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Estimates of the remineralization and burial of organic carbon in Lake Baikal sediments.

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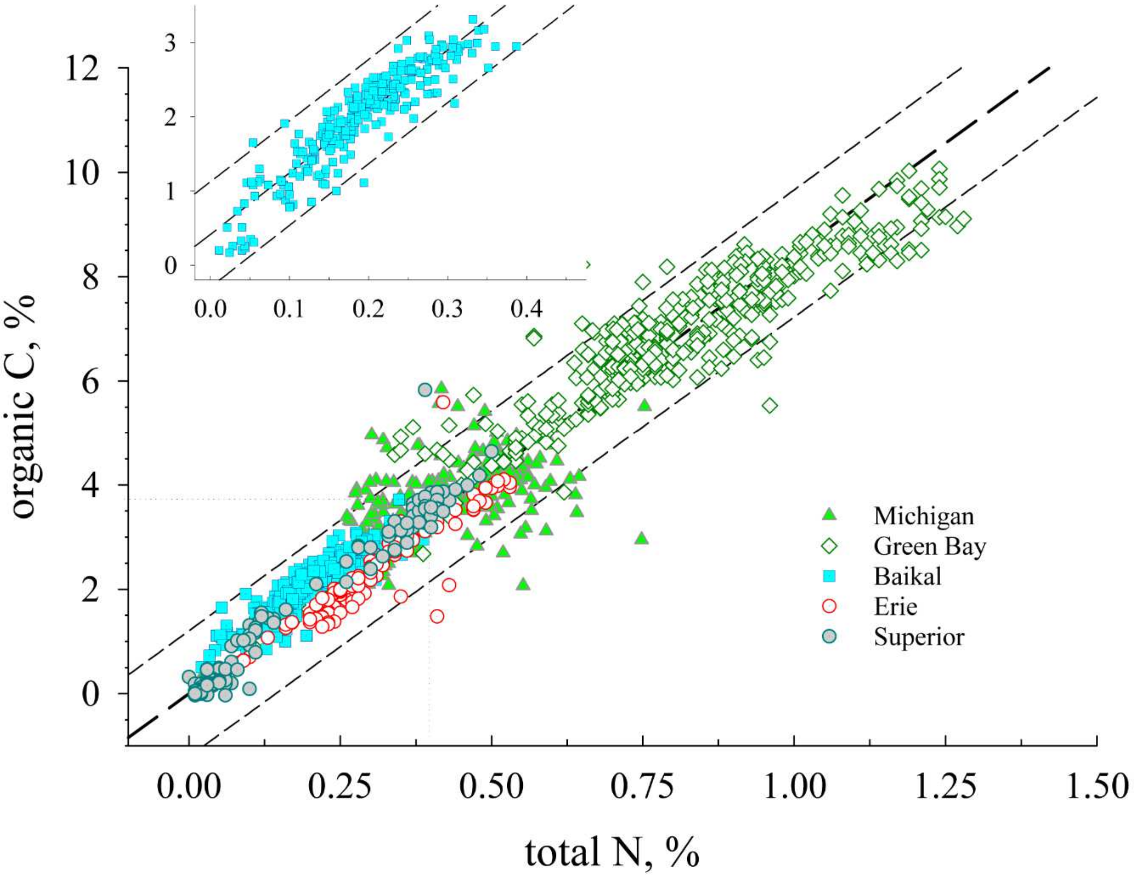
Graphical Abstract



Organic matter content of sediments in large lakes ranges from < 0.5% organic carbon to >10% (by weight) across a spectrum of oligotrophic to hypereutrophic environments. Lake Baikal (plotted alone in insert), the world's deepest (1640 m) and oldest lake, represents an oligotrophic end member on the low end of this range and is similar in this respect to Lake Superior. Sediments are an important sink in lakes and the remineralization of organic matter determines the efficiency with which carbon and other biogeochemically important elements are permanently buried.

Abstract:

Sediment cores collected from several stations throughout Lake Baikal in water depths from 100 meters off the Selenga River delta to the deepest basin of the lake (~1640 meters), have been analyzed for sedimentary organic carbon, nitrogen, and the remineralized components in pore water. The organic carbon content of surface sediments generally varied from 2.3 to 3.2% by weight, and profiles typically showed an exponential decrease in both organic carbon and nitrogen in the upper 20-30 cm of the sediment column. Steady state models of organic matter diagenesis yield first order decomposition rate constants which range from 0.0009 to 0.022 y^{-1}. The calculated residence times for the metabolizable fraction of the organic matter in these sediments increases roughly with increasing water depth and is on the order of 50 to 300 years. Pore water concentration profiles were determined for dissolved inorganic carbon, dissolved organic carbon (DOC), methane, and dissolved ammonium. At depth (25-30 cm) methane concentrations ranged from 50 to 800 umol L_{pw}^{-1} and DOC from 400 to 900 umol L_{pw}^{-1}. Estimation of carbon recycling rates based upon diffusion along pore water concentration gradients at the sediment-water interface, indicate that combined DOC and methane fluxes generally contribute < 15% of the overall turnover of sedimentary organic carbon. Comparisons to Laurentian Great Lakes environments show trends in sediment deposition, organic matter remineralization, and the time scales of carbon recycling across nearly two orders of magnitude with the fraction of organic content buried generally decreasing with decreasing sedimentation rates.

