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Temporal and spatial heterogeneity in lacustrine $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ signatures in a large mid-latitude temperate lake

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ABSTRACT

Modelling limnetic carbon processes is necessary for accurate global carbon models and stable isotope analysis can provide additional insight of carbon flow pathways. This research examined the spatial and temporal complexity of carbon cycling in a large temperate lake. Dissolved inorganic carbon (DIC) is utilised by photosynthetic organisms and dissolved oxygen (DO) is used by heterotrophic organisms during respiration. Thus the spatial heterogeneity in the pelagic metabolic balance in Loch Lomond, Scotland was investigated using a combined natural abundance isotope technique. The isotopic signatures of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and dissolved oxygen ($\delta^{18}O_{DO}$) were measured concurrently on four different dates between November 2004 and September 2005. We measured isotopic variation over small and large spatial scales, both horizontal distance and depth. $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ changed over a seasonal cycle, becoming concurrently more positive (negative) in the summer (winter) months, responding to increased photosynthetic and respiratory rates, respectively. With increasing depth, $\delta^{13}C_{DIC}$ became more negative and $\delta^{18}O_{DO}$ more positive, reflecting the shift to a respiration-dominated system. The horizontal distribution of $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ in the epilimnion was heterogeneous. In general, the south basin had the most positive $\delta^{13}C_{DIC}$, becoming more negative with increasing latitude, except in winter when the opposite pattern was observed. Areas of local variation were often observed near inflows. Clearly $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ can show large spatial heterogeneity, as a result of varying metabolic balance coupled with inflow proximity and thus single point sampling to extrapolate whole lake metabolic patterns can result in error when modelling large lake systems Whilst we advise caution when using single point representation, we also show that this combined isotopic approach has potential to assist in constructing detailed lake carbon models.

Key words: dissolved inorganic carbon, dissolved oxygen, isotopes, photosynthesis, respiration, pelagic

1. INTRODUCTION

Lakes in the boreal and temperate zones are important in global biogeochemical cycles, as significant metabolic activity, respiratory through the breakdown of allochthonous matter, and photosynthetic, links carbon flow from terrestrial organic matter through the aquatic environment and often to the atmosphere. Indeed current research suggests the majority of lakes and near land systems are dominated by respiration and thus sources of carbon to the atmosphere (e.g., Jones 1992; Cole *et al*. 1994, 2000). For this reason the elucidation of how these processes fluctuate over time and space is important to understand the wider global carbon cycle.

Dissolved inorganic carbon (DIC) and dissolved oxygen (DO) are two nutrient pools linked by metabolic processes (Hanson *et al*. 2006). The respective concentrations of these two pools have been used to examine production/respiration balances in aquatic ecosystems for some time (e.g., Juday 1935; Schindler & Fee 1973). However, the use of isotope ratios of carbon ($^{13}C/^{12}C$, $\delta^{13}C$) and oxygen ($^{18}O/^{16}O$, $\delta^{18}O$) for DIC and DO respectively have been used to a lesser extent (e.g., Quay *et al*. 1986, 1995). Each isotope ratio can provide insight into sources and the processes that subsequently amend the respective pools (e.g., Waldron *et al*. 2007).

Several processes govern DIC concentration, [DIC], in freshwater systems. These are the dissolution from carbonate minerals and soil CO_2 from the catchment, influx or efflux of CO_2 from or to the atmosphere, and the balance between photosynthetic CO_2 uptake and respiratory CO_2 production (Clark & Fritz 1997). However, over short time scales, metabolic balance is the key driving force of DIC, and DO, concentration in lakes (Hanson *et al*. 2006; Myrbo & Shapely 2006; Trojanowska *et al*. 2008).

^{13}C is preferentially discriminated against during the uptake of DIC during photosynthesis, resulting in an increase in $\delta^{13}C_{DIC}$. Conversely, respiratory processes such as the breakdown of organic matter or methane have the effect of lowering $\delta^{13}C_{DIC}$ of surrounding lake water through the production of CO_2 that reflects the generally more negative $\delta^{13}C$. The opposite responses of catabolic and anabolic pathways render $\delta^{13}C_{DIC}$ characterisation powerful in providing insight into patterns of lake-metabolism. For example, more positive $\delta^{13}C_{DIC}$

has been interpreted to reflect increased importance of photosynthesis in the epilimnion of stratified lakes (e.g., Quay *et al*. 1986; Keogh *et al.* 1996; Myrbo & Shapley 2006), whilst lower $\delta^{13}C$ in the hypolimnion reflects the lower relative importance of photosynthesis compared to respiration.

Under atmospheric equilibrium the isotope ratio of dissolved oxygen $\delta^{18}O_{DO(aq)VSMOW}$ is approximately 24.2‰ (Kroopnick & Craig 1972). Like DIC, the concentration and $\delta^{18}O_{DO(aq)}$ is mainly driven by the photosynthetic-respiratory balance (Aggarwall & Dillon 1998; Luz & Barkan 2002). ^{18}O is discriminated against during respiratory uptake, thus in general the response of $\delta^{18}O_{DO}$ is opposite to $\delta^{13}C_{DIC}$. Dissolved oxygen produced during photosynthesis lowers $\delta^{18}O_{DO(aq)}$ whilst consumption of DO during respiration increases $\delta^{18}O_{DO(aq)}$. Generally values over 24.2‰ indicate a system where respiration dominates; below this value photosynthesis is considered the dominant metabolic influence.

