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Young, old and weathered carbon (2): using radiocarbon and stable isotopes to identify terrestrial carbon support of the food web in an alkaline humic lake:

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ABSTRACT

Carbon (C) and nitrogen (N) stable isotope analysis (SIA) has been used to identify the terrestrial subsidy of freshwater food webs. However, SIA fails to differentiate between the contributions of old and recently fixed terrestrial C and consequently cannot fully determine the source, age and biochemical quality of terrestrial carbon. Natural abundance radiocarbon ($\Delta^{14}\text{C}$) was used to examine the age and origin of carbon in Lower Lough Erne, Northern Ireland. Radiocarbon and stable isotope values were obtained from invertebrate, algae and fish samples and the results indicate that terrestrial organic C is evident at all trophic levels. High winter $\delta^{15}\text{N}$ values in calanoid zooplankton ($\delta^{15}\text{N} = 24\text{‰}$) relative to phytoplankton and POM ($\delta^{15}\text{N} = 6\text{‰}$ and 12‰ respectively) may reflect several microbial trophic levels between terrestrial C and calanoid invertebrates. Winter and summer calanoid $\Delta^{14}\text{C}$ values show a seasonal switch between autochthonous and terrestrial carbon sources. Fish $\Delta^{14}\text{C}$ values indicate terrestrial support at the highest trophic levels in littoral and pelagic food webs. Radiocarbon therefore has utility in attributing the source of carbon in freshwater in addition to tracing the pathway of terrestrial carbon through the food web.

Keywords: Lake. Food web. Radiocarbon. Stable isotope. Fish.

INTRODUCTION

The investigation of trophic levels in a food web is complex yet fundamental when understanding the dynamics of a freshwater system. Identification of carbon sources can be problematic due to large variation of stable carbon isotope values in freshwater systems, and becomes even more difficult when there is a significant terrestrial subsidy of the food web as terrestrial and freshwater isotope values often overlap. C inputs to lakes can represent a significant component of the diet of lake heterotrophs (organisms unable to synthesise their own organic carbon).

Organic carbon utilised in aquatic food webs is derived from both autochthonous (derived from primary production within the system) and allochthonous (terrestrial) carbon imported from the catchment. Studies showing the influence of terrestrial carbon on food web dynamics have largely dealt with non-eutrophic lakes which are predominantly supported by terrestrial carbon (ÅGren *et al.* 2008; Gratton *et al.* 2008; Seifert and Scheu 2012; Lapierre *et al.* 2013; Wilkinson *et al.* 2013b; Wilkinson *et al.* 2013a). However, lakes with higher trophic status may also be supported by catchment inputs; the terrestrial support of pelagic food webs in such lakes is difficult to ascertain and can be underestimated.

Seasonal changes in productivity affect the delivery of nutrients (Grey 2001; Kritzberg *et al.* 2006b; Neff *et al.* 2006; Rautio *et al.* 2011). Terrestrial carbon can supplant autochthonous carbon in systems with low algal abundance. The availability of this carbon to lake heterotrophs (organisms that cannot fix carbon but utilise organic carbon for growth) is related to its age, which in turn is related to its biochemical composition and nutrient quality (biochemical quality). Bacteria have been shown to metabolise both autochthonous carbon and labile and decayed terrestrial carbon (Guillemette *et al.* 2013) but preference is linked to nutrient content which decreases over time leading to preferential selection of autochthonous

and labile terrestrial carbon sources (Taipale *et al.* 2007; McCallister and Giorgio 2008; Taipale *et al.* 2008; de Kluijver *et al.* 2012; Zigah *et al.* 2012).

Freshwater Carbon sources

Carbon derived from primary production is bio-energetically rich compared to terrestrial input to lakes, particularly previously sequestered detrital carbon which has undergone diagenesis in soil or peat. As carbon sources fluctuate seasonally, heterotrophic organisms can switch between autochthonous or allochthonous sources to exploit high quality carbon sources (Maguire and Grey 2006; Rautio and F Vincent 2007; Taipale *et al.* 2008; Rautio *et al.* 2011).