Key words: Lake Baikal, sedimentation, Great Lakes, carbon and nitrogen cycling

Introduction

In lakes, one of the principal sink terms in biogeochemical budgets for carbon is the deposition and burial, or storage, in permanently accumulating sediments (Cole et al., 2007; Dean and Gorham, 1998). The effectiveness of that sink is largely dependent upon how efficiently organic carbon is remineralized and released back into the overlying water as dissolved organic and inorganic carbon. In marine systems, depth generally translates to longer water column residence times, leading to decreasing fractions of newly produced organic matter exported to the bottom with increasing water depth (Arndt et al., 2013; Lutz et al., 2002; Suess, 1980). Similar to hemipelagic marine systems, large, deep lakes can have water and particle residence times on the order of years to decades. The fraction of the organic matter that ultimately reaches the bottom is dependent upon factors such as settling rates, temperature, and the nature and source of the organic matter itself. The importance of the sediment burial term in biogeochemical budgets for lakes has implications, for example, for whether systems behave as net sinks or sources of carbon to the atmosphere. Trends from autotrophic to increasingly heterotrophic conditions with increasing latitude have been shown in lakes to follow an increasing reliance on allochthonous carbon sources and the percentage of annual primary production buried in sediments (Alin and Johnson, 2007). The extent of organic carbon remineralization is also correlated with the factors affecting exposure to aerobic respiration processes. Low organic carbon burial efficiencies have correlated with longer oxygen exposure times in sediments, which in Baikal have been estimated to range from 15 to >1000 years (Sobek et al., 2009).

The stoichiometry of organic carbon inputs relative to carbon sequestration and burial also determines, in part, the extent to which heterotrophic remineralization exceeds autotrophic production. For example, where carbon is preferentially preserved relative to phosphorus, if C:P ratios for organic matter inputs (either allochthonous or autochthonous) are less than that for burial (and export) then systems trend to be autotrophic (Hessen, et al. 2004; Maranger et al., 2018; Smith et al., 1987, 1991) In some cases it may be easier to construct a stoichiometric mass balance for carbon or nitrogen based upon a phosphorus mass balance since, in practice, inputs are notoriously difficult to measure, open to atmospheric exchange, and highly vary in time. The stoichiometry of those inputs, on the other hand, may be far less variable if the input source functions vary temporally more in magnitude than in composition (Klump et al., 2009).

Here we present data on carbon deposition, remineralization, stoichiometry, and recycling in sediments at a number of stations occupied in two expeditions to Lake Baikal in September of 1988 and 1991. The principal effort of these expeditions was determining the contemporary sediment accumulation rates using the relatively short-lived radionuclides ^{210}Pb and ^{137}Cs (Edgington et al., 1991). Since that time an extensive range of studies have examined sediments and sedimentary processes in Baikal including sediment budgets and mass balances (Callendar and Granina, 1997; Granina, 1997; Müller et al., 2005; Vologina and Sturm, 2017); pore water geochemistry (Granina et al., 2001, 2004, 2007; Maerki et al., 2006; Martin et al., 1998; Pogodaeva et al., 2007, 2017), diagenesis and mineralogy (Demory et al., 2005; Fagel et al., 2005; Och et al., 2012; Ryves et al., 2003; Torres et al. 2014); methanogenesis and methane cycling (Bukin et al., 2018; Pimenov et al., 2014; Zemskaya et al. 2010); unique freshwater gas hydrates, oil seeps, and mud volcanos (Groshkov et al., this issue; Krylov et al., 2008; Minami et al., 2014; Pogodaeva et al., this issue) and others. The objective here in determining the dissolved and particulate carbon and nitrogen components within sediments was to estimate the extent to which carbon is remineralized and released back into the overlying water, thus determining the relative magnitude of burial and the efficiency with which sediments serve as a carbon sink. Baikal sediments are compared here with a range of depositional environments found in the Laurentian Great Lakes. Within this range, Baikal represents an end member in the spectrum of organic carbon burial and regeneration rates in lakes that reflect the time scales of deposition, remineralization, and sediment age resulting from the lake's great depth and enhanced particle residence times in the overlying waters.

Study Site

Lake Baikal, the oldest (20-50 My) and deepest lake in the world, contains fully one-fifth of the world's surface freshwater (Galazi, 1993; Ivanov and Demonterova, 2009; Logatchev, 1993) and is renowned for its high clarity, purity and oligotrophic waters. It is home to thousands of unique species the majority of which (~80%) are believed to be endemic (Sherbakov, 1999; Timoshkin, 1995). With a surface area of 31,722 km^2, a length of 640 km and a maximum width of 79 km, Baikal is similar in size and morphometry to other other large rift valley lakes and contains ~7 km of sediment, the longest continental bound paleo-sedimentary record in the world (Kuzmin et al., 2001). In 1996 Baikal was declared a UNESCO World Heritage Site.

The lake consists of three major basins (Fig. 1), with the central basin containing the deepest sounding (~ 1640 meters), while the southern and northern basins reach maximum depths of 1461 and 900 meters, respectively. The average depth for the lake as a whole is 730 meters (Sherstyankin et al., 2006). Sediment accumulation rates determined from ^{210}Pb and ^{137}Cs geochronologies are low, with average sedimentation within these three basins over the last ~100 years of ~ 0.2 mm yr^{-1} (Edgington et al., 1991; Müller et al., 2005; Och et al., 2012; Roberts et al., 2018). Using measurements of chlorofluorocarbons, Weiss et al. (1991) demonstrated that unlike most temperate lakes which over-turn seasonally, only ~ 12.5% of Baikal's deep waters were estimated to be renewed annually, corresponding to a mean deep-water residence time of ~ 8 years. Based on the ^{137}Cs data, it was estimated that particle residence times were << 20 years (Edgington et al., 1991). Hypolimnetic oxygen concentrations are maintained at no less than 75% saturation, in keeping with the oligotrophic nature of the lake and the low level of organic matter supply to the bottom waters and sediments. Deep water oxygen depletion combined with the renewal rate resulted in a calculated offsetting rate of photosynthetic new production of 2.25 mol C m^{-2} y^{-1} (Weiss et al., 1991) consistent with oligotrophic conditions.

