

## RESEARCH ARTICLE

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## Key Points:

- Significant terrestrial load of DOC, DIC, and CH<sub>4</sub> via groundwater to a boreal lake, even though most water enters via streams
- Terrestrial DIC load accounted for less than 12% of lake CO<sub>2</sub> emission
- Terrestrial DOC was more prone to mineralization and flocculation than lake DOC

## Supporting Information:

- Supporting Information S1

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## High terrestrial carbon load via groundwater to a boreal lake dominated by surface water inflow

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**Abstract** The input of dissolved organic and inorganic carbon (DOC and DIC) via direct groundwater seepage to boreal lakes is often assumed to be small in noncarbonaceous areas. However, measurements are rare. We estimated the terrestrial load of DOC, DIC, and methane (CH<sub>4</sub>) to a small boreal lake for the open water period, on the basis of measured concentrations of carbon species in near-shore groundwater wells and inlet streams, and measured area-specific discharge. The subcatchment directly draining into the lake via groundwater seepage contributed 18% to the total water input during the open water season. Compared to stream and lake water, near-shore groundwater concentrations of DOC were slightly elevated, and groundwater DIC and CH<sub>4</sub> concentrations were highly elevated. Consequently, direct groundwater seepage contributed 27% to the total DOC load, 64% to the total DIC load, and 96% to the total CH<sub>4</sub> load from the catchment to the lake. Groundwater DIC import corresponded only to 5–8% of lake carbon dioxide (CO<sub>2</sub>) emission. In incubation experiments, we observed higher photochemical DOC loss rates in stream and groundwater samples (18–55% DOC loss upon 72 h UV-A exposure) than in lake water (15% DOC loss) and detected significant DOC flocculation in groundwater samples in both light and dark incubations (2–24% DOC loss). We conclude that even in regions where lake hydrology is dominated by surface water inflow via inlet streams, direct groundwater seepage can represent an important carbon source to boreal lakes, and groundwater DOC may be susceptible to in-lake removal via degradation and flocculation.

### 1. Introduction

Inland waters have long been considered to passively transport terrestrial carbon to ocean, but it is now recognized that inland waters process, outgas, and store carbon at significant rates, and hence, they play an important role in the global carbon cycle [Battin *et al.*, 2009; Tranvik *et al.*, 2009]. Particularly in the boreal region, inland waters have been found to be important emitters of CO<sub>2</sub> and CH<sub>4</sub> to the atmosphere, and at the same time, important carbon sinks through organic carbon (OC) burial in the sediments [Bastviken *et al.*, 2004b; Kortelainen *et al.*, 2004, 2006; Wallin *et al.*, 2013], because the boreal forest and wetlands provide high amounts of land-derived dissolved organic carbon (DOC) as well as dissolved inorganic carbon (DIC) to surface waters [Sobek *et al.*, 2007; Öquist *et al.*, 2009]. Land-derived (i.e., allochthonous) DOC is an important energy source for the aquatic microbial community and either accumulates in the food web or mineralized to carbon gases (CO<sub>2</sub> and CH<sub>4</sub>) that can be emitted to the atmosphere. In addition, allochthonous DOC can flocculate and sink to the sediments [von Wachenfeldt and Tranvik, 2008], where it is preferentially buried [Sobek *et al.*, 2009; Chmiel *et al.*, 2015]. The contribution of allochthonous DOC is therefore essential for the metabolic state of lakes, most often resulting in boreal lakes being net heterotrophic systems [Pace *et al.*, 2004]. Together with DOC, land-derived DIC originating from soil respiration or weathering, as well as CH<sub>4</sub> originating from respiration in anoxic soils, can enter surface waters and contribute to the total C emission [Garnett *et al.*, 2013; McDonald *et al.*, 2013; Wallin *et al.*, 2014].

