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ORIGINAL PAPER

# Source and quantity of carbon influence its sequestration in Rostherne Mere (UK) sediment: a novel application of stepped combustion radiocarbon analysis

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**Abstract** We explored the roles of phytoplankton production, carbon source, and human activity on carbon accumulation in a eutrophic lake (Rostherne Mere, UK) to understand how changes in nutrient loading, algal community structure and catchment management can influence carbon sequestration in lake sediments. Water samples (dissolved inorganic, organic and particulate carbon) were analysed to investigate contemporary carbon sources. Multiple variables in a 55-cm sediment core, which represents the last ~ 90 years of accumulation, were studied to determine historical production rates of algal

communities and carbon sources. Fluctuations in net primary production, inferred from sedimentary diatom abundance and high-performance liquid chromatography (HPLC) pigment methods, were linked to nutrient input from sewage treatment works (STW) in the catchment. Stepped combustion radiocarbon (SCR) measurements established that lake sediment contains between 11% (~ 1929 CE) and 69% (~ 1978 CE) recalcitrant carbon, with changes in carbon character coinciding with peaks in accumulation rate and linked to STW inputs. Catchment disturbance was identified by radiocarbon analysis, and included STW construction in the 1930s, determined using SCR analysis, and recent nearby highway construction, determined by measurements on dissolved organic carbon from the lake and outflow river. The quantity of autochthonous carbon buried was related to diatom biovolume accumulation rate (DBAR) and decreased when diatom accumulation rate and valve size declined, despite an overall increase in net carbon production. HPLC pigment analysis indicated that changes in total C deposition and diatom accumulation were related to proliferation of non-siliceous algae. HPLC results also indicated that dominance of recalcitrant carbon in sediment organic carbon was likely caused by increased deposition rather than preservation factors. The total algal accumulation rate controlled the sediment organic carbon accumulation rate, whereas DBAR was correlated to the proportion of each carbon source buried.

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10933-020-00141-1>) contains supplementary material, which is available to authorized users.

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## Introduction

Inland waters play a major role in the global carbon cycle, but carbon dynamics in freshwater lakes are complex. The rate of organic carbon (OC) sequestration in lakes is at least three times higher than that in marine sediments (Cole et al. 2007; Tranvik et al. 2009; Balmer and Downing 2011), yet global emission/sequestration data from inland waters are often incomplete or inaccurate, leading to poorly constrained global models (Tranvik et al. 2013; Hanson et al. 2015). Recent studies, however, show that these water bodies could be important sites of carbon processing and sequestration (Anderson et al. 2013, 2014; Bayer et al. 2016).

Land use changes in lake catchments can influence loading of nutrients and OC, and alter carbon dynamics within lakes. Anthropogenic impacts on freshwater carbon cycles have recently escalated as a consequence of intensified land use and development within catchments (Regnier et al. 2013), and the influence of associated nutrient input from agricultural runoff or sewage discharge is rising in some lakes (Anderson et al. 2014; Deng et al. 2016). Despite efforts that have reduced nutrient loads to water bodies, the influence of historic inputs can persist as a consequence of remobilisation of nutrients such as phosphorus from profundal sediments (Radbourne 2019a). Additionally, mobilisation of terrestrial carbon, through soil disturbance and temperature increases, can influence lake nutrient cycling, with major impacts on primary productivity and organic carbon accumulation rates (Anderson et al. 2012; McGowan et al. 2012; Moorhouse et al. 2014).

The properties of OC in lakes are related to its source and regulate the likelihood of deposition and diagenesis in lake sediment. Allochthonous OC can be labile or recalcitrant and is present in particulate (POC) or dissolved (DOC) forms. This controls whether the OC is remineralised in the water column to CO<sub>2</sub> or CH<sub>4</sub> (Wik et al. 2016) and emitted to the atmosphere, or is deposited directly in the sediment as POC, or after flocculation (Lapierre et al. 2013; Ferland et al. 2014). In contrast, it is commonly

assumed that most OC produced within the lake during primary production by algae and non-vascular aquatic macrophytes is labile, and mineralised rapidly in the water column or at the sediment-water interface. However, recalcitrant autochthonous OC from vascular aquatic plants such as *Phragmites* and *Typha* spp. may also be present, and can be more resistant to decay. Terrestrial vascular sources often contain even greater proportions of refractory OC, a consequence of their geochemical composition (Lacey et al. 2018).

Diatoms can represent a sizeable proportion of the autochthonous OC in sediment, which can be estimated reliably from quantitative counts of valve numbers, if biogenic silica is well preserved, and conversion of abundance values to biovolume and accumulation rates. Diatoms are silica-rich and may sink more readily than non-siliceous algae, contributing to the labile autochthonous OC portion of sediment (Reynolds and Rogers 1976). Presence of other photoautotrophic groups of algae, photosynthetic bacteria and higher plants in lakes may be detected in lake sediments by chlorophyll and carotenoid pigments, which constitute a small, but informative fraction of the organic matter in the deposits (McGowan 2013). Individual pigments vary in lability, but this property is well established for pigments frequently found in sediments. Chlorophyll *a* (Chl*a*) degrades into pheo-pigments such as pheophytin *a* (Pha), and the ratio of the abundances of undegraded and degraded forms can be used as an indicator of preservation (Leavitt and Hodgson 2001).

Carbon source attribution for lake sediments has been identified as a key gap in our understanding of lake carbon dynamics (Hanson et al. 2015; Guillemette et al. 2017). Many factors affect the accumulation of OC in lake sediments, including lake trophic state, life cycles and functional traits of the primary producer community, inputs of allochthonous material from the catchment, lake stratification and oxygen concentrations in the hypolimnion and in upper sediments (Ryves et al. 2006; Gudas et al. 2012; Radbourne 2018). Interpretation of bulk geochemical measures in sediments as indicators of OC source, such as  $\delta^{13}\text{C}$  or carbon/nitrogen (C/N) ratios, are hampered by natural variability and overlapping values between OC pools (Holtvoeth et al. 2016; Lacey et al. 2018). Natural abundance radiocarbon methods have utility for source partitioning of OC in lakes and their sediments (McGeehin et al. 2004; Nara

et al. 2010; Rosenheim et al. 2013; Keaveney et al. 2015). We used  $\Delta^{14}\text{C}$ , defined as the ratio between the international standard  $^{14}\text{C}/^{12}\text{C}$ , corrected for year of measurement (base year AD 1950) and sample  $^{14}\text{C}/^{12}\text{C}$ , both corrected for  $\delta^{13}\text{C}$  fractionation (Stuiver and Polach 1977), to evaluate OC source in Rostherne Mere, UK.

Autochthonous C in contemporary lake and catchment waters can be identified using radiocarbon analysis, particularly in hard-water lakes, which have a Freshwater Reservoir Offset (FRO) (Keaveney et al. 2015a, 2015b; Ascough 2011; Broecker and Walton 1959). The FRO results from dissolution of carbonate bedrock. This carbon is “carbon dead,” i.e. devoid of radiocarbon, and therefore appears to be infinitely old, yielding a depleted, negative  $\Delta^{14}\text{C}$  value. When  $^{14}\text{C}$ -dead carbon enters a lake, an apparent age offset in lake C pools results. This reservoir offset can be considerable and is related to the lake alkalinity (Keaveney and Reimer 2012). Dissolved inorganic carbon (DIC) in lakes surrounded by carbonate bedrock can be used to identify OC produced within the lake, as that DIC is utilised predominantly by phytoplankton, in which the FRO can be detected (Keaveney et al. 2015b). Labile terrestrial organic carbon can be converted to inorganic forms by photo-oxidation or bacterial respiration (Kritzberg 2006), contributing to the DIC pool (Keaveney et al. 2015a). However, in lakes dominated by carbonate bedrock, age offsets are caused primarily by hard-water effects, and are related to the lake water alkalinity (Keaveney and Reimer 2012).

