Long-term perspectives on terrestrial and aquatic carbon cycling from palaeolimnology

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Abstract
Lakes are active processors and collectors of carbon (C) and thus recognized as quantitatively important within the terrestrial C cycle. Better integration of palaeolimnology (lake sediment core analyses) with limnological or modelling approaches has the potential to enhance understanding of lacustrine C processing and sequestration. Palaeolimnology simultaneously assimilates materials from across lake habitats, terrestrial watersheds and airsheds to provide a uniquely broad overview of the terrestrial-atmospheric-aquatic linkages across spatial scales. The examination of past changes over decadal-millenial timescales via palaeolimnology can inform understanding and prediction of future changes in C cycling. With a particular, but not exclusive, focus on northern latitudes we examine the methodological approaches of palaeolimnology, focusing on how relatively standard and well tested techniques might be applied to address questions of relevance to the C cycle. We consider how palaeolimnology, limnology and sedimentation studies might be linked to provide more quantitative and holistic estimates lake C cycling. Finally, we use palaeolimnological examples to consider how changes such as terrestrial vegetation cover, permafrost thaw, the formation of new lakes and reservoirs, hydrological modification of inorganic C processing, land use change, soil erosion and disruption to global nitrogen and phosphorus cycles might influence lake C cycling.
Introduction
Quantification of the terrestrial carbon (C) cycle is paramount to understanding global climate change, and lakes, as “landscape chimneys”, play a key role in terrestrial C processing {Prairie, 2008 #2505}. Most lakes are considered to be net C sources to the atmosphere, emitting carbon dioxide (CO2) and methane (CH4), and are highly active C processing hotspots {Kling, 1992 #2682} {Hanson, 2004 #2487} {Prairie, 2008 #2505} {Tranvik, 2009 #2604}. Yet lakes also simultaneously sequester C in their sediments, comprising one of the largest stores of organic C (OC) on the continents {Dean, 1998 #1921} {Stallard, 1998 #2516} {Alin, 2007 #2665} {Cole, 2013 #2543}. A major challenge therefore exists in trying to quantify relative rates of C evasion versus sequestration in lakes and the influence this has on C fluxes from land, through river basins and to the ocean. Global estimates suggest that annual net lake C evasion exceeds sequestration and inland waters receive 1.9 Pg C yr⁻¹ from streams and rivers of which 0.2 Pg C yr⁻¹ accumulates as sediment, 0.8 PgCyr⁻¹ is evaded to the atmosphere and 0.9 Pg C yr⁻¹ is delivered to the oceans {Cole, 2007 #2472}, although the rates of C evasion in lakes {Tranvik, 2009 #2604} and rivers {Raymond, 2013 #2589} might be higher. Therefore the “active pipe model” highlights that lakes are not simply passive vessels for C transport, but play a critical role in C processing of sufficient magnitude to alter regional C budgets {Cole, 2007 #2472}. In this review we outline the contribution that the long-term and integrative perspective offered by palaeolimnology can make in understanding the complex interplay of physical, chemical and biological processes, which influence these C pathways in lake ecosystems.

C within lake ecosystems can be separated into four major pools (Box 1). Dissolved inorganic C (as CO2) may be fixed into organic form by autotrophs (through photosynthesis or chemosynthesis; autotrophy), and reciprocally organic C can be oxidized/ mineralised through physical, chemical and biological (e.g. respiration; heterotrophy) processes to CO2 (aerobic conditions) or CH4 (anaerobic conditions). The balance of these processes determines whether organic and inorganic C entering a lake is emitted to the atmosphere as a gas, incorporated into the particulate C pool to be collected in sedimentary deposits or exported downstream. Understanding how these processes will change in the future is key to calibrating the terrestrial C cycle {Prairie, 2008 #2505}. One way to address this issue is to use the past as an analogue for future scenarios. Palaeolimnology, the investigation of lake sediments, provides a direct methodology for documenting C inventories in water bodies. Furthermore, through sediment proxies (Figure 1) it is possible to identify past changes in C flux from land to lake as well as gaining qualitative insights into the ways in which it is processed. Distinctive from most limnological approaches, which often focus solely on pelagic measurements (in the water column), palaeolimnology integrates C from all components of the catchment and lake ecosystem, including the benthos. Because benthic production accounts for a large proportion of primary productivity in many lakes {Vadeboncoeur, 2002 #1057} {Ask, 2009 #2657} this integration has the potential to provide a more holistic overview of changes in whole-ecosystem C processing, which can be used to refine regional C budgets {McGowan, 2009 #2671}.

One major unresolved question is how processing of terrestrial C within lakes and wetlands will alter with future global environmental change, because this may be an important feedback for greenhouse gas production or sequestration. Common approaches to this question use surveys across latitudinal gradients to understand how lakes process C within different biomes {Cole, 1994 #2693} {Jansson, 2000 #2634}. This “space for time substitution” approach can provide analogues for how lakes function within different
climatic, edaphic and biogeochemical circumstances, and thus guide likely trajectories of future change. Such approaches are, however only achievable in areas with high lake density and so have been focused in northern latitudes, where the majority of lakes occur {Verpoorter, 2014 #2675}. Spatial surveys are only partially satisfactory for investigating C cycling because many other factors co-vary spatially, particularly between mid-high latitudes where the major climatic and vegetation transitions occur {Tranvik, 2009 #2604} {Sobek, 2007 #1968}. For example, seasonal change in daylength differs substantially between temperate-arctic areas but most measurements of lake C processing have been conducted in boreal and temperate regions, which retain daylight during the winter and have greater anthropogenically-derived nutrient burdens {Elser, 2009 #2694}. The under ice period is important because heterotrophy dominates leading to major CH4 degassing during the ice melt period {Tulonen, 1994 #2656} {Michmerhuizen, 1996 #2658} {Striegl, 1998 #2737}, but little is known of under ice processes, particularly in artic lakes {Hampton, 2015 #2626}. Therefore half or more of the annual lake C cycle within the Earth’s most lake-rich regions is probably inadequately quantified {Verpoorter, 2014 #2675}. Whereas spatial comparisons have limitations for projecting future change in individual regions, the temporal approach of palaeolimnology has the potential to address some of these issues, especially when combined with comparisons across landscapes {McGowan, 2011 #2735} {Anderson, 2014 #2728}.

How can we measure “C cycling” using palaeolimnology?

C cycling is a rather general term, but understanding the role of lakes within the terrestrial C cycle requires knowledge of lake C pools and the processes that alter relative shifts between them. Lake sediments sequentially archive material from the watershed, airshed (allochthonous) and lake environment (autochthonous) allowing direct comparison of how terrestrial, atmospheric and aquatic processes are coupled through time (Figure 1). Although not implicitly process-based, well designed palaeolimnological studies, which use a selection of well chosen proxies are able to address many questions of relevance to C cycling. The section below focuses on routinely applied standard palaeolimnological techniques.

