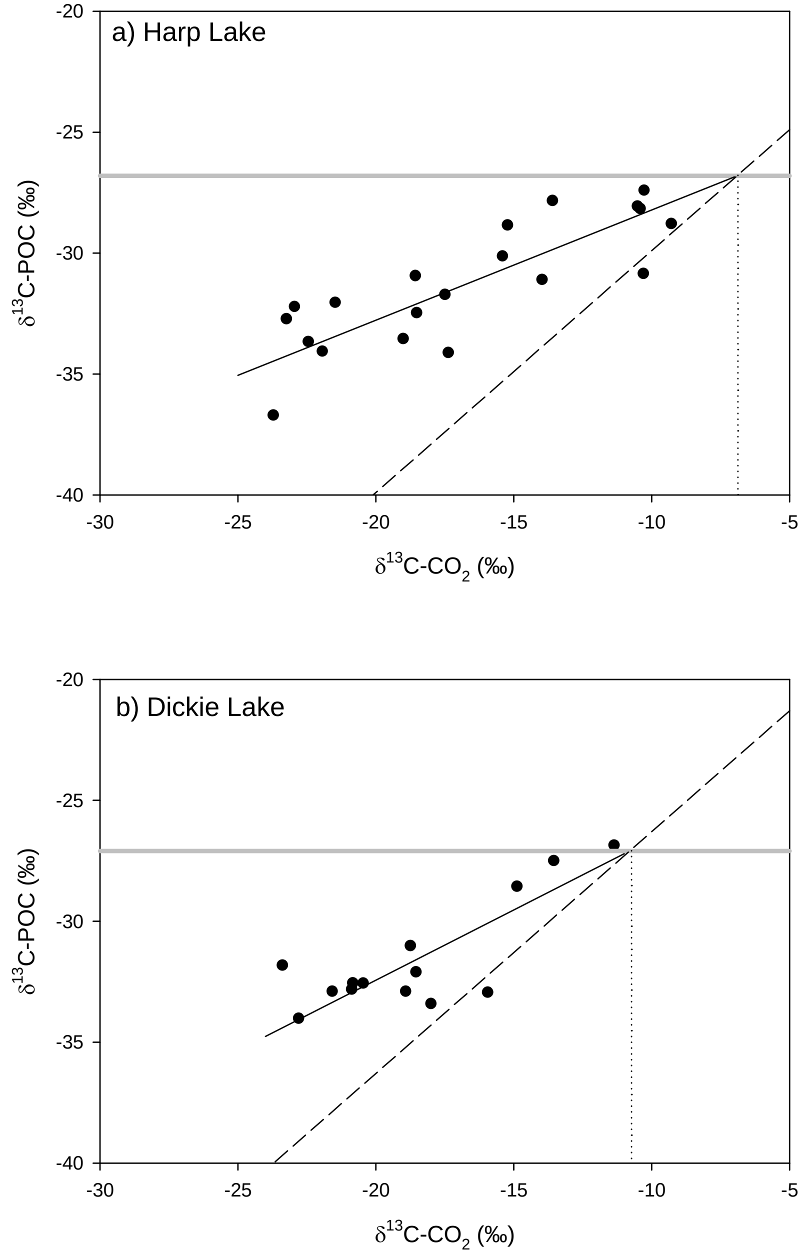


Figure 6.7: The relationship between δ^{13}C-POC and δ^{13}C-CO$_2$ in the surface waters of a) Harp Lake and b) Dickie Lake. Solid grey lines denote the weighted average annual δ^{13}C-DOC of the inflows to the lakes (Harp = -26.8‰, Dickie = -27.1‰), while the solid black lines represent the Model 2 regression line of best fit (Harp: $y = 0.456x - 23.656$, $R^2 = 0.68$; Dickie: $y = 0.581x - 20.817$, $R^2 = 0.65$). The dashed line represents a 1:1 line. The δ^{13}C-CO$_2$ value that corresponds with where the line of best fit intersects the weighted average annual δ^{13}C-DOC of the inflows (grey line) is represented by the dotted line. The point where the dotted line intersects the x-axis is the δ^{13}C-CO$_2$ value that is substituted into Equation 5 to determine the average photosynthetic enrichment factor. For example in Harp Lake, $\varepsilon = \delta^{13}\text{C-POC} - \delta^{13}\text{C-CO}_2 = -26.8‰ - (-6.9 ‰) = -19.9‰$.

Using the methods of Mohamed and Taylor (2009), an average annual (or temporal) photosynthetic enrichment factor was estimated for each lake. Since POC was found to be a good indicator to determine the average fractionation (Mohamed and Taylor, 2009) and does not involve an additional layer of assumptions regarding trophic enrichment that using zooplankton would, the average fractionation was calculated taking into account temporal POC data (and not temporal zooplankton data), and the weighted average annual δ^{13}C-DOC signatures from the inflows to Harp and Dickie Lakes (–26.8‰ and –27.1‰ respectively; Chapter 5). The inflow weighted average annual δ^{13}C-DOC values were used since an average annual photosynthetic enrichment factor was being calculated. Similar to Mohamed and Taylor (2009), the temporal data shows a positive relationship between δ^{13}C-POC signatures and $\delta^{13}CO_2$, demonstrating that as δ^{13}C-CO_2 values increase, there is an associated increase in δ^{13}C-POC values (Harp: $R^2 = 0.68$; Dickie: $R^2 = 0.65$; Figure 6.7). Using the temporal data, the mean photosynthetic enrichments for Harp and Dickie Lakes were calculated as –19.9‰ and –16.3‰ respectively. Should the values of the allochthonous end-members be used instead of just the weighted average annual δ^{13}C-DOC, the mean fractionations for Harp and Dickie Lakes change to –19.3‰ and –15.8‰.

Examination of the relationship between δ^{13}C-POC and δ^{13}C-CO_2 indicates that Harp and Dickie Lakes likely have different amounts of autochthonous POC. It is possible that autochthony is not the sole process that is producing POC since all of the data do not fall directly on the 1:1 line, indicating that the δ^{13}C-POC does not equal the δ^{13}C of algae calculated from measured δ^{13}C-DIC values (Figure 6.7, dashed line). Harp and Dickie Lakes do not closely follow the 1:1 line suggesting they may be more influenced by allochthony.

6.4.6.3 *δ^{13}C-POC created by production (δ^{13}C-CO$_2$ + ε)*

Using a late-summer photosynthetic enrichment of –15.9‰ (Mohamed and Taylor, 2009) the autochthonously derived POC would range on a monthly basis from –27.4‰ to –40.3‰ in Harp Lake and from –30.1‰ to –42.2‰ in Dickie Lake (Figure 6.8a). However, using the estimated enrichment values of –19.9‰ and –16.3‰ from temporal data for Harp and Dickie Lakes respectively, the autochthonous POC would range from –31.5‰ to -44.4‰ in Harp Lake and -30.5‰ to -42.6‰ in Dickie Lake (Figure 6.8b) illustrating the importance of using a temporal photosynthetic fractionation in Harp Lake. The ranges for Dickie Lake do not differ a lot since the temporal fractionation is similar to the average photosynthetic fractionation calculated by Mohamed and Taylor (2009) across their suite of 27 lakes. The δ^{13}C-POC values derived from the temporal ε value were used in conjunction with the estimated relative production in the lakes to calculate weighted average annual δ^{13}C autochthonous end member values.