Materials and Methods:

Sample collection and analysis:

Sediments were collected throughout this study using a Benthos-type gravity corer (7.5 cm diameter), deployed from a deck winch aboard the RV Vereshchagin. Cores were generally

50-80 cm in length and several cores were taken at each station (Table 1). Separate cores were used for solid phase (including geochronology) and pore water analysis. For the former, cores were sectioned via a hydraulic extruder at 0.5 cm intervals to 4 cm, 1 cm intervals to 10 cm, 2 cm intervals to 20 cm, and 5 cm intervals for the remainder of the core. Some cores were sectioned at 0.5 cm intervals to 10 cm to facilitate radiometric dating. Stations ranged in water depth from 100 meters off the Selenga River delta to the deepest basin in the lake (Fig. 1). Depths recorded by the fathometer at the time are of questionable accuracy and therefore have been approximated, curtesy of Oleg Khlystov (pers. comm.), from our coordinates superimposed on recent bathymetry produced by multibeam survey data (http://lin.irk.ru/multibeam/en/) and the 2002 INTAS map (see Sherstyankin et al., 2006).

Sediment porosity was calculated from the weight loss upon drying at 60 C. assuming a dry sediment density of 2.45 g cm^{-3} (Edgington et al., 1991) and is within 2% of the value estimated from organic carbon contents (see Müller et al. 2005). Sedimentary carbon and nitrogen content were determined on a Carlo Erba 1106 CNS analyzer. Carbonate was removed for organic carbon determinations via the addition of 10% H_3PO_4 directly to the tin combustion cups (c.f. Nieuwenhuize et al., 1994). Total carbon and nitrogen were run on unacidified samples. Pore waters were sampled using a modification of the whole core squeezer apparatus described by Jahnke (1988) via porous (70 um) Teflon rods inserted at prescribed depths through Luer fittings on the side of the core to which sample syringes are connected via 3-way stopcocks. Pore waters were expressed directly into gas tight syringes without exposure to air and were suitable for methane analysis. The resolution of the squeezer is centered around each port spaced at 1 cm intervals to 4.5 cm, 2 cm intervals to 14.5 and 3 cm intervals to 32.5 cm. Dissolved phosphate and silicate (not reported) and dissolved ammonium were determined colorimetrically (Presley, 1971) on board the research vessel. Following collection, 2 mL aliquots were titrated with 0.01978 N HCl for total alkalinity using an electronic pipette with 0.5 uL precision and a Ross pH electrode calibrated using standard buffers. ΣCO_2 was calculated from alkalinity via the temperature dependent equilibrium constants (Skirrow, 1975) given by Butler (1982) for freshwater. Accuracy of titrations were checked against standard 1 mM solutions of Na_2CO_3. Dissolved methane was determined using a syringe gas stripping procedure on 5 mL replicates of pore water (Martens and Klump, 1980; McAuliffe, 1971) with flame ionization gas chromatography on a Carle 0111 GC calibrated with known (10 -100 ppm) standards. Dissolved organic carbon (DOC) was determined on pore water filtered through pre-combusted (350° C.) glass fiber filters (0.7 um), acidified with phosphoric acid and stored in pre-combusted glass vials until analysis by high temperature combustion on a Shimadzu 5000 total organic carbon (TOC) analyzer (Benner and Strom, 1993). Sulfate was determined on the filtered samples via liquid ion chromatography (Beckman) with a non-suppressed conductivity detector in our laboratory in the U.S.

Estimates of sediment deposition and burial:

Organic material incorporated into a depositional sedimentary environment is either degraded to soluble forms (remineralized) and released into the overlying water across the sediment-water interface, or it becomes a permanent component of the sedimentary deposit. In this simple formulation, the composition of the sedimentary organic matter may be considered initially to consist of two fractions, one which is permanently buried (G_{bur}) and one which is remineralized or metabolized (G_M). The organic matter deposited to the sediment is represented by the concentration at the sediment-water interface and is equivalent to the sum of these two fractions (G_O). The metabolizable fraction consists, in fact, of a suite of organic constituents which are remineralized over varying time periods determined by their susceptibility to metabolic processes and/or dissolution. This heterogeneity in diagenetic reaction rates is the basis for the "multi-G" models of Berner (Berner, 1980; Westrich and Berner, 1984) and others (Arndt et al., 2013; Boudreau, 1997). For the present purposes, however, where only net deposition and burial are of interest, G_M will be treated as the sum of all remineralized or recycled fractions of sedimentary organic matter and is estimated using the diagenetic expression for first order decomposition kinetics and steady state deposition and burial (Berner, 1980).

$$G_z = G^0_M \exp[(-k/w)*z] + G_{bur} \qquad (1)$$

Where G_z expresses the concentration of organic matter at any depth, z, as the sum of the nonregenerated residual (G_{bur}) and the amount of the initially deposited metabolizable fraction (G^0_M) remaining. k is the first order rate constant and w the mass sediment accumulation rate. In the Baikal sediments analyzed here, sedimentation rates were determined via radionuclide dating using ^{210}Pb and ^{137}Cs and reported by Edgington et al. (1991). The recycled fraction is equal to the difference between the total concentration at the sediment-water interface and the concentration at depth where values reach an asymptotic G_{bur}. The depositional flux ($J_{DEPOSITED}$), the burial flux (J_{BUR}), and the recycled flux ($J_{RECYCLE}$ or J_R) may be calculated for each profile from the concentration of these two end members when multiplied by the mass sediment accumulation rate (w, g cm^{-2} y^{-1}), e.g.

$$J_{RECYCLE} = J_{DEPOSITED} - J_{BUR} = w\,(G^0_M) = w\,(G_O - G_{BUR}) \qquad (2)$$

In fact, the decomposition rates vary with time, hence depth, as the more labile fractions are consumed and modes of remineralization shift to less energetic pathways. To account for this, Middelburg (1989) and Middelburg et al. (1993) presented a model for the decomposition of organic matter in marine sediments that considers organic matter as a whole. In this model the first-order rate parameters (k_t) gradually decrease with time.