Terrestrial C can reach surface waters either via surface water runoff or via groundwater flow. In near-shore, i.e., riparian areas, soils are typically organic rich and wet since the groundwater table is shallow [Seibert *et al.*, 2009]. Groundwater that during transport to surface waters flows through these organic-rich riparian wetland soils get enriched in both organic and inorganic carbon [Öquist *et al.*, 2009; Grabs *et al.*, 2012]. The importance of organic-rich riparian soils for C export to surface waters has been well described for streams [Grabs *et al.*, 2012; Leith *et al.*, 2015], with the high emission of CO<sub>2</sub> and CH<sub>4</sub> observed for streams being attributed to high groundwater input of CO<sub>2</sub> and CH<sub>4</sub> with terrestrial origin [Crawford *et al.*, 2013; Wallin *et al.*, 2014; Kocic *et al.*, 2015]. For lakes, however, detailed studies on the importance

of groundwater C inputs are rare and limited to lakes with high groundwater input [Striegl and Michmerhuizen, 1998; Stets *et al.*, 2009], although large-scale studies [McDonald *et al.*, 2013; Weyhenmeyer *et al.*, 2015] and catchment C budgets [Juutinen *et al.*, 2013] suggest a generally strong contribution. Particularly in studies of boreal lakes dominated by surface water inflow and outflow, groundwater C input has often been argued to be small, even though evidence has been weak [Jonsson *et al.*, 2001; Hanson *et al.*, 2003; Sobek *et al.*, 2006]. However, not only boreal streams but also boreal lakes are often fringed by riparian wetlands, and there is generally a part of the catchment that drains directly into the lake without passing any surface water. Hence, there is no a priori reason as to why direct groundwater input may not be an important pathway of terrestrial C to boreal lakes. However, quantitative evidence is currently lacking.

Moreover, there are indications that groundwater-derived DOC may be more reactive than DOC present in surface waters. For example, very high rates of DOC removal have been reported from streams draining peatland dominated catchments [Dawson *et al.*, 2001; Moody *et al.*, 2013]. Similarly, the photochemical mineralization of DOC in stream water was found to be considerably higher in stream than lake samples [Molot and Dillon, 1997], possibly attributable to streams receiving a higher share of photoreactive groundwater DOC. Also, DOC flocculation was much higher in interstitial water from a mire than in a lake water [von Wachenfeldt *et al.*, 2008]. Even at larger spatial scales it has been observed that DOC of rivers and wetlands was more degradable than DOC of lakes [Lapierre and Del Giorgio, 2014] congruent with the strong negative relationship between the DOC degradation rate in inland waters and water retention time [Catalán *et al.*, 2016]. Hence, multiple lines of evidence indicate that DOC reactivity may be relatively elevated when DOC originating from riparian soils is exposed to surface water conditions, i.e., sunlight and high-oxygen concentration.

Based on these considerations, we hypothesized that C input via groundwater inflow can be an important contributor to the total terrestrial C load to a boreal lake dominated by surface water input. To test this hypothesis, we studied a small boreal lake and conducted a geographic analysis of the subcatchments draining to the lake either via surface water streams or via direct groundwater inflow, established a water budget, and measured riparian groundwater as well as surface water chemistry. We also compared groundwater C inputs with lake exports of C downstream and to the atmosphere in order to gauge the importance of groundwater inflow for the lake C budget. In addition, we conducted a laboratory experiment to test the hypothesis that the DOC derived from riparian soils will be more reactive than lake DOC.