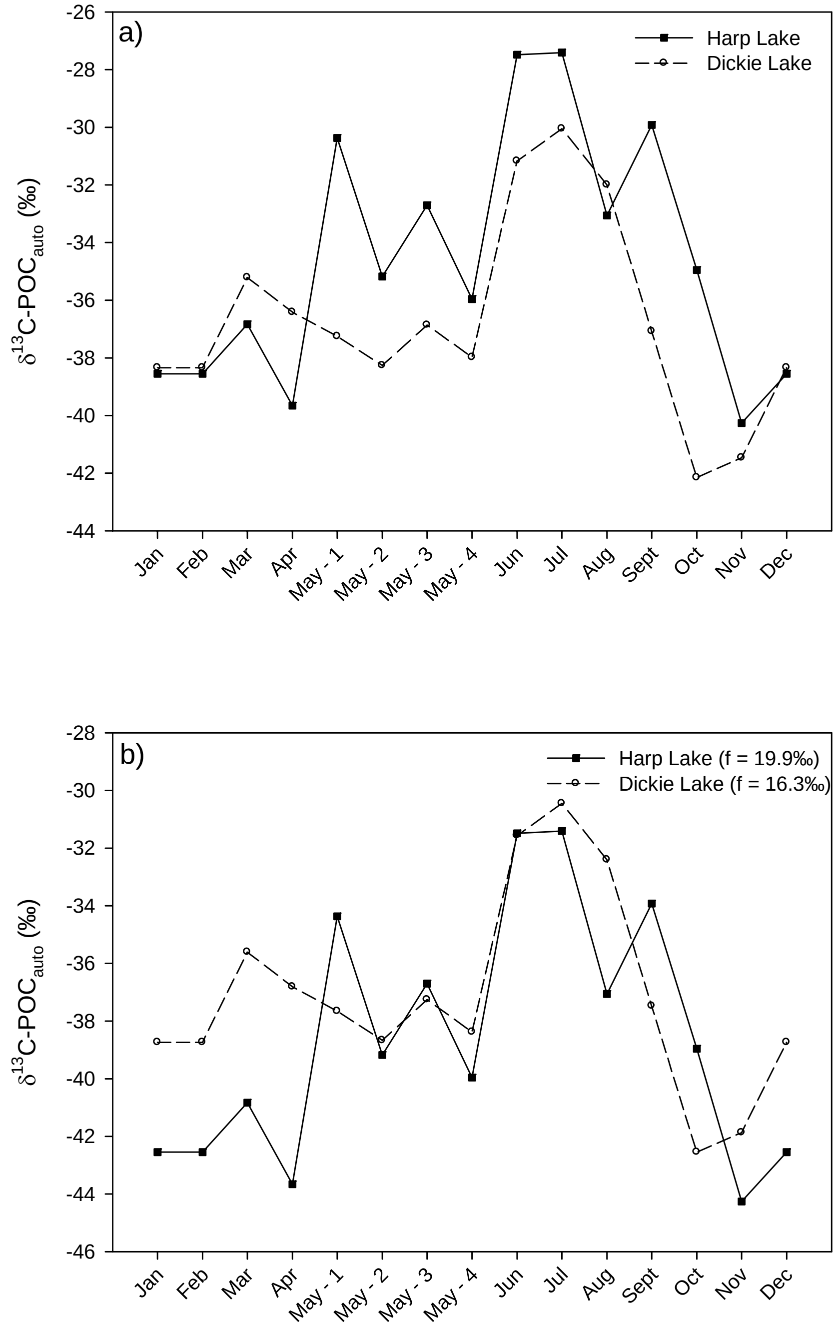


Figure 6.8: The autochthonous δ^{13}C-POC signature of Harp (closed square) and Dickie (open circle) Lakes calculated using a) an average fractionation factor of -15.9‰ (Mohamed and Taylor, 2009), and b) average fractionation factors of -19.9‰ and -16.3‰ for Harp and Dickie Lakes respectively and measured surface water ^{13}C-DIC, CO_2, and DIC. May 1-4 represent four weeks in May when weekly sampling was completed.

Comparing the $\delta^{13}C$ signatures of the weighted average annual autochthonous end member resulting from each of the aforementioned scenarios shows that, between scenarios, the range in the weighted average annual autochthonous end member is 2.9‰ for Harp Lake and 2.2‰ for Dickie Lake (Table 6.3). To determine an average annual POC derived from autochthonous production, the average of production scenarios 1 and 2 were used, assuming an average enrichment of –19.9‰ and –16.3‰ for Harp and Dickie Lakes, respectively. Scenario 3 was not included as it is not likely that productivity is equal throughout the year, especially when the lakes are ice and snow covered during the winter months. The autochthonous $\delta^{13}C$ end member calculated using equal monthly production can be up to ~2‰ different than the other production $\delta^{13}C$ end member values, and shows that using monthly production is important to this calculation. Excluding scenario 3, the range in the autochthonous end member decreases to between ~1.5‰ and 2‰. Since the production curves in scenarios 1 and 2 are from lakes in a similar northern temperate/boreal region that have characteristics similar to Harp and Dickie Lakes, their productions could resemble relative total production at the current study lakes and were therefore used to calculate the $\delta^{13}C_{auto}$. According to the average of scenarios 1 and 2, the $\delta^{13}C_{auto}$ end member is –36.6‰ in Harp Lake and -35.7‰ in Dickie Lake (or -35.5‰ and -35.2‰ if $\delta^{13}C$ allochthonous end-member is used instead of $\delta^{13}C$-DOC inflows). Changing the enrichment factor to the late-summer derived enrichment value of –15.9‰ (Mohamed and Taylor, 2009) changes the average annual POC derived from autochthonous production to –32.6‰ and –35.3‰ for Harp and Dickie Lakes respectively illustrating the sensitivity of the end member to the specific annual fractionation for each lake. It also illustrates the importance of using a temporal average photosynthetic enrichment factor, and not a fractionation calculated in the late-summer. Since it is not likely that fractionation is annually constant in the lakes, temporal data was used to estimate a mean enrichment factor. When the lakes are supersaturated with CO_2, it is expected that photosynthetic fractionation will be large, whereas if CO_2 decreases or becomes limiting, the photosynthetic fractionation will decline, but the reasonable fit of the line in Figure 6.7 suggests that this isn't the case for Harp and Dickie Lakes. It is also important to recognize that there is a positive feedback between $\delta^{13}C$-CO_2 and the autochthonous end-member. As production increases in the lake, the $\delta^{13}C$-CO_2 (and $\delta^{13}C$ of the autochthonous end-member) will increase. Changing the $\delta^{13}C$ of the lake sediments to lower $\delta^{13}C$ values with productivity using end-member mixing is therefore a minimum of the amount of autochthonous carbon required to shift the $\delta^{13}C$ signal since autochthonous carbon is labile and can be more easily degraded than allochthonous carbon in the lake sediments.

Scenario	Modeled after	Winter Production (% of annual production)	^{13}C Autochthonous endmember			
			Harp Lake Average Photosynthetic Enrichment		Dickie Lake Average Photosynthetic Enrichment	
			-15.9 ‰ [a]	-19.9 ‰	-15.9 ‰ [a]	-16.3 ‰
1	Lake Erken	n/a	-32.4	-36.4	-34.3	-34.7
2a	Lake 239	1	-32.0	-36.0	-34.9	-35.3
	Lake 239	5	-32.3	-36.3	-35.1	-35.5
2b	Lake 442	1	-33.1	-37.1	-36.1	-36.5
	Lake 442	5	-33.4	-37.4	-36.2	-36.6
3	Equal montly productivity	n/a	-34.9	-38.9	-36.5	-36.9
	All Scenarios	***average***	***-33.0***	***-37.0***	***-35.5***	***-35.9***
		minimum	*-34.9*	*-38.9*	*-36.5*	*-36.9*
		maximum	*-32.0*	*-36.0*	*-34.3*	*-34.7*
	Scenarios 1 and 2	***average***	***-32.6***	***-36.6***	***-35.3***	***-35.7***
		minimum	*-33.4*	*-37.4*	*-36.2*	*-36.6*
		maximum	*-32.0*	*-36.0*	*-34.3*	*-34.7*

[a] Enrichment factor calculated by Mohamed and Taylor (2009)

Table 6.3: Scenarios used to calculate the possible ^{13}C range of the autochthonous end-member in Harp Lake and Dickie Lake.

In addition to Mohamed and Taylor (2009) who found $\delta^{13}C$-CO_2 signatures to be a good predictor of $\delta^{13}C$-zooplankton in 27 northern temperate lakes, suggesting that CO_2 is a good indicator of autochthonously produced POC in the lakes, many other studies have used $\delta^{13}C$ as a tool to provide information about autochthony. Findlay (2001) found $\delta^{13}C$ values to be useful in differentiating between allochthonous and algal energy sources in CO_2 supersaturated unproductive streams and also found that δ^{13}C-algae was strongly related to δ^{13}C-DIC. McCallister and del Giorgio (2008) used two independent approaches to determine the autochthonous δ^{13}C end member (i.e. the expected δ^{13}C-algae) in 8 boreal lakes and 2 streams in Quebec, Canada. For the first method, they measured δ^{13}C-CO_2 signatures and assumed a –20‰ enrichment value, suggesting that the δ^{13}C for algal biomass produced ranged between –32‰ and –43‰, similar to the range calculated for Harp and Dickie Lakes (Harp: –31.5‰ to –44.4‰; Dickie: –30.5‰ to –42.6‰) using the temporal average enrichment factors (Harp: –19.9‰ and Dickie: –16.3‰). The Harp and Dickie values also overlap the δ^{13}C-biomass derived via lipids in the second method used by McCallister and del Giorgio (2008), although these values differed from the $\delta^{13}C_{auto}$ derived from the δ^{13}C-CO_2 in the above study. McCallister and del Giorgio (2008) suggest that differences between the biomass signature calculated from δ^{13}C-CO_2 and those measured from lipid extraction are due to an overestimation from applying the commonly used –20‰ enrichment factor and propose that photosynthetic enrichment more likely lies between –8‰ and –15‰. This, along with the –15.9‰ enrichment factor from Mohamed and Taylor (2009), and the estimated photosynthetic enrichment factors for Dickie Lake (–16.3‰) supports other recent suggestions that *in situ* fractionation is likely lower than the often used value of –20‰ (e.g. Hecky and Hesslein, 1995; Cole et al., 2002; Bade et al., 2006). However, the estimated average photosynthetic enrichment in Harp Lake (–19.9‰) is very similar to the often-used value of 20‰.