Individually, $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ have been used to assess photosynthetic- respiratory balance between (e.g., Jones *et al*. 2001; Myrbo & Shapley 2006). However, the combining of the two pools in a dual analysis approach is still relatively rare (Wagner & Zalewski 2000; Parker *et al*. 2005; Waldron *et al*. 2007; Trojanowska *et al*. 2008). Here we present preliminary survey data examining spatial and temporal heterogeneity of $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ in a large (71 km^2), temperate lake. Such measurements can reveal variation in the processes that drive elemental cycles in lakes, essential in detailed understanding of role these systems play in the global carbon budget.

In this study we test the hypothesis that $\delta^{13}C_{DIC}$ ($\delta^{18}O_{DO}$) will become more enriched as photosynthesis becomes relatively more important in the summer months, with the opposite being true in winter. We also evaluate the use of single point sampling in large, hydrologically complex lakes when inferring their role in the carbon cycle.

2. METHODS

2.1. Study site and sampling strategy

Loch Lomond is located in west-central Scotland (56°80'N, 4°40'W) (Fig. 1), is the largest surface area mainland United Kingdom lake (71 km^2) and is the third deepest. Loch Lomond is monomictic with one period of mixing per annum, separated by a period of stratification. The loch drains a catchment area of 696 km^2. A geological fault line bisects the lake into two distinct basins. The south basin (~28 km^2) is broad and shallow (up to 8.8 km wide and between 5-30 m deep) and drains a low-altitude, shallowly-sloping, base-rich catchment. The north basin (16.5 km^2) is narrow and deep (up to 1.5 km wide and 200 m deep) and drains a high-altitude, steeply-sloping, base-poor catchment. Stratification is generally stable in the north basin between May and November but regularly breaks down in the south basin during this period due to wind-induced mixing. The south basin is generally mesotrophic-oligotrophic (4 to 6 µg chl-*a* L^{-1}, nitrate 0.17 to 0.25 mg L^{-1}, phosphate 9 to12 µg L^{-1}) and the north basin oligotrophic-ultra-oligotrophic (2 to 3 µg chl-*a* L^{-1}, nitrate 0.12 to 0.15 mg L^{-1}, phosphate 3 to 12 µg L^{-1}) (Krokowski and Doughty 2006). A middle basin (~27 km^2) has also been defined (Fig. 1) which is an intermediary basin between north and south.

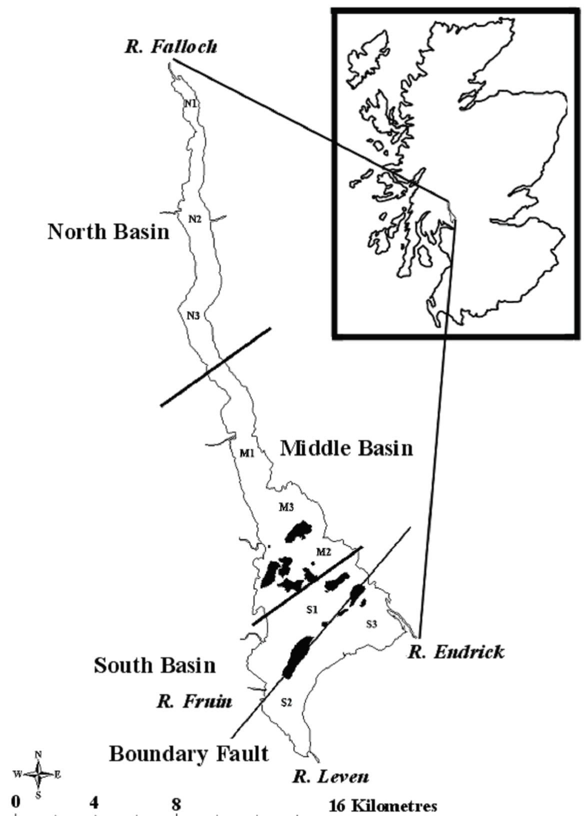

Fig. 1. Loch Lomond, showing sample site locations, basin boundaries used in this study and the locations of the two largest inflows (Rivers Endrick and Falloch) and the main outflow (River Leven). The geological fault line bisecting the south basin is also labelled.

Twenty-one sites were selected across the lake (Fig. 1). For each basin three sample sites were designated (1, 2 and 3) to assess large-scale spatial variation (mean distance between sites 4.73 ± 1.27 km). Around sites N3 in north, M3 in middle and S1 in south four more sites were sampled in close proximity (mean distance from main site 0.49 ± 0.43 km) to assess smaller scale spatial variation. At each of the 21 sample sites three depths were sampled using a Van Dorn sampler: surface water, a middle depth and approximately 3-5 m from the lakebed, except where depths exceeded the limits of our sampling equipment and the sample collected here represents 100 m depth. GPS positions recorded in the first sampling trip were used to reposition and ensured consistency between sampling campaigns.

We carried out four field campaigns between November 2004 and June 2005. In general the north basin was sampled on day one, followed by the middle and south basins 24 hours later. Sampling periods were 3rd/4th November 2004, 7th/8th March 2005, 29th/30th June 2005 and 29th/30th September 2005.

2.2. DIC and DO analysis

Samples for DIC concentration and $\delta^{13}C_{DIC}$ were analysed using a headspace equilibration technique (e.g., Torres *et al*. 2005; Waldron *et al*. 2007). Pre-evacuated 12 mL acid washed glass containers, fitted with a screw cap holding rubber septa (Exetainer™) were filled, underwater with lake water. Prior to evacuation, 200 µL of de-gassed H_3PO_4 had been added to each container. Lake water was sampled using a syringe, and placed into the pre-evacuated containers by piercing the septa. We tested that the vacuum had been adequately maintained by drawdown of the syringe barrel; if this did not occur the sample was rejected. Samples were mixed thoroughly and stored upside down, limiting CO_2 ingression or egression, prior to analysis.