The biochemical quality of allochthonous OC can also be related to its age. Older carbon is generally more recalcitrant, and therefore radiocarbon analysis can help distinguish between the catchment-derived labile and recalcitrant carbon in a lake. “Atomic bomb” carbon, hereafter bomb radiocarbon, can also be found in sub-surface soils. Nuclear weapons testing in the 1950s and 1960s artificially enriched the global atmosphere in  $^{14}\text{C}$  (Reimer and Reimer 2004). Because of soil carbon cycling and turnover, however, atmospheric carbon with enriched bomb  $\Delta^{14}\text{C}$  values can take decades to reach subsurface soil stocks (Trumbore 2009), leading to positive  $\Delta^{14}\text{C}$  values in subsurface soil. This bomb signal can identify another allochthonous end-member (sub-surface soil OC), that can be identified by radiocarbon. Radiocarbon analysis can therefore distinguish between autochthonous

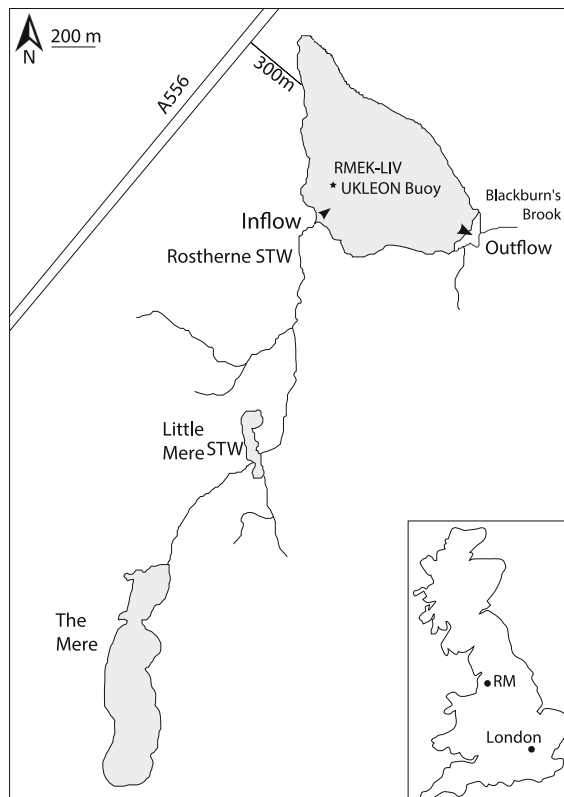
and allochthonous sources and help identify different forms of catchment inputs, i.e. labile dissolved organic carbon (DOC), bomb carbon from sub-surface soils, and recalcitrant carbon from deeper soil/peat stocks (Keaveney et al. 2015).

Stepped combustion radiocarbon (SCR) analysis of sediments can quantify the proportion of each carbon type (labile/recalcitrant) and determine whether these are dominated by autochthonous or allochthonous sources. We conducted analysis of sedimentary diatoms and pigments, along with SCR analysis of multiple OC pools in a lowland eutrophic lake (Rostherne Mere, UK), to investigate the role of productivity and carbon sources in the carbon cycle of this aquatic ecosystem.

#### Study site

Rostherne Mere was selected for study because it has an extensive record of monitoring and sediment analysis (Tattersall and Coward 1914; Reynolds and Rogers 1976; Livingstone and Cambray 1978; Battarbee 1984; Battarbee et al. 2015; Radbourne 2019b), is part of the UK Lake Ecological Observatory Network (UKLEON) project (<http://www.ceh.ac.uk/our-science/projects/uklake-ecological-observatory-network-ukleon>), and hosts an automated water quality station at a central buoy. Multiple studies examined nutrient cycling and sedimentation processes in the lake (Scott 2014; Radbourne et al. 2017, 2019a). A considerable freshwater reservoir offset was identified in the lake because of its high alkalinity ( $\sim 2500 \mu\text{eq L}^{-1}$ ) (Keaveney and Reimer 2012), and as a result, the lake was considered suitable for carbon source identification using novel radiocarbon methods. Furthermore, high organic production, strong stratification and seasonal anoxia at depth (Scott 2014) promote good OC and diatom preservation in the sediments, making the lake suitable for analysis (Livingstone and Cambray 1978; Radbourne 2018).

Rostherne Mere is one of the largest of the Shropshire-Cheshire Meres (Fig. 1), with a surface area of 48.7 ha, a maximum depth of  $\sim 30$  m and a mean depth of 13.6 m. The lake sits in a catchment dominated by limestone bedrock (Reynolds 1979). It is a monomictic, kettle lake and is located downstream from two other lakes (Fig. 1). The upstream lakes are predominantly groundwater fed. Rostherne Mere is fed from these lakes via one large inflow stream



**Fig. 1** Rostherne Mere and catchment and its geographical location in NW England, UK (53.3546° N, 2.3870° W). The core site and UKLEON Buoy are marked, as is the adjacent roadway that was under construction in the years preceding the study (modification of Google Map Data © 2020). Sewage Treatment Works (STW), which were in operation from 1935 to 1991 (Lacey et al. 2018) are also labelled

(Rostherne Brook) and numerous small inflow streams. There is a single surface outflow, Blackburn's Brook, and water residence time is  $\sim 0.8$  year (Radbourne 2018). Lake alkalinity is high ( $> 2500$   $\mu\text{eq/L}$ ).

Two sewage treatment works (STWs) were built upstream, one on the shore of Little Mere in 1935, which discharged directly into the lake (Carvalho et al. 1995). The STWs became overloaded by the 1970–1980s and were closed in 1991, after which sewage effluent was diverted outside the catchment. Prior to closure of the STWs, it was estimated that 72% of phosphorus (P) loading to Little Mere was derived from sewage effluent (Moss et al. 1997). Despite closure of the STWs and the sewage diversion, the lake remains hypereutrophic, as high quantities of

P are remobilised from profundal sediments during seasonal stratification and deep-water anoxia (Radbourne et al. 2019a).

## Materials and methods

### Sediment coring and dating

A 55-cm sediment core (RMEK) was obtained in March 2016 from 26 m water depth in the vicinity of the UKLEON buoy (Fig. 1), using a Hon-Kajak gravity corer with a 1-m tube. (Renberg 1991). The core was extruded at 0.5-cm intervals on site, sealed and stored cold for transport. Dates were assigned to depths in the core by comparison of the distinct stratigraphic profile of organic matter content (%) in a 1.16-m,  $^{210}\text{Pb}$ -dated sediment core (RM-LIV) collected in 2011 from the same location as RMEK (Electronic Supplementary Material [ESM] Fig. S1).

There is a clear and consistent stratigraphic pattern in organic matter content in all deep-water cores from Rostherne Mere over the last decades, i.e. during the period of recent nutrient enrichment (D. Ryves, unpublished data). Distinct features in organic matter %, especially several periods of higher organic matter content, were identified in both the RMEK and RM-LIV cores and formed the basis for stratigraphic correlation. Current sediment accumulation rate in the deepest part of the lake is  $\sim 1$   $\text{cm yr}^{-1}$  (Radbourne 2018), which is consistent with the 7-cm offset between the uppermost samples from the RMEK and RM-LIV cores, which were collected 5 years apart (ESM Fig. S1). Further details about core RM-LIV and its  $^{210}\text{Pb}$  chronology are provided in Radbourne (2018).

### Diatoms

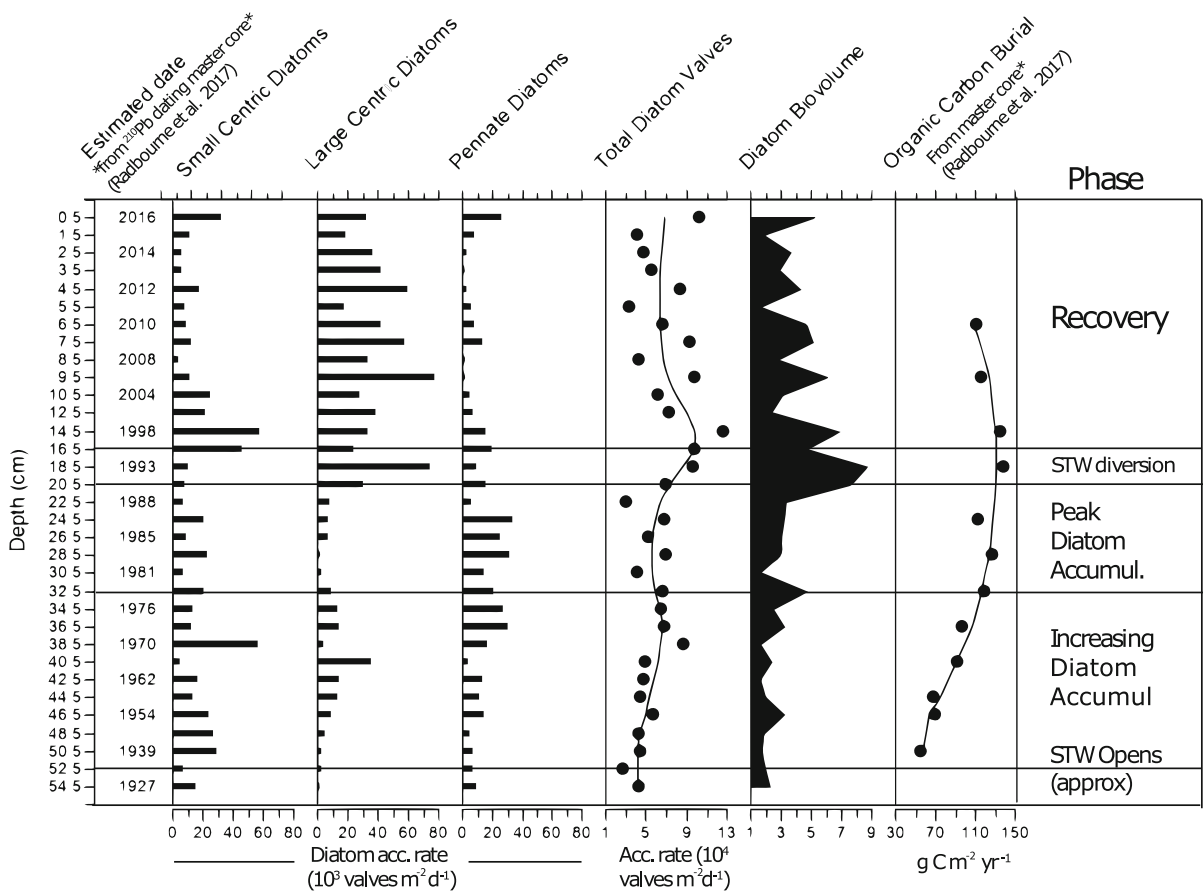
Standard diatom analyses on core samples were undertaken at Loughborough University, to estimate diatom valve abundance and accumulation rates (Renberg 1991; Battarbee et al. 2001), with the modification that we left material for up to 24 h in concentrated  $\text{H}_2\text{O}_2$  solution at room temperature. Labile algal organic matter would have reacted violently had it been heated before this time. A known quantity of microspheres was added to the cleaned diatoms before slide preparation (Battarbee and Kneen 1982). Microspheres and at least 300 diatom valves