6.4.6.4 Average annual δ^{13}C value

To determine the proportion of allochthonous to autochthonous carbon within lake sediments, mean photosynthetic enrichments of –19.9‰ and -16.3‰ for Harp and Dickie Lakes respectively, were used to calculate autochthonous δ^{13}C end members ranges of –36.0‰ to –37.4‰ for Harp

Lake and –34.7‰ to –36.6‰ for Dickie Lake (Table 6.3) using (Equation 6.2. These values are open water values, and do not include carbon fixed by macrophytes. Macrophytes were ~3% of the total autochthonous carbon inputs in the carbon budget of Mirror Lake (Jordan et al., 1985; a lake similar to Dickie Lake) therefore, it is possible that macrophytes may not be a significant contributor to the autochthonous δ^{13}C value. Similarly, macrophytes have low biomass in the oligotrophic lakes on the Canadian Shield (France and Schlaepfer, 2000), located between ThunderBay and the Experimental Lakes Area. Less than 10% of the total surface area of Harp Lake is colonized by macrophytes, and vegetation was present only to depths of 3 m (Wile et al., 1985). Wile et al. (1985) note that the species richness and species composition of Harp and Red Chalk Lakes were similar to other Ontario soft water lakes (Miller, 1977). The average macrophyte biomass of Harp Lake was 73.6 g m^{-2} for the vegetated zone and within the range for oligotrophic lakes (Wile et al., 1985). In a literature survey, France (1995) compiled a range of δ^{13}C values for macrophytes in freshwater lakes, between ~–10‰ and –32‰, while Osmond et al. (1981) show that in British rivers the δ^{13}C of total plant carbon in aquatic macrophytes ranged between –22‰ and –44‰. Therefore, in lakes where macrophyte carbon contributions are high, macrophytes and their δ^{13}C values may play a more important role in sedimentation and the δ^{13}C values of lake sediments.

6.4.7 Allochthonous vs. Autochthonous POC

Using the allochthonous and autochthonous δ^{13}C end member values to calculate the ratio of allochthonous to autochthonous organic carbon in the lake sediments relies on the assumption that the δ^{13}C end-member values do not change over the time frame of the sediment core. It is not likely that local vegetation surrounding the lakes (i.e. C3/C4 plants) would change drastically suggesting that the δ^{13}C of litter and stream POC would not change significantly. Additionally, the $\delta^{13}C$ range of litter (C3 plants) is narrow and although the stream POC $\delta^{13}C$ range has more variation, it will also be small since it is composed mainly of terrestrial material. If the local vegetation remained similar, it is likely that the lability of the allochthonous material did not change.

It is also important to consider how the Suess effect would affect the $\delta^{13}C$-DOC derived from the terrestrial catchment over the history of the core to determine whether the allochthonous end-member is representative for the entire core. Since the industrial revolution, increases in CO_2 and decreases in $\delta^{13}C$-CO_2 have been observed in the atmosphere (Francey et al., 1999). Although plants will uptake the decreased $\delta^{13}C$-CO_2, the DOC in streams, soil water and groundwater surrounding Harp Lake reflect both contemporary plant material and older soil organic matter (Trumbore et al., 1992) although significant amounts of DOC (often >50%) is recent (Schiff et al., 1990). However, extreme ^{14}C values also show the importance of carbon sources prior to the 1960s to DOC formation in some streams and all shallow groundwaters sampled (Trumbore et al., 1992). Since integration of CO_2 into plants occurs slowly over time, and the carbon in the soils incorporates older carbon sources, it is unlikely that the Suess effect will alter the $\delta^{13}C$-DOC (or $\delta^{13}C$-POC) significantly. However, even if the Seuss effect is important to the allochthonous end member $\delta^{13}C$ value by the change in atmospheric $\delta^{13}C$-CO_2 since the industrial revolution will change the allochthonous end member $\delta^{13}C$ value by less than 0.5‰.

It is also possible that the autochthonous signature could be affected by temporal changes in the atmospheric $\delta^{13}C$-CO_2. Although Verburg (2007) suggest that lake sediments in autochthonous and heterotrophic environments should be corrected for the Suess effect, this may not be necessary for the scope of this study. Since the mass balances of Harp and Dickie Lakes are controlled by the terrestrial DOC entering the lakes, it is unlikely that correcting for the Suess effect would significantly affect the proportion of autochthonous carbon in the lake sediments. Changes in the $\delta^{13}C$ of the autochthonous end-member by 0.5‰ only affects the % of autochthonous inputs by <1%. Changes in nutrients (from development), or changes in the degree of fractionation over time could also affect the $\delta^{13}C$ of the autochthonous end-member, and each of these will be discussed later.

The relative proportion of allochthonous POC versus autochthonously derived POC in the lake sediments was calculated using a simple mixing model between the isotopic signatures of the allochthonous (Harp range: –26.9‰ to –27.3‰, Dickie range: –27.5‰ to –28.2‰) and autochthonous (Harp range: –36.0‰ to –37.4‰, Dickie range: –34.7‰ to -36.6‰) end members of Harp and Dickie Lakes. The ranges of allochthonous POC and autochthonous POC are both narrow and do not overlap, indicating that the $\delta^{13}C$ end member values are different. The $\delta^{13}C$ values of Harp and Dickie Lake sediments range between –27.6‰ and -29.9‰ suggesting that sediments must be more allochthonous than autochthonous. Although lake sediments can undergo diagenesis, diagenetic shifts in the $\delta^{13}C$ of the lake sediments with depth are generally absent (e.g. Rea et al., 1980; Hodell and Schelske, 1998; Meyers et al., 1995)

In Harp Lake, the ratio of allochthonous to autochthonous carbon has changed over time, ranging from 2:1 up to 36:1 (corresponding with the percentage of allochthonous carbon changing between 67% and 97% using all $\delta^{13}C_{alloch}$ and $\delta^{13}C_{auto}$ end member scenarios) (Figure 6.9). Similarly, in Dickie Lake, the ratio of allochthonous:autochthonous carbon ranged between 2:1 to 15:1 corresponding with the terrestrial inputs to the sediment record ranging between 66% to 94% (Figure 6.9). As an example, the ratio of allochthonous to autochthonous carbon in the lake sediments using the maximum $\delta^{13}C_{alloch}$ and the minimum $\delta^{13}C_{auto}$ end members is displayed in Table 6.4. Therefore decreases in the $\delta^{13}C$ of the lake sediments can occur due to increases in autochthonous POC or decreases in the contribution of allochthonous POC.

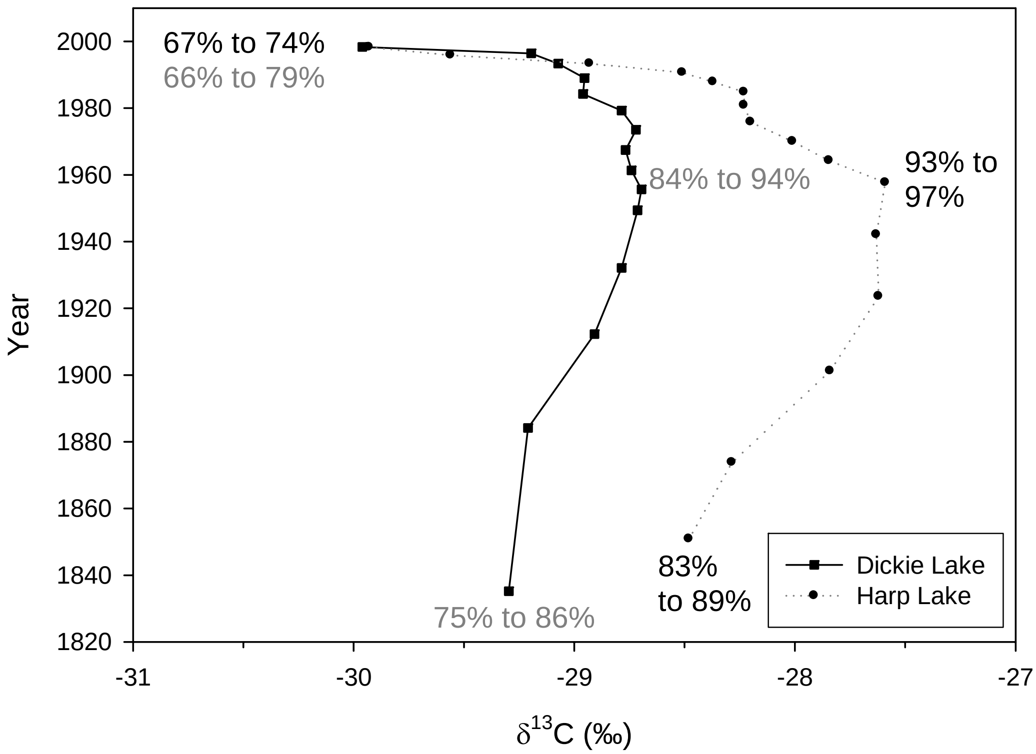


Figure 6.9: δ^{13}C sediment profiles of Harp and Dickie Lakes plotted with age of sediment determined by ^{210}Pb. The % of allochthonous carbon within the sediment is displayed at the top, δ^{13}C peak, and base of the core in black text for Harp Lake, and grey text for Dickie Lake.