DIC concentration and $\delta^{13}C_{DIC}$ were measured by an automated continuous-flow isotope-ratio mass spectrometer (CF-IRMS), using an AP gas preparation interface linked to a VG Optima IRMS. Aqueous DIC standards were prepared with known concentrations in order to correct the unknown samples via linear regression. The $\delta^{13}C_{V\text{-}PDB}$ range of the standards (-24.5 to 2.5‰) was greater than that predicted in freshwater systems (e.g., Meili *et al*. 1996). Precision on replicate standards was ±0.1‰. All standards run in the same batch as samples were prepared and allowed to equilibrate for 24 hours. A more detailed methodology can be found in Waldron *et al*. (2007).

Dissolved oxygen isotope analysis was undertaken using methods described by Barth *et al*. (2004). DO samples were collected in 12 mL exetainers™. $\delta^{18}O_{DO}$ was measured on an AP2003 mass spectrometer and preparation unit, supplied by a XL222 Gilson auto sampler. Air was used as the standard for these analyses and results expressed relative to the international standard VSMOW. Accuracy was generally greater than ±0.3‰. Due to a problem with sample collection data for November 2004 is not available.

2.3. Spatial and statistical analysis

We undertook spatial analysis with ArcGIS version 9.1, using Inverse Distance Weighted (IDW) interpolation to estimate values between data points and contour chosen parameters within the lake. We used a TIN (Triangular Irregular Network) to construct a profile of lake depth that closely matched historical chart data.

As subsurface samples were collected from different depths, spatial comparisons will focus on the epilimnion only. Surveys by the Scottish Environmental Protection Agency (SEPA) suggest a metalimnion between 5.7 and 7.2 m in the south, and 8.4-10.5 m in the north. These data, along with measurements from nearby research station staff (Adams, pers. comm.) support the interpretation of an epilimnion usually between 7-13 m. Thus for calculation of epilimnetic areal DIC concentration, the surface DIC concentration measured in mg L^{-1} was converted to g m^{-3} assumed constant to a 13 m, believed to be the maximal possible extent of the metalimnion. All statistical analyses were carried out on SPSS version 13. Data were analysed using multi-factorial analysis of variance and linear regression models.

In the north and middle basins, all middle and deep sample locations were below our metalimnion boundary. As such from this point onward when referring to the hypolimnion in these two basins we refer to middle and deep sites. This applies in the majority of cases in the south basin and should be assumed unless otherwise stated.

Statistical analyses were carried out on SPSS version 13. Data were analysed using multi-factorial analysis of variance and linear regression models.

3. RESULTS

3.1. Temporal and inter-basin variation in [DIC], $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$

DIC concentration was never under-saturated with respect to the atmosphere, thus atmospheric lake-ingression had no effect on concentration or $\delta^{13}C_{DIC}$. DIC concentration was lowest in the north basin (Fig. 2A), ranging from ~0.08 mM in the hypolimnion, to a maximum of 0.16 mM in the epilimnion. The south basin has the highest concentrations (~0.16 mM in March to ~0.27 mM in June). DIC concentration in the middle basin remained relatively constant (~0.16 mM) throughout the year.

Seasonal patterns of DIC concentration [DIC] in both south and north basin were similar, with a maximum value in June surface waters of 0.27 ± 0.09 mM and 0.17 ± 0.05 mM respectively. Minimum values were recorded in March of 0.17 ± 0.02 mM (south basin, mid depth) and 0.08 ± 0.01 mM (north basin, deep water). All three basins were significantly different, indicating large-scale spatial variability.

Significant variability in $\delta^{13}C_{DIC}$ was observed with depth, basin and month (Fig. 2B). Average $\delta^{13}C_{DIC}$ in the north and middle basin epilimnion in both June and September were above –6‰. Low values (-11 to -13‰) were measured in the north basin hypolimnion in November and March, similar to signatures measured in middle basin hypolimnion water in September. Each basin showed a degree of seasonality in $\delta^{13}C_{DIC}$, although the pattern was variable between basins. The north basin epilimnion had the largest range, with a difference of over 6‰ between March (mean $\delta^{13}C_{DIC}$ = -12.2‰) and June (mean $\delta^{13}C_{DIC}$ = -5.8‰).