$$dG_T/dt = -k(t)G_T \qquad (3)$$

assuming k is constant over an interval dt, k_t can be calculated by:

$$k_t = 1/dt * \ln(G_t/G_{(t+dt)}) \qquad (4)$$

where G_t is the organic matter concentration at a certain time, or in this case depth. The residence time of organic matter in the water column will vary, and the "age" of material when it reaches the sediment-water interface will therefore vary. Empirical results for laboratory studies and profiles of organic matter vs. depths with known ages, produced a relationship found to be valid over 8 orders of magnitude (Middleburg, 1989):

$$k_t = 0.16\,(a+t)^{-0.95} \qquad (5)$$

where a is the apparent initial age and t is the time since the onset of decomposition. Profiles of organic carbon and total nitrogen content were best fit using an error minimization procedure to equation 1, as well as the power function of Middleburg (1989) for estimation of values for G_O, G_{BUR}, and the calculation of apparent initial age (eqn. 5).

Sediment-water pore water gradient supported fluxes:

The fluxes (J) supported by pore water concentration gradients were calculated using Fick's first law, modified for sediments to include an additional pore water burial term (Berner, 1980), although the latter is negligible in Baikal sediments where sedimentation rates are relatively low, and may be ignored, i.e.,

$$J = -\phi_O D_S [dC/dz] + \phi_O C_O \omega_O \qquad (6)$$

where ϕ_O, C_O, and ω_O are the porosity ($cm_{pw}^3 \, cm_{sed}^{-3}$), concentration (mmol L_{pw}^{-1}), and linear sedimentation rate ($cm_{sed} \, y^{-1}$) at the sediment-water interface, respectively. Concentration gradients [dC/dz] were estimated by a simple linear regression or by curve fitting the concentration profile with the general diagenetic exponential (Eq. 1) extrapolated to the sediment-water interface [z=0]. Concentrations at the interface determined by these fits for ΣCO_2, for example, were 1.039 +/- 0.130 mmol L_{pw}^{-1} in good agreement with published bottom water concentrations (Bukin et al., 2018; Falkner et al., 1991, Krylov et al., 2008; and others). Whole sediment diffusivities, D_s, were calculated from molecular diffusion coefficients, D, at ambient temperature (Li and Gregory, 1974) and corrected for tortuosity using the porosity at the sediment-water interface via the relationship, $D_s = \phi^2 D$ (Ullman and Aller, 1982). Molecular diffusivities for DOC were estimated via the relationship to molecular weight given by Burdige et al. (1992), assumed here to be ~1000, consistent with recent measurements in the Laurentian Great Lakes (O'Loughlin and Chin, 2004). Temperature dependence of DOC diffusivities is assumed to follow the Stokes-Einstein relation for slow diffusing constituents (Li and Gregory, 1974). Whole sediment diffusivities used for dissolved inorganic carbon, methane, DOC and ammonium were 0.603, 0.812, 0.160, and 1.06 x 10^{-5} $cm^2 \, sec^{-1}$, respectively.

Results and Discussion:

Sediment pore waters:

The remineralization of the organic matter in sediments proceeds via a complex series of decomposition reactions coupled to microbially mediated oxidation through the well-known sequence of terminal electron acceptors – O_2, NO_3^-, Mn^{4+}, Fe^{3+} and $SO_4^=$, followed by methanogenesis and fermentation (Froelich et al., 1979; and others). The remineralized by-products of organic carbon decomposition, dissolved inorganic carbon, methane and dissolved organic carbon, are released into the interstitial pore waters of the sediment where they may diffuse or advect back into the overlying water often driven by steep concentration gradients. Total dissolved inorganic carbon (ΣCO_2) in sediment pore waters in these Baikal sediments varied from ~1 mmol L_{pw}^{-1} at the sediment-water interface up to 2 mmol L_{pw}^{-1} at 15 to 30 cm depth in the cores (Fig. 2). DOC concentrations in pore water, over this same interval, generally increased from < 200-300 umol L_{pw}^{-1} at the interface to 400-900 umol L_{pw}^{-1} at depth (Fig. 3). Sediments at all stations at which methane concentrations in pore water were measured, showed detectable methane within 4-10 cm of the sediment-water interface, and methane concentrations ranged from 0.2 umol L_{pw}^{-1} at the interface to as high as 50 to 800 umol L_{pw}^{-1} at 25-30 cm (Fig. 3). Methane concentrations were typically higher below the zone of sulfate reduction, and the presence of concave profiles probably reflect both aerobic and anaerobic oxidation in the upper few cm (Bukin et al., 2018; Lomakina et al., 2018; Pimenov et al., 2014; Torres et al., 2014). Subsurface methane gradients would generally, if oxidized, support ~10% of the ΣCO_2 flux across the sediment-water interface. Much higher methane concentrations, in excess of 10 mmol L_{pw}^{-1}, have been found in gas hydrate-bearing sediments and in areas of oil seeps at depths up to 100 cm (Bukin et al., 2018; Lomakina et al., 2018; Pimenov et al., 2014; Zemskaya et al., 2010). Pore water concentrations of dissolved ammonium also indicate active nitrogen regeneration (Fig. 2, see also Maerki et al., 2006; Müller et al., 2005; Pogodaeva et al., 2017).

Estimates of carbon recycling rates based upon Fick's law calculations of diffusion across pore water concentration gradients at the sediment-water interface (eqn. 6) are given in Table 2. ΣCO_2 fluxes calculated range from 38 to 900 mmol m^{-2} y^{-1}. DOC fluxes range from 10 to 63 mmol m^{-2} y^{-1}, and methane fluxes range from 1.2 to 41 mmol m^{-2} y^{-1}. ΣCO_2, therefore, represents the major recycling flux (75-95%) of the carbon back into the overlying water. DOC and methane represent an average of 10% and 2% respectively of the total carbon regenerated.