Table 6.4: The percent allochthonous and percent autochthonous contributions to the ^{13}C-Sediment signature from short cores within a) Harp Lake and b) Dickie Lake using the maximum allochthonous and minimum autochthonous δ^{13}C end-member values as an example.

a) Harp Lake

Year	^{13}C-Sediment (‰)	Allochthonous (%)	Autochthonous (%)	Alloc:Auto
1998	-29.9	67	33	2
1996	-29.6	71	29	2
1993	-28.9	78	22	4
1991	-28.5	83	17	5
1988	-28.4	84	16	5
1985	-28.2	86	14	6
1981	-28.2	86	14	6
1976	-28.2	86	14	6
1970	-28.0	88	12	7
1964	-27.8	90	10	9
1958	-27.6	93	7	13
1942	-27.6	92	8	12
1924	-27.6	92	8	12
1901	-27.8	90	10	9
1874	-28.3	85	15	6
1851	-28.5	83	17	5

b) Dickie Lake

Year	^{13}C-Sediment (‰)	Allochthonous (%)	Autochthonous (%)	Alloc:Auto
1998	-30.0	66	34	2
1996	-29.2	77	23	3
1993	-29.1	78	22	4
1989	-29.0	80	20	4
1984	-29.0	80	20	4
1979	-28.8	82	18	5
1974	-28.7	83	17	5
1967	-28.8	83	17	5
1961	-28.7	83	17	5
1956	-28.7	84	16	5
1949	-28.7	83	17	5
1932	-28.8	82	18	5
1912	-28.9	81	19	4
1884	-29.2	76	24	3
1835	-29.3	75	25	3

Isotopically, the proportion of allochthonous to autochthonous carbon is more sensitive to the δ^{13}C of the average annual allochthonous

POC sources. Altering the average annual $\delta^{13}C$ signatures by 0.5‰ (the average difference between the range of the $\delta^{13}C$ allochthonous end member values calculated in Table 6.2) changes the percentage of allochthonous inputs (to the sediments) by an average of 4.4% and 5.1% in Harp and Dickie Lakes respectively (Harp range: 3.5% to 4.7%, Dickie range: 4.4% to 5.3%). However, changing the average annual $\delta^{13}C_{auto}$ end member by 0.5‰ only changes the percentage of allochthonous inputs to the sediments by an average of 0.7% and 1.0% in Harp and Dickie Lakes respectively (Harp range: 0.3% to 1.7%, Dickie range: 0.7% to 1.8%). Therefore it is likely that large changes to $\delta^{13}C\text{-}CO_2$ (much larger than the Suess effect) or large changes in the degree of fractionation over the time frame of the core would be required to affect these values significantly, emphasizing the important control of allochthonous carbon on the lake sediments.

There is not much difference in the relative proportion of allochthonous to autochthonous carbon if the $\delta^{13}C$-DOC of the inflows is used as the terrestrial signal versus the $\delta^{13}C$ of the allochthonous end-member (i.e. ~2.5% change). The higher sensitivity to changes in the allochthonous $\delta^{13}C$ end-member value than the autochthonous end-member $\delta^{13}C$ value is due to the inferred high proportion of allochthonous material in the sediments. Additionally, had the temporal photosynthetic fractionation factors been calculated using the allochthonous end member instead of the $\delta^{13}C$-DOC entering the lakes been used (–15.8‰ and –18.8‰ for Dickie and Harp Lakes respectively instead of –16.3‰ and –19.9‰), the allochthonous contributions would only change on average by less than 1%.

Harp Lake has less DOC (3.9 mg/L) than Dickie Lake (5.0 mg/L), which is darker in colour (Dillon and Molot, 1997a). According to the mixing model in this chapter, the average POC preserved in the sediments in Harp (from 1850 to 1998) is 87% allochthonous and 13% autochthonous and is 85% allochthonous and 15% autochthonous in the Dickie Lake core sediments dated from 1835 to 1998. The estimated average sediment accumulation rates of Harp and Dickie Lakes are 6.26 g C $m^{-2}y^{-1}$ and 10.1 g C $m^{-2}y^{-1}$ respectively and the DOC retention in Dickie Lake (0.55) is greater than that of Harp Lake (0.42) (Dillon and Molot, 1997a). Dickie Lake has higher estimated sediment accumulation rates and DOC retention than Harp, and it is possible that increases in DOC transport to the lakes could bring additional labile phosphorus to the system, and increase the amount of carbon sedimentation and productivity in the lakes. It is also likely that more autochthonous carbon has sedimented out, but since it is more labile, it was lost to decomposition.

According to Molot and Dillon (1997b), the DOC loss coefficients (σ, from the mass balances) in Harp and Dickie Lakes are very similar to photodecay constants extrapolated to the lakes (k_{lake}). They suggest that photolysis of DOC could be large enough *in situ* to account for all DOC loss to the atmosphere and sediments in lakes with DOC < 4 mg C/L. The σ/k_{lake} increases with increasing DOC concentration, suggesting that in high DOC lakes, nonphotolytic mechanisms could become more important. Since Harp Lake has a DOC concentration of 3.9 mg C/L, it falls below the 4 mg C/L value of Molot and Dillon (1997b) where it is possible that all DOC losses can be attributed to photolysis. However, Molot and Dillon (1997b) assume that as DOC is degraded, DIC forms and can be consumed during photosynthesis to create POC. The data from this study suggests that a larger proportion of the sediment record is composed of terrestrially derived carbon (67% to 97%), and this could be due to the production of POC during DOM photodegradation, contradicting the results of Molot and Dillon (1997b). Similarly, the estimated percentage of carbon in the sediment record that is derived from allochthonous sources in Dickie Lake ranges between 66% and 94%. The DOC of Dickie Lake is 5.0 mg C/L, and above the concentration that Molot and Dillon (1997b) suggest requires nonphotolytic sources of DOC loss. However, since Molot and Dillon

(1997b) did not filter their DOC samples, the actual DOC loss includes any POC production and may underestimate the DOC loss because initial and final DOC samples will contain some portion of initial POC, and POC that is formed from the photodegradation of DOC. In this case, their photodecay constants might change if POC was removed from the DOC. Their initial stream chemistry samples have higher DOC and total iron concentrations than the waters from the Chapter 4 incubations, suggesting that POC should form from the stream water in their study.

Re-examining the relationship between the POC created and the DOC lost from the inflow samples incubated in Chapter 4 shows that the Dickie inflow samples deviate further from the 1:1 line than the Harp Inflow samples (Figure 6.4) and the two statistical outliers in the plot are from Dickie Lake. The plot indicates that as DOM is photodegraded, less POC is being created in Dickie Lake than in Harp Lake. The lack of relationship in the Dickie samples could either indicate that no relationship exists, or there are not enough samples to determine if there is a relationship. It is important to recognize that the average percent of POC created in both the Harp and Dickie inflows was used to estimate the contributions of photodegraded allochthonous end-member since the relationship using only the Dickie Lake samples was weak. This could mean that POC production was underestimated in Harp Lake and over-estimated in Dickie Lake. Further incubations may be necessary to understand the relationship between DOC loss and POC gain from DOM photodegradation in the two lakes.

6.4.8 Sedimentation of Allochthonous and Autochthonous carbon

Examining short cores from the 2 lakes shows that the δ^{13}C increased from the late 1800s until ~1960, where it peaked (Harp: 1957, Dickie: 1955; Figure 6.9). In the late 1800s to the early 1900s (~1870 to 1910) intensive logging occurred in central Ontario followed by road construction in the

1930s and forest regeneration (Paterson, unpublished). In the mid 1950s, where the $\delta^{13}C$ of the lake sediments peak, the 2 end mixing model suggests that 97% and 94% of the carbon in the sediment record is allochthonous (for Harp and Dickie Lakes respectively). During this time, there was increased logging in the area and the peak $\delta^{13}C$ could coincide with cottage development surrounding the lakes. In the mid to late 1950s, a pathway was bulldozed through thick brush and rough terrain, and large boulders were blasted to create the first road to Harp Lake. After that, parts of the surrounding catchment were logged and development began around the lake (Harp Lake Association, 2009). The development around Harp Lake coincides with the peak in the proportion of allochthonous carbon within the sediment cores, suggesting that allochthonous transport to the lake was increased during this time. However, without knowing how the carbon load transported from the watershed changed, this is speculation.

Using the sedimentation rates derived from ^{210}Pb dating for the two cores (Paterson, unpublished) and the percent carbon results from the mixing model, the amount of allochthonous and autochthonous carbon sedimenting within the lakes temporally was calculated (Figure 6.10). In Harp Lake, there was little variability in carbon accumulation from autochthonous sources until the 1960s when autochthonous contributions appear to rise, which coincides with the onset of development surrounding the lake and the peak in the $\delta^{13}C$ signature. However, Figure 6.10 also indicates that the allochthonous carbon contributions have generally increased until 1987, after which, allochthonous carbon contributions are on the decline (coincident with increasing autochthonous contributions). The Harp Lake sediment carbon accumulation rate did not peak at the same time as the peak in $\delta^{13}C$ or the peak in the ratio of allochthonous to autochthonous carbon in Figure 6.9. In Dickie Lake, the autochthonous contribution appears to generally increase until approximately 1980, after which it steadily increases, with a larger increase from 1996 to 1998 (Figure

6.10). The allochthonous contribution within Dickie Lake has generally increased from the base of the core peaking in 1956 with the δ^{13}C of the lake sediments, after which there was a general decrease in allochthonous sedimentation rate. However, it is important to note that at the top of each core the allochthonous contributions are still dominant within the lake sediment.