per slide were identified following standard methods (Battarbee et al. 2001). Total diatom abundance was calculated from the diatom to microsphere ratio, using methods outlined in Battarbee and Kneen (1982), with diatom valve accumulation rate calculated from sediment dry density and bulk sedimentation rate. Diatom biovolume was calculated for taxa with > 3% abundance in an individual sample. Biovolume calculations followed methods outlined in Hillebrand et al. (1999), with 25 representative examples from a range of slides measured to determine the mean biovolume (Fig. 2) for each taxon.

Pigments

High performance liquid chromatography (HPLC) analysis was undertaken at the University of

Nottingham. Pigments were extracted quantitatively overnight in an acetone:methanol:water (80:15:5) mixture at - 4 °C, filtered with a PTFE 0.2-µm filter and dried under nitrogen gas. A known quantity was re-dissolved into a solution of a 70:25:5 mixture of acetone, ion-pairing reagent (IPR; 0.75 g of tetrabutyl ammonium acetate and 7.7 g of ammonium acetate in 100 ml water) and methanol, and injected into an Agilent 1200 series HPLC unit. Pigment extracts were separated using a modification of Chen et al. (2001), and the system was calibrated and pigments identified with reference to commercial standards (DHI Denmark). Pigment concentrations are expressed per g organic matter, estimated by loss-on-ignition at 550 °C (Dean 1974). Carotenoid and chlorophyll pigments were used to infer algal community shifts and the seven carotenoids were summed to assess overall



**Fig. 2** Selected diatom valve accumulation rates in the RMEK sediment core and organic carbon sequestration from the RM-LIV core. RMEK ages are estimated from the <sup>210</sup>Pb data from

the RM-LIV core and matched through organic matter % (see Electronic Supplementary Material)

changes in carotenoid concentration in the sediment organic fraction.

### Radiocarbon analysis of water samples

Water samples were collected from the lake inflow and outflow sites in March 2016, and in April, September and December 2017. Nalgene® bottles and lids were soaked in 10% HCl overnight before collection and rinsed with Milli-Q® water (1 L bottles were used for DIC and 1.5 L for DOC and POC because of the low concentration of organic carbon in the lake). For DIC/DOC/POC samples, bottles were rinsed once in lake water before water was collected from approximately 30 cm below the water surface. Bottles were closed under water to ensure that no air was trapped in them. For DIC analysis, BaCl<sub>2</sub> was added in the field to a 1-L sample bottle from each site, along with 2–3 pellets of NaOH to convert DIC to a BaCO<sub>3</sub> precipitate, which could be measured in the laboratory. Some samples, collected on later expeditions were shipped and the DIC was precipitated in the lab. There were no significant differences in DIC values from those treated in the field when compared to those treated in the lab.

Back in the laboratory samples were processed for <sup>14</sup>C analysis according to methods detailed in Keaveney et al. (2015), Landmeyer and Stone (1995), Burr et al. (2001) and Nakata et al. (2016). POC was filtered onto Fisherbrand® glass microfibre filters (GF/F pore size 0.7 µm), which had been combusted overnight at 500 °C. This was the smallest pore size that could be used because of the need to pre-combust filter papers to avoid contamination. POC on filters was acidified with 4% HCl to remove carbonates. DOC was obtained by concentrating the sampled lake water using rotary evaporation, which was acidified with 4% HCl to remove carbonates and lyophilised overnight. POC filter papers and DOC samples were loaded into pre-combusted quartz tubes with silver and copper oxide, sealed under vacuum, and combusted at 850 °C overnight to generate CO<sub>2</sub> gas. DIC samples were acidified with 86% orthophosphoric acid under vacuum (Landmeyer and Stone 1995; Nakata et al. 2016), and the CO<sub>2</sub> gas was cryogenically collected. Blank GF/F filter papers were processed by each method and were either combusted or hydrolysed (DIC). They yielded no measurable carbon. Carbon yields were low in some samples and thus were not graphitised, leading

to some missing POC and DIC values. DOC results from samples collected in 2016 showed a range of values, so DOC was retrieved from multiple sites in 2017 to try and identify the source of lake DOC.

Whereas the DIC method is susceptible to contamination (Nakata et al. 2016), the high alkalinity in Rostherne makes the dissolution of CO<sub>2</sub> from external sources unlikely. As the alkalinity of Rostherne Mere is so high any contamination if present will be diluted and would not affect the results significantly. The results were reproducible both temporally and spatially in this study, and between samples pre-treated in the field and the lab. Additionally, the results were in agreement with previous analyses in Rostherne Mere and we are confident that contamination was not an issue in this setting.

### Stepped combustion radiocarbon (SCR)

SCR followed the method of McGeehin et al. (2001). Bulk sediment samples were halved, acidified with 4% HCl, and dried. One aliquot (200–300 mg) underwent standard combustion overnight in a vacuum-sealed quartz tube with CuO at 850 °C. The second aliquot (400–500 mg) was initially combusted at 400 °C overnight and the CO<sub>2</sub> produced was collected. The remainder of the sample was re-combusted at 850 °C overnight and the CO<sub>2</sub> produced was collected.

### Graphitisation and AMS measurement

The CO<sub>2</sub> from each sample was graphitised in the presence of an iron catalyst at 560 °C for 4 h, according to the Bosch-Manning hydrogen reduction method (Manning and Reid 1977; Vogel et al. 1987). The graphite produced was analysed on a 0.5 MV National Electrostatics compact accelerator mass spectrometer (AMS) at the <sup>14</sup>CHRONO Centre in Queen's University, Belfast. The sample <sup>14</sup>C/<sup>12</sup>C ratio was background-corrected and normalised to the HOXII standard (SRM 4990C; National Institute of Standards and Technology).

Two pairs of secondary standards were run with each AMS wheel and included one pair of IAEAC6 (ANU sucrose) and a pair of either TIRI/FIRI inter-comparison standards (Scott 2003) or an in-house tree ring sample of known age. The background samples were anthracite or Icelandic spar calcite.

$\Delta^{14}\text{C}$  was calculated using Eq. 1:

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

where  $y$  is the year of collection (2016 or 2017 for this study) and  $\text{F}^{14}\text{C}$  is the ratio of the sample  $^{14}\text{C}/^{12}\text{C}$  and standard  $^{14}\text{C}/^{12}\text{C}$ , both corrected for isotope fractionation using AMS  $^{13}\text{C}$  (Reimer et al. 2004).