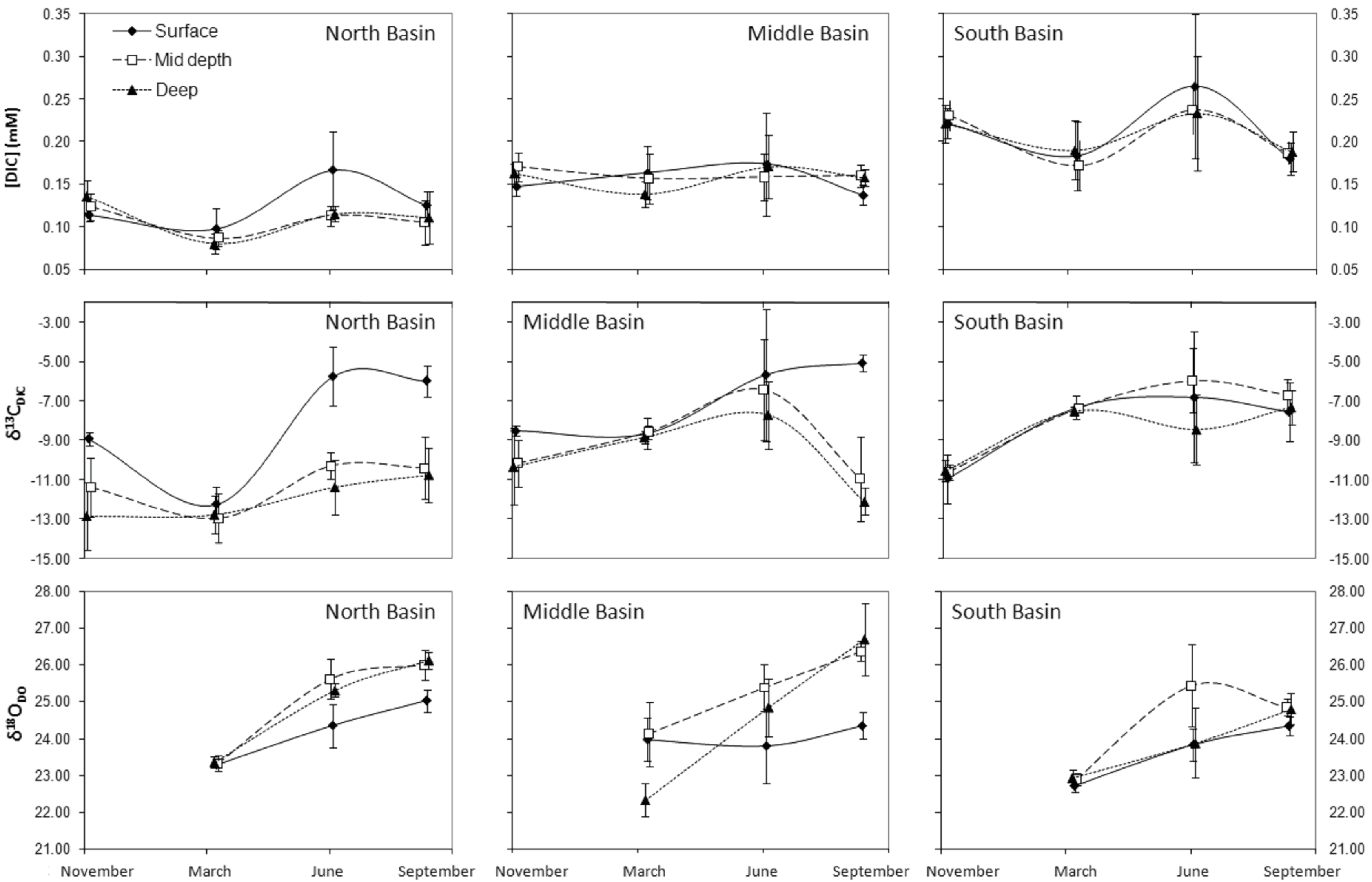

Fig. 2. Seasonal DIC concentration, $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$. Lake divided into basins (north, middle and south) and depths (surface, middle and deep). In general, middle and deep values represent the hypolimnion water, and surface values the epilimnion. Error bars represent standard deviation of the basin average (n = 7).

$\delta^{18}O_{DO}$ varied from 22.3‰ (March, mid-basin, mid-water) to 26.7‰ (September, mid-basin, mid-water) (Fig. 2C). $\delta^{18}O_{DO}$ is significantly affected by depth, basin and month. In all three basins there was a significant increase in $\delta^{18}O_{DO}$ between March and September with higher values in the hypolimnion compared to the epilimnion. Whole lake averages (ignoring basin and depth) show an increase from 23.2 ± 1.5 to 25.4 ± 1.0‰ between March and September (P <0.005). Overall, basin effect is significant (P <0.005) but middle and north basin are not statistically different from each other (P = 0.341).

3.2. *GIS supported spatial analysis of [DIC], $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$*

For all four sampling trips there was a gradient of decreasing DIC concentration with distance north (Fig. 3A). In November and September the highest concentrations (~37-41 g m^{-2}) were estimated in the southeast corner near the inflow of the River Endrick (see Fig. 1). In March, highest concentrations were slightly further west, in the middle region of the south basin. The highest DIC concentration and greatest spatial variation was modelled in June. As in March the highest concentrations were in the middle and western areas of the south basin (55-57 g m^{-2}). In contrast to November and September, the south-east corner near the River Endrick was an area of lower concentration in June. Further north the concentration fell again, but unlike November, March and September, increases again on approach to the mouth of the River Falloch in the north basin (Fig. 1).

Substantial spatial variability in $\delta^{13}C_{DIC}$ epilimnion was modelled (Fig. 3B). In November the south basin exhibits the most negative $\delta^{13}C_{DIC}$ with higher values occurring throughout the middle and north basins. This contrasts with March where the opposite pattern was observed. The most positive $\delta^{13}C_{DIC}$ were measured in June (whole loch mean = -6.3 ± 1.8‰). As in March, there was depletion further north, but to a lesser extent. The most significant area of depletion in June was next to the River Endrick inflow. A similar pattern to June was observed in September, with the most positive $\delta^{13}C_{DIC}$ in the middle basin and more negative values in the far north and south. Significant depletion in $\delta^{13}C_{DIC}$ the southeast corner in September was no longer evident; instead the most ^{13}C-depleted values were recorded in the southwest near the outflow into the River Leven. As with June and March, $\delta^{13}C_{DIC}$ were lower towards the River Falloch inflow in September.

An overall increase in $\delta^{18}O_{DO}$ between March and September was observed, along with smaller scale spatial variability (Fig. 3C). In March, the south basin had a uniform distribution with little variation. $\delta^{18}O_{DO}$ increased in the middle basin, before lowering again approaching the north basin. The distribution of more positive $\delta^{18}O_{DO}$ expands in June. The south basin had enriched areas in the southeast corner, as well as areas of the middle basin. $\delta^{18}O_{DO}$ remained relatively constant at ~23.8‰ for the north basin until a large increase near the mouth of the River Falloch. The most ^{18}O-enriched values were observed in September, with the highest values in the southwest corner of the south basin and the far north of the north basin. $\delta^{18}O_{DO}$ for the middle basin were less positive than the north and south basin, and no significant temporal variability was observed (P <0.001).

