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The role of sediments in the carbon budget of a small boreal lake

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running head: Role of sediments in lake C budget

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Abstract

We investigated the role of lake sediments as carbon (C) source and sink in the annual C budget of a small (0.07 km²) and shallow (mean depth, 3.4 m), humic lake in boreal Sweden. Organic carbon (OC) burial and mineralization in the sediments were quantified from ²¹⁰Pb-dated sediment and laboratory sediment incubation experiments, respectively. Burial and mineralization rates were then upscaled to the entire basin and to one whole year using sediment thickness derived from sub-bottom profiling, basin morphometry, and water column monitoring data of temperature and oxygen concentration. Furthermore, catchment C import, open water metabolism, photochemical mineralization as well as carbon dioxide (CO₂) and methane (CH₄) emissions to the atmosphere were quantified to relate sediment processes to other lake C fluxes.

We found that on a whole-basin and annual scale, sediment OC mineralization was three times larger than OC burial, and contributed about 16% to the annual CO₂ emission. Other contributions to CO₂ emission were water column metabolism (31%), photochemical mineralization (6%), and catchment imports via inlet streams and inflow of shallow groundwater (22%). The remainder (25%) could not be explained by our flux calculations, but was most likely attributed to an underestimation in groundwater inflow.

We conclude that on an annual and whole-basin scale (1) sediment OC mineralization dominated over OC burial, (2) water column OC mineralization contributed more to lake CO₂ emission than sediment OC mineralization, and (3) catchment import of C to the lake was greater than lake-internal C cycling.

Introduction

Inland waters are important and active constituents in the global carbon (C) cycle by transporting and processing carbon on its way from land to sea, by accumulating and storing carbon in their sediments, and by emitting carbon dioxide (CO₂) and methane (CH₄) to the atmosphere (Tranvik et al. 2009; Aufdenkampe et al. 2011; Raymond et al. 2013). At present, global estimates of freshwater CO₂ emission and C burial in sediments amount to about 2.1 Pg C yr⁻¹ and 0.6 Pg C yr⁻¹, respectively (Tranvik et al. 2009; Raymond et al. 2013), illustrating the large-scale importance of these C fluxes. However, there is a high uncertainty in each of these global estimates as they are based on compilations of a limited amount of data that were often collected for different purposes. Therefore, in depth studies that address inland water C cycling and its underlying mechanisms are needed to improve our understanding of freshwater C fluxes (Hanson et al. 2015).

In the boreal zone, lakes and rivers often cover a large proportion of the landscape, and receive large amounts of organic carbon (OC) and inorganic carbon (IC) from the terrestrial environment (Sobek et al. 2003; Raymond et al. 2013; Weyhenmeyer et al. 2015). These high latitude aquatic ecosystems are sites of intensive C cycling, and are typically supersaturated with CO₂ with respect to the atmosphere (Cole et al. 1994; Weyhenmeyer et al. 2012; Wallin et al. 2014). Lakes, however, also accumulate C in their sediments, which removes C from the short-term C cycle (Kortelainen et al. 2004). Hence, quantifying the ratio of C emission to C accumulation of boreal lakes is essential for our understanding of lakes as C sources and C sinks. For instance, a study in Finland demonstrated that the C evasion-to-accumulation ratio of 82 lakes varied greatly (range,

4-86; Kortelainen et al. 2013), but the reasons behind this variability remain poorly understood.

Lake sediments play a central role in the C budgets, not only because they bury OC, but also since mineralization of sedimentary OC provides a source for CO₂ and CH₄. Studies that addressed the role of sediments in the C budget of boreal lakes yielded widely different results (Jonsson et al. 2001; Algesten et al. 2005; Kortelainen et al. 2006). For instance, OC mineralization in sediments was about equal to open-water OC mineralization in a large humic lake in Sweden (Jonsson et al. 2001), whereas a study of 15 boreal and subarctic lakes concluded that areal CO₂ emission from the lake surface to the atmosphere was on average 10-fold higher than sediment OC mineralization (Algesten et al. 2005). It was previously suggested that the contribution of sediment OC mineralization depends on the sediment area-to-water volume ratio (A_s/V_w ; den Heyer and Kalff 1998), and that in deep lakes with low A_s/V_w values, sediments contribute less to the overall OC mineralization than in shallow lakes with higher A_s/V_w values. Furthermore, there is evidence that the burial efficiency (BE; OC buried / OC deposited onto sediment surface) of sediments at the deepest point of lakes is much higher compared to whole-basin integrated BE (Sobek et al. 2009; Ferland et al. 2014). Hence, the morphometry of the lake basin needs to be considered when assessing the role of lake sediments in C cycling.

Important regulatory factors of OC mineralization and OC burial in aquatic sediments are temperature and oxygen. OC mineralization rates in sediment and water increase with temperature (Carignan et al. 2000; del Giorgio and Williams 2005; Gudas et al. 2010). Also, the presence of oxygen greatly enhances OC mineralization compared

to rates occurring under anoxic conditions (Sobek et al. 2009; Fenner and Freeman 2013). Anoxic environments, however, favor CH₄ production, which by weight is a 28 times stronger greenhouse gas than CO₂ (IPCC 2013). Thermal conditions and oxygen concentration in lakes vary with depth and over time depending on external forces, i.e., air temperature, wind, solar radiation, and on lake properties such as basin morphometry, lake water color, and trophic state (Fee et al. 1996). Previous studies on the role of sediments as a C source and C sink have addressed these factors (i.e., den Heyer and Kalff 1998; Sobek et al. 2009; Gudas et al. 2010), however, until now no study has integrated these regulatory mechanisms across the temporal and spatial scales of a lake basin.

Here, we evaluate the role of sediments as a C sink and C source in a small boreal lake on a whole-basin scale and over an entire year. We accounted for spatial variability in sediment accumulation, temporal and spatial dynamics in temperature and oxygen, and for the morphometric properties of the lake basin. Furthermore, we assessed the role of sediments in the annual lake C budget by comparing sediment OC burial and sediment OC mineralization to other C fluxes of the lake. We hypothesized that, on an annual whole-basin scale, (1) sediment OC mineralization contributes significantly to annual lake C emission, and that (2) the C flux by sediment OC mineralization is larger than the sediment OC burial flux.

Methods

Study lake

The study was conducted in a small and humic-rich lake (Lake Gäddtjärn, Fig. 1) in central Sweden (59.51 °N and 15.11 °E), which has characteristics common to lakes of the Scandinavian boreal zone (Algesten et al. 2003; Verpoorter et al. 2012). Lake Gäddtjärn has a surface area of 0.07 km², a maximum and mean depth of 11 m and 3.4 m, and a brownish water colour related to a high content of land-derived dissolved organic carbon (DOC; mean, 17 mg L⁻¹; Kokic et al. 2015). Two inlet streams are located SE and E of the lake, and one outlet stream is located in the NW. The theoretical water retention time (volume / annual average discharge) of Lake Gäddtjärn is 68 days. The 0.23 km² catchment consists of 84% coniferous forest, 12% wetland, and 4% lakes and streams (Kokic et al. 2015), and the entire area is underlain by crystalline bedrock (mostly gneiss) covered by a < 5 m thick till soil. Lake Gäddtjärn was studied during one year from September 2011 to September 2012. Mean annual air temperature during the study period was 5.5 °C and annual precipitation equaled 958 mm, which was both slightly higher than the long-term mean values (4.5°C and 900 mm, respectively, for the period 1961-1990; data obtained from the Swedish Meteorological and Hydrological Institute, SMHI).