A mass balance equation (Eq. 2) was used to determine the fraction of labile carbon ( $\text{LC}_f$ ) present in bulk sediment using  $\text{F}^{14}\text{C}$  values (Table 2). The mass balance equation for estimating the fraction of labile sediment OC composition ( $\text{LC}_f$ ) is:

$$\text{F}^{14}\text{C}_{\text{BULK}} = \text{LC}_f * \text{F}^{14}\text{C}_{\text{LOW}} + (1 - \text{LC}_f) * \text{F}^{14}\text{C}_{\text{HIGH}} \quad (2)$$

where  $\text{F}^{14}\text{C}_{\text{BULK}}$  = Bulk  $\text{F}^{14}\text{C}$ , which underwent standard single step combustion (at 850 °C).  $\text{F}^{14}\text{C}_{\text{LOW}}$  =  $\text{F}^{14}\text{C}$  of sample combusted at low temperature (400 °C).  $\text{F}^{14}\text{C}_{\text{HIGH}}$  =  $\text{F}^{14}\text{C}$  of sample recombusted at high temperature (850 °C).

## Results

### Diatom valve and biovolume accumulation rates

Total diatom valve accumulation rate (DAR; valves  $\text{cm}^{-2} \text{yr}^{-1}$ ) increased after the establishment of the STWs (Fig. 2), and associated increases in lake nutrient concentrations (Lacey et al. 2018; Radbourne 2018). The pattern of DAR paralleled that of the OC sequestration rate, yet with a slight reduction in DAR during the peak nutrient phase, shortly before STW diversion in 1991. Immediately after STW diversion, DAR increased to its highest level in the sediment record, before declining, concurrent with a lower OC sequestration rate. The diatom biovolume accumulation rate (DBAR) emphasised the increasing diatom accumulation rate, together with greater numbers of larger diatom taxa. These larger centric diatoms were found at highest abundance close to and immediately after STW diversion, as OC accumulation rates fell, and both the DAR and DBAR subsequently stabilised.

### Pigments

Prior to the period of peak carbon sequestration, before ca. 1980, concentrations of carotenoids and chlorophylls *a* and *b* were lower than in later times (Fig. 3).

The phase of peak carbon sequestration was preceded by a marked decline in all pigments, after which all carotenoids and chlorophyll *b* (from chlorophytes) increased. Almost all pigment concentrations declined during the period of STW closure and sewage diversion. Subsequently, most, but not all pigment concentrations increased during the recovery phase. Abundance of pigments from cyanobacteria (echinenone and myxoxanthophyll), chlorophytes (chlorophyll *b*) and all algae ( $\beta$ -carotene), increased in the early 1980s and maintained higher, but variable abundances thereafter. Cryptophyte pigments (alloxanthin) increased more gradually through time and pigments from siliceous algae (highly labile fucoxanthin) were variable, with no long-term trends. Pigment preservation throughout the core was inferred using the ratio of *Chla* to *Pha* (Fig. 3). Although the preservation index varied, overall preservation was shown to be good throughout the core.

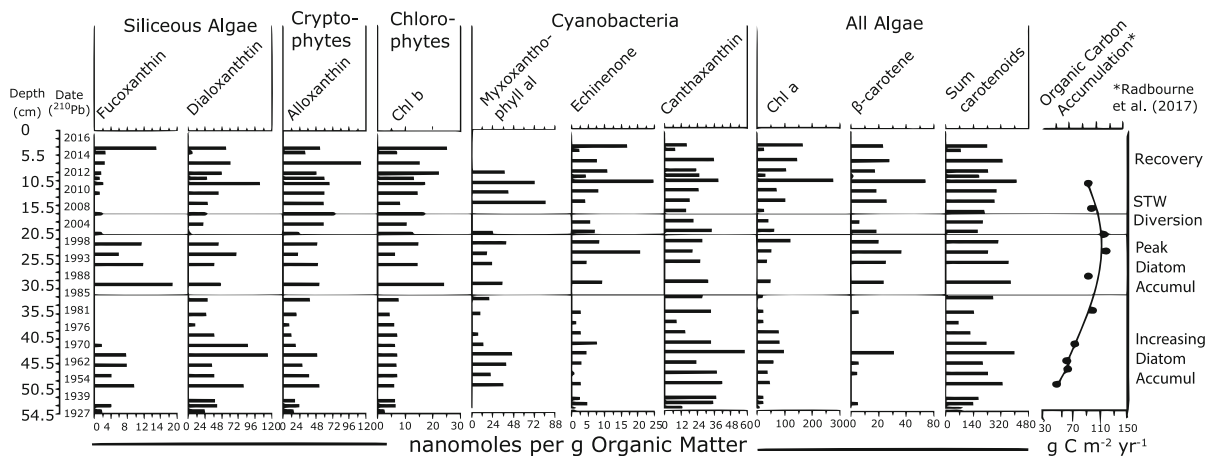
### Autochthonous and allochthonous carbon: Radiocarbon analysis

#### Carbon sources in water

DIC and POC in water samples exhibited depleted  $\Delta^{14}\text{C}$  values (Figs. 4 and 5; Table 1), supporting the findings of Keaveney et al. (2012), who found an FRO in the water DIC ( $\Delta^{14}\text{C} = -127 \pm 3.6\%$ ). DIC  $\Delta^{14}\text{C}$  values from lake water collected in 2016/2017 were substantially depleted ( $\Delta^{14}\text{C} = -147 \pm 3.6\%$ ), as were POC values (September 2016  $\Delta^{14}\text{C} = -161 \pm 2.7\%$ ; March 2017  $\Delta^{14}\text{C} = -152 \pm 4.0\%$ ).

To confirm enrichment in lake water DOC, more comprehensive sampling was undertaken in 2017 to determine if there was DOC enrichment in the upstream and downstream lakes and incoming rivers. Upstream  $\Delta^{14}\text{C}$  DIC/DOC/POC values were depleted, indicating a FRO. As Rostherne Mere water is primarily sourced from alkaline groundwater, this was expected.

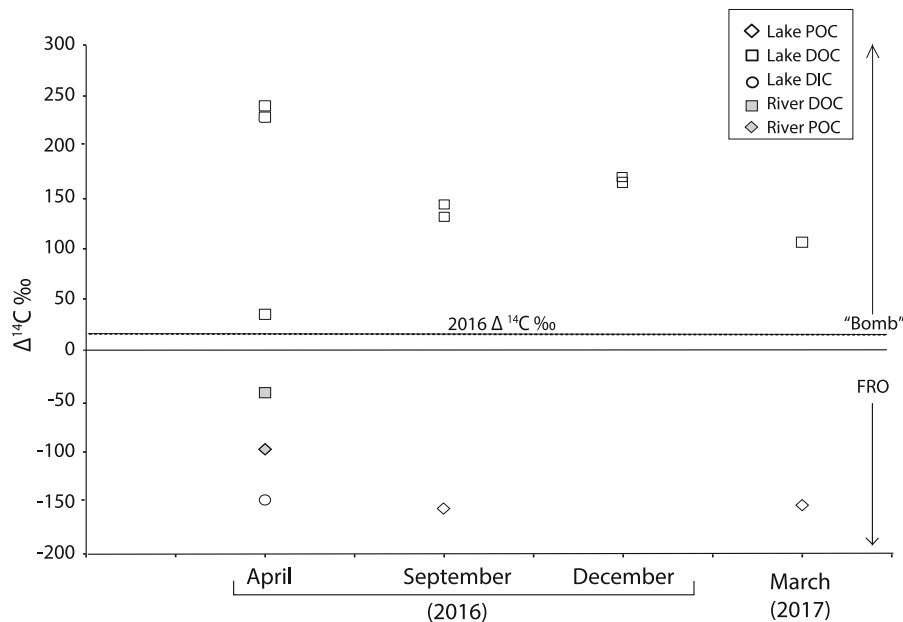
DIC is the inorganic component of the carbon pool derived from dissolution of the carbonate bedrock, and is part of the carbon pool in Rostherne Mere water. The DIC pool was depleted, evidence for an FRO.