(a) C inventories

Palaeolimnology can directly measure the amount of C sequestered within lacustrine basins (the C standing stock) and variability in past rates of C accumulation. Sedimentary C content can be estimated through by loss-on-ignition (LOI) after burning at 550 °C (organic) and 925 °C (carbonate) following corrections for C content {Heiri, 2001 #2662} {Dean, 1974 #1067}, or via an elemental analyzer on acidified (to remove inorganic carbonates) or non-acidified sediments {Meyers, 2001 #1846}. These straightforward methods estimate the relative C in organic and inorganic (usually carbonate) forms versus minerogenic material (including biogenic silica) {Tenzer, 1997 #2663}. In areas where lake formation dates are known, regional estimates of lake C stocks are possible using lake morphometry and volumetric density-corrected calculations of sediment {Dean, 1998 #1921} {Campbell, 2000 #2541} {Kastowski, 2011 #2628}. Sediment cores dated using a combination of 210Pb, 137Cs, radiocarbon (14C) and other techniques can be used to quantify changes in the C accumulation rate (CAR), for an overview of changes in C processing over longer timescales {Anderson, 2009 #2664}. Most palaeolimnological studies are based on a single sediment core taken from the deepest central part of the basin where sediment focusing occurs (fine particles are preferentially deposited in deeper parts of the lake basin) {Anderson, 1989 #292}. Estimates of whole-basin CARs require correction for sediment focusing, which can be achieved in recent sediments using the ratio of sediment 210Pb flux: regional atmospheric 210Pb flux {Anderson, 2013 #2466} {Anderson, 2014 #2676} or through multiple coring {Kortelainen,
2004 #2570}. Seismic surveys are informative in larger or deeper lake basins with heterogeneous sediment coverage {Kortelainen, 2004 #2570} {Ferland, 2012 #2480} {Lowag, 2012 #2666}, or where gas hydrates might be important for C budgets {Vanneste, 2001 #2667}.

(b) Morphological “fossil” macro- and micro-scopic remains
Terrestrial pollen, spores and plant macrofossils provide a relatively direct assessment of land vegetation cover {Prentice, 2011 #2738} and, by inference, the presence of allochthonous C pools, soil development and precipitation (Figure 1). Therefore these proxies may be used to estimate the potential for changes in dissolved organic C (DOC) runoff or soil erosion into lakes {Heggen, 2010 #2668} {Leng, 2012 #2464}. Other allochthonous and wind-borne morphological remains indicative of processes relevant to C-cycling may derive from coal-fired power stations, which emit soot particles and pollutants {Rose, 1996 #2669}, or from fires on land, which release charcoal into lake air- and watersheds {Whitlock, 2001 #2670}. Many autochthonous primary producers in lakes leave identifiable remains in sediments, especially diatoms (frustules), chrysophytes (cysts and scales), cyanobacteria (kinetes), dinoflagellates (cysts) and the chlorophyte alga *Pediastrum* (cell walls) {Bunting, 2007 #1637}. If fluxes are quantified from dated cores a provisional estimate of changes in primary productivity of the source organism is possible {Anderson, 1995 #2672}. However, sedimentary remains are only a remnant of the original community because of decomposition and differential preservation, and some remains such as cysts are formed during particular life stages {Ryves, 2001 #786}. Therefore, most estimates of past microfossil flux are used to infer relative measures of productivity changes through time rather than whole-basin estimates (c.f. {Anderson, 1989 #292}). Nevertheless estimation of microfossil flux is a relatively straightforward but under-utilized technique to quantify variability in autochthonous C sequestration rates by individual groups of biota. Numerous primary and secondary consumers also leave sedimentary remains (e.g. chironomids, cladocera, orabatid mites, sponge spicules {Smol, 2002 #2629}). Indicator taxa tolerant to oxygen stress (e.g. *Chironomus*) can be used to infer hypolimnetic anoxia, which has implications for sediment C preservation and methanogenesis {Brodersen, 2004 #2736}. Using a combination of proxies it is possible to reconstruct paleo-food webs {Rawcliffe, 2010 #2673} to infer past changes in lake functioning. For example, major shifts between benthic and pelagic primary and secondary production in shallow lakes can infer changes in major habitats for autotrophic C production, processing and energy flows {Davidson, 2010 #2674} {Wiik, 2015 #2731}.

(c) Biochemical indicators of C processing
Many morphological remains decompose before deposition in sediments and in these cases biochemical markers (biomarkers) may be used as sedimentary proxies {Meyers, 1993 #2500}. These may include chlorophyll and carotenoid pigments, indicative of certain algal and bacterial groups (e.g. cryptophytes, cyanobacteria) and used to estimate autochthonous primary production {McGowan, 2013 #2677}. Some bacteriochlorophylls and carotenoids from obligate anaerobic photosynthetic bacteria (e.g. Chlorobiaceae, Chromatiaceae) can be used to infer anoxia, with associated implications for the preservation of sedimentary C. Other ultraviolet radiation (UVR)- screening pigments such as scytonemin and derivatives are produced by some microbes on exposure to UVR and so their production relative to other pigments can quantify water staining by coloured dissolved organic matter (CDOM) {Leavitt, 1997 #340}. Other lipid biomarkers include a range of hydrocarbons and carboxylic acids, alcohols and ketones, which can be used as individual biomarkers e.g. dinostanol (a steryl chlorin ester biomarker for dinoflagellates) {Tani, 2002 #1245}, phenolic compounds (from coniferous trees) {Meyers, 1993 #2500}, hopanoid biomarkers from heterotrophic bacteria
Inventories, Whils macrofossil palaeoproductivity of aquatic macrophyte remains have been used to reconstruct depletions of chironomids due to their fresh metabolic CO₂ release (including OM deposition). Although the basis of these correlations remains unclear, near infra-red spectroscopy (NIRS) is a non-destructive spectral measure of sediment properties which correlates with lake water column DOC concentrations at the time of sediment deposition, although the basis of this correlation remains uncertain. C stable isotopes are widely used in palaeolimnology and whilst the principles underlying isotopic fractionation are theoretically well understood, interpreting bulk (c.f. organism-specific) lake δ¹³C ratios in sediment profiles requires thorough understanding of the lake-catchment system. Sedimentary δ¹³C can be measured within the organic (δ¹³Corg) and inorganic (δ¹³Cinorg) sediment fractions and may record shifts in terrestrial/aquatic contributions to the lake basin and changes in process (including diagenesis) (Galman, 2008 #2482) (Tolu, 2015 #2806). For example δ¹³C values in dissolved inorganic C (DIC) fixed during photosynthesis may depend on lake-atmosphere CO₂ exchange, algal productivity rates and decomposition of terrestrial OM into DIC, which is then incorporated into algal material (Maberly, 2013 #2499). DIC derived from CH₄ depleted δ¹³C ratios that may be effectively incorporated and preserved in the head capsules of chironomids (Van Hardenbroek, 2013 #2641) (Frossard, 2014 #2642) and the δ¹³C values of aquatic macrophyte remains have been used to reconstruct HCO₃⁻ concentrations (Herzschuh, 2010 #2648). Changes in catchment vegetation (e.g. C₃ versus C₄ plants) are also important drivers of sedimentary δ¹³Corg (Wooller, 2003 #2680), but extraction of isotopes from isolated organic fractions such as leaf waxes can refine terrestrial vegetation reconstructions (Huang, 2001 #2679). Biogenic silica (BSi) analysis is a rapid alternative to microfossil analysis for quantifying sedimentary concentrations from siliceous biota (Conley, 1988 #71) and the fractionation of stable silicon isotopes δ³⁰Si can indicate palaeoproducivity (Panizzo, 2015 #2632). Radiocarbon dating of terrestrial plant macrofossil and contemporary sediments frequently show offset ages (Björck, 1998 #63). Whilst these discrepancies are regarded as troublesome for deriving accurate chronologies, they are informative about past lake water equilibration with atmospheric CO₂ and incorporation of “old” C from the catchment (e.g. through permafrost melt), which can become incorporated into sedimentary OM (Dutta, 2006 #2681).