4. DISCUSSION

Dissolved inorganic carbon is the primary source of carbon for photosynthetic utilisation. Previous work showed DIC concentration can be closely associated with photosynthetic production (Hein 1997; Jones *et al*. 2001), especially when studying short (diel-seasonal) timescales. Volume changes in Loch Lomond were insufficient to account for the observed changes in DIC concentration. DIC concentration varied between 0.07 and ~0.25 mM, consistent with other lake studies (e.g., Heinn 1997; Hanson *et al*. 2006). Concentration of DIC peaked in the summer months, corresponding to the likely periods of high photosynthesis. This is in contradiction to some other work (e.g., Hanson *et al.* 2006) where in all of the seven lakes sampled maximum DIC concentration was reached in the winter months. We suggest this is a reflection of high concurrent respiration rates, an interpretation supported by the $\delta^{18}O_{DO}$ signatures above 24.2‰. Concurrent algal and bacterial production measurements carried out in other work (Bass 2008) add credence to this idea, showing pelagic respiration rates to significantly exceed photosynthesis. The relative importance of respiration compared to photosynthesis was supported by DIC concentration variation and $\delta^{18}O_{DO}$.

The south basin generally had higher DIC concentration than the middle and north. Two major inflows join the loch in the south basin, the Rivers Endrick and Fruin (Fig. 1), and account for 47.7% of total inflow into the lake on average (Maitland 1981; Smith *et al*. 1981). The Endrick and Fruin had the highest annual average inflow DIC concentration (Tab. 1), measured at 0.939 ± 0.54 mM (n = 9) and 0.443 ± 0.21 mM (n = 7) respectively.

Tab. 1. DIC concentration, $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ for the three largest inflows into Loch Lomond.

	November	March	June	September
[DIC] (mM)				
Endrick	0.77 ± 0.11	0.65	1.74 ± 0.27	0.60 ± 0.03
Fruin	0.44 ± 0.02	0.34 ± 0.12	0.73 ± 0.10	0.26 ± 0.11
Falloch	0.28 ± 0.09		0.18	0.18 ± 0.08
$\delta^{13}C_{DIC}$ (‰)				
Endrick			-8.6 ± 2.3	-13.8 ± 0.9
Fruin	-14.8 ± 0.3	-11.3 ± 0.7	-12.7 ± 0.5	-10.1 ± 0.7
Falloch	-13.0 ± 1.1		-10.0 ± 2.1	-13.3 ± 0.2
$\delta^{18}O_{DO}$ (‰)				
Endrick		24.4 ± 0.2	23.4 ± 0.2	25.2 ± 0.3
Fruin		24.2 ± 0.1	25.4 ± 0.2	24.5 ± 0.6
Falloch		25.1 ± 0.7	23.4 ± 0.4	25.1 ± 0.1