**Fig. 3** Selected diatom and algal pigments in the RMEK sediment core and organic carbon sequestration from the RM-LIV core. RMEK ages are estimated from the <sup>210</sup>Pb data from

the RM-LIV core and matched through organic matter % (see Electronic Supplementary Material)

**Fig. 4**  $\Delta^{14}\text{C}$  values from Rostherne Mere river and lake samples collected in 2016. Error bars correspond to a 1 $\sigma$  uncertainty. The solid line indicates 0  $\Delta^{14}\text{C}$  ‰, above which samples have incorporated atmospheric bomb carbon. The dashed line indicates the 2016 radiocarbon activity of 10  $\Delta^{14}\text{C}$  ‰ (Hammer et al. 2017). Lake samples were collected at the UKLEON buoy site (Fig. 1). River samples were taken from the inflowing river (Fig. 1)



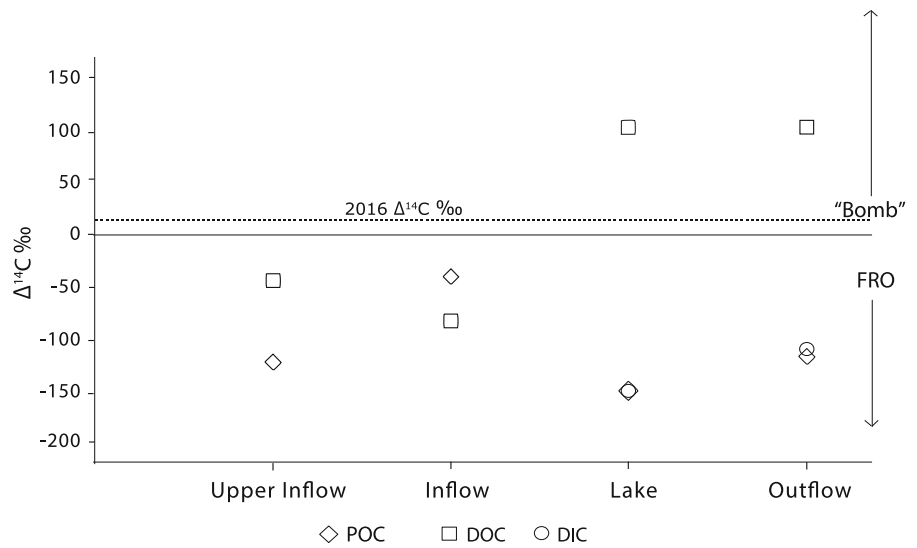
POC  $\Delta^{14}\text{C}$  from the lake was also depleted and within the range of DIC  $\Delta^{14}\text{C}$ , making it clear that the POC came primarily from an autochthonous source such as algae, which had used the inorganic carbon pool for photosynthesis. Surface lake water DOC  $\Delta^{14}\text{C}$  values, however, were enriched, and no FRO was evident in this carbon pool.

There was high variability in bulk sediment radiocarbon values (Fig. 6; Table 2) particularly during the

operation of the STWs. The 54 cm sample (ca. 1927)  $\Delta^{14}\text{C}$  values display significant  $\Delta^{14}\text{C}$  depletion (high temperature (HT) combustion  $\Delta^{14}\text{C} = -222 \pm 3.5\%$ , bulk  $\Delta^{14}\text{C} = -145 \pm 4.1\%$ , low temperature (LT)  $\Delta^{14}\text{C} = -135 \pm 3.9\%$ ). The  $\Delta^{14}\text{C}$  value of the 50 cm (ca. 1939) sample was also significantly depleted (HT combustion  $\Delta^{14}\text{C} = -393 \pm 3.9\%$ , bulk  $\Delta^{14}\text{C} = -349 \pm 2.7\%$ ), beyond what can be explained by old carbon in the DIC.



**Fig. 5**  $\Delta^{14}\text{C}$  values from Rostherne Mere river and lake samples collected on one day in March 2017. Error bars correspond to a  $1\sigma$  uncertainty. The dashed line indicates the 2016 radiocarbon activity of 10  $\Delta^{14}\text{C}$  ‰ (Hammer et al. 2017)



**Table 1** Radiocarbon results from lake and river dissolved inorganic, dissolved organic and particulate organic carbon. Small samples (< 0.3 mg) were accepted, as long as yields were satisfactory and ran successfully on the AMS

Lab identifier	Sample type and location	Mg C	$^{14}\text{C}$ Years BP $\pm 1\sigma$	$F^{14}\text{C} \pm 1\sigma$	$\Delta^{14}\text{C} \pm 1\sigma$
UBA-31830	March River inflow POC	0.54	760 $\pm$ 26	0.9098 $\pm$ 0.0033	- 97 $\pm$ 3.2
UBA-31829	2016 River inflow DOC	0.35	276 $\pm$ 29	0.9663 $\pm$ 0.0034	- 41 $\pm$ 3.6
UBA-31826	Lake DIC	0.92	1212 $\pm$ 29	0.86 $\pm$ 0.0031	- 147 $\pm$ 3.6
UBA-31827-1	Lake DOC	0.45	- 1794 $\pm$ 22	1.2502 $\pm$ 0.0034	240 $\pm$ 2.7
UBA-31827-2	Lake DOC	1.00	- 1721 $\pm$ 27	1.239 $\pm$ 0.0042	229 $\pm$ 3.4
UBA-32984	Lake DOC	0.87	- 344 $\pm$ 19	1.0438 $\pm$ 0.0025	35 $\pm$ 2.4
UBA-32985-1	September Lake DOC	1.00	- 1142 $\pm$ 24	1.1527 $\pm$ 0.0034	144 $\pm$ 3.0
UBA-32985-2	2016 Lake DOC	0.55	- 1056 $\pm$ 56	1.1405 $\pm$ 0.0063	131 $\pm$ 5.6
UBA-32987	Lake POC	0.37	1345 $\pm$ 25	0.8459 $\pm$ 0.0026	- 161 $\pm$ 3.1
UBA-33695	December Lake DOC	0.25	- 1317 $\pm$ 29	1.1782 $\pm$ 0.0042	169 $\pm$ 3.6
UBA-33695	2016 Lake DOC	0.34	- 1292 $\pm$ 20	1.1745 $\pm$ 0.0029	165 $\pm$ 2.5
UBA-34673	March River inflow DOC	1.00	595 $\pm$ 21	0.9286 $\pm$ 0.0024	- 79 $\pm$ 2.6
UBA-34675	2017 River inflow POC	0.69	235 $\pm$ 25	0.9711 $\pm$ 0.0030	- 37 $\pm$ 3.1
UBA-34677	River inflow DIC	0.63	3000 $\pm$ 33	0.6883 $\pm$ 0.0028	- 317 $\pm$ 4.1
UBA-34678	River upper inflow POC	1.00	281 $\pm$ 26	0.9656 $\pm$ 0.0031	- 42 $\pm$ 3.2
UBA-34680	River upper inflow POC	0.66	954 $\pm$ 23	0.888 $\pm$ 0.0025	- 119 $\pm$ 2.9
UBA-34683	Lake DOC	1.00	- 876 $\pm$ 19	1.1152 $\pm$ 0.0026	106 $\pm$ 3.4
UBA-34685	Lake POC	0.27	1258 $\pm$ 27	0.855 $\pm$ 0.0029	- 152 $\pm$ 4.0
UBA-34687	River outflow DIC	0.39	851 $\pm$ 32	0.8995 $\pm$ 0.0036	- 108 $\pm$ 4.0
UBA-34688	River outflow DOC	1.00	- 873 $\pm$ 18	1.1153 $\pm$ 0.0024	106 $\pm$ 0.0
UBA-34689	River outflow POC	1.00	916 $\pm$ 29	0.89230 $\pm$ 0.0032	- 115 $\pm$ 3.6

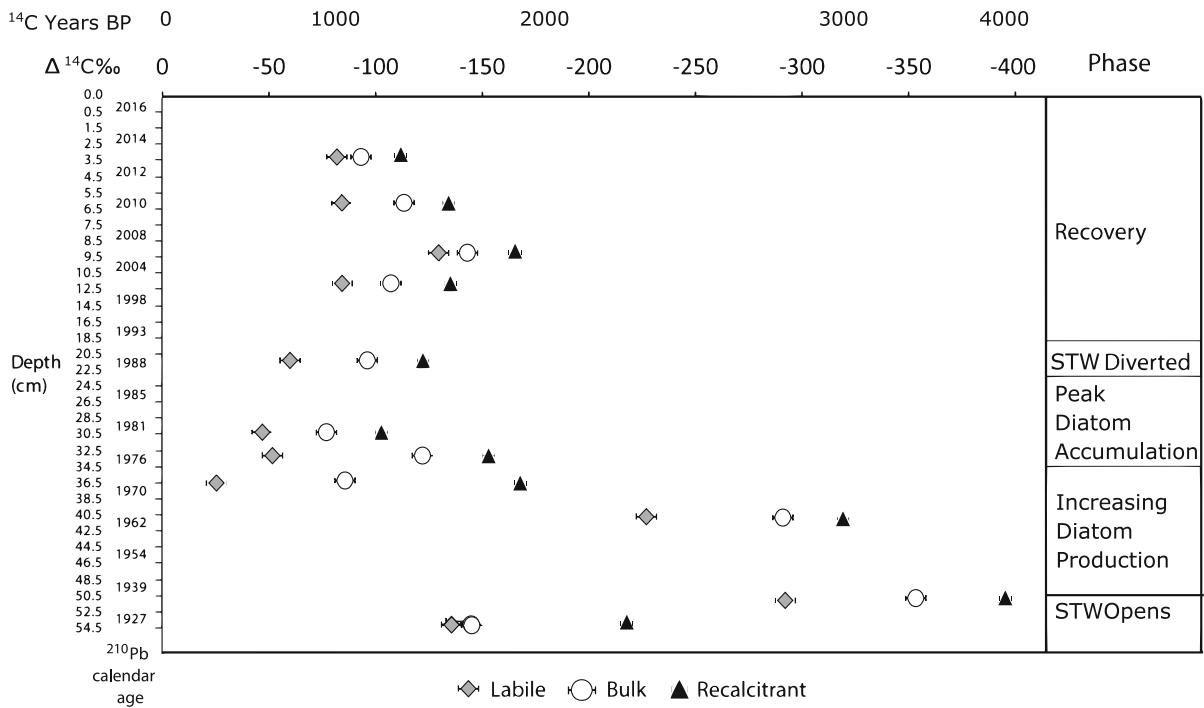
*Sediment carbon composition*

From 38 cm (ca. 1970) upwards, when productivity driven by nutrient output from the STWs was at its

peak, all  $\Delta^{14}\text{C}$  values were enriched relative to samples at the bottom of the core (Fig. 6). SCR results indicated the presence of multiple carbon sources in bulk sediment. Samples combusted at 400 °C were