Quantitative integration of palaeolimnology and limnology
The examples above describe how palaeolimnology can be used to directly quantify lake C inventories, changes in C accumulation rates and changes in the materials accumulated in
lake basins, thus playing a major role in understanding C sequestration and associated processes (Figure 2). Improvements in the application of palaeolimnology might be achieved by a more critical consideration of sediment redistribution and focusing processes {Hilton, 1986 #2798} which need to be accounted for when comparing sediment accumulation rates among different lakes {Anderson, 2013 #2466}. However, quantitative interpretation of palaeolimnology also requires stronger integration with limnology and sedimentation studies. Commonly, linkages between the sediment record and limnological conditions are established by correlating limnological conditions with sediments through space or time. For example, more C is generally sequestered in productive than unproductive lakes (c.f. 11 m of sediment in Denmark with 2 m Greenland over the Holocene; {Bradshaw, 2005 #1602} {Anderson, 2009 #2664}). However, direct correlations between lake productivity and C sequestration are far too simplistic because they ignore the roles of allochthonous C delivery, the processes, which cause decomposition and preservation of C in the water column and sediment focusing. Measurements in the water column and sediments can complement palaeolimnological observations to facilitate improved interpretations. Below we explore how lake sediments are formed and the processes that change them during and after deposition in the sediments to consider how this influences the interpretation of the C cycle using palaeolimnology.

Sedimentation of C first requires production of particulate C which is composed of sources from inside and outside of the lake. Allochthonous POC can be significant components in lake sediment records from erodible catchments with organic soils {Turcq, 2002 #2688} {McGowan, 2008 #1694} {Kortelainen, 2004 #2570} whereas in-lake production of POC depends strongly on internal lake processing. Up to 95% of DOC may be removed from lake pools by photochemical mineralization to CO₂, which in turn is influenced by physical processes such as lake mixing {Forsius, 2010 #2700} {Cory, 2014 #2545}. It is not possible to directly measure such gaseous emissions from lakes using palaeolimnology, but sediments may provide a means of validating and guiding limnological measurements. For example, sedimentary δ¹³C analyses might identify whether methanogenesis is likely to be important to the overall lake C budget to suggest whether temporally discontinuous gas measurements, are effectively capturing all relevant processes {Eller, 2005 #2702} {Cole, 2013 #2543}. Microbrial processing of DOM also provides a pathway for POC (sediment) production because heterotrophic organisms utilize DOM as an energy source and are an important component of the POC pool {Jansson, 2007 #2809}. Heterotrophic consumption of DOM releases nutrients (“the microbial loop”), which can fertilize growth of autotrophic algal POC, but productivity rates are moderated by light absorption by CDOM {Tranvik, 2009 #2604}. Each of these POC sources is available for consumption and incorporation into higher parts of the lake food web {Marcarelli, 2011 #2636}. These factors interact to determine the overall composition, abundance and fate of the POC pool, and hence the sediment record that is ultimately preserved and thus detectable by palaeolimnology {Hanson, 2011 #2486} {Kritzberg, 2014 #2492}.

Sedimentation studies demonstrate that only a small fraction of the C fixed or processed in lakes ends up in sediments {Leavitt, 1993 #259} {Cuddington, 1999 #617}. For example approximately 90% of algal pigments and 85% of C is oxidized before leaving the epilimnion so that ca. 6% of C reaches lake sediments {Meyers, 1993 #2500}. Models describe how lake depth and morphometry greatly influences these values because shorter sinking times for seston provide fewer opportunities for mineralization and so incorporation of C should be most efficient in shallow lakes {Cuddington, 1999 #617} {Sobek, 2009 #2597} resulting in greater C sequestration rates {Ferland, 2012 #2480}. Counteracting this is the influence of
BIOTURBATION, RESUSPENSION, OXYGENATED SEDIMENT CONDITIONS AND GENERALLY FASTER Flushing RATES THAT EXIST IN SHALLOWER LAKES, WHICH CAN ENHANCE DEGRADATION AFTER DEPOSITION AND ENCOURAGE EXPORT FROM THE LAKE THEREBY REDUCING C BURIAL EFFICIENCY {KRISTENSEN, 1992 #913} {DONG, 2008 #2729} {MACKAY, 2012 #2701}. LAKE MORPHOMETRY IS ALSO IMPORTANT BECAUSE C SEQUESTRATION VARIES SPATIALLY WITHIN BASINS, WITH SEDIMENT FOCUSING IN THE DEEPER AREAS DISTAL FROM DEGRADATION PressURES IN THE LITTORAL Zone {DEN HEYER, 1998 #2689} {ANDERSON, 1990 #293}. SUCH PROCESSES ARE HIGHLY RELEVANT FOR C Budgets IN LAKE-RICH LANDSCAPES BECAUSE MOST LAKES GLOBALLY ARE SMALL AND SHALLOW {VERPOORTER, 2014 #2675}. BENTHIC ALGAL PRODUCTION USUALLY EXCEEDS PLANKTONIC PRODUCTION IN SHALLOW LAKES BUT THE RELATIVE INFLUENCE THAT THIS HAS ON C SEQUESTRATION IS POORLY QUANTIFIED {VADEBONCOEUR, 2002 #1057}. BECAUSE SOME PALEOLIMNINLOGICAL PROXIES SUCH AS DIATOMS CAN INDICATE RELATIVE PLANKTONIC: BENTHIC PRODUCTION FOR COMPARISON WITH C SEDIMENTATION RATES, SEDIMENT CORE ANALYSES PROVIDE A SIMPLE MEANS TO QUANTIFY HOW BENTHIC-PELAGIC BALANCES INFLUENCE NET C SEQUESTRATION.