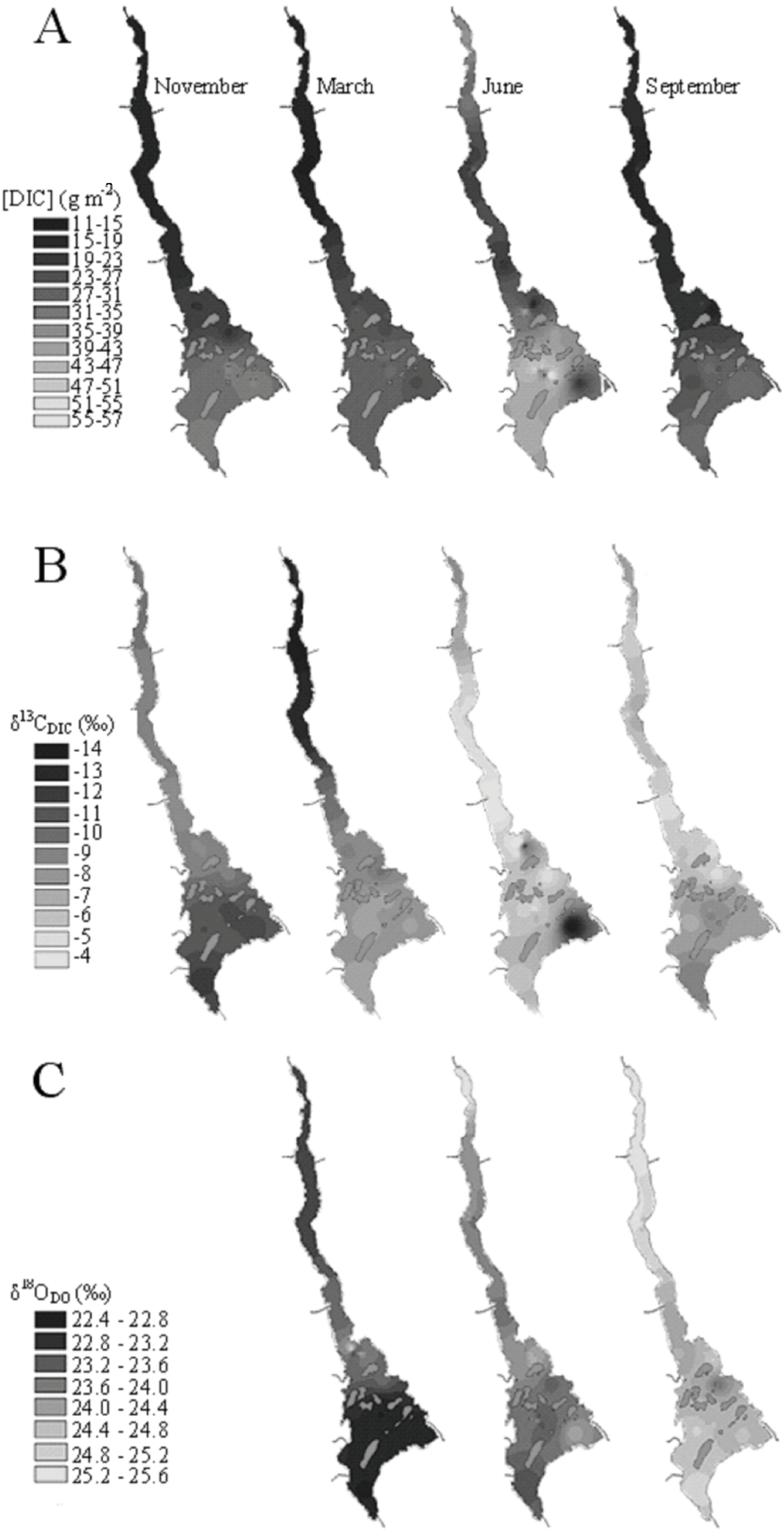

Fig. 3. Epilimnetic distribution of (**A**) dissolved inorganic carbon (g m^{-2}), (**B**) $\delta^{13}C_{DIC}$ and (**C**) $\delta^{18}O_{DO}$ for four months sampled. Solid green areas show island locations.

The high concentration of DIC in the south basin is likely a combination of higher rate of pelagic respiration, and increased DIC import from the catchment.

Previous studies have shown increases in the epilimnetic $\delta^{13}C_{DIC}$ in summer months caused by higher photosynthetic activity (Herczeg 1987; Hollander & McKenzie 1991; Wang & Veizer 2000). The same pattern was observed in this study (Fig. 2), though temporal variation was higher. Quay *et al*. (1986) showed the temporal range in $\delta^{13}C_{DIC}$ of the epilimnion of Lake Washington to be 3.2‰, and in small Minnesota and Montana lakes (all less than 325 ha and 17.5 m deep) $\delta^{13}C_{DIC}$ varied by approx 8‰ (Mybro & Shapely 2006). $\delta^{13}C_{DIC}$ in Loch Lomond changed by 11‰ through the seasons. Bade *et al*. (2004) used various statistical models to show that although the "potential" $\delta^{13}C_{DIC}$ for a lake is set by the geochemical characteristics of the watershed, metabolism can give significant variation around this baseline. The observed temporal and inter-basin variability in Loch Lomond $\delta^{13}C_{DIC}$ is likely a reflection of photosynthetic/respiratory balance and contributions from substantial inflows.

The observed range in $\delta^{13}C_{DIC}$ in the north and south basins was similar, contrary to expectations if primary production alone dictated these values. The north, oligotrophic basin would be expected to become less-enriched in the spring summer than the mesotrophic south. Direct productivity measurements in 2006 and 2007 (Bass *et al*., in press) showed the south basin supported significantly greater levels of bacterial production during the productive periods (spring and summer) than the north, likely due to greater concentrations of allochthonous DOC and POC. Although photosynthetic rates in the south may be higher, the greater level of secondary production may be limiting the potential enrichment of the DIC pool, and both north and south basin appear similar. This scenario demonstrates the potential complexities of $\delta^{13}C_{DIC}$ systematics in morphologically and hydrologically complex lakes.

The measured decrease in $\delta^{13}C_{DIC}$ with depth in the stratified water column supports the interpretation that metabolic balance drives the observed variability in $\delta^{13}C_{DIC}$, and $\delta^{18}O_{DO}$. If the observed changes in $\delta^{13}C_{DIC}$ (more positive in the summer, more negative with depth) were caused a shift between photosynthetic and respiratory dominance, we would expect the opposite pattern in the $\delta^{18}O_{DO}$ (more negative in summer, more positive with depth). $\delta^{18}O_{H2O}$ showed no significant variability throughout the lake (annual mean = -6.9 ± 0.2‰, n = 249) so is likely not a significant factor in the observed $\delta^{18}O_{DO}$ variability.

$\delta^{18}O_{DO}$ became more positive over the summer months and peaked in September, three months after the peak in $\delta^{13}C_{DIC}$. Respiration increases concomitant with photosynthesis as the phytoplankton supply a valuable source of autochthonous, labile dissolved organic material (Lancelot 1983; Jumars *et al*. 1989). Thus we hypothesise that $\delta^{18}O_{DO}$, and therefore the relative importance of respiration, continue to increase after the autotrophic peak has subsided. Even after the bloom event large quantities of organic material may remain from the dead/dying autotrophs that supply a food source for heterotrophs. This accompanied by the return of early autumnal weather, with storms, increased run off and the fall of leaves bringing more allochthonous organic material into the lake and a re-suspension of organic material from the lake sediments, likely fuel significant respiratory rates.

Distribution of $\delta^{18}O_{DO}$ in the epilimnion varied between month and basin (Fig. 3c). Mean epilimnetic $\delta^{18}O_{DO}$ in the middle basin remained the same during the study period. One interpretation of this pattern is that, unlike the north and south, the middle basin is lacking a large inflow thus nutrient concentrations may be more stable, and production, and subsequently isotopic composition may reflect this.

Often the south basin had lower $\delta^{18}O$ than the north basin and this may reflect higher primary production in the south basin. The north basin is usually oligotrophic, and regularly ultra-oligotrophic in the winter months. Primary production is effectively non-existent at these times (Bass *et al*., in press). Respiration is the dominant process for most, if not all of the year, particularly when considering depth-integrated values due to the large areas of hypolimnion, which are subject to little algal carbon supply.