Lake C budget

We described the annual C budget of Lake Gäddtjärn by the following mass balance equation:

$$\text{TOC}_{\text{INL}} + \text{DIC}_{\text{INL}} + \text{TOC}_{\text{GW}} + \text{DIC}_{\text{GW}} = \text{TOC}_{\text{OUT}} + \text{DIC}_{\text{OUT}} + \text{TOC}_{\text{B}} + \text{CO}_{2\text{E}} + \text{CH}_{4\text{E}} \quad (1)$$

where TOC_{INL} and DIC_{INL} denote the import of total organic carbon (TOC) and dissolved inorganic carbon (DIC) via the two inlet streams, TOC_{GW} and DIC_{GW} indicate the direct inflow of TOC and DIC via shallow groundwater, not passing any stream, TOC_{OUT} and DIC_{OUT} are the exports of TOC and DIC via the lake outlet stream, TOC_{B} is the burial of TOC in the lake sediments, and $\text{CO}_{2\text{E}}$ and $\text{CH}_{4\text{E}}$ are emissions of CO_2 and CH_4 to the atmosphere.

Leaf litter input and direct inputs via precipitation were considered of minor importance in the C budget (Sobek et al. 2006) and therefore not included in the mass balance equation. The presence of particulate inorganic carbon was also considered negligible due to the low pH in the streams (pH 4-6; Kokic et al. 2015) and since no solid-phase carbonate was detected in the sediment of Lake Gäddejärn (Chmiel et al. 2015).

Basin morphometry and sediment mapping

The entire lake basin was mapped with an acoustic sub-bottom profiler (BSS+3 system, *Specialty Devices Inc.*), coupled to a Differential Global Positioning System (DGPS) as described in (Ferland et al. 2012). This system depicts the water-sediment and the sediment-bedrock interfaces, which were used to spatially resolve water column depth and sediment volume. Data points were collected in a spatial distance of 5 m to each other, resulting in a grid resolution of 25 m² for each cell (2485 cells in total). The measured data were spatially interpolated using natural neighbor interpolation in ArcGIS 10.0 (ESRI).

Water column monitoring

Temperature, dissolved oxygen (DO), pH, and conductivity were monitored in the water column over the study period (see supporting information). During the ice-free season, parameters were logged hourly, except DO, which was logged every 20 minutes. Under ice, all parameters were logged at 8-hour intervals. In addition to the monitoring, manual depth profiles of temperature and DO were taken at the deepest point of the lake at approximately monthly intervals ($n=12$).

Quantification of sediment C fluxes

OC burial

To quantify permanent OC burial we used ^{210}Pb -based data on OC accumulation rates, derived from a sediment core taken from the deepest part of the lake (Chmiel et al. 2015). The core was analyzed in 5 mm increments for OC content, dry bulk density, and sedimentation rates based on measurements of the unsupported ^{210}Pb activity, and by applying the constant rate of supply (CRS) model (Appleby and Oldfield 1978, 1983). The upper 1.5 cm of sediment, corresponding to < 25 years of age, were disregarded for calculation of OC burial, to account for potential loss of OC due to ongoing degradation during early years after deposition (Gälman et al. 2008).

Whole-basin OC burial was estimated by first relating the mean OC burial rate to the sediment thickness of the sampled location (i.e., OC burial rate / sediment thickness). Assuming that sediment focusing in the lake has been constant over time, this ratio was applied to derive OC burial rates as a fractional difference for other sediment thicknesses across the basin. Sediment areas with the same sediment thickness were then multiplied

with the corresponding OC burial rate to derive a spatially weighted average of whole-basin OC burial.

OC sedimentation

The sedimentation flux of OC in the water column was quantified from sediment traps consisting of cylindrical, darkened plastic tubes (diameter = 15.2 cm²; Wachenfeldt and Tranvik 2008). The traps were deployed in the deepest part of the lake at 1 m below the water surface ($n=4$) and at 1 m above the sediment surface ($n=4$). The traps were emptied at four to six week intervals during the ice-free period, and once after ice melt (May 2012). The dry weight of the material was quantified after freeze-drying, and the C and N contents were measured on an elemental analyzer (Costech Elemental Combustion System, CHNS-O).

Whole-basin OC sediment deposition onto the sediment surface was calculated in two ways: (1) by multiplying annual OC-fluxes measured by the sediment traps with the lake area assuming spatially homogenous sedimentation across the basin, and (2) by using the same approach as for the calculation of whole-basin OC burial.

Sediment OC mineralization

We used dark incubation experiments to quantify sediment OC mineralization rates, and applied a temperature relationship of OC mineralization for upscaling. Sediment cores were sampled at three different lake depths and incubated in the laboratory at measured *in-situ* temperatures at both oxic and anoxic conditions. In oxic incubations, mineralization rates were determined as the production of CO₂ and the consumption of

O₂ over time, and in anoxic incubations as the production of CO₂ and CH₄ over time (see supporting information for details).

Whole-basin sediment OC mineralization was calculated by first fitting an exponential regression between temperature and measured sediment OC mineralization (Gudas et al. 2010). Secondly, we used the water temperatures from the continuous data set to calculate daily OC mineralization rates of sediment located within an oxygenated water layer at each meter-increment depth in the lake, for each day of the study period. Thirdly, the calculated daily rates were multiplied with the sediment area located within each meter depth (Fig. 1 and Supporting Table S1), and the daily whole-lake sediment DIC production was summed up to an annual value. For the period of anoxic conditions in the lake water, results from the anoxic core incubations were applied to anoxic water layers.

OC burial efficiency

We calculated the basin-wide sediment OC burial efficiency (OCBE, %) which is defined here as the ratio of OC burial to OC deposition onto the sediment surface, in two different ways: (1) based on sediment trap data (OCBE_S) and (2) based on sediment mineralization data (OCBE_M):

$$\text{OCBE}_S = \text{OC}_B / \text{OC}_S \times 100 \quad (2)$$

$$\text{OCBE}_M = \text{OC}_B / (\text{OC}_B + \text{OC}_M) \times 100 \quad (3)$$

where OC_B, OC_S, and OC_M are basin-wide fluxes in t C yr⁻¹ of OC burial, OC sedimentation, and sediment OC mineralization, respectively.