ANOTHER IMPORTANT PROCESS TO BE CONSIDERED IS CHANGES TO THE SEDIMENT RECORD FOLLOWING DEPOSITION {COLE, 2013 #2543}. MOST SEDIMENT DECOMPOSITION OCCURS IN THE FIRST FIVE YEARS AFTER DEPOSITION (E.G. AROUND 20% OF THE C AND 30% OF THE N IS MINERALIZED OVER THIS TIMESCALE) {Cuddington, 1999 #617} {Galman, 2008 #2482} {Sobek, 2014 #2616}. SELECTIVE LOSS OF NITROGENOUS OM IN THE UPPER SEDIMENTS REFLECTS THE LABILITY OF COMPOUNDS SUCH AS PROTEINS AND CHLOROPHYLLS IN COMPARISON TO TERRESTRIAL MATERIALS SUCH AS LIGNINS AND CELLULOSE {Cranwell, 1976 #275}. BELOW THIS ZONE THE PRESERVATION OF SEDIMENTARY OM IS MORE STABLE {Cuddington, 1999 #617}, AND THEREFORE MANY LAKE C SEQUESTRATION STUDIES EXCLUDE THE LESS STABLE UPPER CA. 10CM OF SEDIMENT BECAUSE IT IS UNREPRESENTATIVE {AndERSON, 2013 #2466}. MINERALIZATION OF C IN LAKE SEDIMENTS IS POSITIVELY CORRELATED WITH LAKE TEMPERATURE, WITH PROJECTED FUTURE TEMPERATURE INCREASES LEADING TO A 4-27% DECLINE IN LAKE OC BURIAL {GUDASZ, 2010 #2485}. HOWEVER, WARMING ALSO INCREASES THE DELIVERY OF PELAGIC OC TO SEDIMENTS, WHICH MAY OFFSET A REDUCTION IN BURIAL EFFICIENCY OF OC FROM MINERALIZATION {KRITZBERG, 2014 #2492}. THE IMPORTANCE OF THE SEDIMENT-WATER INTERFACE IN METHANOCESIS IS ALSO BECOMING MORE WIDELY RECOGNIZED {ELLER, 2005 #2702} {COLE, 2013 #2543}. IN THE LIGHT OF THESE COMPLEX AND INTERACTING PROCESSES, PALEOLIMNOLOGY IS ABLE TO INTEGRATE NET C SEQUESTRATION UNDER DIFFERENT CLIMATIC CONDITIONS TO PROVIDE AN OVERVIEW OF LIKELY C SEQUESTRATION TRAJECTORIES. FOR EXAMPLE, COMPARISONS OF HOLONIC SEDIMENT CORES IN AN UNDISTURBED REGION OF GREENLAND SHOW THAT MEAN C ACCUMULATION RATES (CARs) DO NOT DIFFER SUBSTANTIALLY BETWEEN WARMER AND COOLER PERIODS, SUGGESTING THAT ALTHOUGH C PRODUCTION AND MINERALIZATION RATES MIGHT HAVE CHANGED, OTHER FACTORS THAT INFLUENCE C SEQUESTRATION (E.G. LAND TO LAKE DOC FLUX, C PRODUCTION CHANGES ASSOCIATED WITH WATER LEVEL FLUCTUATIONS) HAVE COMPENSATED FOR THEM {ANDERSON, 2009 #2664}. THIS IS SUPPORTED BY HOLONIC CORE SURVEYS IN EUROPE AND NORTH AMERICA THAT ATTRIBUTE FLUCTUATIONS IN CARs TO LAND USE RATHER THAN CLIMATE {KASTOWSKI, 2011 #2628}. THESE EXAMPLES DEMONSTRATE HOW CARs IN COMBINATION WITH SUPPORTING MULTI-PROXY PALEOLIMNOLOGICAL ANALYSES CAN BE USED TO INVESTIGATE MECHANISMS ASSOCIATED WITH CHANGES IN CARs. COMPARING AND INTEGRATING LAKE MEASUREMENTS OF WATER COLUMN PRODUCTIVITY/MINERALIZATION RATES AND SEDIMENT DECOMPOSITION PROCESSES WITH PALEOLIMNOLOGICAL MEASUREMENTS PROVIDES MORE HOLISTIC LAKE C BUDGETS AND THE POTENTIAL TO IDENTIFYING COMPONENTS (SUCH AS BENTHIC AND UNDER-ICE ACTIVITIES) THAT MIGHT BE MISSING OR UNDER-ESTIMATED.

Global environmental change and the C cycle
Many global environmental change (GEC) processes which influence lakes and their watersheds operate on timescales that cannot be effectively addressed with using ‘real-time’ physiological, limnological or sedimentation measurements (Figure 2). Palaeolimnology can be used to understand GEC processes retrospectively where lakes were not measured and provides information on the decadal-millennial timescales which are relevant to many GEC processes. The next section considers possible future trends in C dynamics in lakes, with examples of how lake sediment records can be used to understand the fate of C within changing terrestrial-aquatic systems.

(a) Climate-driven vegetation changes

Climate change can alter the type and density of terrestrial vegetation cover (Tape, 2006 #2805) with implications for the availability and quality of C transported (usually as DOC) from land to water {Sobek, 2005 #2515} {Marcarelli, 2011 #2636} {Lapierre, 2012 #2493}. As the northward spread of shrubs into tundra regions indicates, vegetation biomes are changing and will continue to change with future warming {Bhatt, 2010 #2698} {Tape, 2011 #2518} {Cahoon, 2012 #2699} {IPCC, 2013 #2199}. Climate also affects DOC delivery to lakes by altering precipitation and flow paths, which are themselves influenced by soil and vegetation development {Hanson, 2011 #2486} {Kothawala, 2014 #2572}. These influences on C cycling are evident when comparing lakes over different biomes (Figure 3). Some of the differences in lake C processing described in Figure 3 can be detected in surface sediments of lakes collected across vegetation transitions indicating the potential for palaeolimnology. Pollen and macrofossils are well established indicators of terrestrial vegetation used to identify vegetation assemblages on regional to continental scales {Prentice, 1996 #2651}. NIRS analysis of surface sediments demonstrates that DOC concentrations are lower in Swedish lakes above treeline (e.g. Figure 3b) compared to those with forested catchments where the DOC supply is more abundant (Figure 3a) {Rosén, 2000 #572}. In line with this observation, relative abundance of algal UVR-screening compounds are higher (clearer water) and C:N ratios lower (less terrestrially derived C) in surface sediments of lakes above treeline {Reuss, 2009 #1836}. Presence of tree cover appears to suppress autotrophic production (measured as sedimentary pigments) in lakes with forested catchments, because light is limited in brown-stained lakes {Reuss, 2009 #1836} {Jansson, 2000 #2634} {Sobek, 2003 #2512}. Lakes with limited catchment soil and vegetation development (e.g. Antarctic, High Arctic and montane lakes; Figure 3d) often have extremely low DOC concentrations and UVR-screening pigments such as scytonemin can form a significant proportion of the sedimentary pigment assemblage {Michelutti, 2002 #2808} {Hodgson, 2004 #1509} {Verleyen, 2005 #1986}. These spatial surveys validate the utility of certain palaeolimnological proxies in detecting the presence and effects of vegetation cover around lakes.