Biogeochemical and physical process driving horizontal spatial distribution in epilimnetic $\delta^{13}C_{DIC}$ (Fig. 3B) were often evident in $\delta^{18}O_{DO}$ (Fig. 3C). For example, in June lower $\delta^{13}C_{DIC}$ in the southeast corner and the east coast of the middle basin, corresponds with increasing $\delta^{18}O_{DO}$. A similar response was also observed in the southwest corner, near the River Leven outflow in September. Thus variation in metabolic balance can occur over small distances (<0.5 km) in some lakes.

Heterogeneity in lakes is not a newly realised phenomenon, indeed there has been much evidence in the past that planktonic horizontal distributions can vary due to wind (George & Edwards 1976), edge effects (Laybourne-Parry & Rogerson 1993) and variable catchment characteristics (George & Jones 1987). However, this work represents one of few detailed spatial surveys, over a combined horizontal and vertical gradient, of stable carbon and oxygen isotopes in a water body of this size and complexity.

We have observed significant temporal and horizontal epilimnetic heterogeneity in $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ of Loch Lomond. The different trophic status of the north, middle and south basins may be reflected in latitudinal variation as productivity and the production: respiration (P:R) ratio changes. However this was not observed and significant intra-basin variation exists for example, in the south basin water around the mouth of the Endrick in June was over 6‰ more negative than the rest of the basin.

More temporal and spatial detail is needed to make predictions on metabolic balance changes. Loch Lomond is a complex water body and numerous factors affect the hydrological as well as biological patterns. The north basin is relatively simple in structure, being a deep, narrow trough. Water enters mainly through the Falloch inflow (in the north) and drains south. Predicting patterns in isotope change for this basin may be possible as the inflowing water from the Falloch is likely the driving force behind the isotope values for much of the time, and this isotope value (either higher or lower depending on time of year) seems to spread south. South basin spatial variation is complicated by other factors. The islands in the south basin lead to complex hydrological patterns. Coupled with varying wind direction, water flow directions can change significantly.

We have presented data that shows the significant effect metabolism has on the isotope distributions of DIC and DO in a temperate lake. Perhaps more significantly however, we have shown evidence that the balance between photosynthesis and respiration can change substantially over both small and large spatial scales. This has implications when incorporating inland water bodies into carbon models, as single point sampling may be inappropriate and lead to significant error. We advise consideration of this fact in future work.

5. CONCLUSIONS

$\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ in Loch Lomond showed substantial temporal and spatial variation over one sampling year. Opposite and discernable responses in $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ have allowed significant variation in the photosynthesis-respiration balance to be interpreted, identifying local areas of high relative respiratory activity, likely coupled to supplies of terrestrial DOC from the main inflows. Process-controlled predictable changes with depth are also apparent.

The spatial variation we observed suggest that single point sampling for Loch Lomond would risk significant errors, except maybe in the winter months such as March. Whether this applies to smaller lakes with simpler hydrological regimes is currently unknown, but until known not to be important, that natural variation exists need to be accommodated.

The uses of $\delta^{13}C_{DIC}$ are ever expanding e.g., to infer heterotrophic processes in lakes (Jones *et al.* 2001) and track oceanic water masses (Itou *et al.* 2003), and likely more applications will be explored in future work. However, when used in large lakes we have shown spatial variation exists on relatively small scales and this may complicate extrapolation to ecosystem level for modelling purposes, unless suitable numbers of sampling locations are chosen. Conversely, spatial changes in $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ present a potentially useful method for elucidating patterns in metabolism in other aquatic systems.

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REFERENCES

Aggarwall, P.K. & M.A. Dillon. 1998. Stable isotope composition of molecular oxygen in soil gas and groundwater: A potentially robust tracer for diffusion and oxygen consumption processes. *Geochim. Cosmochim. Acta*, 62: 577-584.

Bade, D.L., S.R. Carpenter., J.J. Cole., P.C. Hanson & R.H. Hesslein. 2004. Controls of $\delta^{13}C_{DIC}$ in lakes: geochemistry, lake metabolism, and morphometry. *Limnol. Oceanogr.*, 49: 1160-1172.

Barth, A.C., A. Tait & M. Bolshaw. 2004. Automated analysis of $^{18}O/^{16}O$ ratios in dissolved oxygen from 12-ml water samples. *Limnol. Oceanogr. Meth.*, 2: 35-41.

Bass, A.M., S. Waldron., C.E. Adams & T. Preston. (2010). Net pelagic heterotrophy in mesotrophic and oligotrophic basins of a large, temperate lake. *Hydrobiologia*: (in press).

Clark, I.D. & P. Fritz. 1997. *Environmental isotopes in hydrology*. Lewis Publishers, New York: 328 pp.

Cole, J.J., N.F. Caraco, G.W. Kling & T.K. Kratz. 1994. Carbon dioxide super saturation in surface waters of lakes. *Science*, 265: 1568-1570.

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

George, D.G. & R.W. Edwards. 1976. The effect of wind on the distribution of chlorophyll-*a* and crustacean plankton in a shallow eutrophic reservoir. *J. Appl. Ecol.*, 13: 667-690.

George, D.G. & D.H. Jones. 1987. Catchment effects on the horizontal distribution of phytoplankton in five of Scotland's largest freshwater lochs. *J. Ecol.*, 66: 133-155.

Hanson, P.C., S.R. Carpenter., D.E. Armstrong., E.H. Stanley & T.K. Kratz. 2006. Lake dissolved inorganic carbon and dissolved oxygen: Changing drivers from days to decades. *Ecol. Monogr.*, 76: 343-363.

Heinn, M. 1997.Inorganic carbon limitation of photosynthesis in lake phytoplankton. *Freshwat. Biol.*, 37: 545-552.

Herczeg, A.L. 1987. A stable carbon isotope study of dissolved inorganic carbon cycling in a soft water lake. *Biogeochemistry*, 4: 231-263.