Water-column metabolism

OC mineralization in the water column was quantified by (1) assessing net DO consumption in open water and under ice from the DO monitoring data, and by (2) converting net DO consumption into DIC production using the respiratory quotient ($RQ = CO_2 \text{ production} / O_2 \text{ consumption}$) determined from incubated lake water samples.

Briefly, we applied the diel oxygen technique (Staehr et al. 2010) to the DO monitoring data in order to assess net ecosystem production (NEP), gross primary production (GPP), and respiration (R) on a daily scale. Furthermore, we quantified net DO consumption from quasi-linear declines in DO, which were observed over several days at periods of highly stable summer stratification and over 134 days during ice cover (see supporting information and Fig. S1). In addition, water samples from different depths were incubated in the laboratory according to the setup of the sediment mineralization experiment, and RQ values were calculated from DIC production and O_2 consumption in the water. Based on these data, we derived the temperature sensitivity of oxic respiration in the water column and used the monitored water temperatures to calculate daily DIC production for the oxygenated lake volume, which were summed to obtain the annual estimate.

Photochemical mineralization

Photochemical DOC mineralization was simulated for every day of the study period (see supporting information) using spectra of apparent quantum yields, chromophoric dissolved organic matter (CDOM) absorption spectra (Supporting Fig. S2) and solar

irradiance as described in detail in Koehler et al. (2014). The simulated daily photomineralization rates were summed over the study period to obtain the annual estimate. During the ice-covered period, when snow covered the ice most of the time, we assumed zero irradiance transmittance into the lake and hence absence of photochemical DIC production.

CO₂ and CH₄ emission

CO₂ emissions were calculated based on six manual sampling campaigns of the partial pressure of CO₂ ($p\text{CO}_2$) in the lake, hourly measurements of $p\text{CO}_2$ in the lake outlet stream, and gas transfer velocity (k_{CO_2}) estimated from wind speed measured at a meteorological station located in 4 km distance from the lake (see supporting information). The annual CO₂ emission was calculated as the sum of daily CO₂ emissions. CO₂ emission during ice cover was set to zero and CO₂ emission at ice melt, which was not covered by our measurements, was taken from emission measurements at ice melt of the same lake during the following year (Denfeld et al. 2015) and added to the annual emission estimate.

CH₄ emission was estimated from floating chamber measurements carried out during summer stratification in 2008 (see supporting information). Water stratification and O₂ profile patterns were similar between the studied years indicating comparable conditions for CH₄. The observed summer mean CH₄ flux was applied to upscale CH₄ emission to the lake area over the stratification period. CH₄ emission during holomixis in spring and autumn were estimated as lowered proportions of the summer mean flux assuming that the production of CH₄ in the sediment is about four-fold reduced and the

oxidation of diffusive CH₄ in the water column about two-fold reduced at a temperature decrease of 10°C (Bastviken 2009; Yvon-Durocher et al. 2014). The potential storage flux of CH₄ at autumn and spring lake turnover was estimated from CH₄ concentration profiles in the water column (see supporting information).

Catchment C fluxes

The inflow and outflow of DOC, particulate OC (POC) and DIC via streams to Lake Gäddtjärn were taken from the detailed study of Kokic et al. (2015) for the same time period. The inflow of DIC and DOC via shallow groundwater discharge directly into the lake without passing any stream was determined for Lake Gäddtjärn in 2013 (Einarsdóttir et al. unpubl.; see supporting information).

During the study period, local authorities unexpectedly resumed a previously halted liming program. Sweden runs a liming program of surface waters with the purpose of remediating acidification. Lake Gäddtjärn was limed on July 17th 2012, with 4.59 t of calcium carbonate (CaCO₃), equaling 0.55 t C, which was deposited by helicopter directly onto the lake surface (Swedish county administration board; <http://kalkdatabasen.lansstyrelsen.se>). The pH data from *in-situ* monitoring indicated that the added lime only affected the epilimnion, and was flushed from the epilimnion within about 2 months after deposition (see supporting information and Fig. S3). Therefore, the amount of inorganic carbon added by liming to the lake (0.55 t C) was subtracted from the outlet export of DIC.

Uncertainty estimates

Uncertainties were calculated as 95% confidence intervals (CI) of measurements of C fluxes conducted at different sites and/or time points, except for photochemical mineralization where a minimum and a maximum value of annual DIC production was determined using the minimum and maximum observed absorbance spectrum (Fig. S2).

Uncertainty of OC sedimentation was calculated as the 95% CI of dry mass sedimentation and OC content of the trapped material, and for OC burial as the 95% CI of the OC mass accumulation rates derived from ^{210}Pb -dating. For sediment and water OC mineralization we used the 95% CI of the slopes in the temperature regressions, and the annual DIC production was calculated with each of the slopes. The 95% CI of the annual CO_2 emission was calculated by taking into account the spatial variability in $p\text{CO}_2$ in the surface water and the temporal variability in daily average wind speed to account for uncertainties in k_{CO_2} . For CH_4 emission, we accounted for the 95% CI of the measured summer mean flux, however, due to the limited data on spring and fall storage turnover fluxes it was difficult to assign uncertainties to these terms. Uncertainties in catchment C fluxes were taken from Kokic et al. (2015).

Results

Lake morphometry

The total sediment area (A_s) of Lake Gäddejärn equaled $67,501 \text{ m}^2$, and 57% of A_s was located above a water depth of 3 m (Supporting Table S1). The maximum and mean sediment thickness was 6.4 and 2.2 m, respectively (Fig. 1b), and the total sediment volume (V_s) equaled $147,239 \text{ m}^3$. The water volume (V_w) of the lake was $259,160 \text{ m}^3$, and the ratio of sediment area to water volume (A_s/V_w) was 0.29 (Table S1). Water level

fluctuations of up to 0.4 m during the study period, obtained from the YSI depth sensors, correspond to maximal changes in water volume of 27,000 m³.

Stratification and mixing periods

Lake Gäddejärn was stratified at the beginning of the study period in September 2011, with anoxic conditions ($<0.5 \text{ mg O}_2 \text{ L}^{-1}$) below 6.5 m water depth (Fig. 2). Holomixis was reached on October 21st 2011 and lasted until ice formation at the beginning of December 2011. The permanent ice cover on the lake lasted for 134 days during which the water column was inversely stratified. Ice melted in mid-April 2012, and the water column mixed again until summer stratification was established at the end of April 2012. Hypolimnetic anoxia was detected at the beginning of July below 9 m water depth (Fig. 2).

Sedimentation and burial of OC

Sedimentation of OC in the water column, obtained from sediment traps in the surface water, equaled $43.8 \pm 3.7 \text{ g C m}^{-2} \text{ yr}^{-1}$ (mean \pm standard error, SE), and molar C:N ratios of trap material ranged from 7 to 18. Sediment traps deployed in the bottom water at 9 m depth gave an almost identical value of $43.9 \pm 1.8 \text{ g C m}^{-2} \text{ yr}^{-1}$ and a similar range in C:N ratios (7-20). OC burial, calculated from the vertical sediment profile for sediment layers older than 25 years, averaged $7.8 \pm 1.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ between 1912 and 1981 AD. The C:N ratios of the sediment layers ranged between 18 and 20.