In addition to this relative composition, the stoichiometry of sedimentary organic matter remineralization may also be estimated. Berner (1977) demonstrated that stoichiometry can be deduced from the concentration of the remineralized elements released to pore water. Assuming steady state diagenesis, and including the effects of differential diffusion and adsorption, the carbon to nitrogen ratio may be estimated from ΣCO_2 and NH_4 in pore water from the expression:

$$ {}^{C}\!/_{N\ remin} = d\Sigma CO_2/dNH_4 \cdot \frac{\omega + kD_s^C}{\omega\,(1+K_N)+kD_s^N} \qquad (7) $$

where ω is the linear sedimentation rate (here ~ 0.02-0.04 cm y^{-1}, Edgington et al., 1991), K_N the adsorption coefficient for the reversible ion exchange of ammonium on to sediment particles (= 1, Klump et al., 2009; Machin and Aller, 1984; Rosenfeld, 1979), k the first order steady state decomposition rate constant (~0.012 y^{-1}, Table 3, eqn.1), and D_s^x the whole sediment diffusivity, corrected for tortuosity, of 1.0 and 0.6 x 10^{-5} cm^2 sec^{-1}, for dissolved ammonium and inorganic carbon, respectively. In this instance, the calculated ratio is relatively sensitive to the effects of differential transport, but not for the correction for adsorption. ΣCO_2 vs. NH_4 concentrations are shown in Fig. 4 for stations within each basin. Variability amongst stations is high; but nevertheless, estimates of the $C{:}N_{remin}$ ratio vary from an average of 6.6 to 9.2 to 7.8 in the Central, Northern and Southern basins, respectively. A regression of all the combined data yields an average calculated C:N ratio of ~8 (r^2 ~ 0.53). Considering the addition of methane and DOC would add another 12% to the estimated C:N stoichiometry for the metabolizable fraction, or approximately 7.3, 10.2 and 8.6, for the Central, Northern and Southern basins, respectively. These values may be used to cross check a sedimentary mass balance for deposition and burial because the change in C:N with depth should be consistent with the C:N stoichiometry of the remineralized fraction.

Organic carbon deposition and burial

During steady state diagenesis the concentration of organic carbon is expected to decrease with time and age of the sediment. Inspection of sedimentary organic carbon and nitrogen profiles in Baikal shows the generally expected exponential decrease in concentrations typically within the upper 10-20 cm of the sediment column (Fig. 5). At the mass sediment accumulation rates determined for these cores (2 to 22 mg cm^{-2} y^{-1}, Edgington et al., 1991), this represents extrapolated ages of 100 to over 600 years at 10 cm depth (Fig. 6). The estimated values for G_o and G_{bur}, (Tables 3 and 4) were then used to impose limits for organic carbon and nitrogen deposition, burial and benthic remineralization and recycling (eqn. 2). Values for the Laurentian Great Lakes of Superior, (perhaps the most closely aligned with Lake Baikal in terms of trophic status), the main basins of Lake Michigan, and the eutrophic sediments of Green Bay are shown for comparison (Table 3).

The average burial rate for organic carbon estimated here is 233 and 93 mmol C m^{-2} y^{-1} for the southern and central basins respectively, and ~ 160 mmol C m^{-2} y^{-1} for all stations, (Table 2). This agrees well with Müller et al. (2005) estimates of 220 and 125 mmol C m^{-2} y^{-1} for the southern and northern basins, respectively. Estimates for carbon recycling based upon the simple formulation given by the difference between depositional and burial fluxes (eqn 2), indicate that, on average, approximately 50% of the carbon deposited (as estimated from the organic carbon content within top 0.5 cm of these cores), is remineralized and recycled. Ignoring the extremely high diffusive fluxes at stations 103 and 109, the average combined porewater concentration gradient supported fluxes of ΣCO_2, DOC and methane give higher recycling flux estimates, closer to 75%, than the diagenetic mass balance calculations. There is no *a priori* explanation for this difference. Solid phase measurements of sedimentary organic carbon were determined for only about half of the cores analyzed for porewater, variability is significant, seasonal effects seem unlikely (i.e. changing pore water concentration gradients), and 50% would be more consistent with other estimates.

A stoichiometric mass balance may also be used to check carbon and nitrogen turnover. The C:N ratio typically increases with depth in the core, presumably the result of preferential remineralization of nitrogen relative to carbon. For example, carbon recycling may be given in terms of nitrogen fluxes (J^N) and C:N stoichiometry (Klump et al., 2009):

$$J_R^C = J_R^N\ [C:N]_R = J_{DEPOSITED}^{\ N}\ [C:N]_{DEPOSITED} - J_{BUR}^N\ [C:N]_{BUR} \qquad (8)$$

Similarly, the fraction recycled ($f_{recycled}$) may also be given in terms of the stoichiometries alone, e.g., for carbon:

$$f_{recycled} = \frac{[N{:}\mathrm{C}]_{BUR} - [\mathrm{N{:}C}]_{DEPOSITED}}{[\mathrm{N{:}C}]_{BUR} - [\mathrm{N{:}C}]_{R}} \qquad (9)$$

Based upon the relationship between estimated depositional and burial for organic carbon and nitrogen, the average stoichiometries for these fluxes are 11.4 and 13.1, respectively (fig. 7). The former is essentially the same as organic matter collected in sediment traps which was observed to have a C:N ratio of 11.3 (Müller et al., 2005). The C:N ratio of the buried organic matter is higher than that of the deposited organic matter, most likely indicating that nitrogen is preferentially remineralized relative to carbon, consistent with C:N ratio of the remineralized fraction (~ 8) being lower than that of the deposited material.