Hollander, D.J. & J.A. McKenzie. 1991. CO_2 controls on carbon isotope fractionation during aqueous photosynthesis. *Geochim. Cosmochim. Acta*, 19: 929-932.

Itou, M., T. Ono & S. Noriki. 2003. Provenance of intermediate waters in the western North Pacific deduced from thermodynamic imprint on $\delta^{13}C$ of DIC. *J. geophys. Res.*, 10: 3347.

Jones, R.I. 1992. The influence of humic substances on lacustrine planktonic food chains. *Hydrobiologia*, 229: 73-91.

Jones, R.I., J. Grey., C. Quarmby & D. Sleep. 2001. Sources and fluxes of inorganic carbon in a deep, oligotrophic lake (Loch Ness, Scotland). *Global Biogeochem. Cycles*, 15: 863-870.

Juday, C. 1935. Dissolved oxygen as an ecological factor in lakes. *Ecology*, 16: 654-654.

Jumars, P.L., D.L. Perry., J.A. Baross., M.J. Perry & B.W. Frost. 1989. Closing the Microbial Loop: Dissolved carbon pathway to heterotrophic bacteria by incomplete ingestion, digestion and absorption in animals. *Deep Sea Res*., 36: 483-495.

Keogh, J.R., M.E. Viersen & C.A. Haley. 1996. Analysis of a Lake Superior coastal food web with stable isotope techniques. *Limnol. Oceanogr*., 41: 136-146.

Kroopnick, P.M. & H.C. Craig. 1972. Atmospheric oxygen: Isotopic composition and solubility fractionation. *Science*, 175: 54-55.

Lancelot, C. 1983. Factors affecting phytoplankton extracellular release in the Southern Bight of the North Sea. *Mar. Ecol. Prog. Ser*., 12: 115-121.

Laybourne-Parry, J. & A. Rogerson. 1993. Seasonal patterns of protozooplankton in Lake Windermere, England. *Arch. Hydrobiol*., 129: 25-43.

Luz, B. & E. Barkan. 2002. The isotope ratios $^{17}O/^{16}O$ in molecular oxygen and their significance in biogeochemistry. *Geochim. Cosmochim. Acta*, 69: 1099-1110.

Maitland, P.S. 1981. An introduction to catchment analysis. In: Maitland, P.S. (Ed.), *The ecology of Scotland's largest lochs: Lomond, Awe, Ness, Morar and Shiel*. Dr W. Junk Publishers, The Hague: 1-27.

Meili, M., G.W. Kling., B. Fry., R.T. Bell & I. Ahlgren. 1996. Sources and partitioning of organic matter in a pelagic microbial food web inferred from the isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) of zooplankton species. *Arch. Hydrobiol. Spec. Iss. Adv. Limnol*., 48: 53-61.

Mybro, A. & M.D. Shapley. 2006. Seasonal water-column dynamics of dissolved inorganic carbon isotopic compositions ($\delta^{13}C_{DIC}$) in small hardwater lakes in Minnesota and Montana. *Geochim. Cosmochim. Acta*, 70: 2699-2714.

Parker, S.R., S.R. Poulson, C.H. Gammons & M.D. Degrandpre. 2005. Biogeochemical controls on diel cycling of stable isotopes of dissolved O_2 and dissolved inorganic carbon in the Big Hole River, Montana. *Environ. Sci. Technol*., 39: 7134-7140.

Quay, P.D., S.R. Emerson., B.M. Quay & A.H. Devol. 1986. The carbon cycle for Lake Washington – A stable isotope study. *Limnol. Oceanogr*., 31: 596-611.

Quay, P.D., D.O. Wilbur, J.E. Richey, A.H. Devol, R. Benner & Forsberg. 1995. The ^{18}O:^{16}O of dissolved oxygen in the rivers and lakes in the Amazon basin: Determining the ratio of respiration to photosynthesis in freshwaters. *Limnol. Oceanogr*., 40: 718-729.

Schindler, D.W & E.J. Fee. 1973. Diurnal-variation of dissolved inorganic carbon and its use in estimating primary production and CO_2 invasion in lake-227. *J. Fish. Res*., 30: 1501-1510.

Smith, B.D., S.P. Cuttle & P.S. Maitland. 1981. The Profundal Zoobenthos. In: Maitland, P.S. (Ed.), *The ecology of Scotland's largest lochs: Lomond, Awe, Ness, Morar and Shiel*. Dr W Junk Publishers, The Hague: 205-222.

Torres, M.E., A.C. Mix & W.D. Rugh. 2005. Precise $\delta^{13}C$ analysis of dissolved inorganic carbon in natural waters using automated headspace sampling and continuous flow mass spectrometry. *Limnol. Oceanogr. Meth*., 3: 349-360.

Trojanowska, A., D. Lewicka-Szcebak., M.O. Jędrysek., M. Kurasiewicz., L.I. Wassenaar & K. Izydorczyk. 2008. Diurnal variations in the photosynthesis-respiration activity of a cyanobacterial bloom in a freshwater dam reservoir: An isotopic study. *Isot. Environ. Healt. S*., 44: 163-175.

Wagner, I. & M. Zalewski. 2000. Effect of hydrological patterns of tributaries on biotic processes in a lowland reservoir- consequences for restoration. *Ecol. Eng*., 16: 79-90.

Waldron, S., M. Scott & C. Soulsby. 2007. Stable isotope analysis reveals lower-order river dissolved inorganic carbon pools are highly dynamic. *Environ. Sci. Technol*., 41: 6156-6152.

Wang, X. & J. Veizer. 2000. Respiration-photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada. *Geochim. Cosmochim. Acta*, 64: 3775-3786.

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