## 2. Methods

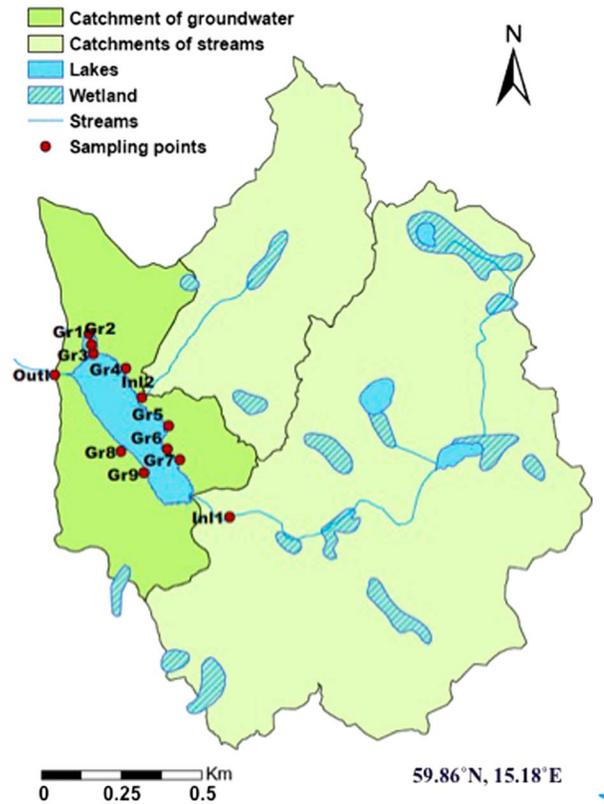
### 2.1. Study Site

The study was conducted in the Lake Gäddtjärn catchment located in mid-Sweden (59.86°N, 15.18°E). The 229 ha large catchment is mainly covered by forest (84%), followed by wetland (12%) and surface water (4%) (Figure 1). The forest is dominated by Norwegian spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). The main soil type of the area is brown forest soil and podzol, lying on Svecofennian intrusive rock, which is rich in iron and manganese oxide deposits [Stephens, 2009]. Annual mean temperature for the area is 4.5°C, and annual mean precipitation is 700 mm (Swedish Meteorological and Hydrological Institute, SMHI).

The area of Lake Gäddtjärn is 6.7 ha with mean depth of 3.4 m and a water volume of about 260,000 m<sup>3</sup>. The theoretical water retention time of Lake Gäddtjärn is around 2 months [Denfeld *et al.*, 2015]. The lake has two visible inlet streams and one outlet stream. The main inlet stream (Inlet 1) drains about 138 ha of the catchment, and the smaller inlet stream (Inlet 2) drains about 45 ha. The remaining 39 ha of the catchment drain directly into the lake via groundwater without passing any stream (Figure 1). In boreal Sweden, which is characterized by till soils, the groundwater table is generally shallow (< 1 m below the soil surface) due to the progressive increase in lateral saturated hydraulic conductivity toward the soil surface. This results in that the majority of the lateral groundwater flow occurs in superficial flow paths [Rodhe, 1987; Bishop *et al.*, 2004]. For this reason, we can assume that the groundwater flow paths largely follow the water divide determined at the soil surface.

### 2.2. Hydrology

The water level and temperature of the Inlet 1 and outlet streams were monitored automatically (hourly) during the open water season, from 3 May to 20 November 2013. Two identical setups consisting of a pressure



**Figure 1.** Map of the catchment of Lake Gäddtjärn divided to three subcatchments. The subcatchment areas draining into one of the two inlet streams are marked light green, and the subcatchment area that drains directly to the lake via groundwater discharge is marked dark green. Dots present sampling sites for groundwater (Gr1-Gr9), the two inlet streams (Inl1 and Inl2), and the outlet stream (Outl). Lake water sampling sites were located near-shore next to Gr3 (Lake1), Gr6 (Lake 3), and Gr9 (Lake2). © Lantmäteriet Gävle (2010): Permission I 2010/0058.

the area of the Inlet 1 subcatchment. We therefore estimated the discharge of groundwater directly into the lake from the discharge measured at Inlet 1 and applying the area ratio of the two subcatchments (29%):

$$Q_{gw} = \frac{Q_{Inlet} * A_{gw}}{A_{Inlet}} \quad (1)$$

where  $Q_{gw}$  is the discharge of groundwater directly into the lake,  $Q_{inlet}$  is the measured discharge at Inlet 1,  $A_{gw}$  is the subcatchment area draining directly into the lake, and  $A_{inlet}$  is the subcatchment area of Inlet 1. We base this approach on the observed homogeneity in area-specific discharge of Inlets 1 and 2 (see above).