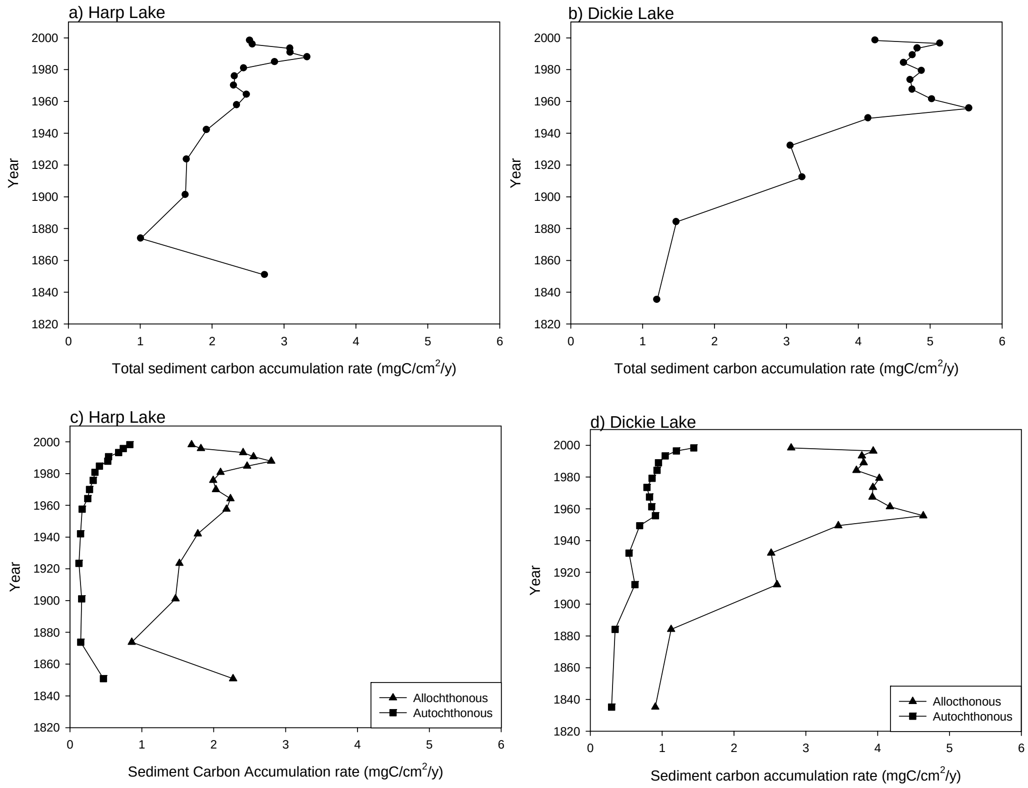


Figure 6.10: Total sediment carbon accumulation rates for a) Harp Lake, and b) Dickie Lake, and the allochthonous and autochthonous sediment carbon accumulation rates for c) Harp Lake, and d) Dickie Lake. Accumulation rates are calculated using allochthonous and autochthonous proportions derived from the maximum allochthonous ^{13}C end-member and the minimum autochthonous ^{13}C end-member scenario and the sedimentation rates from the cores.

Overall, these results suggest that although allochthonous contributions increased within the lakes from the early 1800s to the 1960s, productivity generally did not, contradicting the conventional interpretation of the δ^{13}C sediment record which indicates that productivity is decreasing during this time frame. After 1960, productivity began to increase (corroborated by the δ^{13}C sediment record) and allochthonous contributions to lake sediments became more variable. The switch to increased productivity and decreased allochthonous inputs to the lake sediments appear to coincide with increased development in the region, and the shift from cottages to permanent homes possibly reflecting increased transport of phosphorus to the lakes. Additionally, from the late 1980s until 2004 mean average annual temperatures were generally greater than the climatic normals between 1960 and 1990, and coincide with decreases in the allochthonous inputs to the lake sediments. Total precipitation was also greater than the climatic normals from the mid 1980s to the mid 1990s. The surface of the cores suggests that productivity is rising and allochthonous contributions to lake sediments is decreasing, however, allochthonous contributions remain the main component of lake sediments.

The results from the δ^{13}C-POC mixing model of allochthonous and autochthonous carbon and the carbon sedimentation rates from the short cores imply that the sediment record is primarily composed of allochthonous material and therefore records not only a lake productivity signal, but also changes to the allochthonous inputs to the lake. Furthermore, the contributions of allochthonous and autochthonous carbon to the sediment record have changed historically. Shifts in the allochthonous contributions to the mass balances of these lakes will change the δ^{13}C of the lake sediments (Chapter 5) corroborating that lake sediments provide information about carbon mass balances. In addition, changes in the δ^{13}C record of lake sediments can potentially record both productivity and mass balance information; however, this study shows that it is also possible that productivity changes occurring within the lakes cannot always be inferred by changes in the δ^{13}C of lake sediments.

6.5 Summary

Inflow and surface samples from two oligotrophic Shield lakes reveal that significant changes in δ^{13}C-POC and δ^{13}C-DIC are observed monthly. These values were used in conjunction with estimated POC balances to calculate δ^{13}C values for the allochthonous and autochthonous end members. Estimated POC, litter, and incubations tracking the phototransformation of DOC to POC were used to calculate the δ^{13}C allochthonous end member signal. Using the novel technique of Mohamed and Taylor (2009), average annual photosynthetic enrichments for Harp and Dickie Lakes were calculated (–19.9‰ and –16.3‰ respectively) and applied to surface water δ^{13}C-CO$_2$ and seasonal productivity curves, to calculate the POC created by phytoplankton. The POC created from allochthonous and autochthonous sources have distinct δ^{13}C values that lie on opposite sides of sediment δ^{13}C values indicating that lake sediments are a combination of allochthonous and autochthonous carbon.

Using these distinct average annual δ^{13}C end member values, and assuming that they do not change over the time represented by the cores, the proportion of allochthonous and autochthonous carbon within the lake sediments was assessed. Even if the δ^{13}C end member values change, the variation would be small, therefore not affecting the main conclusions that lake sediments are affected by, and primarily composed of, allochthonous carbon. The allochthonous contributions to the sediments have varied between 66% and 97% within the cores from Harp and Dickie Lakes. Contrary to interpretations derived from δ^{13}C sediment records alone, sedimentation rates of allochthonous and autochthonous carbon suggest that the autochthonous contribution of POC to lake sediments was relatively constant in Harp Lake and increased slightly in Dickie Lake until the 1960s, after which productivity increased within both the lakes. This suggests that changes to the δ^{13}C of the lake sediments of Harp and Dickie

Lakes were controlled by changes in the allochthonous carbon contribution to lake sediments until the late 1950s. Allochthonous contributions generally increased throughout the history of the cores, however, they have been on the decline and have become more variable since the 1980s. Therefore, the sediment $\delta^{13}C$ value has the potential to record both changes in productivity and changes in the allochthonous carbon load entering and sedimenting in high DOC retention lakes.

This study has important implications for paleoecology studies. Not only does it reveal that $\delta^{13}C$ sediment records can record changes in productivity and in carbon mass balances, but it also shows that changes in the $\delta^{13}C$ sediment records may not always reflect changes in productivity. This research also demonstrates that stream POC contributes to lake sediments. It was estimated that 9% to 24% of the allochthonous POC could be transported to the lakes as POC in the inflows, therefore 6% to 23% of the lake sediments could be derived from the streams. Since the $\delta^{13}C$ and C/N ratios of stream POC suggest algal contributions, productivity measured or inferred from lake sediments could include stream and wetland productivity. Thus, the "aquatic signal" recorded in lake sediments includes aquatic processes (and aquatic cellulose) from adjoining wetlands and streams.

Chapter 7:

Conclusions and Recommendations

7.1 Conclusions

The overall objectives of this thesis are to use stable carbon and oxygen isotopes as tools to examine the fate of allochthonous DOM in northern temperate lakes, and to examine the importance of DOC in lake carbon mass balances and in the $\delta^{13}C$ of lake sediments. Many northern temperate lakes retain a large proportion of allochthonous DOC, and photodegradation alone can account for the DOC loss (mineralization and sedimentation) that is observed within these lakes (Molot and Dillon, 1997b). To understand the impacts of allochthonous DOC on the sediment record, it is necessary to understand how abiotic processes (such as the photodegradation of DOM) affect stable oxygen and carbon isotopes relative to biotic processes (i.e. respiration) and to use this information to calculate isotope values for the carbon end-members of which the sediment is comprised.