Pore water stoichiometry yields estimates for the C:N ratio of the recyclable fraction of ~ 8.6, 7.2 and 10.2 for the southern, central and northern basins when accounting for DOC and methane (fig. 4). The fraction recycled calculated via equation 9 is variable and results in estimates that range from 29% to 19% to 53% for organic carbon and from 38% to 29% to 59% for nitrogen across these three basins. Using the ratio derived from flux values generated by equation 2 for the recycled fraction of ~7.9 (Fig. 7) gives estimates of 40% and 50% for sedimentary organic carbon and nitrogen recycling, respectively. This is somewhat less, approximately 10% in absolute terms, than the sedimentary mass balance calculation (Tables 2 and 3).

The mean residence time for the recycled fraction, G^0_M, may be estimated by dividing the total inventory of G_M within the sediment column by the flux of the recycled component back into the overlying water (Klump and Martens, 1987; Martens and Klump, 1984). The standing stock of "metabolizable" material may be estimated by integrating equation 1 for the expression for G_M over the depth interval of interest. The residence time, τ, is given by:

$$\tau = \frac{\frac{G_M^0}{k/\omega}\left[1-\exp\left(-\frac{k}{\omega}z\right)\right]}{G_M^0\,\omega} \qquad (10)$$

With the exception of station 107 on the Akademichesky Ridge, a known site of low sediment accumulation (Edgington et al., 1991), the estimated residence time for metabolizable organic carbon in Baikal sediments ranges from 40 to nearly 400 years (Table 3), with ~ 50% of the remineralization occurring within a mean of 60 years post-deposition. This is consistent with the oxygen exposure times, estimated from the depth of oxygen penetration into the sediments divided by the linear sedimentation rate, of a few years to several hundred years (Sobek et al. 2009; Remsen and Klump, unpub. data).

Comparison with the Laurentian Great Lakes:

Comparison with the shallower Laurentian Great Lakes, where water depths in depositional environments range from 10 meters to 400 meters, demonstrates that sedimentary organic matter diagenesis in freshwater sediments in large lakes show consistent correlations across a variety of parameters with water depth as an approximate surrogate for residence time in the overlying water, and carbon deposition, a function of trophic status. Data for organic carbon (Table 3) are included for sediments, within the Laurentian Great Lakes, of Lake Superior (Klump et al., 1989), the bay of Green Bay in Lake Michigan (Klump et al., 2009), and Lake Michigan (Klump unpublished). For example, the residence time for metabolizable carbon increases roughly with increasing water depth as does the “apparent initial age” (Fig. 8). For Baikal the apparent initial age of deposited organic carbon is, on average, approximately 45 years, probably reflecting both a longer residence time within the water column and a lower sediment accumulation rates which allow material to age at the sediment surface before being buried. Bottom water renewal times in Baikal have been estimated to be on the order of years (Killworth et al., 1996; Weiss et al., 1991).

Despite being much shallower, the organic matter-rich sediments of Lake Michigan’s Green Bay, have a calculated initial age that is still quite long, on the order of a few years, reflecting physical mixing of recently deposited material with older sediments in the upper 2-3 cm and rapid linear sedimentation rates that reach a cm per year (Klump et al., 2009). Regardless, similar to what has been shown in marine sediments, the relationship between mass sediment accumulation rates and the modeled decomposition rate constants is approximately linear (fig. 9a). Removal of the shallow organic-rich sediments in Green Bay improves the fit somewhat, but the uncertainty in lakes would be high. Across these large lake environments, the flux of carbon to the sediment varies by over 2 orders of magnitude (<0.1 to >5 mol m^{-2} y^{-1}). The relationships between these organic carbon depositional fluxes and the first order decomposition rate constants is similar to the relationship with mass sedimentation rates (fig. 9b). Modeled decomposition rate constants vary approximately linearly with flux of organic carbon, perhaps even with a somewhat tighter fit. In marine systems this relationship has been portrayed as having potential for estimating approximate sedimentation rates based upon modeling organic carbon diagenesis (Berner, 1978; Toth and Lerman, 1977; Arndt et al., 2013).

Comparisons of deep oligotrophic lakes to oceanic environments have characterized these lake sediments as pelagic to hemipelagic in character consistent with their scale as inland seas (Johnson et al., 1982; Klump et al., 1989). Carbon cycling conforms to many of the same trends as found in marine systems (Li et al., 2012; Arndt et al., 2013). One such trend was shown by Suess (1980) in relating the carbon flux to sediments relative to primary production (sometimes referred to as an export ratio) as a function of depth in the oceans. Others have similarly examined "burial efficiency" in lakes, i.e. the ratio of organic carbon burial to primary production (Alin and Johnson, 2007; Sobek et al., 2009). Figure 10 shows this ratio plotted vs. mass sedimentation rate for the three lake regimes here: Baikal, Michigan and Superior combined, and Green Bay (in the latter case the two shallowest, river input influenced stations have been omitted from the regression). Higher sedimentation rates correlate to a higher fraction of primary production becoming permanently buried. It is possible that higher sediment accumulation rates could be driven in part by allochthonous inputs of older terrestrial and soil carbon, subject to more extensive weathering, and therefore more refractory in nature. Higher sedimentation rates also generally translate to an accelerated onset of anaerobic conditions often associated with enhanced preservation of organic matter and/or more extensive geopolymerization and reduced degradability (Arndt et al., 2013). Regardless, this data suggests the burial efficiency for Baikal is less than 25% in keeping with a > 75% remineralized fraction. Particle settling rates have been estimated at < 1 meter/day which, for much of the lake, would result in residence times in the overlying water equivalent to years. Based on sediment trap data Müller et al. (2005) estimated that 30% of the organic carbon and 20% of the nitrogen was decomposed within the water column, leaving ~ 50% of the carbon recycling process taking place within the sediments. The diagenetic modeling results given here are consistent with these estimates.