These subcatchment areas for Inlet 2 and direct drainage into the lake were used in conjunction with the area-specific discharge measured at Inlet 1 to estimate the discharge at Inlet 2 and to estimate the groundwater that was directly discharged to the lake without passing any stream. Catchment area identifications were made by using a digital elevation model (2 m resolution; the Swedish Land Survey) in ArcGIS 10.1.

Hourly air pressure, wind speed, humidity, and air temperature (measured at a weather station in Klotten; 59.52°N and 15.15°E, approximately 7 km from Lake Gäddtjärn; SMHI 2013) and net irradiance (modeled at 22 × 22 km grid scale, SMHI; <http://strang.smhi.se>) were used to calculate evaporation from Lake Gäddtjärn [Penman, 1948; Shuttleworth, 1993] according to

$$E = \frac{mR_n + \gamma * 6.43(1 + 0.536 * U_2) \delta e}{\lambda(m + \gamma)} \quad (2)$$

transducer (MJK Expert 3400) and a temperature sensor (TOJO Skogsteknik Soil, TO3R) connected to a data logger (CR1000, Campbell Sci.) were used. The discharge ( $Q$ ) of the streams was manually measured at different discharge regimes during the study by the salt (NaCl) dilution method described by Day [1976]. A power fit regression between water level and measured discharge was used to convert hourly logged water level to hourly discharge (Inlet 1:  $n = 10$ , and  $R^2 = 0.97$ ; outlet;  $n = 11$ , and  $R^2 = 0.94$ ; data not shown). Manual measurements of discharge at Inlet 2 using the salt dilution method ( $n = 10$ ) revealed that discharge of Inlet 2 was on average ( $\pm$ SD) 33.5% ( $\pm$ 4.8%) of the manually measured discharge at Inlet 1. This was in close agreement with the subcatchment area of Inlet 2 being 33% of the subcatchment area of Inlet 1 (Figure 1), and thereby suggesting a relatively homogeneous area-specific discharge across the Lake Gäddtjärn catchment. Hourly discharge of Inlet 2 was therefore calculated from the measured hourly discharge of Inlet 1 and the discharge ratio of the two inlet streams (33.5%).

Similarly, groundwater discharge directly into the lake was calculated by determining the subcatchment area not draining into one of the inlet streams but directly via groundwater discharge into the lake (Figure 1), which corresponds to 29% of

where  $E$  is the evaporation rate ( $\text{mm d}^{-1}$ ),  $m$  is the slope of the saturation vapor pressure curve ( $\text{kPa K}^{-1}$ ),  $R_n$  is the net irradiance ( $\text{MJ m}^{-2} \text{d}^{-1}$ ),  $U_2$  is the wind speed at 2 m height ( $\text{m s}^{-1}$ ),  $\delta e$  is the vapor pressure deficit (kPa),  $\lambda_v$  is the latent heat of vaporization ( $\text{MJ kg}^{-1}$ ), and  $\gamma$  is the psychrometric constant expressed as

$$\gamma = \frac{C_p * P}{\lambda_v * MW} \quad (3)$$

where  $C_p$  is the specific heat of air at constant pressure,  $P$  is the atmospheric pressure and  $MW$  is the ratio of molecular ratio of water vapor to dry air.