Such spatial observations are reflected in temporal changes of sediment records. In montane lakes that have transitioned between forested and alpine conditions, scarcity of vegetation-derived DOC inhibits primary production through UVR damage during alpine periods {Leavitt, 2003 #1482}. This response is more subtle in Swedish lakes at boreal-tundra treeline where low-intermediate DOC concentrations allow autotrophic production by increasing light availability, but due to greater baseline DOC abundance no UVR-screening pigments are produced {Reuss, 2010 #2027}. Treeline changes in the Tamyr Peninsula, Russia increased the fluxes of terrestrial derived C (with low δ13C values) during warmer and more humid conditions in the earlier Holocene and increased autochthonous uptake of CO2 (with high δ13C values) when treeline retreated {Wolfe, 1997 #752}. Similarly at Kharinei Lake, (NE Russia) spruce forest expansion coincided with high NIRS-inferred DOC
concentration in the water column and after tree-line retreat, optical transparency of the lake increased {Jones, 2011 #2635}. As well as promoting DOC delivery to lakes, enhanced precipitation promotes mire formation (inferred from pollen and peat studies) and both processes can control lake water total organic C (TOC), pH (inferred from diatoms) and colour (inferred from NIRS) {Rosén, 2007 #2508}. Fire frequency (measured as charcoal) is also important in removing catchment vegetation and, despite temporary charcoal inputs, leads to lower lake-water TOC concentrations {Rosén, 2007 #2508}. This and other studies suggest that the simple presence of vegetation is not always the primary driver of lake C processing. For example shrub expansion in the Alaskan tundra had less influence on lake biota (diatoms and chironomids) than flooding caused by thermokarst expansion {Medeiros, 2014 #2580}. Similarly, fluxes of terrestrial DOC and POC (measured as C:N ratio and macrofossils of *Coenococcum, Sphagnum* and *Empetrum*) in lakes from Greenland increased during the wetter Neoglacial conditions, but changes in lake C processing (as δ13C) were most pronounced where changes in lake hydrological balance (and hence C delivery) were greatest {Leng, 2012 #2464}. Together these palaeolimnological studies argue that precipitation/hydrology (delivery of DOC) might have a greater influence than vegetation cover (availability of DOC) {Engstrom, 1987 #2478} over lake C fluxes and processing {Medeiros, 2014 #2580} {Kokfelt, 2009 #2489}, providing guidance on how conceptual models developed from spatial observations (Figure 3) might be further developed.

(b) Permafrost thaw

In the next century substantial near-surface permafrost degradation is projected to occur and thaw depth will increase {IPCC, 2013 #2199}. Permafrost soils store immense amounts of frozen C, but warming threatens to activate that store {Kling, 1992 #2682} {Walvoord, 2007 #2732} {Frey, 2009 #2650} {Grosse, 2011 #2484} {Schuur, 2008 #2739}. The presence of water bodies and wetland areas is a key control on C processing in permafrost areas as it can shift frozen C sinks into C sources {Yvon-Durocher, 2014 #2652} {Nauta, 2015 #2613}. Thermokarst ponds and lakes form on peaty soils or on yedoma (deep deposits of ice-rich silt) across large parts of Siberia, Alaska and Canada when thawing of frozen ground results in volume loss and mass failure of the land surface {Lee, 2011 #2496}. These water bodies are active sites for methanogenesis and CO2 ebullition {Abnizova, 2012 #2640} and may have released sufficient quantities of CH4 to influence global thermal forcing {Walter, 2007 #2610} {Packalen, 2014 #2614}. However, over the past 15,000 years some estimates suggest that thaw lakes have buried more C than they emitted {Sobek, 2014 #2616} {Anthony, 2014 #2457}. Although much permafrost research has focused on C-rich areas of the Arctic and subarctic, many Arctic areas (e.g. High Arctic, polar deserts) currently have thinly developed soils due to exceptionally low temperatures, low productivity and a lack of liquid water. In the High Arctic, as temperature increases, and soils develop they are expected to become net CH4 {Jørgensen, 2015 #2703} and CO2 {Lupascu, 2014 #2615} sinks. Consequently, the High Arctic has the potential to remain a strong C sink when other permafrost regions are transformed to a net C source as a result of future warming {Lupascu, 2014 #2615}.

Permafrost thaw should increase the influx of C (DOC and POC) and other nutrients to lakes (Figure 3). Indeed, palaeolimnological records of δ13C and organic δ15N imply greater fluxes of N as well as C from soils into lakes when hydrological pathways are open {Wolfe, 1997 #752}. Thermokarst processes that increase flooding cause greater DIC and N influx into lakes (as recorded by higher δ15Norg and lower δ13Corg) leading to changes in aquatic biota {Medeiros, 2014 #2580}. In contrast with these predictions, limnological analyses show that lakes with thermokarst slumps are clearer and have lower nutrient concentrations than ones
without slumps [Mesquita, 2010 #2733] [Thompson, 2012 #2603] and palaeolimnology shows that periphytic diatom abundance and diversity increases after slumping suggesting that water gets clearer [Thienpont, 2013 #2602]. After formation of thermokarst ponds, DOC concentrations systematically decline and C pools in waters shift from soil-derived to autochthonous (algal-derived) [Pokrovsky, 2011 #1935]. These studies suggest that there is no simple and synchronous lake response to permafrost melt and highlight the need for systematic regional-scale palaeolimnological investigations, although the issues for sediment dating in such studies in permafrost areas where “old C” is actively redistributed need addressing [Bouchard, 2011 #2691].

(c) Formation of new lakes
Glacial recession, as projected over the next century [IPCC, 2013 #2199] could form entire lake districts with exceptionally lake-rich landscapes. Palaeolimnology shows that newly exposed land surfaces after glacial recession have very specific characteristics. Carbonate can be abundant in certain glacial deposits and weathering of this material is intense in the first few centuries after recession [Engstrom, 2000 #698] [Norton, 2011 #2705]. Sediments deposited shortly after the formation of a small lake (SS2, South-west Greenland) are predominantly composed of carbonate because active weathering sequesters CO$_2$ as HCO$_3^-$ [Tank, 2012 #2517] resulting in very high (>30g C m$^{-2}$ yr$^{-1}$) CARs in this early period (Figure 4a). Newly created lake waters are usually ion-rich and, if receiving glacial meltwater have a high loading of glacial flour leading to high minerogenic sedimentation rates [Anderson, 2012 #2395]. DOC is usually scarce because of the absence of terrestrial vegetation and thus the water is very UVR transparent with glacial flour scattering the light and creating an environment suited to cyanobacteria with UVR-screening pigments [Leavitt, 2003 #1482] [Anderson, 2008 #1693]. Marl-secreting charophytes often thrive in these early post-glacial base-rich conditions and diatom diversity is low [Birks, 2000 #746]. However, this condition is reliant on the availability of alkaline glacial till material and may not characterise areas of non-carbonate geology or non-erosive glacial regimes [Jones, 1989 #1696] [Michelutti, 2007 #2339]. Generally though, OC production shortly after lake inception is focused within benthic areas, and limited to specialized taxa but IC sequestration is often dominant. After this initial period of rapid inorganic C sequestration, which usually lasts a few centuries, soil development (dependent on climate) begins to influence lake C processing [Fritz, 2004 #2654] [Norton, 2011 #2705]. Lake catchments in humid climates may develop thick peaty soils, which are a rich DOC source, but the delivery of C to lakes depends on hydrological pathways (e.g. permafrost presence, delivery of groundwater, podsolization) [Fritz, 2013 #2557]. The consequences of this successional change are that lake water pH and calcium (Ca) usually decline whereas C and N increase [Engstrom, 2000 #698]. Although the effects of this on overall C fluxes are unknown, it is clear from Lake SS2 that C sequestration declined five-fold after soil development (Figure 3a). Along with soil development, vegetation succession can influence C cycling by impeding sediment transport from land [Dearing, 1991 #2706] and influencing N availability through presence of N$_2$-fixing plants such as alder [Engstrom, 2006 #2653].