**Table 2**  $\Delta^{14}\text{C}$  values from sediment. Samples were combusted at 400 °C and recombusted at 850 °C. Bulk samples were combusted once, at 850 °C.  $\pm$  Errors correspond to  $1\sigma$  uncertainty on radiocarbon measurements

Combustion	Lab identifier	Age estimate ( $^{210}\text{Pb}$ )	Top of interval	mg C	AMS $\delta^{13}\text{C}$	$^{14}\text{C}$ years BP $\pm 1\sigma$	$\text{F}^{14}\text{C} \pm 1\sigma$	$\Delta^{14}\text{C}$	Fraction recalcitrant carbon
400 °C	UBA-32724-1	2014	3–4	1.00	-33.4	63 $\pm$ 29	0.9244 $\pm$ 0.0033	-83 $\pm$ 3.61	0.38
850°	UBA-32724-2			1.00	-31.8	915 $\pm$ 27	0.8924 $\pm$ 0.0030	-115 $\pm$ 3.36	
Bulk	UBA-32723			1.02	-30.9	737 $\pm$ 31	0.9123 $\pm$ 0.0035	-95 $\pm$ 3.86	
400 °C	UBA-32726-1	2010	6–7	1.01	-30.1	653 $\pm$ 26	0.9219 $\pm$ 0.0030	-85 $\pm$ 3.24	0.58
850°	UBA-32726-2			1.00	-32.1	1132 $\pm$ 27	0.8685 $\pm$ 0.0030	-138 $\pm$ 3.36	
Bulk	UBA-32725			1.02	-30.8	929 $\pm$ 26	0.8908 $\pm$ 0.0029	-116 $\pm$ 3.24	
400 °C	UBA-32245-1	2008	9–10	0.87	-34.5	1040 $\pm$ 32	0.8786 $\pm$ 0.0035	-128 $\pm$ 3.98	0.38
850°	UBA-32245-2			0.87	-28.7	1395 $\pm$ 31	0.8406 $\pm$ 0.0032	-166 $\pm$ 3.86	
Bulk	UBA-32531			0.99	-28.1	1173 $\pm$ 35	0.8642 $\pm$ 0.0038	-143 $\pm$ 4.36	0.45
400 °C	UBA-32246-1	2004	12–13	1.00	-28.1	637 $\pm$ 31	0.9238 $\pm$ 0.0035	-84 $\pm$ 3.86	
850°	UBA-32246-2			1.00	-27.1	1123 $\pm$ 43	0.8696 $\pm$ 0.0046	-137 $\pm$ 5.35	
Bulk	UBA-32532			1.00	-28.9	852 $\pm$ 35	0.8994 $\pm$ 0.0039	-108 $\pm$ 4.36	
400 °C	UBA-32247-1	1991	20–21	1.00	-26.8	413 $\pm$ 33	0.9499 $\pm$ 0.0039	-58 $\pm$ 4.1	0.58
850°	UBA-32247-2			1.00	-27.1	997 $\pm$	0.8833 $\pm$ 0.0037	-124 $\pm$ 3.23	
Bulk	UBA-32533			1.00	-26.8	747 $\pm$ 35	0.9112 $\pm$ 0.0040	-96 $\pm$ 4.36	
400 °C	UBA-32248-1	1981	30–31	1.00	-23.7	294 $\pm$ 29	0.964 $\pm$ 0.0035	-44 $\pm$ 3.61	0.54
850°	UBA-32248-2			1.00	-26.6	807 $\pm$ 32	0.9044 $\pm$ 0.0036	-103 $\pm$ 3.98	
Bulk	UBA-32534			1.00	-30.3	566 $\pm$ 29	0.9319 $\pm$ 0.0033	-76 $\pm$ 3.61	0.69
400 °C	UBA-32728-1	1978	33–34	1.00	-29.8	307 $\pm$ 24	0.9625 $\pm$ 0.0029	-45 $\pm$ 2.99	
850°	UBA-32728-2			1.00	-27.2	1265 $\pm$ 27	0.8543 $\pm$ 0.0029	-152 $\pm$ 3.36	
Bulk	UBA-32727			1.01	-29.4	960 $\pm$ 27	0.8874 $\pm$ 0.0030	-120 $\pm$ 3.36	0.42
400 °C	UBA-32730-1	1976	36–37	1.00	-30.1	108 $\pm$ 28	0.9867 $\pm$ 0.0035	-21 $\pm$ 3.49	
850°	UBA-32730-2			1.00	-32	1451 $\pm$ 39	0.8347 $\pm$ 0.0040	-172 $\pm$ 4.85	
Bulk	UBA-32729			1.00	-31.3	642 $\pm$ 25	0.9232 $\pm$ 0.0028	-84 $\pm$ 3.11	0.69
400 °C	UBA-32249-1	1969	40–41	1.00	-26.8	1876 $\pm$ 34	0.7917 $\pm$ 0.0330	-215 $\pm$ 4.23	
850°	UBA-32249-2			1.00	-26.8	2957 $\pm$ 39	0.6921 $\pm$ 0.0034	-313 $\pm$ 4.85	
Bulk	UBA-32535			1.00	-26.2	2607 $\pm$ 36	0.7229 $\pm$ 0.0032	-283 $\pm$ 4.48	0.60
400 °C	UBA-32250-1	1939	50–51	1.00	-28	2623 $\pm$ 33	0.7214 $\pm$ 0.0030	-284 $\pm$ 4.11	
850°	UBA-32250-2			1.00	-24.4	3951 $\pm$ 32	0.6115 $\pm$ 0.0024	-393 $\pm$ 3.98	
Bulk	UBA-32536			1.00	-29.7	3387 $\pm$ 44	0.656 $\pm$ 0.0036	-349 $\pm$ 5.48	0.11
400 °C	UBA-32251-1	1927	54–55	1.00	-28.3	1099 $\pm$ 31	0.8721 $\pm$ 0.0033	-135 $\pm$ 3.86	
850°	UBA-32251-2			1.00	-26.2	1951 $\pm$ 28	0.7844 $\pm$ 0.0027	-222 $\pm$ 3.49	
Bulk	UBA-32537			1.00	-27.8	1190 $\pm$ 33	0.8623 $\pm$ 0.0035	-145 $\pm$ 4.11	



**Fig. 6**  $\Delta^{14}\text{C}$  values from Rostherne Mere sediment, combusted at different temperatures. Bulk samples, denoted by black circles, are always depleted relative to low temperature (400 °C) and (850 °C) values. Error bars correspond to  $1\sigma$  uncertainty.

Calendar ages on the y-axis were estimated using  $^{210}\text{Pb}$  dates from a master core, matched to RMEK through organic matter % (see Electronic Supplementary Material).  $^{14}\text{C}$  Years BP are only shown as a guide to the age of samples

consistently more enriched in  $\Delta^{14}\text{C}$  than those re-combusted at 850 °C (Fig. 6), which were depleted relative to bulk samples. At least two carbon pools were present in bulk sediment, and a mass balance equation demonstrated that the proportion of each changed over time (Fig. 7).