Calculated evaporation and measured precipitation (Kloten weather station, SMHI 2013) were integrated for the lake area to calculate daily changes in water storage of Lake Gäddejtjärn. The water storage of the lake at daily time steps was estimated from

$$\Delta S_l = Q_{in} + Q_{gw} + P_l - Q_{out} - E_l \quad (4)$$

where  $\Delta S_l$  is the volume change in water storage of the lake,  $Q_{in}$  is the discharge of the inlet streams,  $Q_{gw}$  is the direct groundwater inflow to the lake,  $P_l$  is the direct precipitation onto the lake,  $Q_{out}$  is the discharge of the outlet stream, and  $E_l$  is the evaporation from the lake. Calculated lake water storage according to equation (4) was compared with estimated changes of water storage that was calculated from manual measurements of the lake water level at the sampling occasions and the lake area.

### 2.3. Water Chemistry

Nine groundwater tubes (50 mm diameter) were installed around the lake, 5–10 m from the lakeshore. The belowground part of each tube was approximately 1 m long and perforated with 5 mm holes to collect groundwater. The locations were selected to cover the present gradients in soil types and topographies. Accordingly, four tubes (Gr1-Gr3 and Gr5) were located in a near-shore sloping wetland, another three (Gr4, Gr6, and Gr7) in a steeply sloping forested mineral soil, and two in a gently sloping forested mineral soil (Gr8 and Gr9) (Figure 1). In addition, the study covered the open water season and therefore included both low-flow and high-flow periods. For these reasons, we are confident that our study represents the main drivers of variability in groundwater characteristics. In addition to the groundwater tubes, three stream sites (Inlets 1 and 2 and outlet) as well as three lake sites by the shore (Lakes 1–3) were monitored within the study.

The groundwater tubes were sampled by slowly pumping with a peristaltic pump (Cole-Parmer Masterflex), avoiding turbulence in order to minimize gas loss during sampling. Samples were collected from all tubes for analysis of DOC ( $n = 48$ ), DIC ( $n = 42$ ), and  $\text{CH}_4$  ( $n = 34$ ) (Table 1). After every sampling occasion, the remaining water of each tube was pumped out the tube which was then sealed with a rubber stopper. Surface water (streams and lake) samples were taken at approximately 10 cm below the water surface (Table 1). All water samples were put on ice and kept dark after sampling for transport and then stored dark at  $4^\circ\text{C}$  until further analysis. At all groundwater and surface water sampling sites, water level, conductivity, dissolved  $\text{O}_2$  concentration, and temperature were measured using a HQ40d portable meter. pH was measured in the laboratory on the same day after return from sampling (Metrohm, Aquatrode Plus).

For DOC and DIC analyses, water was collected into glass vials (40 mL for DOC and 17 mL for DIC; closed without headspace). All samples were stored dark and cold ( $4^\circ\text{C}$ ) until they were analyzed. The DIC samples were analyzed within 24 h on a Sievers 900 TC analyzer. Samples for DOC analyses were filtered in the laboratory through precombusted glass fiber filter (25 mm Whatman GF/F) and analyzed with a Shimadzu TC analyzer within 48 h from sampling. Particulate organic carbon (POC) has been earlier found to be a quantitatively insignificant contribution to the terrestrial C load to Lake Gäddejtjärn [Kokic *et al.*, 2015] and was therefore not measured in this study.

Partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) in ground and surface water was determined using the headspace equilibration method [Sobek *et al.*, 2003]. Water was directly collected carefully into a 60 mL polypropylene syringe, avoiding bubbles, and closed with a three-way stopcock. Twenty mL of the sample water were then equilibrated by shaking with 20 mL of ambient air for 1 min. The headspace was transferred to a second syringe