Summary:

Within this largely closed basin, the sediments of Lake Baikal play a significant role in the biogeochemistry of the system. The fractional recycling and turnover of carbon and nitrogen in these sediments compares to that of much shallower environments, with a significant fraction of the deposited organic matter being relatively labile. At higher carbon deposition rates found in the Laurentian Great Lakes, the fraction of the carbon preserved by burial reaches approximately 65%, i.e. at high carbon deposition rates about 35% of the organic carbon is recycled. At the low end of deposition, i.e. where many of the sediments in Lake Baikal reside, the fraction of primary production that is remineralized and recycled appears to be perhaps as high as 75% based upon organic carbon burial efficiencies relating primary production to permanent accumulation. Estimates here indicate that the majority of carbon recycling results in the production of dissolved inorganic carbon (ΣCO_2) while the DOC and methane fluxes generally contribute < 15% of the overall turnover of organic carbon in Lake Baikal sediments.

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Figure captions:

1. Station locations: Lake Baikal.
2. Sediment pore water concentration profiles for dissolved ΣCO_2, $SO_4^=$, and NH_4^+: a) 100 series b) 300 series cores in Fig.1.
3. Sediment pore water concentration profiles for dissolved organic carbon (DOC) and methane (CH_4).
4. Stoichiometry of remineralized sedimentary carbon and nitrogen as determined from pore water ΣCO_2 and NH_4^+ (eqn. 7) yields C:N ratios of 7.8, 6.6 and 9.2 for the southern, central and northern stations, respectively, with an average of ~ 8 (exc. 107). Taking into account DOC and CH_4 raises the average C:N ratio to ~ 9.

5. % organic carbon and nitrogen content in the upper 30 cm of Baikal sediments showing fit to simple first order diagenetic model given by equation 1 (dotted line)..
6. % organic carbon content of sediments (data in figure 5) plotted against age of sediment as extrapolated from sedimentation rates determined by Edgington et al. (1991).
7. Ratio of the depositional ($J_{deposited}$) and burial (J_{burial}) fluxes of sedimentary organic carbon and total nitrogen (eqn. 2) yield C:N stoichiometries for sedimentary organic matter of ~ 11.4 and 13.1 for input and burial, respectively (right panel). The ratio of the fluxes of the recycled component yields a C:N stoichiometry for recycling of 7.9, indicative of preferential nitrogen remineralization (left panel).
8. The residence time of metabolizable carbon (eqn. 10) and the apparent initial age of sedimentary organic carbon (eqn. 5) based on the diagenetic models of Berner (1980) and Middelburg (1989), respectively, as a function of water depth for sediments in Lakes Baikal, Superior, Michigan, and Green Bay (Lake Michigan).
9. The relationships between a) sedimentation rates and the first order decomposition rate constants, and b) organic carbon deposition and the first order decomposition rate constants for freshwater depositional environments in Lake Baikal and the Laurentian Great Lakes varying in carbon flux over two orders of magnitude (<0.1 to >5 mol m^{-2} y^{-1}).
10. Burial efficiency (defined as the ratio of organic carbon burial in sediments to primary production) vs. mass sediment accumulation rate for three groups of sediments: Baikal, Superior, Michigan, and Green Bay.

Table 1: Station locations: Lake Baikal

Station	Lat ° N	Long ° E	Approx. Depth (m)*
101	51.78	104.47	1150
102	51.73	105.23	1430
103	52.38	106.15	217
104	52.37	106.22	101
105	52.42	105.98	667
106	53.18	107.77	1619
107	53.53	107.97	403
108	53.92	108.42	888
109	52.92	107.88	815
110	52.98	107.85	996
305	51.83	105.07	1415
307	51.82	105.45	1425
311	52.95	107.82	1173
312	53.37	108.20	1609
314	54.18	108.77	888
315	54.50	108.98	897
317	54.80	109.17	889
321	55.27	109.42	825
324	55.55	109.50	650

*Interpolated from coordinates curtesy of Oleg Khlystov (± 2-10 m)

Table 2 Summary of pore water concentration gradients and diffusive fluxes across the sediment-water interface for recycled carbon

	ΣCO_2		CH_4		DOC	
Station	gradient uM cm^{-1}	flux mmol m^{-2} y^{-1}	gradient uM cm^{-1}	flux mmol m^{-2} y^{-1}	gradient uM cm^{-1}	flux mmol m^{-2} y^{-1}
305	70	126				
307	112	202	1.2	2.9	160	63
311	160	289	2	4.9	30	14
312	150	271	0.5	1.2	33	16
314	150	271	0.9	2.2	90	43
315	200	361	0.5	1.2	35	17
317	130	235	0.9	2.2	20	10
321	215	388	0.7	1.7	85	41
324	180	325	17	41.4	65	31
ave	*152*	*274*	*3.0*	*7.2*	*65*	*29*
% total		88%		2%		10%
101	172	311				
102	58	105				
103	500	903				
104	77	139				
105	188	340				
106	156	282				
107	21	38				
109	324	585				
ave all		*304*				

Table 3 Comparison of diagenetic model parameters (eqns. 2 and 5) for sedimentary organic carbon in Lake Baikal with the Laurentian Great Lakes. Data sources: Baikal (this paper), Superior (Klump et al. 1989), Michigan (Klump, unpub.), Green Bay (Klump et al. 2009).