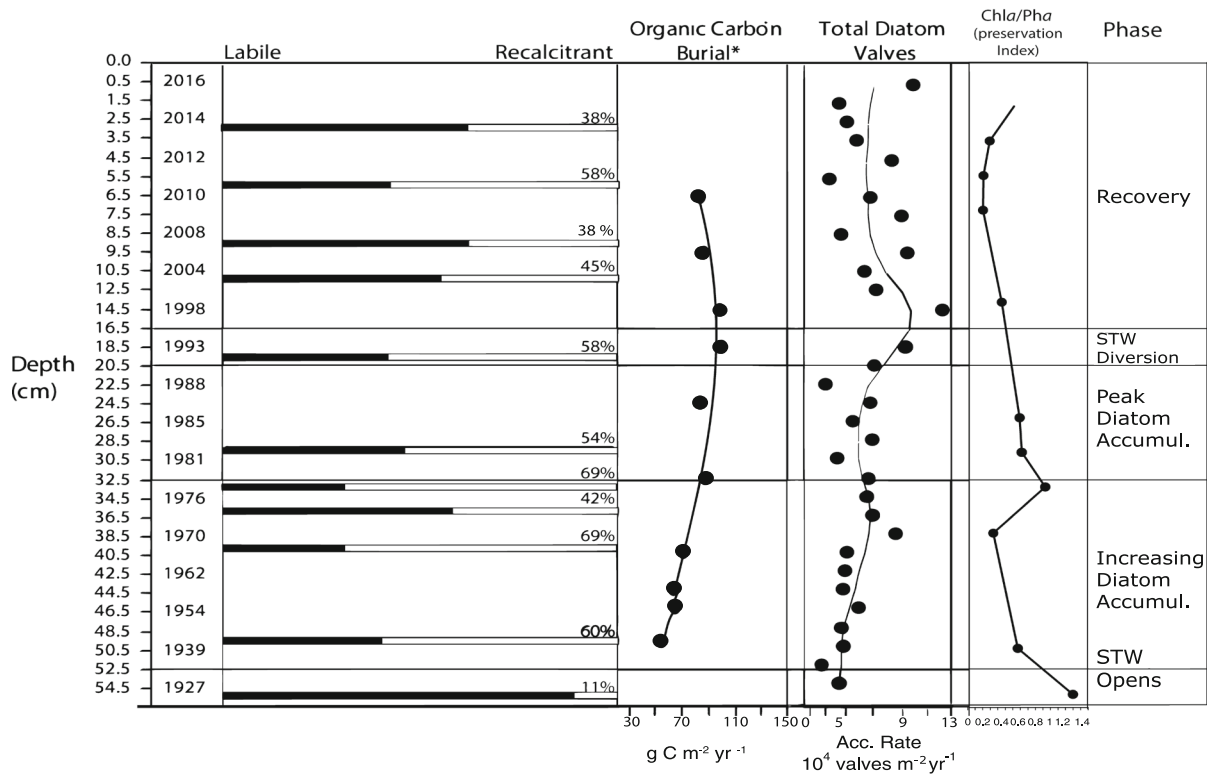
At the base of the core, ca. 1927, organic carbon in sediment consisted of 11% recalcitrant and 89% labile material (Fig. 7). The basal sample is thought to be representative of the system prior to STW operation. The proportion of labile carbon in the sediment core dropped dramatically thereafter, to 40% at the time of STW construction (Fig. 7). Thereafter, productivity increased and diatom valve accumulation rate rose, as did the proportion of labile carbon, before dropping again and remaining at 40–50% during the period of peak STW operation. After sewage diversion in 1991, the percentage of labile carbon in sediment increased (> 50%), associated with a peak in DBAR (Fig. 7), which reached a maximum of 62% in the top sample. There was, however, a slight decline in the proportion

of labile carbon in 2010 (to 42%), which coincided with a peak in the *Chla/Pha* ratio.

## Discussion

### Rostherne Mere productivity

Rostherne Mere has been impacted by anthropogenic activities such as the operation of STW upstream, and more recently, highway construction in the catchment. Sediment core analyses showed that as nutrient concentrations increased, so too did algal productivity (inferred from DBAR and pigment concentration), and the proportion of cyanobacteria in the phytoplankton increased, also indicating eutrophication. The diatom communities responded to rising nutrient concentrations with increasing DAR, showing a rise similar to the OC sequestration rate (Fig. 2). Furthermore, during that time there was a shift to larger Si-rich, centric diatom species as the production potential increased from anthropogenic nutrient enrichment (Radbourne



**Fig. 7** Summary of analyses of Rostherne Mere sediment core. **a** Proportion of labile to recalcitrant carbon, along with a 2-step moving average trend line. **b** Organic carbon sequestration rate taken from a master core collected from the lake in 2016 and matched to this study's core using loss on ignition (Electronic

Supplementary Material). **c** Diatom valve accumulation rates. **d** Pheophytin *a* to Chlorophyll *a* ratio, a measure of pigment preservation in sediments. Defined zones and sub-zones are shown. Chronology was determined by <sup>210</sup>Pb dating, using the Constant Rate of Supply model

et al. 2019a), emphasising the increase in DBAR as nutrient concentrations rose.

At the peak of nutrient concentrations around the 1980s, there were declines in DAR and DBAR, likely caused by a spring depletion of available dissolved Si from intensive spring diatom production, driven by high concentrations of P, which can influence diatom growth and community composition (Ryves et al. 2013). As diatoms became limited by Si depletion, they were succeeded by cyanobacteria and chlorophytes (Radbourne et al. 2019a), which can also suppress diatom productivity through shading.

Following sewage diversion in 1991, a peak in DAR and DBAR occurred as direct inputs from the STW were reduced. That gave a competitive advantage to diatoms over cyanobacteria, perhaps as light shading was reduced. Nevertheless, Si depletion in the upper waters was still occurring by summer (Radbourne 2018). As lake nutrient recovery continued, the

DAR decreased, in line with the decline in OC sequestration rate, as lakewide OC production fell.

Pigment results support diatom accumulation rate data (Fig. 4), indicating that, while overall DAR remained relatively stable, all pigment concentrations declined before the peak carbon sequestration phase. During this peak phase the community shifted towards dominance of chlorophytes and cyanobacteria.

The Chla/Pha index (Fig. 7) indicates a weak inverse relationship with the amount of recalcitrant carbon in the sediment. This suggests that the variability in pigment data was the result of deposition processes, rather than diagenetic effects. Previous studies demonstrated that preservation of biogeochemical variables and biological remains in Rostherne Mere sediment is excellent (Livingstone and Cambray 1978; Lacey et al. 2018; Radbourne et al. 2019a), supported by the very good preservation of sedimentary pigments and diatom valves in the present study.

### Carbon sources in water

Radiocarbon analysis of carbon in Rostherne Mere water samples collected in 2016/2017 (Figs. 5 and 6) documented substantial  $\Delta^{14}\text{C}$  depletion, which has been linked with the alkalinity of the lake (Keaveney and Reimer 2012). Depleted 2016/2017 DIC and POC  $\Delta^{14}\text{C}$  values indicated both were predominantly comprised of autochthonous carbon, derived from the DIC pool. DOC samples, however, had positive  $\Delta^{14}\text{C}$  values ( $\Delta^{14}\text{C} > 200\text{‰}$ ; Fig. 5), which was also the case for samples collected in 2017 (Fig. 6). This positive radiocarbon signal can only have been derived from a source containing bomb carbon.

The degree of enrichment in Rostherne Mere DOC, not seen in any other carbon pool in the water, is difficult to explain. Ordinarily, this magnitude of enrichment is attributed to irradiated medical waste or nuclear activity. Neither factor, however, could influence the enrichment seen in Rostherne Mere DOC. There are no nuclear power or fuel reprocessing stations close enough to impact the lake catchment, and the majority of lake water is derived from groundwater. The catchment is in a Ramsar protected area that is monitored regularly for dumping and other illegal activity. No reports of such material were found and any enrichment from such sources would also be evident in other carbon pools in the lake.

The high radiocarbon activity in Rostherne Mere lake DOC dates to the early 1960s to 1980s (CALIBomb (Reimer and Reimer 2004)). There is no such enrichment in the inflow waters, Rostherne Brook, which provides 75% of the lake's inflow, and drains 7 km<sup>2</sup> of the catchment (Carvalho et al. 1995) (Fig. 6). This implies that the <sup>14</sup>C-enriched material entered the lake laterally, from the catchment. Keaveney et al. (2015) found that subsurface carbon in the catchment of Lough Erne, NW Ireland, contributed to the DOC pool in the lake water. Although catchment soil was not analysed in this study because of funding and time constraints, we suggest that subsurface carbon was also the source of DOC in Rostherne Mere.

The source of enriched  $\Delta^{14}\text{C}$  values cannot be the inflow river or groundwater, which appear older because of the FRO. As this FRO is present in upstream DIC/POC/DOC, this enriched bomb <sup>14</sup>C source does not contribute to the upstream rivers or lakes. <sup>14</sup>C-enriched DOC values were also measured in the outflow river (Fig. 6), showing that some DOC

was transported downstream. As a consequence of the  $\Delta^{14}\text{C}$  enrichment, not present upstream of the lake, we suggest that the enriched DOC is likely from disturbance of sub-surface soil in the vicinity of Rostherne Mere, which is then transported to the outflow stream.