**Table 1.** Sampling Occasions and Concentration of C Species<sup>a</sup>

Sampling Dates	Outlet/Lake			Inlet Streams			Groundwater		
	DOC (mg/L)	DIC (mg/L)	CH <sub>4</sub> (μg C/L)	DOC (mg/L)	DIC (mg/L)	CH <sub>4</sub> (μg C/L)	DOC (mg/L)	DIC (mg/L)	CH <sub>4</sub> (μg C/L)
3 May	11.6 (n = 1)	1.6 (n = 1)	ND	13.1 ± 0.6 (n = 2)	0.8 ± 0.0 (n = 2)	ND	ND	ND	ND
21 May	12.4 (n = 1)	0.7 (n = 1)	ND	13.6 ± 0.4 (n = 2)	1.1 ± 0.1 (n = 2)	ND	ND	ND	ND
8 Jul	12.1 ± 0.1 (n = 2)	ND	ND	18.7 ± 3.6 (n = 2)	ND	ND	42.6 ± 4.2 (n = 6)	ND	ND
31 Jul	9.2 ± 0.1 (n = 4)	5.2 ± 0.0 (n = 4)	ND	20.6 ± 3.6 (n = 2)	1.3 ± 0.1 (n = 2)	ND	20.0 ± 2.5 (n = 7)	7.0 ± 1.0 (n = 7)	ND
22 Aug	9.2 ± 0.0 (n = 4)	5.4 ± 0.0 (n = 4)	8.1 (n = 1)	15.8 ± 3.3 (n = 2)	1.3 ± 0.0 (n = 2)	6.5 ± 3.8 (n = 2)	28.5 ± 4.3 (n = 7)	14.9 ± 1.8 (n = 7)	60.7 ± 23 (n = 6)
11 Sep	9.3 ± 0.1 (n = 4)	5.6 ± 0.1 (n = 4)	10.4 ± 2.8 (n = 4)	14.9 ± 3.5 (n = 2)	1.6 ± 0.0 (n = 2)	7.7 ± 1.0 (n = 2)	24.9 ± 2.4 (n = 7)	14.3 ± 2.1 (n = 7)	1212 ± 471 (n = 7)
3 Oct	9.5 ± 0.1 (n = 4)	5.7 ± 0.1 (n = 4)	10.3 ± 4.9 (n = 4)	11.4 ± 2.7 (n = 2)	1.4 ± 0.2 (n = 2)	6.8 ± 0.1 (n = 2)	31.6 ± 8.1 (n = 7)	11.8 ± 1.5 (n = 7)	1109 ± 495 (n = 7)
29 Oct	11.3 ± 0.7 (n = 4)	5.6 ± 0.1 (n = 4)	5.8 ± 1.4 (n = 4)	22.7 ± 3.6 (n = 2)	1.0 ± 0.2 (n = 2)	2.7 ± 0.5 (n = 2)	33.4 ± 11.3 (n = 7)	7.1 ± 2.0 (n = 7)	255 ± 210 (n = 7)
20 Nov	14.2 ± 0.8 (n = 4)	4.4 ± 0.3 (n = 4)	4.0 ± 1.3 (n = 4)	17.6 ± 0.8 (n = 2)	0.8 ± 0.1 (n = 2)	2.1 ± 0.3 (n = 2)	28.4 ± 9.7 (n = 7)	5.6 ± 2.0 (n = 7)	150 ± 87 (n = 7)

<sup>a</sup>Samples taken in 2013 during open water season. Values of concentration are expressed in mean ± SE.

and analyzed with an Infrared Gas Analyzer (Environmental Gas Monitor (EGM-4) PP Systems). Atmospheric  $p\text{CO}_2$  and atmospheric pressure were measured at every sampling occasion.

Partial pressure of  $\text{CH}_4$  ( $p\text{CH}_4$ ) was measured using the headspace equilibration method as described above. 10 mL of the equilibrated headspace was injected through a rubber stopper of a 25 mL glass vial, filled with supersaturated salt (NaCl) solution. While injecting the headspace gas, the vial was turned upside down and the corresponding volume of salt solution was pressed out from a second needle placed in the rubber stopper. Since  $\text{CH}_4$  does not dissolve in saturated salt solution, this method allows storage of the headspace gas without dilution. These samples as well as ambient air samples were analyzed on a gas chromatograph (GC-FID, Agilent Technologies), directly connecting the vials to the GC inlet port. Gas concentrations and partial pressures were calculated using temperature adjusted Henry's constants [Weiss, 1974; Yamamoto et al., 1976].