Terrestrial organic matter has been shown to enter aquatic food webs in a number of ways. Terrestrial dissolved organic carbon (DOC) can be utilised by mixotrophic (utilising a mixture of autotrophic and heterotrophic modes) and heterotrophic bacteria (Tittel *et al.* 2009; Cole *et al.* 2011; Rottberger *et al.* 2013). Particulate organic matter (POM) of terrestrial origin often forms important foci for bacterial production. Subsequent consumption of bacteria can also be an important pathway into food webs (Kritzberg *et al.* 2006a; Cole *et al.* 2011).

Stable Isotope Analysis of food webs

Food web utilisation of terrestrial organic subsidies in lakes has been demonstrated for many widely distributed global locations, and for the most part these involve the use of natural abundance or artificially enriched stable isotopes of carbon and nitrogen (Perga and Gerdeaux 2004; Carpenter *et al.* 2005; Kritzberg *et al.* 2006a; Marty 2007; Taipale *et al.* 2008).

Detecting the source of carbon can be problematic however when using SIA. Kinetic stable isotope fractionation leads to differences in pelagic (open water) and littoral (near shore) areas of the lake, and between organisms and their dietary sources (Fry 1991). It is difficult to

physically isolate phytoplankton samples and to accurately measure the baseline isotopic signature required in models detecting the carbon source utilised in food web studies (Hamilton *et al.* 2005; Cole *et al.* 2011; Smyntek *et al.* 2012). Isotope signatures of terrestrial, littoral and pelagic sources can overlap considerably preventing source discrimination. In addition, mobile predators can integrate carbon from a number of sources resulting in a mixed dietary pattern which can be difficult to explain (Layman *et al.* 2012; Phillips *et al.* 2014). Allochthony in higher trophic levels may therefore not be detected. While the terrestrial subsidy of food webs can sometimes be established, the age (and therefore biochemical/nutrient quality) of carbon cannot be determined using stable isotopes alone.

Radiocarbon in the food web

Radiocarbon (^{14}C) has utility for examining freshwater carbon dynamics. $\Delta^{14}\text{C}$ (see methods for derivation) of freshwater carbon is governed by its source and is corrected for fractionation, removing the problem of kinetic fractionation experienced in stable isotope analyses. “Modern/Recent” (atmospheric, modern photosynthetic terrestrial plant production) radiocarbon will be equivalent to that of the modern atmosphere. “Labile” terrestrial carbon can be derived from terrestrial material that has undergone minor decomposition. Complex soil/peat dynamics can mean that although the carbon is chemically labile, it may have a lower than modern radiocarbon content (Trumbore 2009). Therefore, carbon that is ^{14}C -depleted, relative to modern values may still be labile, despite its age, and available for microbial catabolisation.

Due to soil carbon cycling and turnover, carbon can take decades to be released from subsurface soil (Trumbore *et al.* 1989; Polsenaere *et al.* 2013). As such, carbon is released which contains “Bomb” radiocarbon, enriched relative to the modern atmosphere due to nuclear testing in the 1950s and 1960s, resulting in positive $\Delta^{14}\text{C}$ values (Reimer *et al.* 2004).

“Sub-fossil” carbon originates from stored terrestrial soil/peat carbon which can be substantially ^{14}C -depleted depending on its age and mineralogy, which may be significantly degraded (Neff *et al.* 2006; Guo *et al.* 2007; Raymond *et al.* 2007; Caraco *et al.* 2010; Butman *et al.* 2012; Raymond *et al.* 2013).

The $\Delta^{14}\text{C}$ value of dissolved inorganic carbon (DIC) (and autotrophic producers utilising DIC) may be partially derived from the weathering of carbonaceous bedrock (via atmospheric CO_2 or soil carbon) with no radiocarbon content (“ ^{14}C dead”). This leads to depleted ^{14}C values and a radiocarbon ages older than the contemporary atmosphere. This difference is known as a freshwater reservoir offset “FRO” (Deevey *et al.* 1954; Broecker and Orr 1958; Broecker and Walton 1959; Ascough *et al.* 2007; Ascough *et al.* 2010; Keaveney and Reimer 2012).

Radiocarbon and stable isotope measurements of autotrophs and their consumers can be therefore be used to determine the age and contributions of autochthonous and terrestrial carbon to the food web. A study was carried out using radiocarbon and SIA to identify the carbon sources utilised in a complex lake to determine the age and influence of terrestrial carbon subsidies of the food web.