Photodegradation of DOM uses O_2 to convert recalcitrant DOM to more labile carboxylic acids, other smaller organic compounds, and dissolved inorganic carbon (DIC); therefore DOM photodegradation, O_2, and carbon dynamics in aquatic systems are linked. Previously published studies have examined the effects of photodegradation on O_2 and carbon (e.g. DIC, CO_2, DOC) concentrations, however, studies of the changes in the $\delta^{18}O$-O_2, $\delta^{13}C$-DIC, $\delta^{13}C$-DOC, and $\delta^{13}C$-POC during photolytic processes are few or do not exist. In this thesis, incubations on northern temperate stream waters reveal that DOC loss was concomitant with O_2 loss, DIC gain, and POC gain. O_2 consumption and DIC production rates normalized for the DOC lost differed between streams indicating that there were inherent differences in DOM photolability. O_2 consumption rates and DIC production rates were an order of magnitude greater in incubations under natural sunlight in comparison to dark conditions. Additionally, the rates among different treatments (filtered, inoculated, and sterile) were similar, indicating that photolysis was greater than respiration and other abiotic processes in the light-exposed treatments. Although photolytic effects cannot be directly quantified, the differences in consumption and production rates in the dark incubations (in which photolysis does not occur and abiotic and/or respiration could occur) were minimal suggesting that the effects observed in the light incubations were primarily the cause of DOM photodegradation. Photolysis could therefore be an important, though neglected, component in oxygen and carbon mass balances used to determine P:R ratios and ecosystem metabolism in aquatic systems. In O_2 models, the loss of O_2 during DOM photodegradation could be misinterpreted to be the result of respiration suggesting that respiration could be overestimated in aquatic systems. Similarly, DIC gain in carbon studies could be due to the photodegradation of DOM, not respiration, again indicating that respiration could be overestimated. If this is the case, then photosynthesis could be more important compared to respiration than previously believed.

DOM photodegradation affects the δ^{18}O-O_2, δ^{13}C-DIC, and δ^{13}C-DOC. Few other DOM photodegradation studies have examined the δ^{13}C-DIC and δ^{13}C-DOC and no other studies have looked at changes to the δ^{18}O-O_2, or the production and carbon isotope ratios of the POC produced. The incubations in the present work indicate that during O_2 consumption, photolysis and other abiotic reactions fractionated oxygen isotopes, preferentially consuming the lighter $^{16}O^{16}O$ isotopomer, similar to respiration. Calculated $\delta^{18}O-O_2$ photolysis fractionation factors (α) were the same for all treatments within a stream, and were confined to a narrow range for the three different streams (α range = 0.988 – 0.995) under both light and dark regimes. Furthermore, fractionation factors were not dependent on O_2 consumption rates, which differed among the wetland and upland streams. This suggests that the range of fractionation factors calculated in this study could be applied to other ^{18}O studies.

The α values calculated from dark incubations (for respiration and abiotic processes occurring within the dark) were larger than α_R (fractionation due to respiration) values reported for large rivers and marine systems. As O_2 and $\delta^{18}O-O_2$ applications in aquatic system studies currently do not separately include DOM photodegradation and other abiotic processes, respiration rates in shallow, high DOC aquatic systems, could be overestimated since they could incorporate all three processes. This could affect P:R ratios directly constrained using combined O_2 and $\delta^{18}O$ models (e.g. Quay et al., 1995) and could have effects on ecosystem implications.

The $\delta^{13}C$-DIC value decreased with DIC production in all incubations, contrary to two out of three samples from the one other study of this type (all three samples inoculated; Opsahl and Zepp, 2001). The DIC produced is created from the breakdown of DOC, which has a lower initial $\delta^{13}C$-DOC signature than the initial $\delta^{13}C$-DIC value thereby decreasing the $\delta^{13}C$-DIC as more DIC is produced. The calculated $\delta^{13}C$-DIC gained was within 1‰ between the incubations of the same stream water (H5 and D10) performed on different dates (mid June and early July) suggesting that the carbon source, not total irradiation, was the cause of the changing $\delta^{13}C$-DIC value. Presumably, the $\delta^{13}C$-DIC value would eventually match the $\delta^{13}C$-DOC value if enough DIC was produced and the δ^{13}C-DOC source remained constant. This suggests that the δ^{13}C-DIC gained was dependent on the δ^{13}C and the quality of the source DOC and must be calculated independently for different systems. However, similar to the δ^{18}O-O_2, the δ^{13}C-DIC values are affected by DOM photodegradation, therefore models that include DIC production could be incorporating all DIC producing processes including photolysis. Cole et al. (2006) created a dual isotope flow (DIF) model that simulated the flow of carbon (^{12}C and ^{13}C) and ^{13}C in a lake food web. Although they considered that DOC was lost by photooxidation and particulate carbon formation in the model, DIC was not gained by photooxidation but is presumably included in their total respiration component, possibly overestimating respiration. Additionally, similar to ^{18}O/^{16}O studies, carbon isotope studies in aquatic systems do not consider DOM photodegradation and other abiotic processes as processes affecting the δ^{13}C-DIC values suggesting that ^{13}C/^{12}C studies could be missing an important component and possibly confusing the processes (or balance of processes) affecting the δ^{13}C-DIC (and δ^{13}C-CO_2) within surface waters of high DOC systems.

Another important aspect of this research is that with DOM photodegradation, the residual DOC became isotopically heavier than the initial δ^{13}C-DOC, illustrating that the isotope value of the allochthonous DOC entering lakes can be altered from its original δ^{13}C value. The degree of change in the incubations (up to 8‰) appears to be related to the amount of degradation that has occurred, and changes could be due to either preferentially breaking off the lighter ^{12}C molecules, or due to functional groups that are being cleaved having more depleted isotope ratios than the bulk DOM. DOC enrichment factors (ε) during DOM photodegradation range between 1‰ and 3.5‰ over two sets of incubations with an average ε value of approximately 2‰. This has implications for ^{13}C/^{12}C studies that are using δ^{13}C-DOC to isolate DOC sources or using δ^{13}C-DOC as a terrestrial end member value in aquatic systems since the alteration of δ^{13}C-DOC during photodegradation can confuse the origin of DOC. It is possible to use the calculated average enrichment factor from the current work in models such as the DIF model presented by Cole et al. (2006) where they assume that the δ^{13}C-DOC does not change due to photodegradation. Additionally, without incorporating the δ^{13}C-DOC changes from DOM photodegradation, ^{13}C/^{12}C studies that use δ^{13}C-DOC as a terrestrial end member in food web studies or in studies that examine the ratio of allochthonous to autochthonous carbon contributions could underestimate the importance of allochthonous carbon. For example, Pace et al. (2004) use a terrestrial isotope value of –28‰ in their two end mixing model to determine the origin of POC in lakes, potentially underestimating the importance of allochthonous carbon if DOM photodegradation occurs within their system. Since carbon isotopic studies in aquatic systems currently do not consider DOM photodegradation as a process that affects δ^{13}C-DOC values, sources of DOC could be misinterpreted and ^{13}C/^{12}C studies in shallow, high DOC systems could be missing an important component.

The δ^{13}C-DOC lost during photodegradation did not match the δ^{13}C-DIC produced, suggesting that there was an alternative loss pathway not accounted for. In the first set of incubations, particulate matter was also created during DOM photodegradation, but was not quantified. The second set of incubations was designed to examine the importance of POC formation during the degradation of DOM. The amount of POC created accounted for 20% to 91% of the DOC lost, indicating that a significant portion of DOC can transform to POC. In most cases, the δ^{13}C-POC was within 1‰ of the initial DOC in this study, suggesting that if this POC were to settle to the lake sediments, it would have a δ^{13}C value close to the source DOC. If the difference between the δ^{13}C-POC created and its source

δ^{13}C-DOC was larger in other systems, then studies that use the δ^{13}C of settling POC to examine the importance of allochthonous carbon to lake sediments could underestimate the importance of allochthonous carbon depending on the amount of photoflocculation occurring.

After exposure to sunlight, the C/N ratios of the photolyzed DOC decreased. This could mean that DOC sources could be misinterpreted as a shift in source from terrestrial inputs to increased algal or microbial inputs. C/N ratios of the POC created during photolysis were between the initial DOC C/N value and final DOC C/N ratio after photodegradation, indicating that the C/N ratios of the POC created is not similar to the DOC source. Furthermore, the C/N ratios of POC suggest a combination of terrestrial and algal inputs although no algae or microbes are present. Therefore, the origin of POC created during the photodegradation of DOC in surface waters could be misinterpreted as a combination of POC from productivity and terrestrial sources and the source of POC in sediments cannot be determined from C/N ratios.

Absorbances decreased after the stream waters were exposed to natural sunlight, indicating the aromaticity, colour, and UV absorption of the DOC decreased which has implications for biota in aquatic systems (Schindler and Curtis, 1997). McKnight et al. (1997) note that the scarcity of aromatic fulvic acid derivatives causes increased UV penetration in high latitudes. Decreases in colour and UV absorption resulting from photodegradation could increase UV exposure and decrease UV protection to freshwater communities, and Curtis and Schindler (1997) suggest that lakes with small catchments in boreal regions could be at risk since there is a rapid selective loss of coloured DOC. The optical index of molecular weight also increased in most samples indicating that, generally, the molecular size of the DOC was decreasing.