Palaeolimnology is also well placed to investigate lakes formed in other ways. Holocene connectivity between land and sea has altered through relative sea level changes [Holmes, 1998 #2787] including glacio-isostatic adjustments [Bradley, 1996 #247] [Willén, 2001 #2786] leading to isolation of lake basins from the sea. Most palaeolimnology studies to date have focused on reconstruction of past sea levels using isolation basins [Long, 1999 #2789]. However, marine-freshwater transitions cause fundamental changes in ecosystem structure such as changes in water residence time and stratification, nutrient limitation, and biota.
Major transitions in sediment stratigraphies show that isolation basin sediments are more C-rich than marine basins {Long, 2011 #2790} and physical connectivity with the sea influences C accumulation rates in coastal fjords {Lewis, 2013 #2788}. Reservoir creation through damming has greatly altered C fluxes from land to sea through the trapping of sediments {Rosenberg, 2000 #2793}. Reservoirs can be a particularly important methane source, especially when reservoirs flood land vegetated with C-rich soils, particularly in the tropics {Fearnside, 2005 #2794} {Barros, 2011 #2811}. Reservoir sediment accumulation is strongly correlated with reservoir methane production, highlighting a role for palaeolimnology in tracking potential changes in methane fluxes {Maeck, 2013 #2803}. As reservoirs get older, intensity of C processing from the flooded terrestrial OM may subside and be replaced by autochthonous production dependent on external nutrient supply {Hall, 1999 #538}. There is great potential to explore these issues using palaeolimnology, but issues associated with heterogeneous sedimentation in the disturbed reservoir environments must be considered {Tibby, 2010 #2795} {Teodoru, 2013 #2800}.

(d) Hydrological change and inorganic C processing

Inorganic C dynamics are important components of the C cycle in saline and hard-water lakes {Tranvik, 2009 #2604} {Marcé, 2015 #2730}. Allochthonous IC sources to lakes usually depend on catchment geology and surficial deposits with groundwater inputs being important in limestone regions {Webster, 2000 #1267} {Hodell, 2005 #2707}. Calcium carbonate (CaCO₃) can form directly from photosynthesis if soluble Ca²⁺ ions are present causing “lake whiting” during phytoplankton blooms (Equation 1). In this case CaCO₃ precipitates around algal cells because the alkaline microenvironment caused by photosynthesis causes cells to act as nucleation sites {Schultze-Lam, 1997 #2620}. This process is an effective vector for particulate inorganic C (PIC) deposition into sediments and can be enhanced during warmer years in some lakes {Hodell, 1998 #2621}. Several types of aquatic plants are also well known for CaCO₃ (marl) precipitation and can be important contributors to the sediment C sink {Wiik, 2013 #2708} {Pukacz, 2014 #2734}. Inorganic precipitation and sedimentation of carbonates can also occur in lakes through simple concentration, which is common in closed-basin (endorheic) lakes that lack an outflow and become saline when there is a precipitation deficit {McGowan, 2003 #1093} (e.g. Figure 4b). Sustained CaCO₃ precipitation may cause lake waters to become dominated by sulphate rather than bicarbonate {Gorham, 1983 #2709} and this process also has implications for lake-atmosphere C fluxes because it causes CO₂ enhancement of lake water at high salinities {Barkan, 2001 #2623}:

\[
Ca^{2+} + 2HCO_3^- = CaCO_3(s) + CO_2(aq) + H_2O
\]  

[Equation 1]

These precipitation legacies preserved in lake sediments as PIC are useful in explaining present day patterns in water chemistry {Anderson, 2001 #603}. Saline lakes (>1000 μS cm⁻¹ conductivity and comprising one fifth of the global lake surface area) are considered especially important in the C cycle {Duarte, 2008 #1933} because CO₂ exchange with the atmosphere is chemically enhanced (by up to three-fold) by hydration reactions of CO₂ with hydroxide ions and water molecules in the lake boundary layer {Wanninkhof, 1996 #2710}.

Palaeolimnology shows that past climate changes had a marked influence on IC cycling in many lakes, especially endorheic basins that are particularly responsive to climate {Last, 2002 #2618}. Lake hydrological closure often leads to deposition of sediments that are more enriched in carbonates, as external sedimentary inputs decline {Verschuren, 2001 #2711}. However, higher relative abundance of IC may not necessarily translate to an increase in C sequestration rates (Figure 4). Concentration of lake waters through hydrological closure can increase carbonate sequestration and induce a switch from calcite to aragonite deposition as
lake closure progresses {Valero-Garcés, 1997 #739}, but excessive evapo-concentration may cause a switch from carbonate to gypsum (CaSO.2H2O) {Hodell, 2005 #2707}. In-lake processes such as meromixis and localized evaporation at lake margins can also affect ratios of calcite: gypsum deposition {Last, 2002 #2618}. Transition from prairie to forest in North America around 4000 years ago led to the abrupt loss of annual carbonate-C laminations and predominantly organic C burial in hydrologically-closed lake basins {Dean, 1999 #2548} {Dean, 1998 #1921}. The converse transition from forest to prairie close to this region led to heavier δ13C in sedimentary carbonates indicating that less DIC was derived from isotopically light terrestrial sources or lake primary producers {Valero-Garcés, 1997 #739}.

(e) Land use change and soil erosion
Land disturbance by humans has altered C sequestration in lake basins for millennia in many regions {Evans, 2013 #2479} {Einsele, 2001 #2712}, and over mid- to late-Holocene timescales humans can have a greater impact on sediment loads than climate {Dearing, 2003 #2713} {Kastowski, 2011 #2628} {Anderson, 2013 #2466}. Agricultural development alters vegetation cover and hydrological pathways, e.g. via land drainage {Foster, 2003 #2714}, and so can directly influence DOC and POC fluxes to lakes {Enters, 2006 #2715}. For example, lakewater TOC concentrations in Sweden have been extensively influenced over the past ca. 500 years by changes in agricultural practices {Cunningham, 2011 #2546} {Meyer-Jacob, 2015 #2639}. Sediment delivery following major human impact can increase 5–10-fold {Dearing, 1991 #2706} {Dearing, 2003 #2713}. Although erosion of C-rich soils might enhance CARs in lakes, the relationship between lake C cycling and soil erosion is rarely this simple because erosion associated with the removal of forest cover often leads to minerogenic inwash (registered as higher sedimentation rates and lower sedimentary C content). Soil erosion is also often associated with eutrophication, which increases autochthonous OC production {Enters, 2006 #2715} (Figure 5). Therefore, abrupt increases in sediment accumulation rate often follow on from land disturbance, but it is unclear whether they result in increased CARs as much of the input is minerogenic {Battarbee, 1978 #2624} {Leavitt, 1999 #348} {McGowan, 2012 #2177}. Many tropical regions are now experiencing major land disturbance associated with development which, when associated with intense monsoon rains, may have a significant influence on allochthonous POC loads {Kim, 2000 #2697}.