Sediment mineralization

Mineralization rates in oxygenated sediment samples ranged from 9 to 88 mg C m⁻² d⁻¹ and were lower at 4°C than at 15°C (t-test, $P < 0.0001$, $n = 23$; Table 1). The calculated temperature dependence ($\text{DIC}_{\text{sed}}(T) = 10^{(0.032T + 1.360)}$; $P < 0.0001$; $R^2 = 0.64$; $n = 23$) was similar to the dependence reported for sediment of a nearby lake of similar character (Lake Svarttjärn; Gudas et al. 2010). Mineralization rates in anoxic sediment samples were about 20% of oxic mineralization rates at 9 °C and CH₄ accounted for 6% of the total anoxic OC mineralization (Table 1).

Water column metabolism

Over the vast majority (92%) of diel cycles, DO did not display the expected pattern of increase during daytime and decrease during nighttime. Hence the diel oxygen technique could only be applied to 8 days in summer 2012 (Table S2) when NEP was mostly negative (range, -198 to -54 mg O₂ m⁻³ d⁻¹) except for one diel cycle (88 mg O₂ m⁻² d⁻¹). NEP calculated from the weekly-scale quasi-linear declines in DO during periods of strong stratification equaled -130 and -146 mg O₂ m⁻³ d⁻¹, respectively (Table S2).

Oxic OC mineralization rates in incubated lake water samples equaled 13.0 ± 0.2 mg C m⁻³ d⁻¹ at 4.5 °C, and the RQ measured during these incubations was 0.95 ± 0.16 . Accordingly, free-water OC mineralization rates derived from diel DO cycles and weekly-scale DO declines ranged between 17 and 71 mg C m⁻² d⁻¹ at mean temperatures between 13.8 and 15.8 °C, respectively (Table S2). Long-term under-ice OC mineralization in the water column corresponded to 10.6 ± 1.8 mg C m⁻³ d⁻¹ at a mean temperature of 3.5 °C (Table S2). Collectively, these data indicate that Lake Gäddejärn was net heterotrophic during the study period. The temperature dependence of respiration

in the water column of Lake Gäddejärn derived from the results above was $DIC_{\text{wat}} = 3.300T - 1.147$ ($p < 0.05$; $R^2 = 0.97$).

Photochemical DOC mineralization

DOC photomineralization rates, simulated using the mean absorbance spectrum for the ice-free period ($n=232$ days) varied between 1 and 55 $\text{mg C m}^{-2} \text{ d}^{-1}$ and averaged 24.8 ± 1.0 $\text{mg C m}^{-2} \text{ d}^{-1}$. Given the small temporal variation in CDOM absorbance over time in this brown-water lake (Fig. S2), annual simulation using the minimum and maximum observed CDOM absorbance spectrum resulted in nearly identical mean photochemical mineralization estimates of 23.6 and 24.8 $\text{mg C m}^{-2} \text{ d}^{-1}$.

CO₂ and CH₄ emissions

The $p\text{CO}_2$ in the surface water of Lake Gäddejärn varied between 1438 and 2267 μatm . Daily average wind speed during the study period varied between 0.3 and 5.1 m s^{-1} (SMHI), and returned an average daily k_{CO_2} between 0.26 and 0.77 m d^{-1} (mean $k_{\text{CO}_2} = 0.36 \text{ cm h}^{-1}$). The resulting mean daily flux of CO₂ from the surface water to the atmosphere for the entire ice-free period was 406 $\text{mg C m}^{-2} \text{ d}^{-1}$ (range, 186-894 $\text{mg C m}^{-2} \text{ d}^{-1}$).

Floating chamber measurements at Lake Gäddejärn revealed a mean CH₄ flux of 8 $\text{mg C m}^{-2} \text{ d}^{-1}$ to the atmosphere (range, 3-20 $\text{mg C m}^{-2} \text{ d}^{-1}$), with 52% being attributed to ebullition. The storage CH₄ flux calculated for spring was < 1 kg C, and for autumn turnover about 7 kg C, respectively.

Annual C budget

Basin-wide OC burial was estimated at 0.33 t C yr^{-1} or $4 \text{ g C m}^{-2} \text{ lake area yr}^{-1}$ (Table 2). OC sedimentation flux in the water column equaled 2.96 t C yr^{-1} ($44 \text{ g C m}^{-2} \text{ yr}^{-1}$) if assuming homogenous sedimentation, and 1.86 t C yr^{-1} ($28 \text{ g C m}^{-2} \text{ yr}^{-1}$) if upscaling according to the fractional difference in sediment thickness. Sediment OC mineralization was estimated at 0.99 t C yr^{-1} ($15 \text{ g C m}^{-2} \text{ yr}^{-1}$; Table 2). Hence, the basin-wide OCBE_s was calculated at 11% (95% CI; 8-15%) assuming spatially homogenous sediment deposition, and 18% (14-24%) assuming non-homogenous sediment deposition. Calculating the basin-wide OCBE_M from sediment OC mineralization instead returned a mean value of 25% (20-29%).

OC mineralization in the water column accounted for 2.00 t C yr^{-1} ($30 \text{ g C m}^{-2} \text{ yr}^{-1}$) of net DIC production, and photochemical DIC production equaled 0.39 t C yr^{-1} ($6 \text{ g C m}^{-2} \text{ yr}^{-1}$; Table 2). Hence, total OC mineralization in the water was 2-fold higher than in the sediment. The total annual CO₂ emission equaled 6.36 t C yr^{-1} ($94 \text{ g C m}^{-2} \text{ yr}^{-1}$), and the estimate of annual CH₄ emission was 0.11 t C yr^{-1} ($2 \text{ g C m}^{-2} \text{ yr}^{-1}$; Table 2). During the study period, 17.6 t of DOC ($261 \text{ g C m}^{-2} \text{ yr}^{-1}$) and 1.4 t of DIC ($21 \text{ g C m}^{-2} \text{ yr}^{-1}$) were supplied to the lake through stream and groundwater inputs, while 13.9 t DOC and 0.6 t DIC left the lake again via stream outflow (Table 2; Kokic et al. 2015).

Considering the mass balance (Eq. 1), we can summarize the budget (Table 2) by equaling inputs to outputs, such that $13.0 + 0.5 + 4.6 + 0.9 = 13.9 + 0.6 + 0.3 + 6.4 + 0.1$, or $19 = 21.3$ (all fluxes expressed in t C yr^{-1}). Considering only OC, inputs were similar to losses (17.6 and 16.6 t C yr^{-1} , respectively), while for IC, inputs were smaller than losses (4.8 and 7.0 t C yr^{-1} , respectively).