Understanding that DOM photodegradation can change $\delta^{13}C$ values and C/N ratios allows for a better understanding of the processes that could affect aquatic systems with high DOC. Dillon and Molot (1997a) indicate that according to mass balances, approximately equal amounts of carbon are evaded to the atmosphere and lost to sedimentation within a suite of temperate lakes from southern Ontario. Furthermore, Molot and Dillon (1997b) found that photodecay constants from incubations on stream inflow water, once extrapolated to lakes, are similar to those from DOC loss in the mass balances of Dillon and Molot (1997a). The incubations performed in the current study corroborate that a significant portion of the DOC lost could be transformed, however, contrary to Molot and Dillon (1997b) who believe that sedimentation is the result of CO_2 fixation, the loss pathway in the current study includes the abiotic formation of particulate carbon, which can settle out and thus affect the mass balance of lakes.

Two independent methods were used to determine the importance of DOC on lake sediments. One of the methods used stable carbon isotope analyses on stream and lake POC, litter, POC created from photodegradation, DIC, and zooplankton and suggested that allochthonously and autochthonously derived POC are isotopically distinct. Using a 2 end member mixing model, the allochthonous to autochthonous ratio in the $\delta^{13}C$ of the lake sediments was calculated, indicating that the isotopic signature of sediment organic matter can be affected by the ratio of autochthonous and allochthonous contributions. This suggests that climate change and/or anthropogenic changes to the landscape, and the concomitant changes in DOC inputs to lakes can be recorded in the sediment record. The $\delta^{13}C$ of lake sediments can thus be affected by the amount of particulate carbon created through the photodegradation of DOC, POC entering lakes, and litter fall onto lakes, suggesting that sediment records are not just a productivity signal, but a mass balance signal in high DOC retention lakes. Furthermore, once the allochthonous to autochthonous ratio is applied to sedimentation rates from the cores, it becomes evident that the autochthonous contribution to the lakes does not always change. Therefore, $\delta^{13}C$ of lake sediments may not always be recording productivity within lakes, which goes against classic $\delta^{13}C$ lake sediment interpretations. Consequently, productivity changes inferred from $\delta^{13}C$ lake sediment records could be incorrect, and may be overestimated in aquatic systems.

Furthermore, it was estimated that up to 25% of the lake sediments could be derived from POC originating from lake inflows. The $\delta^{13}C$ and C/N ratios of stream POC suggest that stream POC is a combination of algal contributions and terrestrial inputs and that in stream (or wetland) productivity can be incorporated into the lake sediments. Therefore, productivity measured or inferred from lake sediments could include stream and wetland productivity suggesting that, the "aquatic signal" recorded in lake sediments includes aquatic processes (and aquatic cellulose) from adjoining wetlands and streams.

A second independent method used annual carbon mass and stable isotope balances for Harp and Dickie Lakes to determine the impacts of allochthonous carbon on the $\delta^{13}C$ of lake sediments and corroborated that long-term DOC changes affect lake sediment records. The small range in the mass-weighted average annual $\delta^{13}C$ values suggest that for most of the parameters the values are well constrained. However, calculated $\delta^{13}C$ values of the lake sediment differ from the measured $\delta^{13}C$ sediment values, suggesting that there was either a problem with the carbon mass balance or the isotope balance of the lakes. In an attempt to isolate why the calculated $\delta^{13}C$ of the lake sediments did not match the measured $\delta^{13}C$ value, a dynamic mass and isotope budget model was created to examine the sensitivity of the $\delta^{13}C$ values and masses of carbon of the different inputs to the lakes were to the sediment signature.

The model revealed that changing the DOC mass entering lakes by small amounts (i.e. 5%) does not appear to significantly alter the $\delta^{13}C$ of the lake sediment. However, the $\delta^{13}C$ of the lake sediments can change up to 2.5‰ when the long-term annual variability of DOC entering the lakes (i.e. 40% change) is applied. According to the model, the $\delta^{13}C$ of the lake sediments is also sensitive to the areal water discharge rate (q_s), which controls the mass of DOC exiting the lakes. Harp Lake is also sensitive to pH and the CO_2 gas exchange coefficient. Although the carbon mass and isotope balances are sensitive to different parameters, the $\delta^{13}C$ of lake sediments in both lakes are affected by changes to the long-term DOC load entering the lakes.

Overall, this thesis demonstrates that the photodegradation of DOM can change stable oxygen ($\delta^{18}O$-O_2) and carbon ($\delta^{13}C$-DIC, $\delta^{13}C$-DOC) isotopes and affect the interpretation of isotope studies in aquatic systems with high DOC (or high DOC loss due to photodegradation). Particulate carbon is created during the photolytic breakdown of DOC, and could account for a large portion of the allochthonous DOC loss in lakes. Since allochthonous and autochthonous POC are isotopically distinct, estimates of POC balances in Harp and Dickie Lakes suggest that allochthonous POC (from litter, as POC entering streams, and POC created by DOM photodegradation) can account for ~65% to 100% of organic carbon within lake sediments. Furthermore, a dynamic carbon mass and isotope budget model corroborates that long-term changes to the DOC entering lakes can affect the $\delta^{13}C$ of lake sediments illustrating, by a second independent method, the importance of allochthonous carbon to lake sediments.

7.2 Recommendations

Broadly, this thesis can be split into 2 components: the effects of DOM photodegradation on the concentrations and isotopes of O_2, DIC, DOC, and POC, and the use of carbon mass balances to examine the importance of allochthonous carbon to lake sediments. Suggestions to improve future studies of this nature will be suggested in the following sections.

7.2.1 i) DOM photodegradation experiments

In this thesis, O_2 consumption rates, DIC production rates, O_2 fractionation factors, and the δ^{13}C-DIC produced for the combined effects of respiration, photolysis, and other abiotic reactions were calculated. Although the experiments indicate that DOM photodegradation is the main process affecting these concentrations and isotope ratios in the incubations, future work could differentiate between the effects of respiration, photolysis, and other abiotic reactions. Separating abiotic and respiratory effects from photolysis in the light treatments would require sampling the dark incubation bags concurrent with the light incubations to ensure that incubation conditions (i.e. temperature, hours, etc) are consistent. Additionally, other aquatic environments could be examined to determine whether the isotope fractionations and ratios presented in this thesis can be applied to other systems.

O_2 consumption and DIC production rates differed in different streams even when normalized for the DOC concentration lost, indicating that there were inherent differences in DOM photolability. Annual and/or seasonal changes in DOM lability suggest that O_2 consumption and DIC production rates may be different with changes in DOM quality, and that these experiments should be performed on DOM collected from different seasons. Schumacher et al. (2006) have used CP-MAS ^{13}C-NMR (cross polarization magic-angle spinning ^{13}C nuclear magnetic resonance) spectroscopy to examine seasonal differences in the chemical composition of DOM from boreal catchments. Completing ^{13}C-NMR analysis on incubation samples could provide a better understanding of the changes to DOM during photodegradation possibly providing insight into the structural changes of DOM, perhaps identifying the functional groups cleaved.

However, ^{13}C-NMR spectroscopy of humic substances assumes the equal distribution of isotopically enriched carbon among different carbon moieties (McKnight et al., 2003), which might not be the case.

The stream water used in the incubations was collected in spring, however, it was not incubated until mid summer when the length of daylight was at a maximum. Although not quantified for the duration of the incubations, it is also possible that the O_2 loss and DIC production rates could be affected by the amount and/or intensity of sunlight the stream water was exposed to. Incubating sterile treatments of Harp Inflow 5 and Dickie Inflow 10 water during incubations conducted in the middle of June and the beginning of July show that the O_2 consumed and DIC produced (both normalized for the amount of DOC lost) were lower in the June incubations than in the July incubations for Dickie Inflow 10 samples, but similar for the Harp Inflow 5 samples. This suggests that there might be differences in DOM photolability and that different intensities or amounts of total irradiation might affect the amount and rate of photodegradation. Additionally, von Wachenfeldt et al. (2008) show that light stimulated particulate matter formation and that the POC produced decreased with decreases in photosynthetically active radiation (PAR), indicating that amount of photoflocculation in the current incubations could change seasonally with changes to PAR. Performing photolytic experiments using DOC samples collected over the course of a year could also show the importance of POC formation to lake mass balances.

Particulate matter formation can also be related to metal concentrations (e.g. Mn, Fe) within natural waters and these were not quantified in these experiments. As metals are bound to DOM, transport of metals from the catchment could also change temporally with hydrological changes flushing DOC from the catchments to the lakes. It is possible that the amount of particulate matter created could be related to the metals in the stream water and, therefore, the amount of particulate matter created could change temporally. It could be useful in future incubations to track the concentrations of metals or manipulate the metal concentrations for a better understanding of what drives the amount of particulate matter created by photodegradation. Additionally, the δ^{13}C-POC created during DOM photodegradation could be tracked during these incubations to determine whether POC production (and enrichment in δ^{13}C-POC from the source DOC) is constant with different amounts of DOC loss.

7.2.2 ii) The importance of allochthonous carbon to lake sediments

In this thesis, the importance of allochthonous carbon to lake sediments was investigated using two independent methods: estimated POC mass balances, and combined DOC and DIC mass balances.