A major indirect effect of land disturbance is that nutrients are more efficiently transferred from the land to lakes, and/or applied as fertilizers in intensive agricultural regimes. The resultant change in lake nutrient balances can fuel a greater proportion of algal-derived C as algal growth is fertilized (Figure 5) {Moorhouse, 2014 #2716}. Hence, OC and diatom accumulation rates increased after Medieval land disturbances in Sweden {Anderson, 1995 #2717}. Changes to land cover may also influence sediment C preservation because sediment laminations sometimes cease after removal of forest cover indicating greater physical mixing in the water column {Fritz, 1989 #154} {Scully, 2000 #874}. In contrast, bottom-water anoxia may be initiated by lake catchment disturbance, as occurred with early native Iroquoian horticultural activity (AD 1268-1486) in North America {Ekdahl, 2004 #1422}. Meta-analysis of multiple sediment cores has shown that agricultural intensification has increased C sequestration rates up to 8-fold in lakes from North America {Heathcote, 2012 #2564} {Anderson, 2013 #2466} and Europe {Anderson, 2014 #2676}, although increases in Europe have been sustained for longer throughout the 20th century. Therefore in highly
disturbed mid-latitude regions (30-50°N), human induced burial of C in lakes generally exceeds that driven by climatic changes.

(f) Disruptions to lake biogeochemistry
The chemical balance of many lakes has been greatly altered through the delivery of human-derived pollutants during the Anthropocene {Lewis, 2015 #2718}. To service human population growth and urban expansion, lakes have been used as receptacles for sewage or sewage effluent {Edmonston, 2005 #1665}. Unprocessed sewage has a high OM content and so may stimulate heterotrophic bacterial activity and CO₂ efflux from lakes. Secondary-treated sewage effluent has less OM but remains enriched in nitrogen and phosphorus which fertilize autotrophic algal growth and so CO₂ uptake. The apparent benefit of enhancing C sequestration capability of lakes through fertilization is, however, offset by reduction in water quality and other ecosystem services {Jeppesen, 2000 #863}, and general resilience of lakes to be forced into net autotrophy {Cole, 2000 #1469}. However, it is clear that relatively more sediment OM derives from autochthonous sources after lake fertilization {McGowan, 2012 #2177} (Figure 5). Increased sedimentation rates are a positive feedback for enhancement of OM preservation {Cuddington, 1999 #617}, but severe sediment anoxia can lead to methanogenesis, which may cancel out the C sequestration benefits {Hollander, 2001 #2655} {Deines, 2006 #2719}. In shallow lakes, fertilization can stimulate planktonic production at the expense of benthic plants and algae, which are very efficient C sequesterers {Vadeboncoeur, 2003 #1167}. These compensatory whole-ecosystem effects are very difficult to monitor using standard limnological techniques and here sedimentary analyses can provide a useful overview {McGowan, 2005 #1679}. Lake eutrophication can shift algal communities over longer timescales, as described by the Si depletion hypothesis {Schelske, 1995 #1822} whereby P fertilization initially stimulates diatom production and sedimentary C sequestration, but long-term burial of Si leads to eventual replacement of siliceous algae with cyanobacteria {Anderson, 1989 #292}. As well as creating a water quality issue, little is known of the effects on mass C sequestration of such changes in algal communities.

Major modifications to the N cycle through fossil fuel combustion and artificial fertilizer production have led to the fertilization of many remote lakes through atmospheric deposition. Palaeolimnology has highlighted the widespread nature of this issue using ¹⁵N stable isotopes as tracers {Holtgrieve, 2011 #2720}. It is estimated that 1.0-2.3 Gt C yr⁻¹ of terrestrial C storage may have been stimulated by anthropogenic increases in nitrogen deposition in the past century {Schindler, 1993 #2721}, but lakes are not well integrated into this estimate, despite the knowledge that N deposition can significantly modify lake ecology and, hence, C sequestration potential {Wolfe, 2001 #1826} {Hu, 2014 #2722}. Atmospheric pollution also causes acidification of surface waters in poorly buffered acid-sensitive regions {Schöpp, 2003 #2723}, leaving strata of soot particles and metal pollution in lake sediments {Rose, 1996 #2669} {Jones, 1990 #2724}. Acidification makes lake waters more transparent because it coagulates, bleaches and oxidises coloured DOM {Schindler, 1996 #2725} {Molot, 1996 #2502} and therefore alters habitat availability for lake biota {Findlay, 1999 #507} {Frost, 2006 #2726}. Palaeolimnology shows how acidification-induced water clarity increases (traced using UVR pigments) lead to either expansion of benthic algal growth (increased C sequestration) {Vinebrooke, 2002 #1025} or when acidification is extreme, suppression of algal production through UVR damage {Leavitt, 1999 #160}. Acidification can also lead to long-term Ca depletion in lakes, altering lake biota, with implications for IC cycling {Jeziorski, 2015 #2727}. In recent decades, there is evidence for widespread lake water browning through increasing DOC concentrations, as lakes recover from acidification
across North America and Europe {Monteith, 2007 #1762} {Solomon, 2015 #2807}. Understanding how such processes interact with the recovery of in-lake biota and other stressors will be critical in quantifying changes in lake C processing in the future {Curtis, 2014 #2692}.

Conclusions
Many of the routine methods and techniques used in palaeolimnological studies can contribute to the interpretation of terrestrial-aquatic C cycling. Previous palaeolimnological studies applied to address other research questions often present findings which are of relevance to C cycling and there is scope for further exploitation of this knowledge base. In comparison with limnological techniques, palaeolimnology has the specific advantages of being able to address questions on timescales of relevance to many GEC processes and of providing information that integrates spatially (habitat-lake-watershed-airshed) and temporally (annual-decadal). This integrative perspective is highly valuable in identifying which sources and processes might be quantitatively important to overall lake C budgets and in directing where limnological investigations need to be focused. Palaeolimnology techniques are well suited to quantifying C sequestration rates in lake basins but, unlike limnological techniques, cannot be directly used for indicating gas fluxes. However, closer integration of limnology and palaeolimnology together with quantitative sediment trap studies is key to providing holistic and quantitative understanding of lake C cycles and their relevance for earth system processes.

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References

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Figure 1: Schematic showing the origin and processing pathways of commonly used palaeolimnological proxies in lake sediments (orange), including the influence of modifications by anthropogenic and natural processes (agriculture, fossil fuel combustion and changes in terrestrial vegetation cover). C pools in lake waters (blue) include PIC (particulate inorganic carbon), DIC (dissolved inorganic C), POC (particulate organic carbon) and dissolved organic carbon (DOC).