STUDY SITE AND METHODS

Study site

Carbon dynamics in Lower Lough Erne (Figure 1) are complicated by seasonal changes in terrestrial subsidies and productivity (Keaveney *et al.* 2015). The lake was chosen as a suitable study site to build on the substantial amount of research carried out in the lake (Maguire and Gibson 2010). A radiocarbon study (using fish and water samples) was carried out in the lake that showed an FRO of ca. 500 ^{14}C years was present due to the alkalinity of the lake (Keaveney and Reimer 2012). While the FRO was relatively large, it was lower than

would have been predicted from the hardness of lake water; most likely due to the contribution of younger allochthonous organic carbon in the lacustrine food web.

Figure 1 Lower Lough Erne, Fermanagh, Northern Ireland. River Bannagh and lake sites that were sampled are marked on the map. LE1, LE3 and LEP are pelagic sites, LEA1-LEC are littoral sites

Lough Erne in Northwest Ireland is a system composed of two interconnected lakes. The limnology of the system has been well studied since the 1970s (Gibson *et al.* 1980; Gibson *et al.* 1993; Zhou *et al.* 2000; Gibson *et al.* 2003; Gibson *et al.* 2005; Maguire and Gibson 2010). It is a relatively large, humic (DOC c. 12 mg l⁻¹) and alkaline lake (alkalinity ≈ 1.5 meq l⁻¹). The lake is eutrophic on the basis of total phosphorous (TP) (> 50 µg L⁻¹ since 1975 (Battarbee 1986; Foy *et al.* 1993; Maguire and Gibson 2010) but light limitation due to high DOC loading results in secchi depths of 1-3m.

Chlorophyll a concentrations were reduced due to the presence of zebra mussels (*Dreissena morpha*) (Foy *et al.* 1993; Maguire and Gibson 2010) since the late 1990s (Rosell *et al.* 1998). Expanding zebra mussel population with associated decreases in phytoplankton abundance have been shown by stable isotope analysis to shift Lower Lough Erne

zooplankton production towards greater allochthony (Maguire and Grey 2006). There is no indication in these studies whether this terrestrial carbon is derived from modern or detrital material.

Field Sampling

Site ID	Coordinates	
River Bannagh	54°32'02"N	7°46'55"W
LE1	54°29'07"N	7°50'37"W
LE3	54°23'51"N	7°40'12"W
LEP	54°21'30"N	7°39'40"W
LEA1 & 2	54°23'09"N	7°40'08"W
LEB	54°28'20"N	7°51'51"W
LEC	54°24'38"N	7°41'50"W
	Irish Grid Reference	Depth
K30	025 607	1 to 4 m
Pollan Survey (PS)	110 610 to 130 600	20 to 30m
	060 590 to 130 580	

Table 1: Location data for sampling sites including depths of fish net placement.

Field sampling was conducted in February, March, May, August and October of 2011 and details of methodology are described in supplemental information (also, Keaveney *et al.* 2015). The lake did not stratify during the study. DIC, DOC, POM, phytoplankton and zooplankton were isolated from water samples collected at sites LE1, LE3 and LEP (Figure 1, Table 1).

Littoral invertebrates were sampled once in July 2011 at 3 sites (Figure 1), using hand searches and 300 µm dip nets. Biofilm was collected from macrophyte stems and the upper surface of rocks using a toothbrush with matter rinsed into sample containers using Milli-Q® water.

Fish samples were obtained from routine surveys conducted for population and biomass studies at a number of spatially distinct sites carried out by the Agricultural and Food Biosciences Institute. Fish were caught using gill nets in 2010 using the survey methodology described by Rosell (2000) and were stored frozen prior to sampling for isotope samples.

Laboratory Sample preparation

Samples were pre-treated and combusted for radiocarbon and stable isotope analysis as described in (Keaveney *et al.* 2015). The opercular bone obtained from fish samples was demineralised using 4% HCl for approximately 24 hours until CO₂ evolution was no longer evident. Paired opercular bones were homogenised using a Retsch MM200 Mixer Mill for SIA; lipid removal was deemed unnecessary based on previous work in the lake (Keaveney and Reimer 2012).

Isotopic measurements:

The ¹⁴C/¹²C ratio of the sample relative to an international standard (F¹⁴C) and its associated uncertainty were calculated according to Reimer *et al.* (2004) and van der Plicht & Hogg (2006) and incorporated a fractionation correction (Stuiver and Polach 1977) based on δ¹³C measured by AMS.