The first method used estimated POC mass balances to calculate average temporal allochthonous and autochthonous δ^{13}C end member values. The allochthonous value was composed of litter, POC entering through streams and POC created through photodegradation. POC concentrations and litter fall into the lakes were only estimated in this study, however, their calculated δ^{13}C values were similar. If POC concentrations and litter fall were quantified, it could provide a better understanding of their contributions to the lake sediments. Additionally, incubations using stream samples collected from different times of the year could provide additional information on both the amount and the δ^{13}C of POC formed during DOM photodegradation. Since a two end-member mixing model was used to examine the proportion of allochthonous to autochthonous carbon in lake sediments, the ratio is affected by the δ^{13}C autochthonous end member signal. Since productivity curves were also assumed in this study, having a better understanding of production within Harp and Dickie Lakes could provide a more accurate autochthonous δ^{13}C end-member value.

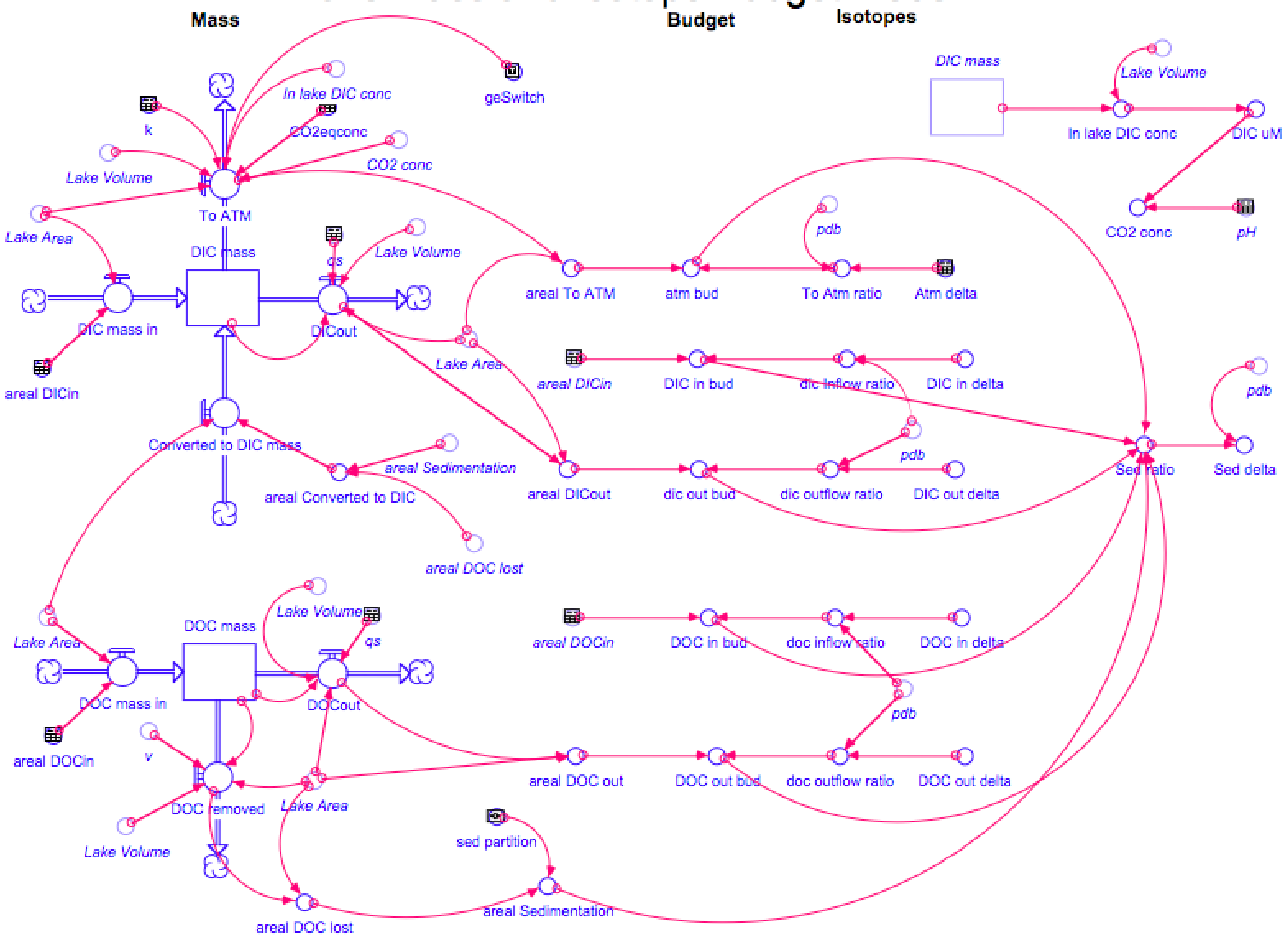
The second method used to examine the importance of allochthonous carbon to lake sediments involved creating a combined mass and isotope budget model. The average carbon masses within the model for Harp and Dickie Lakes did not match the mass balances (averaged over 8 years) provided by Dillon and Molot (1997a) even though their input variables (i.e. q_s, v, pH etc) were used to calculate the masses. To determine whether this was due to the technique used to estimate the balances or the model, it might be useful to input variables for one year (instead of an average of 8 years), to assess whether the masses within the model balance. However, this would involve further assumptions (e.g. the partition between sedimentation and gas exchange remains constant) that would require further consideration.

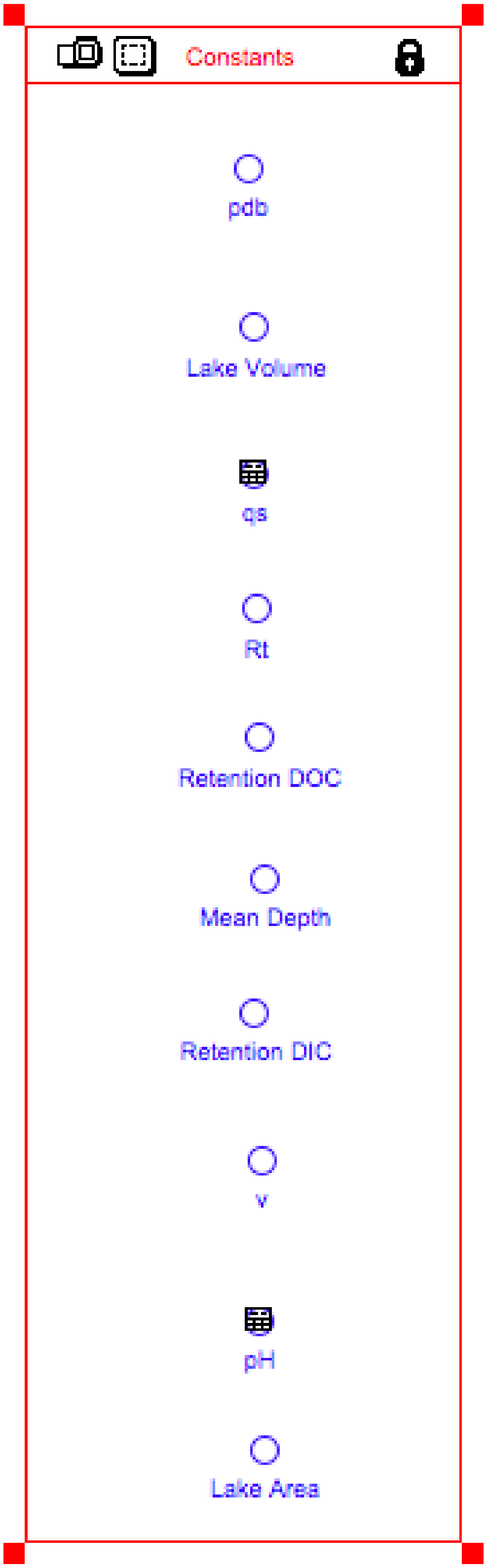
The model indicated that the amount of carbon exiting the lakes was highly dependent on the gas exchange coefficient used in the model. This variable was estimated based on temporal wind speed data; however, improvements could be made through tracer experiments to determine the annual variability of this parameter or by installing flux towers around the lakes. Additionally, a closer look at the input parameters to the model suggest that the $\delta^{13}C$-CO_2 evaded to the atmosphere is a key parameter in completing the isotope balances, and calculating the $\delta^{13}C$ of the sediments. Flux calculations suggest that detailed lake surface measurements must be collected at the onset of and times surrounding the fall turnover for accurate calculation of $\delta^{13}C$-CO_2 lost to gas exchange. This key point was missed in the sampling efforts and could account for the mismatch between the calculated and the measured $\delta^{13}C$ sediment values. Future studies should recognize the importance of CO_2 evasion in the fall, and account for its impact in sampling strategies.

Appendix A

A forester diagram of the dynamic mass and isotope budget model used to calculate the $\delta^{13}C$ of the lake sediments in Chapter 5 is presented on the following page.

Lake Mass and Isotope Budget Model




Constants
pdb
Lake Volume
qs
Rt
Retention DOC
Mean Depth
Retention DIC
v
pH
Lake Area

References

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