Comparing the different in-lake processes on a monthly scale, demonstrates strong variability throughout the year (Fig. 3a). During winter months (December-February) sediments and the water column contributed about equally to the DIC gain in the lake, whereas from spring onwards and over summer microbial OC mineralization in the water column became progressively more important. The highest contribution of photochemical mineralization to in-lake DIC production was in spring and early summer 2013. Of the total annual CO₂ emission, a large fraction (43%) was emitted from the lake in autumn 2011, about 20% was emitted in spring 2012, and 37% was emitted in summer 2012 (Fig. 3b).

Discussion

The role of sediments in the lake C budget

This study shows that both OC burial and OC mineralization in sediments played in terms of quantity a rather small role in the annual C budget of a small boreal lake (Fig. 4). The production of DIC in the sediments accounted on average for 16% of the total annual lake CO₂ emission, and OC burial, even though an important long-term C sink in the boreal landscape (Kortelainen et al. 2004), accounted on average for only 2% of the total catchment export of OC to the lake.

Earlier studies on sediment OC mineralization have come to partially different conclusions, with sediment OC mineralization being either very important (Jonsson et al. 2001; Kortelainen et al. 2006) or moderately important as a source of CO₂ emission from boreal lakes (Algesten et al. 2005; Brothers et al. 2012). These studies, however, were based on data that were either not resolved on a basin-wide scale, or limited to a

particular season of the year. Based on annually resolved and whole-basin data, our study concludes that sediments are on an annual scale only a moderate source to the CO₂ emission (~16%) from the studied boreal lake. The potential to apply this conclusion to other boreal lakes, relies on the knowledge of the morphology of the lake basin, i.e., the sediment As:Vw ratio. In shallow lakes with a higher As:Vw ratio comparatively more sediment is deposited in shallow areas where it warms up in summer, resulting in greater sediment OC mineralization (den Heyer and Kalff 1998; Gudas et al. 2010) and stronger sediment contribution to lake CO₂ emission.

The small C flux of OC burial in the budget is in agreement with earlier reports of low OC burial in boreal lakes (Kortelainen et al. 2004; Ferland et al. 2012). Similarly to our study, OC burial was found to be only 13-14% of gross sedimentation in a small boreal Finish lake (Einola et al. 2011). Furthermore, Kortelainen et al. (2013) showed that CO₂ emission is on average 30 times larger than OC burial in boreal lakes (range, 4-86 times). In Lake Gäddejärn, CO₂ emission was about 20 times greater than OC burial.

The OCBE_S (8-24%) and OCBE_M (21-30%) of Lake Gäddejärn display a slight divergence in numbers depending on the method of calculation, which could be related to inaccurate estimation of the sinking sediment flux by the sediment traps (i.e., underestimation due to OC degradation or overestimation due to zooplankton migration or sediment resuspension) or to the upscaling of OC mineralization. However, all estimates indicate that the whole-basin OCBE is in the range of 8-30%. This is much lower than the 64% reported for the deepest point of Lake Gäddejärn only (Sobek et al. 2009), but comparable to the whole-basin OCBE of boreal lakes in Quebec (mean, 22%; Ferland et al. 2014). For the Quebec lakes, whole basin OCBE was well correlated to the

dynamic ratio (DR), which is calculated as the square root of lake area (LA; km²) divided by the mean depth of the lake (d; m). The DR of Lake Gäddejärn is 0.73, for which the regression reported by Ferland et al. (2014) returns a whole-lake OCBE of 10%, which is in the lower range of our estimates. Apparently, expressing the OCBE for an entire basin (as opposed to the deepest point of the lake basin only) leads to a relative reduction of OC burial, as littoral sedimentation is lower compared to sedimentation at the deepest point (Fig. 1). In addition, whole-basin sediment OC mineralization is higher than sediment OC mineralization at the deepest point, since higher temperatures of littoral sediments during summer stratification and a higher availability of dissolved oxygen result in greater OC mineralization (Gudas et al. 2010; Sobek et al. 2009). However, it should finally be noted here that despite the comparatively small flux of OC burial in the annual C budget, it is the only flux which leads to a permanent removal of C from the active cycling loop, and therefore represents an important long-term C sink in the boreal landscape (Kortelainen et al. 2004).

In-lake OC processing

Lake Gäddejärn was a net heterotrophic system during the study year, evident in the C budget by a lake-internal net OC loss of 3.4 t C through mineralization (Table 2, see also discussion in supporting information). Water-column NEP was the quantitatively most important OC mineralization pathway (2.0 t C), followed by sediment OC mineralization (1.0 t C), and photochemical DOC mineralization (0.4 t C; Table 2). Water-column NEP determination using the diel oxygen technique was only possible on 8 out of 150 days of open-water DO measurements, which was surprising given that the method is widely and

successfully applied (i.e., Staehr et al. 2010; Solomon et al. 2013; Sadro et al. 2014). The difficulties in applying the diel DO technique are probably related to the highly humic and dystrophic nature of Lake Gäddejärn. The lake water is strongly colored and humic-rich, creating a highly unfavorable light climate for phytoplankton (Karlsson et al. 2009), supported by low concentration of chlorophyll *a* in surface water during the open-water season ($0.1\text{--}1.3\ \mu\text{g L}^{-1}$; $n=3$; Sobek et al. 2003). Accordingly, diel DO cycles could only be observed during mid-June to mid-July, when solar irradiance was at its annual maximum (Table S2).

The photochemical estimate covers only direct photooxidation of DOC to DIC, disregarding potential light-mediated production of more labile substrates for bacterial respiration from recalcitrant DOC (Bertilsson and Tranvik 1998). The C loss due to photo-stimulation of bacterial respiration via DOC cleavage can be similar to C loss by direct photomineralization (Miller and Moran 1997). This may perhaps explain why *in-situ* water column OC mineralization was often higher than when determined from dark laboratory incubations (Table 1). Interestingly, direct photomineralization was of similar magnitude as OC burial ($0.3\ \text{t C}$), and a similar conclusion was recently drawn in a large-scale study across Swedish lakes and for the global scale (Koehler et al. 2014).

The monthly resolved data on OC mineralization (Fig. 3a) display a changing importance of each process over the year. Sediment OC mineralization and NEP in the water column followed in general the annual temperature curve, with a declining trend in DIC production from early autumn to early winter, low DIC production during months of ice-cover, and a positive trend from spring towards summer. In winter, sediment OC mineralization slightly dominated over water-column metabolism. However the latter

became progressively more important towards summer, resulting in about twice as much DIC produced by water-column OC mineralization than by sediment OC mineralization (Fig. 3a). In general, these observed trends display the combined effect of basin morphology, i.e., the $A_s:V_w$ ratio, and temperature dependences of OC mineralization in sediment and in water.

The seasonal trends in sediment OC mineralization and water column metabolism are also in agreement with temporal dynamics in allochthonous OC loading. During the ice-free season, the lake received a large amount of OC via stream inflow, which consisted to 96% of DOC (Kokic et al. 2015). Even if a proportion of the DOC may have flocculated in the lake and contributed to sedimentation of OC (Wachenfeldt and Tranvik 2008), a large proportion of the imported DOC was also available for utilization by bacteria in the water column. Given that photochemical reactivity was determined only once during the study period, and hence assumed to be constant in the model simulations, the simulated photomineralization peaked in May-July during the maximum in solar irradiation intensity (see also discussion in supporting information).