Site	Sta.	Depth	sed. rate	Org.C_o	$C_{deposition}$	C_{burial}	$C_{recycled}$	k	res. time	apparent	$f_{recycled}$
		m	mg cm^{-2} y^{-1}	%	-----	mol m^{-2} y^{-1}	-----	y $^{-1}$	yr	age, y	
Baikal	101	1150	18	2.78	0.417	0.161	0.256	0.0139	72	20	0.61
Baikal	102	1430	8	3.21	0.214	0.067	0.147	0.0089	127	34	0.69
Baikal	103	217	22	2.77	0.509	0.324	0.184	0.0098	102	50	0.36
Baikal	104	101	22	3.20	0.587	0.405	0.182	0.0220	41	34	0.31
Baikal	105	667	14	3.27	0.382	0.210	0.172	0.0183	55	21	0.45
Baikal	106	1625	9	3.01	0.225	0.158	0.068	0.0172	58	34	0.30
Baikal	107	403	3	1.85	0.046	0.006	0.041	0.0009	1085	60	0.88
Baikal	108	888	4	2.65	0.088	0.020	0.068	0.0038	262	35	0.77
Baikal	109	815	6	2.65	0.133	0.044	0.089	0.0027	365	115	0.67
Baikal	110	996	6	2.90	0.145	0.077	0.068	0.0100	100	45	0.47
Ave.		*829*	*11*	*2.83*	*0.275*	*0.147*	*0.127*	*0.0108*	*227*	*45*	*0.55*
Ave. (ex. 107)		*876*	*12*	*2.94*	*0.300*	*0.163*	*0.137*	*0.012*	*131*	*43*	*0.52*
L.Superior	HB	30	81	1.62	1.09	0.64	0.45	0.016	63	35	0.41
L.Superior	IP	132	58	3.42	1.65	1.12	0.54	0.025	40	35	0.32
L.Superior	EB	323	40	3.82	1.27	1.08	0.19	0.016	63	75	0.15
L.Superior	1377	323	55	4.40	2.03	1.58	0.45	0.031	32	26	0.22
Ave.		*202*	*58.5*	*3.32*	*1.51*	*1.11*	*0.41*	*0.022*	*50*	*43*	*0.28*
L.Mich.	2076	89	22	3.91	0.70	0.29	0.41	0.023	44	10	0.59
L.Mich.	2077	105	18	4.40	0.65	0.31	0.34	0.021	49	13	0.52

L.Mich.	2080	182	146	4.43	5.37	4.27	1.09	0.072	14	12	0.20
L.Mich.	2082	160	67	4.40	2.46	2.01	0.45	0.035	29	29	0.18
L.Mich.	2085	82	46	3.36	1.28	0.42	0.86	0.019	52	6	0.67
L.Mich.	2086	50	24	4.42	0.87	0.53	0.34	0.017	58	26	0.39
Ave.		*111*	*54*	*4.15*	*1.89*	*1.31*	*0.58*	*0.031*	*41*	*16*	*0.43*
Green Bay	9	9	85	5.72	4.05	0.92	3.13	0.051	20	4	0.77
Green Bay	12	12	75	7.26	4.54	1.44	3.10	0.045	22	5	0.68
Green Bay	17	14	44	8.17	2.99	1.72	1.27	0.038	26	10	0.42
Green Bay	21	17	52	7.79	3.38	2.38	0.99	0.030	33	20	0.29
Green Bay	25	21	46	8.71	3.34	1.73	1.61	0.048	21	6	0.48
Green Bay	26	22	59.5	9.09	4.50	2.93	1.58	0.045	22	11	0.35
Green Bay	30	20	73.5	8.97	5.49	3.68	1.82	0.109	9	5	0.33
Green Bay	31	25	75	8.94	5.59	4.19	1.40	0.078	13	9	0.25
Green Bay	32	24	160	8.49	11.32	6.67	4.65	0.083	12	5	0.41
Green Bay	33	16	102	8.25	7.01	2.98	4.04	0.049	20	6	0.58
Green Bay	38	28	45	9.26	3.47	2.33	1.15	0.080	13	6	0.33
Green Bay	39	28	61	9.78	4.97	3.00	1.97	0.071	14	5	0.40
Green Bay	43	33	33	9.80	2.69	1.79	0.91	0.036	28	14	0.34
Green Bay	47	32	35	10.13	2.95	1.75	1.20	0.035	28	11	0.41
Green Bay	48	32	22	10.16	1.86	1.10	0.76	0.023	43	18	0.41
Green Bay	25-31	23	69	8.81	5.06	3.28	1.79	0.035	29	14	0.35
Green Bay	30-31	22	70	8.33	4.86	3.44	1.42	0.028	36	22	0.29
Green Bay	31-38	26	60	8.60	4.30	3.00	1.30	0.032	31	18	0.30
Green Bay	31-39	26	68	10.33	5.85	3.46	2.40	0.063	16	6	0.41
Ave		*23*	*65*	*8.77*	*4.64*	*2.72*	*1.92*	*0.052*	*23*	*10*	*0.41*

Table 4 Diagenetic model parameters for sedimentary nitrogen in Lake Baikal, based upon profiles (Fig. 5) and equations 2 and 5.

Station	$TN_{z=o}$	$N_{deposition}$	N_{burial}	$N_{recycled}$	$f_{recycled}$	res. time	apparent
	%	--------- mmol m^{-2} y^{-1} ---------				y	age, y
101	0.280	36.0	6.0	30.0	0.84	52	8
102	0.351	20.1	5.1	14.9	0.74	77	14
103	0.288	45.0	24.0	22.0	0.48	99	37
104	0.343	54.0	30.0	24.0	0.44	71	27
105	0.324	32.0	13.0	19.0	0.60	69	18
106	0.346	22.2	14.8	7.5	0.34	103	55
107	0.257	5.5	0.6	4.9	0.89	683	133
108	0.314	9.0	2.7	6.3	0.70	135	26
109	0.271	11.6	2.1	9.5	0.82	367	75
110	0.296	12.7	6.0	6.7	0.53	60	12
Ave.	*0.308*	*26.2*	*10.9*	*15.3*	*0.65*	*184*	*44*
Ave.(ex.107)	*0.31*	*27.0*	*11.5*	*15.5*	*0.61*	*115*	*30*