Major engineering works in the catchment to the west and north, during the construction of the A556 Bypass, began in 2014 and resulted in excavation of parts of the catchment to depths of several metres during 2015–2016. In the absence of any other plausible explanation, we suggest that this construction, which occurred ~ 300 m from the NW lake shore (Fig. 1), mobilised subsurface OC, which entered the lake and was incorporated into the DOC pool. Archaeological investigations were completed in advance of the road construction, which involved trial trenching (Highways Agency 2013). It is unclear whether such trenching would have caused soil disturbance that could explain the sediment  $\Delta^{14}\text{C}$  value at the top of the core, but it is clear that recovery measures under the Water Framework Directive and motorway construction have impacted carbon sources in Rostherne Mere water and sediment.

Although internal loading under seasonal anoxia maintains high phosphorus concentrations in the lake (Carvalho et al. 1995; Moss et al. 2005; Radbourne 2018), it is unlikely that mobilisation of DOC from lake sediments, observed from monitoring (Scott 2014) explains the unusual DOC results. If the bomb C was derived from remobilised lake sediment OC, we would also expect the signal to be evident in the uppermost sediment sample (~ 2014), lake POC, or DIC from bacterial metabolism of DOC (Kritzberg et al. 2006), as is evident in Lower Lough Erne DIC  $\Delta^{14}\text{C}$  values (Keaveney et al. 2015). The bomb signal in lake surface DOC also persisted beyond the estimated residence time of the lake (0.8 year; Radbourne 2018), indicating that <sup>14</sup>C inputs to the lake from disturbed soil were ongoing over the period of the study. As road construction was completed in March 2017, and the catchment soils stabilised as vegetation developed, this hypothesis could be tested by measuring <sup>14</sup>C in lake water and surface sediment C pools again in the near future, given the short water residence time of the lake.

## Sediment carbon composition

### *Establishment of catchment STWs*

At the approximate time of the establishment of the STWs, ca. 1935,  $\Delta^{14}\text{C}$  values in sediment at 50–51 cm from all three temperature fractions were depleted beyond what can be explained by the FRO (Fig. 7). Although we cannot definitively explain this  $\Delta^{14}\text{C}$  depletion, we suggest that it was caused by input of glacial soil/peatland that was disturbed during construction of the STWs or earlier projects, which, coupled with the large FRO, yielded the  $^{14}\text{C}$ -depleted sample. Lacey et al. (2018) observed a sharp increase in the sediment accumulation rate at that time in independently dated cores. Increased loading of recalcitrant terrestrial OC from old glacial soil/peat, which entered the lake from inflows that drained a disturbed catchment, could explain the sudden increase in DAR, as well as the apparent  $^{14}\text{C}$  age of the sample (i.e. before any bomb carbon effect). Our inability to analyse additional samples (e.g. soil/peat samples), precluded explanation of the  $\Delta^{14}\text{C}$  depletion in these sections of the core, but this remains an avenue for further research.

### *STWs and “bomb” carbon input*

During the operation of the STWs, sediment  $\Delta^{14}\text{C}$  values were enriched relative to samples at the base of the core (Fig. 7). At that time the atmospheric  $\Delta^{14}\text{C}$  was about + 500‰ (Levin et al. 2010). The high radiocarbon concentration of this input counteracted the FRO effect in the lake, causing enrichment of sediment  $\Delta^{14}\text{C}$  values relative to the bottom of the core, but they are still depleted relative to the 1970 atmosphere radiocarbon activity. This indicates that the terrestrially derived bomb carbon did not overwhelm the autochthonous FRO signal, demonstrating that labile carbon is derived from both allochthonous and autochthonous sources.

### *Recalcitrant carbon during the peak lake production phase*

After 1970, the proportion of recalcitrant carbon in sediment increased to 42–69% (Fig. 7). During the peak STW phase, inferred cyanobacteria-driven production and sediment accumulation rates were highest,

and the proportion of labile carbon in sediment decreased. The recalcitrant fraction during the peak STW phase (1980s) is in agreement with modern lake DIC  $\Delta^{14}\text{C}$  values. Terrestrial vegetation from the 1970s to 1990s (Fig. 7) would have bomb  $\Delta^{14}\text{C}$  values, which are not evident in the recalcitrant fraction. The slightly depleted  $\Delta^{14}\text{C}$  values from the peak STW phase indicate that, although thermally stable vascular material derived from terrestrial/emergent aquatic plants may contribute to this recalcitrant carbon fraction, the larger fraction was from submerged aquatic material that utilised DIC and incorporated an FRO.

### *Post-STW closure*

After sewage was diverted in 1991, pigment analyses and diatom counts indicate that the phytoplankton community changed, with an increase in diatom abundance (Figs. 2 and 3). At that time, the percentage of labile carbon in sediment began to rise and  $\Delta^{14}\text{C}$  values became somewhat more depleted (Figs. 6 and 7), indicating an increase in autochthonous carbon deposition, likely the result of greater diatom sedimentation. Nevertheless, overall organic carbon accumulation rates declined. The proportion of labile organic carbon in sediments, 25 years after sewage diversion, is still far lower than it was before the STWs opened (Fig. 7), emphasising that the lake has not yet returned to a pre-STW phase in terms of its C dynamics, consistent with observations that it is on a slow path of recovery to oligotrophy (Radbourne 2018).

In  $\sim$  2010 (6 cm), however,  $\Delta^{14}\text{C}$  values became enriched once more (labile  $400^\circ\text{C}$   $\Delta^{14}\text{C} = -85 \pm 3.6\text{‰}$ ) and the proportion of recalcitrant carbon again rose (Figs. 6 and 7). This may also be explained by the input of bomb carbon. As discussed earlier, DOC  $\Delta^{14}\text{C}$  values from Rostherne Mere water collected in this study were all positive ( $> 200\text{‰}$   $\Delta^{14}\text{C}$ ). This carbon entering the DOC pool is derived from sub-surface soil carbon that contains bomb carbon from the 1960s through the 1980s (CaliBomb; Reimer and Reimer 2004; Levin et al. 2010). After 2010, sediment with enriched  $\Delta^{14}\text{C}$  values indicates that a small amount of allochthonous carbon, derived from subsurface soil carbon containing bomb radiocarbon, is present in both the labile and recalcitrant OC fractions. Lacey et al. (2018) found that the

predominant source of terrestrial carbon entered the lake via DOC from soil. The DOC  $\Delta^{14}\text{C}$  results in this study show that in 2016, inputs came from sub-surface catchment OC. Whereas lake DOC largely appears to be transported downstream, rapid deposition of OC from a shallow subsurface catchment source may explain this slight increase in  $\Delta^{14}\text{C}$  values at the top of the sediment core. As we have argued, construction of the A556, which began in 2014, and associated soil disturbance, can explain the unusual water DOC  $\Delta^{14}\text{C}$  values measured in this study. Although the scope of this study precluded analysis of terrestrial catchment material, developments in the region and soil disturbance during environmental impact assessments ca. 2010 can be invoked to explain these recent sedimentary excursions in  $^{14}\text{C}$  activity.

## Conclusions

Organic carbon accumulation in Rostherne Mere sediment over the last century was largely regulated by autochthonous production (both labile and recalcitrant), although sources of allochthonous C were significant at times, influenced by sewage discharge and road development in the catchment. Recent highway construction allowed lateral transfer of allochthonous carbon from the catchment, as evidenced by DOC  $\Delta^{14}\text{C}$  values. Construction, overloading, and eventual closure of the sewage treatment works, and diversion of sewage from the basin, marked changing phases of lake productivity and organic carbon accumulation.

Application of SCR analysis to C pools in lake water and lake sediments, coupled with analyses of diatoms and pigments in lake deposits, can shed light on sources of C within the lake-catchment system today and in the past. These novel methods can help identify sources of carbon in lake sediment and determine whether they are stored in sediment, or transported downstream. Lakes and their catchments are threatened by multiple anthropogenic impacts (e.g. directly through construction and development, and indirectly through effects on nutrient loading), which affect both allochthonous and autochthonous C pools. Identification of carbon sources in sediment can clarify whether catchment inputs promote carbon burial, and whether additional allochthonous inputs are stored in sediment. Stepped Combustion

Radiocarbon analysis can determine the quantity and character of carbon sequestered in sediment and as such is a uniquely valuable tool in freshwater carbon-cycle analysis.

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