In contrast, during months of ice-cover, reduced allochthonous OC input might have limited OC mineralization in the water column as winter progressed, whereas the large OC pool in sediment may continue to be degraded at similar rate throughout winter (Denfeld et al. 2015).

The role of CH₄ in the lake C budget

CH₄ emission was the smallest measured flux in the annual lake C budget that accounted for 1-3% to the total lake C emission. However, by mass-equivalent CH₄ is a 28 times

stronger greenhouse gas than CO₂ at a 100-year timescale (IPCC 2013). Accounting for this, CH₄ contributes to about 14% (7-21%) to the total global warming potential emitted of the lake, indicating the importance of CH₄ emission from Lake Gäddejärn, in spite of its small share in the lake C budget. However, since the measurements in our study on internal lake CH₄ dynamics are limited, the annual CH₄ emission estimate is a relatively uncertain term in the overall lake C budget, calling for future studies investigating the importance of CH₄ in lake C budgets.

The catchment impact on the C budget

In terms of the C mass balance (Eq. 1), the lateral C import via streams and groundwater, as well as stream C export from the lake had a much larger impact on the C budget than in-lake processes (Table 2, Fig. 4). From the budget numbers, and given the limited rates of primary production (Table S2), it is evident that allochthonous OC mostly dominated the C pool in the lake. The calculated loading rate of allochthonous OC (261 g C m⁻² yr⁻¹) is within the range of loading rates (9-740 g C m⁻² yr⁻¹) reported in other budget studies of small sized boreal lakes, where allochthonous OC contributed 20-98% of the total OC pool (Sobek et al. 2006; Einola et al. 2011).

Likewise, the DIC loading rate of 21 g C m⁻² yr⁻¹ compares to the range of reported values (0.3-85 g C m⁻² yr⁻¹; Sobek et al. 2006; Einola et al. 2011). The contribution of stream and groundwater DIC to the estimated CO₂ emission (22%) was smaller than the contribution of in-lake DIC production (53%) in Lake Gäddejärn, even though the remainder (25%) may possibly be related to inaccurate estimation of groundwater C input (see supporting information). This shows that even in strongly net

heterotrophic lakes, hydrologic C input can be an important contributor to CO₂ emission (Stets et al. 2009; Weyhenmeyer et al. 2015).

Budget uncertainties

When calculating sediment C budgets there is an inherent mismatch in timescales, since OC burial is calculated over timescales of past decades, while OC mineralization or OC deposition in sediment traps is determined at daily or weekly timescales. However, sediment core data suggest that in Lake Gäddtjärn, OC mass accumulation rates have varied very little over the past century and that the OC, once buried in the sediment, undergoes very little degradation (Chmiel et al. 2015). Accordingly, even if we calculate the OCBE only using the most recent OC burial estimate of 9 g C m⁻² yr⁻¹ (which was excluded from calculations because of presumably incomplete degradation), very similar numbers of whole-lake OC burial (0.36 t C yr⁻¹) and burial efficiency (28%, if calculated via OC mineralization) are returned. Hence, our conclusions for the sediment C budget of Lake Gäddtjärn seem to be robust despite the difference in temporal scales.

Moreover, despite uncertainties associated with each of the C flux estimates in the entire Lake Gäddtjärn C budget (see supporting information), many of them related to upscaling in both space and time, C inputs of 19 t C yr⁻¹ are close to being balanced by C outputs of 21.3 t C yr⁻¹ (Eq 1; Table 2). Annual OC gain (17.6 t C; 95% CI: 14.6-21.1 t C) was similar to OC loss (16.6 t C; 13.3-20.1 t C). DIC gain (4.8 t C) was on average smaller than DIC loss (7.0 t C), however the confidence intervals overlap (3.5-5.8 t C and 5.5-7.7 t C, respectively). While some of the discrepancies may be related to C fluxes that we did not assess within this study (e.g., atmospheric OC deposition), uncertainties

deriving from assumptions and up-scaling of C flux estimates are large, as evidenced by the confidence intervals (Table 2). Probably the largest uncertainty in the C budget is related to the estimate of groundwater C supply to the lake (see supporting information). Nevertheless, these approximate estimates of subsurface DOC and DIC inputs indicate that shallow groundwater inflow has an important role in the lake C budget that should not be neglected.

Conclusions

By assembling a detailed C budget that accounts for both temporal and spatial variability of C fluxes, this study supports the initial hypotheses that on an annual whole-basin scale (1) sediment OC mineralization contributed a significant, but comparatively small share (~16%) to lake CO₂ emission, and that (2) the flux of sediment OC mineralization dominated over the flux of OC burial. Also, the large difference in whole-basin vs. deepest-spot OC burial efficiency (Sobek et al. 2009) highlights the importance of integrating whole systems when assessing carbon dynamics in inland waters (Hanson et al. 2015). The importance of sediments for the C budget of boreal lakes will however vary depending on basin morphometry (sediment area-to-water volume ratio), stratification patterns and, as a consequence, temperature and oxygen regimes. At a catchment scale, CO₂ emission by the headwater streams and lakes was more than twice the annual C emission from the study lake (Kokic et al. 2015). However, for an integrated assessment of aquatic C fluxes both burial and emission need to be quantified at the catchment-scale, including small headwater lakes and wetlands.

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Tables

Table 1. Mean (\pm SE) mineralization rates measured as dissolved inorganic carbon (DIC) and methane (CH_4) production during the incubation experiments. RQ is given as the molar ratio of CO_2 production to O_2 consumption.

	T °C	DIC mg C m ⁻² d ⁻¹	CH₄ mg C m ⁻² d ⁻¹	RQ
Oxic incubation ($n=11$)	4.4	31.7 \pm 2.9	n.d.	0.73 \pm 0.09
Oxic incubation ($n=12$)	15.0	69.1 \pm 3.3	n.d.	1.27 \pm 0.05
Anoxic incubation ($n=11$)	9.0	8.6 \pm 1.4	0.7 \pm 0.2	n.a.

n.d. = not determined, n.a. = not applicable

Table 2: Annual carbon budget of Lake Gäddtjärn. Numbers denote OC and DIC gain and loss in t C yr⁻¹, including fluvial C-flux from the catchment (Kokic et al. 2015)¹ and input via groundwater (Einarsdóttir et al. unpubl.)². Values in parenthesis express 95% confidence levels. Asterisks (*) indicate the range of photochemical DIC production when using the minimum or maximum observed CDOM absorbance spectra for annual simulation.