Δ¹⁴C is defined in Stuiver and Polach (1977) as the relative difference between the absolute international standard (base year 1950) and sample ¹⁴C/¹²C ratio corrected for age and δ¹³C fractionation. The Δ¹⁴C age correction accounts for decay that took place between collection/death and the time of measurement so that two measurements of the same sample taken years apart will produce the same Δ¹⁴C result, which is calculated using the equation:

$$\Delta^{14}\text{C} = [\text{F}^{14}\text{C} * e^{\lambda(1950 - x)} - 1] * 1000$$

X is the year of collection or growth (2010 for fish samples analysed, 2011 for all other samples).

The AMS δ¹³C measurements (not given) include any fractionation which may occur during sample preparation and AMS analysis and therefore are only used for fractionation correction. All other stable isotope measurements were made using a Thermo Scientific EA-IRMS. Samples were corrected using a one point calibration (R041 L-Alanine). Other standards were measured at intervals (USGS 41 and Leucine) and results plotted to make a

two point calibration. The effect of applying one point and two point correction to samples was compared and the difference was negligible. The precision of the EA-IRMS is $< 0.1\%$ for $\delta^{13}\text{C}$ and $< 0.15\%$ for $\delta^{15}\text{N}$. Isotope values were expressed relative to the known standards ($\delta^{13}\text{C}_{\text{VPDB}}$, $\delta^{15}\text{N}_{\text{AIR}}$).

Statistical Analyses.

In order to determine the percentage contribution of sources to the diet of Lower Lough Erne fish, mixing models were generated using SIAR (version 4.2) (Parnell *et al.* 2008), a Bayesian isotope mixing model in R (version 2.12.1). The model utilises mean stable isotope values and associated standard deviations from dietary sources to generate a mixing model which incorporates these uncertainties associated with multiple sources.

Trophic enrichment factors (TEF) were $\Delta^{13}\text{C} = 1.63 \pm 0.5\%$, $\Delta^{15}\text{N} = 2.9 \pm 0.32\%$ (Caut *et al.* 2009). SIAR models have been criticised for sensitivity to variable trophic enrichment factors, which in this study were obtained from the literature (Caut *et al.* 2009; Bond and Diamond 2011; Phillips *et al.* 2014). Changes made to the TEF when generating SIAR models with data from this study had little influence on the results of the model. However, large differences in stable isotope signatures can make the model less sensitive to trophic enrichment factors (Jensen *et al.* 2012). As such the model was thought unreliable for radiocarbon data and was only utilised and assumed to be robust for stable isotope data. Models were generated from measurements of the largest fish groups (perch: *Perca fluviatilis*, pollan: *Coregonus autumnalis* and roach: *Rutilus rutilus*) and source prey collected from Lower Lough Erne in 2011. Data utilised in models may be found in supplemental information. All other statistics (regression, ANOVA) were performed in R using Hmisc (version 3.14-0 (Harrell Jr *et al.* 2007)) and ggplot (version 0.9.3.1 (Ginestet 2011)) packages.

RESULTS

Lower Lough Erne Fish

Figure 2 Stable carbon and nitrogen isotope results from Lower Lough Erne fish species collected in 2010.

Stable isotope analyses of Lower Lough Erne fish show distinct differences between species (Figure 2). Samples from deep water surveys (20-30 m, Table 1) – Pollan (*Coregonus autumnalis*, n=11) and trout (*Salmo trutta*, n=3) were ^{13}C -depleted ($\delta^{13}\text{C} < -28$ ‰). Elevated $\delta^{15}\text{N}$ (> 17 ‰) suggests the fish are more predatory than others measured in the study. Perch (*Perca fluviatilis*, n= 16) collected in the same location had similarly elevated $\delta^{15}\text{N}$, yet perch were also more ^{13}C -enriched than pollan and trout. The $\delta^{13}\text{C}$ values of perch collected in a shallower, more littoral sample (depth < 4 m) vary from -29.0 to -21.5 ‰; $\delta^{15}\text{N}$ values also differ (13.1 to 18.6 ‰). Perch stable isotope results indicate a more mixed diet than pollan or trout with smaller fish feeding in the littoral area. Roach (*Rutilus rutilus*, n = 26) isotopes also fluctuate showing a mixed diet with a littoral influence.