Figure 2: Conceptual model illustrating how palaeolimnology integrates with other methodologies in quantification of terrestrial-aquatic C cycling, and the elements that can be best quantified by each method (arrows). The width of the shapes indicates how widely the methodology has been applied at each timescale and the intensity of shading indicates the relative frequency that each type of technique has generally been applied. The majority of C cycling studies in lakes thus far have focused on physiological/chemical and limnological processes, although there are a growing number of palaeolimnological studies dedicated to this topic. In comparison there are fewer quantitative studies of C sedimentation using techniques such as sediment traps to understand whole lake C budgets; such studies are vital to bridge the gap between palaeo/limnological methods. Timescales of operation for a range of global environmental change processes discussed in the latter half of the review are presented for comparison.

Figure 3: Representation of how temperature and precipitation influence DOC fluxes and processing within lakes and watersheds from mid-high latitudes during the summer ice-free growth periods of different climatic zones (after {Mulholland, 2002 #2503}). The size of the arrows indicates the relative flux or influence of each component. In “humid and warm” boreal regions with forest cover (a) lakes are generally net heterotrophic because allochthonous DOC from terrestrial vegetation and soils is the dominant lakewater C pool, staining waters brown, limiting light penetration for autotrophic photosynthesis and providing an energy source for heterotrophs (“the microbial loop”) {Molot, 1996 #2502} Sobek, 2003 #2512} {Tranvik, 2009 #2604}. (b) In cooler regions above treeline with high-moderate precipitation (e.g. shrub tundra, tundra heath) where permafrost restricts DOC transport and low temperatures impede terrestrial vegetation decomposition {Sjögersten, 2009 #2741} {Pries, 2012 #2506}, lake waters with intermediately-coloured with DOC {Pokrovsky, 2011 #1935} and lakes are usually weakly heterotrophic. (c) In areas of low precipitation with warm growth season temperatures (e.g. continental interiors with prairie/steppe or savannah vegetation), terrestrial vegetation growth and external DOC transport is limited by moisture availability, recalcitrant and colourless DOC characterises the lakewaters {Anderson, 2007 #1712} {Hanson, 2011 #2486} {Kothawala, 2014 #2572} and DIC is usually the most abundant C pool in waters {Finlay, 2015 #2740} leading to optimal conditions for autotrophic production. (d) In cold regions with low precipitation and minimal vegetation development (High Arctic, polar deserts, montane) allochthonous DOC sources are scarce and nutrients may strongly limit autotrophic processes with the C (and nutrient) budgets often supplemented by wind-blown dusts {Barrett, 2007 #2684}. Severe lack of DOC may limit algal growth through UVR damage {Bothwell, 1994 #2394} {Hodgson, 2004 #1509}. Note
that the diagram represents only growth season conditions, and complete estimates lake autotrophy/heterotrophy must include the winter period which is usually ice-covered.

Figure 4: Inorganic and organic C accumulation rates (not focusing-corrected) over the past ca. 8000 years in (a) freshwater Lake SS2 {Anderson, 2008 #1693} and (b) closed-basin oligosaline lake Braya Sø {McGowan, 2003 #1093} which are located with a few kilometres of each other in the Kangerlussuaq area of West Greenland. The high inorganic calcium carbonate deposition around 8000 years ago Lake SS2 sediments is most likely cause by intense weathering of carbonate minerals derived from glacial till, which declined when soils established. The absence of this feature in Braya Sø indicates heterogeneity of carbonate deposition in this area. Afterwards, mean uncorrected CARs were similar in both lakes, but the much greater variability in Braya Sø is caused by fluctuations in water levels, and hence altered conditions for organic C production and deposition, including periods of anoxia in the bottom of the lake when autotrophic purple sulphur bacteria (that leave purple bands in the sediment- inset) were important in C processing. Distinct carbonate laminations in the Braya Sø sediments (inset) indicate periods of intense IC deposition, and yet IC is proportionally much less important than OC in these sediments. In both lakes, although there was a transition from warmer to cooler conditions ca. 4500 years ago, this had little impact on CARs; instead it appears that the hydrological balance had a greater impact on CAR in the closed-basin and hydrologically-sensitive Braya Sø.

Figure 5: Sediment core measurements from Blelham Tarn, a small lake in the English Lake District taken from {Moorhouse, 2014 #2716} showing changes in (a) OC burial rates (focusing corrected) and loss-on-ignition (LOI) at 550°C as an estimate of the % organic content and (b) concentrations of the cyanobacterial pigment aphanizophyll expressed relative to the organic content of the sediment. The proportional increase in aphanizophyll relative to OM in the sediment indicates that cyanobacteria associated with lake eutrophication, became proportionally more important within the lake C budget after ca. 1950 when piped water and sewerage systems were installed in the village within the lake catchment. The general increase in CAR started before 1950 and is associated with agricultural intensification, with peak CARs during the 1980-90s associated with high livestock densities, and soil erosion. Soil erosion led to a decline in LOI, due to dilution of the %OM by minerogenic material, but the CARs show that it had the net effect of stimulating C burial, probably from enhanced eutrophication. The upper sediments have very high LOI, possibly due to incomplete C degradation, but also because of the decline in soil erosion when livestock densities were reduced.
Box 1: Forms of carbon in lake ecosystems

**DIC** - Dissolved inorganic carbon. Carbon dioxide (CO$_2$) is the major DIC pool and either passes into lakes from the atmosphere by diffusion, or is produced *in situ* by respiration and oxidation of organic material. When dissolved in water to form carbonic acid it can dissociate as follows dependent on pH:

\[
\text{CO}_2 (g) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+
\]

DIC is important for the C cycle because it links atmospheric and aquatic C pools.

**PIC** - Particulate inorganic carbon includes solid inorganic carbonate material, usually calcium carbonate (which can be produced as aragonite or calcite). In lakes PIC usually accumulates in sediments, but is sometimes found suspended in the water column when mass production by phytoplankton causes “whiting events”. PIC precipitation is common in lakes within carbonate-rich catchments and closed-basin lakes where salts accumulate. Charophytes commonly become encrusted in calcium carbonate deposits, sometimes called “marl”, which can be a significant component of the lake sedimentary C pool.

**DOC** - dissolved organic carbon includes molecules in water usually classified as < 0.45µm in size. Dissolved organic matter (DOM) is also used to describe organic material. Allochthonous DOM delivered to lakes is often brown-coloured (CDOM) deriving from partly decomposed terrestrial vegetation (cellulose and lignin) and soils including humic and fulvic acids, which are large molecules and smaller molecules such as amino acids, fats, proteins, carbohydrates with a low molecular weight. Autochthonous sources of DOC/DOM include lower molecular weight and usually colourless C compounds, many of which are released as metabolic by products by lake microbes and organisms. DOM is an important component of the terrestrial C cycle because it is highly mobile and therefore important for C transport and can be utilized by heterotrophic bacteria as an energy source.

**POC** - Particulate organic carbon (and particulate organic matter, POM) includes particles > 45µm, which exist in lakes either suspended in the water column or collected in the lake bottom as sediments. Autochthonous POM may include living organisms such as bacteria, phytoplankton, zooplankton and plants or detrital remains of decaying organisms. Allochthonous POM includes particulate matter such as vegetation remains and soil erosion washed into lakes and air-transported materials such as dust, pollen and particulate contaminants.
Fig 5