Process	OC (t C yr ⁻¹)		DIC (t C yr ⁻¹)	
	gain	loss	gain	loss
sediment burial	-	0.3 (0.2-0.4)	-	-
sediment mineralization	-	1.0 (0.8-1.1)	1.0 (0.8-1.1)	-
open water respiration	-	2.0 (1.5-2.5)	2.0 (1.5-2.5)	-
photomineralization	-	0.4 (0.3-0.4)*	0.4 (0.3-0.4)*	-
CO ₂ emission	-	-	-	6.4 (5.1-7.0)
CH ₄ emission	-	0.1 (0.1-0.2)	-	-
stream inflow ¹	13.0 (10.8-15.6)	-	0.5 (0.4-0.6)	-
stream outflow ¹	-	13.9 (11.5-16.7)	-	0.6 (0.4-0.7)
groundwater inflow ²	4.6 (3.8-5.5)	-	0.9 (0.7-1.1)	-
sums of C-import and -export	17.6 (14.6-21.1)	16.6 (13.5-20.0)	4.8 (3.7-5.7)	7.0 (5.5-7.7)

Figure caption

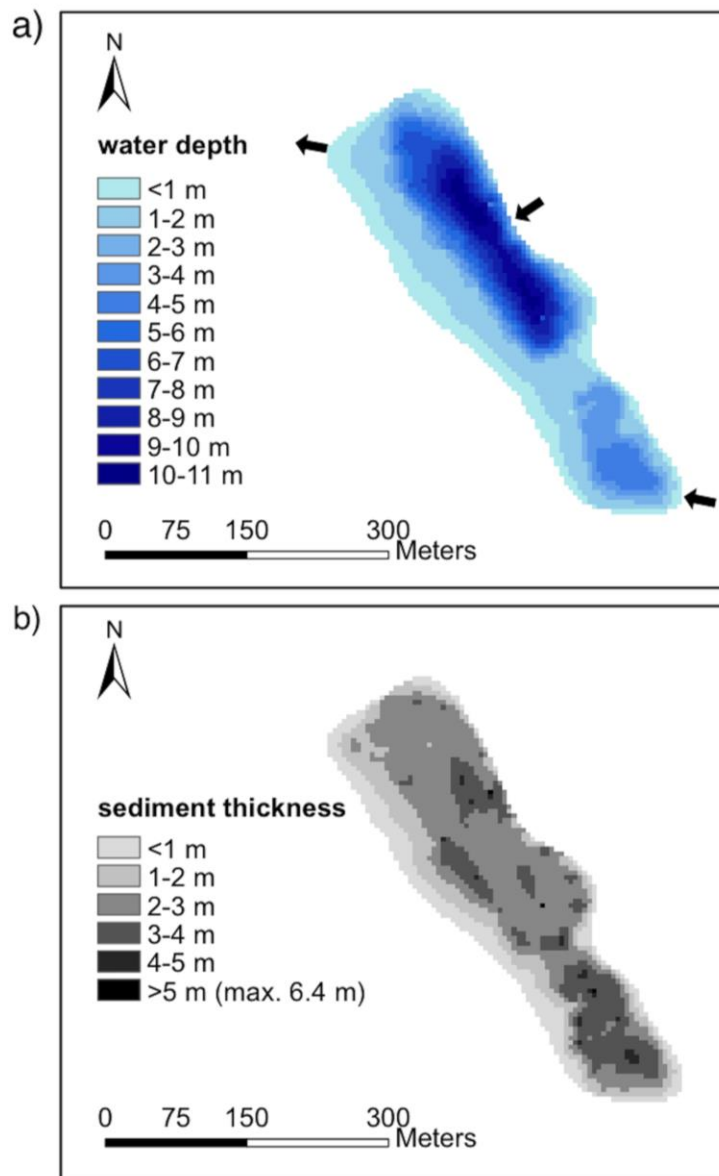


Fig. 1. Water depth (a) and sediment thickness (b) across the basin of Lake Gäddtjärn. Black arrows in (a) indicate the two inlet streams and the outlet stream.

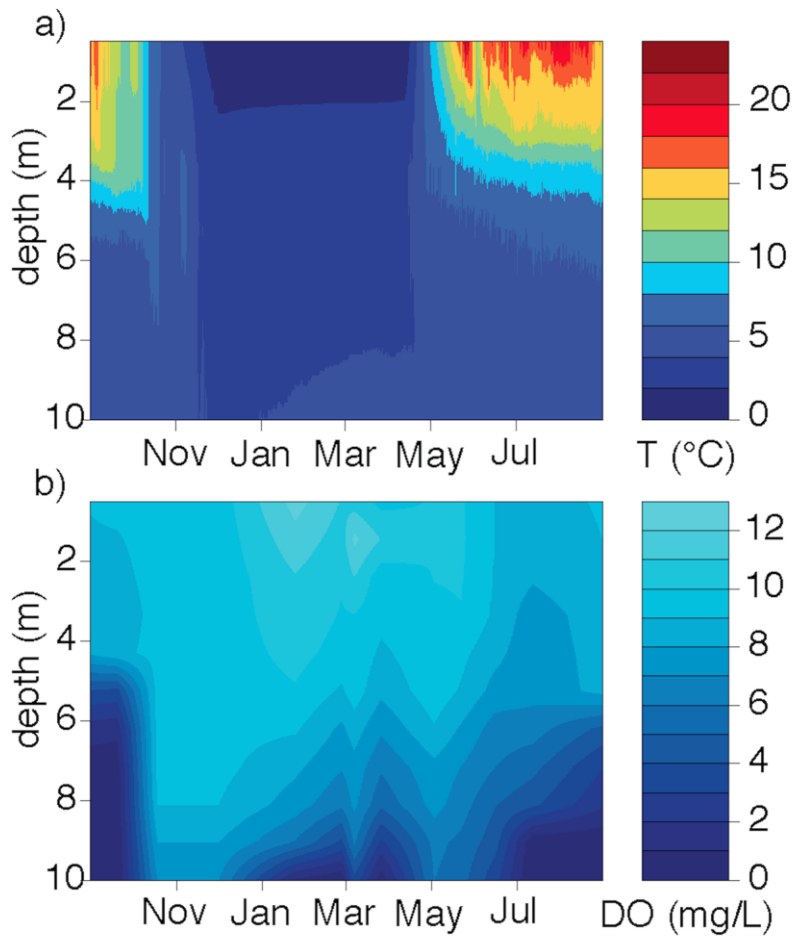


Fig. 2. Thermal conditions (a) and DO concentration (b) in Lake Gäddtjärn during the study period (Sep 2011-Aug 2012). Monthly DO data were linearly interpolated between measurement dates. No temperature sensors were deployed in the surface water from winter 2011 to spring 2012, and data were interpolated from manual measurements during ice-cover ($n=6$).