Figure 3 a-c: Proportions of dietary sources contributing to the diets of perch (*Perca fluviatilis*, Figure 3a), pollan (*Coregonus autumnalis*, Figure 3b) and roach (*Rutilus rutilus*, Figure 3c). Mixing models were generated using SIAR version 4.2, R version 2.12.1 and are described in more detail in the text. Shaded grey levels in plot refer to 5, 25, 75 and 95% confidence intervals.

Based on the outputs generated in the mixing model, sources (labelled in Figure 3, detailed values in supplemental information) contribute to the diet in different proportions according to species. Littoral invertebrates ($n = 21$) constitute approximately 23 – 61 % of perch diet (Figure 3a), 0 – 23 % of pollan diet (Figure 3b) and 62 – 79 % of roach diet (Figure 3c). Pollan diet as indicated by the mixing model is strongly influenced by calanoid zooplankton (19 – 62 %) and to a lesser extent *Daphnia spp.* (1.4 – 33 %). Percentage contributions of sources to diet listed in the text are measured at 95% confidence level and data can be found in supplementary information.

In short, as indicated by the stable isotope data (Figure 2) the mixing model suggests that pollan have less influence from littoral sources than perch which have a more evenly mixed diet. Roach have the highest littoral contribution to their diet. However, the variation evident in the mixing model results, although due to source sample size issues, is evidence of the issues of stable isotope analysis and the clarity of conclusions that can be drawn from such data.

Figure 4: $\delta^{14}\text{C}$ and stable carbon isotope measurements from Lower Lough Erne fish. Error bars represent the

uncertainty on measurements. Horizontal lines denote the mean $\Delta^{14}\text{C}$ as measured from calanoid zooplankton in winter and summer. Winter calanoid $\Delta^{14}\text{C}$ results are analogous to those of modern terrestrial carbon, summer to autochthonous algal $\Delta^{14}\text{C}$.

Figure 5: Stable isotope values of Lower Lough Erne pelagic invertebrate species. Points with error bars denote mean algal and POM isotope values with their associated standard deviations.

The sample size of stable isotope measurements of some sources was small, but the sample size of radiocarbon measurements for these sources was smaller still (see supplementary information). Large ranges of $\Delta^{14}\text{C}$ values within a consumer/prey cohort lead to high standard deviations, again affecting the reliability of the model; consequently the model results are not presented here.

Figure 4 however gives an indication of the differences in the dietary information provided by the utilisation of $\Delta^{14}\text{C}$ measurements not shown by SIA. Error bars represent the statistical uncertainty of $\Delta^{14}\text{C}$ measurements. There is no correlation between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ ($R^2 = 0.05$, $p = 0.0885$). The variation in species suggests there is no relationship between collection location and individual species $\Delta^{14}\text{C}$ value (ANOVA, $F = 0.765$, $p = 0.3856$).

It is clear from radiocarbon measurements that individual fish from all species utilise divergent carbon sources. $\Delta^{14}\text{C}$ of the majority of fish are enriched relative to summer calanoid $\Delta^{14}\text{C}$. Three small perch (TL = 9 cm, 9.3 cm, 9.4 cm) have the most depleted $\Delta^{14}\text{C}$ (-68.2 ‰, -52.7 ‰ and -60.8 ‰ respectively).

Invertebrate diet

Stable isotope analysis of Lower Lough Erne invertebrates demonstrates distinction between groups of invertebrates (Figure 5). ^{15}N values (winter = 23.4 ± 1.2 ‰, summer = 16.6 ± 3.7 ‰) of the calanoid zooplankton *Eudiaptomus gracilis* samples in winter are highly enriched relative to phytoplankton, POM and the other components of the food web including predatory fish and while they drop in summer they are still higher than expected from an algal diet. *E. gracilis* is an omnivorous species which preferentially feeds on phytoplankton (Maguire and Grey 2006; Ger *et al.* 2011). Their $\delta^{13}\text{C}$ (winter = -32.3 ± 2.5 ‰, summer = -33.4 ± 2.4 ‰) is inconclusive – it could describe an algal ($\delta^{13}\text{C} = -33.4 \pm 3.8$ ‰, $\delta^{15}\text{N} = 9.3 \pm 4.7$ ‰) or particulate organic matter ($\delta^{13}\text{C} = -31.4 \pm 1.3$ ‰, $\delta^{15}\text{N} = 13.4 \pm 7.3$ ‰) carbon source. Their $\Delta^{14}\text{C}$ values are more clear – winter values are enriched and within the range of lake DOC values (mean winter calanoid $\Delta^{14}\text{C} = -4.0 \pm 6.1$ ‰). However, the summer results are within range of algal sample $\Delta^{14}\text{C}$ values ($\Delta^{14}\text{C} = -50 \pm 4.1$ ‰).

Figure 6: Invertebrate $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measured from selected Lower Lough Erne invertebrate species. Winter samples were collected in February and March, and summer samples in May and August 2011. Points with error bars denote mean algal and POM isotope values with their associated standard deviations. Mean DOC $\Delta^{14}\text{C}$ (relatively consistent over the duration of the study) is shown as a horizontal line – $\delta^{13}\text{C}$ values were unreliable for DOC samples. Dashed lines denote the error associated with the mean.

Daphnia spp. ^{15}N is also enriched but more so in the summer ($\delta^{15}\text{N}$ in winter = $+12.8 \pm 1.7$ ‰, summer = $+17.5$ ‰) despite increased algal abundance. *Daphnia* $\Delta^{14}\text{C}$ values (Figure 6)

are depleted ($\Delta^{14}\text{C} = -108.1 \pm 5.2 \text{ ‰}$ $-91.9 \pm 3.6 \text{ ‰}$) and are within the range of sub-fossil POM values ($\Delta^{14}\text{C} = -83.1 \pm 4.0$ to $-191.9 \pm 12.4 \text{ ‰}$).

DISCUSSION

The results from Lower Lough Erne samples show evidence three dietary carbon sources exist in the lake.

Autochthonous fraction – carbon partially derived from bedrock weathering is utilised in primary production leading to a mean algal value of $\Delta^{14}\text{C} = -58.8 \pm 9 \text{ ‰}$ (excluding May cyanobacteria sample). This ^{14}C -depletion results from the freshwater reservoir offset and is linked to water alkalinity (Keaveney and Reimer 2012).

Modern/recent Radiocarbon: Riverine DOC sampled in October 2011 had a positive bomb radiocarbon signal ($\Delta^{14}\text{C} = + 51.9 \pm 2.9 \text{ ‰}$) indicating a modern or recent photosynthetic carbon source (Levin *et al.* 2013).

Labile allochthonous carbon: Lake DOC is ^{14}C -enriched ($\Delta^{14}\text{C} = -17.4 \pm 19.4 \text{ ‰}$) relative to DIC and POC in the lake, yet depleted relative to modern values. It is consistent with that from incoming River Bannagh in winter indicating a terrestrial source.

Sub-fossil allochthonous carbon: POM $\Delta^{14}\text{C}$ values are depleted relative to anything else in the lake indicating the presence of a sub-fossil terrestrial carbon source in the lake ($\Delta^{14}\text{C} = -122.3 \pm 61.3 \text{ ‰}$).

Invertebrate food web

While the sample size of invertebrate prey was small, there is clear evidence that terrestrial support of the food web is extensive. Invertebrates utilise both energetically rich autochthonous and terrestrial carbon of lower nutritional value. Within the terrestrial carbon pool both sub-fossil, detrital carbon with low nutrient value, and chemically labile carbon are consumed by different invertebrates.

The highly positive $\delta^{15}\text{N}$ values of calanoid zooplankton indicate the presence of a microbial loop with bacteria metabolising terrestrial carbon which is then consumed by other species (Meyer 1994). The existence of a microbial loop is an indicator of a terrestrial diet but stable isotope analysis does not indicate whether the terrestrial source utilised by Lower Lough Erne calanoid zooplankton is detrital, or whether it is a labile terrestrial carbon source.

$\Delta^{14}\text{C}$ values of calanoid zooplankton measured in winter and summer demonstrate the significant differences in carbon sources utilised (Figure 6). $\Delta^{14}\text{C}$ measurements from winter calanoid zooplankton (winter = -7.5 ± 14.7 ‰) are within the range of lake DOC $\Delta^{14}\text{C}$ (-4 to -40 ‰, Figure 6). In the summer, calanoid $\Delta^{14}\text{C}$ values are comparable to algal $\Delta^{14}\text{C}$, showing a clear dietary switch with algal blooms. The calanoid invertebrates are clearly selecting bio-energetically richer carbon – labile terrestrial carbon in the winter with low algal abundance and a switch to an algal diet in the summer. They are not utilising sub-fossil carbon sources showing a clear selection against detrital carbon.