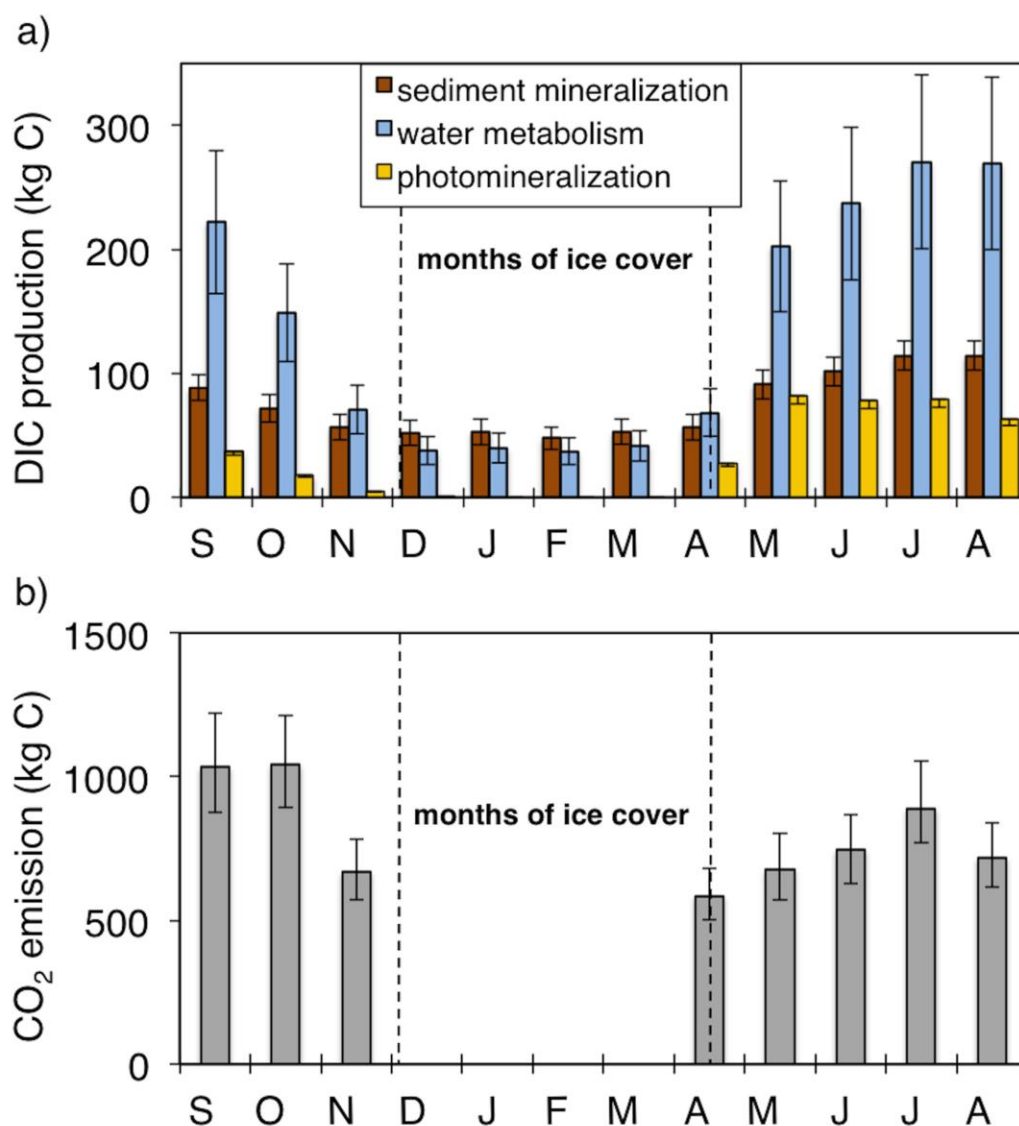


Fig. 3 Monthly net DIC production (a) by sediment respiration, respiration in lake water, and photomineralization in Lake Gäddtjärn. Error bars indicate minimum and maximum estimates of 95% confidence levels except for photomineralization where error bars indicate the total range of estimates using the minimum and maximum CDOM absorbance spectra. (b) Monthly CO₂ emission from Lake Gäddtjärn. Error bars indicate minimum and maximum estimates of 95% confidence levels.

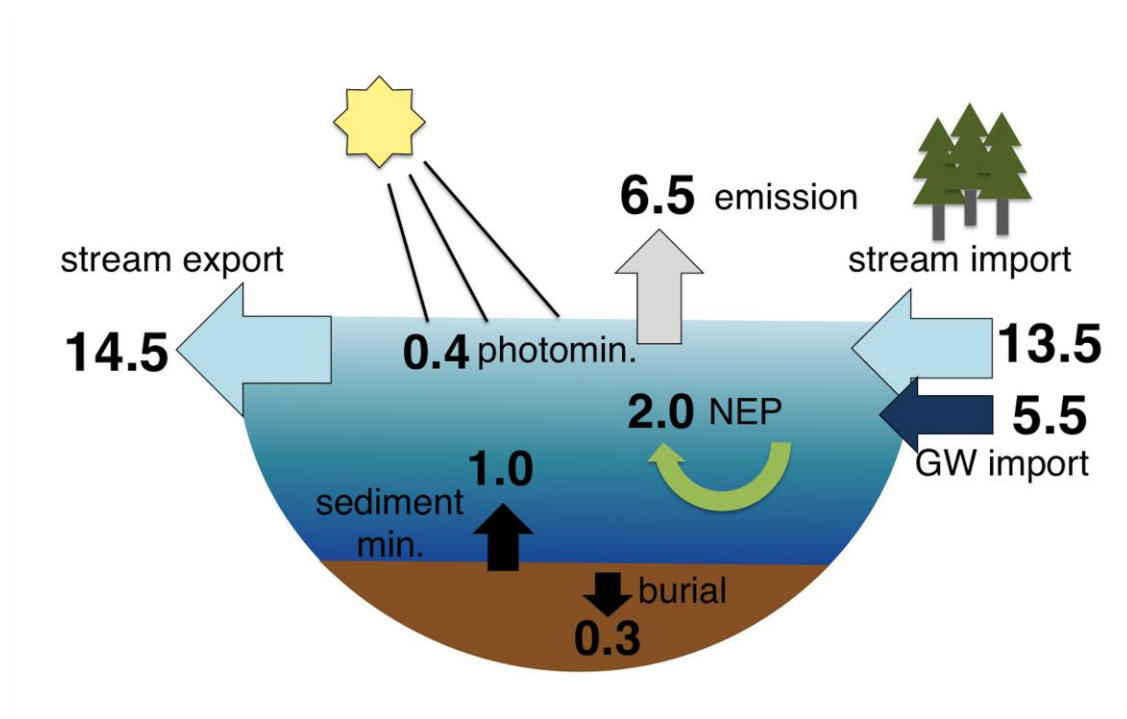


Fig. 4. A simplified annual carbon budget of Lake Gäddtjärn, showing the means (expressed as t C yr⁻¹) of OC burial, sediment OC mineralization, net water OC mineralization, photochemical OC mineralization, CO₂ and CH₄ emissions, C import from the catchment via surface water and groundwater, and C export from the lake via the outlet stream.