Daphnia $\Delta^{14}\text{C}$ values are more depleted than algal $\Delta^{14}\text{C}$. *Daphnia* have been shown to feed on the algal portion of the POM (Rautio *et al.* 2011). However, *Daphnia* $\Delta^{14}\text{C}$ values indicate that they are consuming a sub-fossil carbon source which is older than the algal carbon pool – suggesting that they are also feeding on a detrital terrestrial portion of POM.

The availability and biochemical quality of carbon seems to drive the dietary preferences of calanoid zooplankton, while *Daphnia* spp. derive carbon from particulate sources of detrital sub-fossil carbon.

Fish

The stable isotope values of fish are as expected; benthic/planktonic pollan have a strongly predatory signal and their isotope values reflect their specialised diets. Roach and perch, again as expected have a more mixed littoral and pelagic diet showing their less selective diet. The evidence for terrestrial subsidy of fish diet is not as clear when using SIA alone as

$\delta^{13}\text{C}$ overlaps with terrestrial values. The evidence for terrestrial support of all fish species is only found in the results from radiocarbon analysis.

A range of $\Delta^{14}\text{C}$ values are evident in individual Lower Lough Erne fish. While stable isotopes can indicate that terrestrial carbon may be a component of diet of Lower Lough Erne invertebrates, $\Delta^{14}\text{C}$ clearly shows that individual fish within and between species can obtain carbon through different food web pathways including those supported by terrestrial carbon. Even $\Delta^{14}\text{C}$ values of open/deep water fish (*e.g.* pollan) are enriched indicating that terrestrial carbon has been transferred to the highest trophic levels.

An individual pollan and roach each had positive $\Delta^{14}\text{C}$ values indicating the presence of bomb radiocarbon in their diet. No invertebrate species measured in this study had an equivalent bomb radiocarbon signal. However, DOC from a tributary river to Lower Lough Erne, the River Bannagh (see Figure 1), collected in October 2011, had a highly positive $\Delta^{14}\text{C}$ ($= + 51 \pm 2.9 \text{ ‰}$) which corresponds to atmospheric ^{14}C from 2005-2009 (Hua and Barbetti 2004; Levin and Kromer 2004; Levin *et al.* 2008; Levin *et al.* 2013), so represents modern/recent photosynthetic carbon from leaf fall, grass or riparian plant material.

A modern terrestrial carbon source is clearly a part of the food web of fish with positive $\Delta^{14}\text{C}$ values although it is unclear the mechanism by which this carbon enters the food web.

Enriched bomb $\Delta^{14}\text{C}$ as seen in Lower Lough Erne can only be obtained from the products of a terrestrial plant or its consumer. Much of the shore line of the lake consists of shrubs or trees while the more sheltered bays have extensive beds of emergent macrophytes which could be contributing a source of modern carbon via leaf fall and plant senescence. The enriched $\Delta^{14}\text{C}$ values of the individual pollan and roach show they must be utilising prey consuming this modern source of terrestrial material in addition to autochthonous and terrestrial food sources. This prey source is missing from our analysis; we did not measure

any source contributing to diet other than riverine DOC that had sufficient enrichment to cause these $\Delta^{14}\text{C}$ values.

The utilisation of methane can result in ^{14}C -enriched/depleted results depending on the source of methane (Billett *et al.* 2012; Garnett *et al.* 2013). However, samples in Lower Lough Erne are not sufficiently ^{13}C -depleted to provide evidence for methanogenesis in the system (Pasche *et al.* 2011). The absence of an enriched $\Delta^{14}\text{C}$ bomb signal in the pelagic invertebrate species measured in this study suggests that there may be a benthic source of modern carbon which was not sampled in the current study.

Perch have a mixed pelagic and littoral diet according to the relatively large range of $\delta^{13}\text{C}$ values. The majority of perch $\Delta^{14}\text{C}$ measurements fall within the range of those of zooplankton with an algal diet such as summer calanoid samples. They do not appear to have a sub-fossil carbon source; all except three are enriched relative to mean calanoid zooplankton $\Delta^{14}\text{C}$. The exceptions are the three oldest perch which clearly have a prey source consuming a slightly older source of carbon although $\Delta^{14}\text{C}$ indicates they are still within the range of autochthonous carbon sources. They were collected from K30 (Table 1), at a depth of 1-4 m. These perch are amongst the smallest and are likely to feed in the littoral zone – as indicated by the stable isotopes; $\Delta^{14}\text{C}$ may also indicate a littoral carbon source (values are within 2 σ error of littoral zone food sources such as *Asselus aquaticus* ($\Delta^{14}\text{C} = -57.3 \pm 3 \text{ ‰}$) and biofilm ($\Delta^{14}\text{C} = -56.6 \pm 12.2 \text{ ‰}$).

Roach are omnivorous and this is clearly shown in the stable isotope and radiocarbon measurements. The range of $\Delta^{14}\text{C}$ values indicates they are consuming invertebrates feeding in terrestrial and/or autochthonous carbon pools. None are more depleted than algal $\Delta^{14}\text{C}$ indicating that terrestrial carbon is more important in the food web of roach. One roach, like the pollan sample, is enriched with bomb radiocarbon indicating they are consuming prey utilising a modern terrestrial carbon pool.

CONCLUSION

The use of the radiocarbon method in analysing the Lower Lough Erne food web has elucidated the sources of carbon utilised in the lake. Terrestrial support of the food web was expected given previous research and water chemistry (*e.g.* DOC loading, chlorophyll *a* values). The method allows for clear separation of modern/recent, labile and sub-fossil terrestrial carbon in addition to the partitioning of terrestrial and autochthonous carbon sources. The method also shows the extent to which the pelagic food web is driven by terrestrial carbon sources, to the highest trophic levels – terrestrial support is underestimated or overlooked with stable isotope analysis alone.

The distinction between modern, labile, and detrital, sub-fossil terrestrial carbon in the food web made using radiocarbon analysis is essential when analysing carbon dynamics in freshwater lakes. The data have implications for biodiversity management as the proliferation of invasive species takes place. Terrestrial subsidies of freshwater lakes are likely to increase with climate and land use changes; this information is of paramount importance in the overall management of freshwater areas, and their catchments in the near future.

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FIGURE CAPTIONS:

Figure 1: Lower Lough Erne, Fermanagh, Northern Ireland. Lake and river sites that were sampled are marked on the map. LE1, LE3 and LEP are pelagic sites, LEA1-LEC are littoral sites

Figure 2: Stable carbon and nitrogen isotope results from Lower Lough Erne fish species collected in 2010.

Figure 3a-c: Proportions of dietary sources contributing to the diets of perch (*Perca fluviatilis*, Figure 3a), pollan (*Coregonus autumnalis*, Figure 3b) and roach (*Rutilus rutilus*, Figure 3c). Mixing models were generated using Siar version 4.2, R version 2.12.1 and are described in more detail in the text. A = littoral invertebrates. B = chironomid. C = calanoid zooplankton. D = Daphnia. E = roach fry. F = perch fry. Shaded grey levels in plot refer to 5, 25, 75 and 95% confidence intervals.

Figure 4: $\Delta^{14}\text{C}$ and stable carbon isotope measurements from Lower Lough Erne fish. Error bars represent the uncertainty on measurements. Horizontal lines denote the mean $\Delta^{14}\text{C}$ as measured from calanoid zooplankton in winter and summer. Winter calanoid $\Delta^{14}\text{C}$ results are analogous to those of modern terrestrial C, summer to autochthonous algal $\Delta^{14}\text{C}$.

Figure 5: Stable isotope values of Lower Lough Erne pelagic invertebrate species. Points with error bars denote mean algal and POM isotope values with their associated standard deviations.

Figure 6: Invertebrate $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measured from selected Lower Lough Erne invertebrate species. Winter samples were collected in February and March, and summer samples in May and August 2011. Points with error bars denote mean algal and POM isotope values with their associated standard deviations. Mean DOC $\Delta^{14}\text{C}$ (relatively consistent over the duration of the study) is shown as a horizontal line – $\delta^{13}\text{C}$ values were unreliable for DOC samples. Dashed lines denote the error associated with the mean.

TABLE CAPTIONS

Table 1: Location data for sampling sites including depths of fish net placement.