### 2.4. C Load

Daily time series of DOC, DIC, and  $\text{CH}_4$  concentrations for the period 1 May to 30 November were created by linear interpolation between sampling days. For the groundwater, the mean ± standard error of measured concentrations in seven groundwater tubes (observations from Gr4 and Gr7 were excluded as they were dry during most of the study period) from each sampling occasion were used in the interpolation. Daily load by groundwater and surface water of each C species was estimated by multiplying C concentrations with mean daily discharge. As groundwater measurements did not start until July for DOC and DIC, and not until August for  $\text{CH}_4$  (Table 1), the mean concentration of each carbon species of all sampling occasions was used to calculate the load for the months before groundwater concentration measurements commenced. The standard error for each load was calculated as the sum of standard error of concentration and standard error of discharge. The monthly area-specific load was calculated for each subcatchment by dividing the monthly load of the respective subcatchment (Inlets 1 and 2 and direct groundwater drainage to lake) with its area.

Lake Gäddejärn is part of the Swedish liming program, aimed at counteracting the adverse effects of acid precipitation. While the liming of Lake Gäddejärn had previously been halted, it was unexpectedly recommenced when a series of field investigation of the lake and its catchment had started [Denfeld et al., 2015; Kokic et al., 2015; Chmiel et al., 2016]. Lime was spread directly on the lake by helicopter on 1 July 2013, corresponding to 1.6 t inorganic carbon (IC) (information obtained from the Swedish county administrative board: kalkdatabasen.lansstyrelsen.se). Because of the long water retention time during the study period, the liming gave lasting effects throughout the study period and increased lake DIC concentration by about  $4 \text{ mg L}^{-1}$ . Hence, the liming affects estimates of DIC outflow and  $\text{CO}_2$  emission to a certain degree (see section 4) but does not affect reported catchment C loads to the lake, since not the catchment but the lake itself was limed.

## 2.5. Lake CO<sub>2</sub> Emission

The emission of CO<sub>2</sub> from the lake was calculated for the period of 1 May until 20 November 2013, when the first ice was detectable on the lake. Daily time series of *p*CO<sub>2</sub> were created by linear interpolation between means of the three near-shore lake *p*CO<sub>2</sub> measurements at each sampling occasion. The emission was calculated using following equation:

$$Em_{CO_2} = K_{CO_2} * (CO_{2Lake} - CO_{2Air}) \quad (5)$$

where  $Em_{CO_2}$  is the water-atmosphere CO<sub>2</sub> emission of the lake.  $K_{CO_2}$  is the gas transfer velocity (cm h<sup>-1</sup>),  $CO_{2Lake}$  is the CO<sub>2</sub> concentration of the lake water, and  $CO_{2Air}$  is the concentration of CO<sub>2</sub> in the water when it is in equilibrium with the atmosphere. CO<sub>2</sub> concentrations were calculated from *p*CO<sub>2</sub> using Henry's law according to Weiss [1974].  $K_{CO_2}$  was calculated using the Schmidt number (*Sc*) for CO<sub>2</sub> [Jähne et al., 1987]:

$$K_{CO_2} = k_{600} / (600 / Sc_{CO_2})^{-0.66} \quad (6)$$

where  $k_{600}$  is the gas transfer velocity that has been normalized for CO<sub>2</sub> at 20°C and -0.66 is the power dependence of *Sc* when the wind speed is lower than 3.5 m s<sup>-1</sup>, and with  $Sc_{CO_2}$  calculated as

$$Sc_{CO_2} = 1841 * e^{-0.0549T} \quad (7)$$

where *T* is the temperature in °C. For  $k_{600}$ , the wind speed parameterization by Cole and Caraco [1998] was used:

$$k_{600} = 2.07 + 0.215 * U_{10}^{1.7} \quad (8)$$

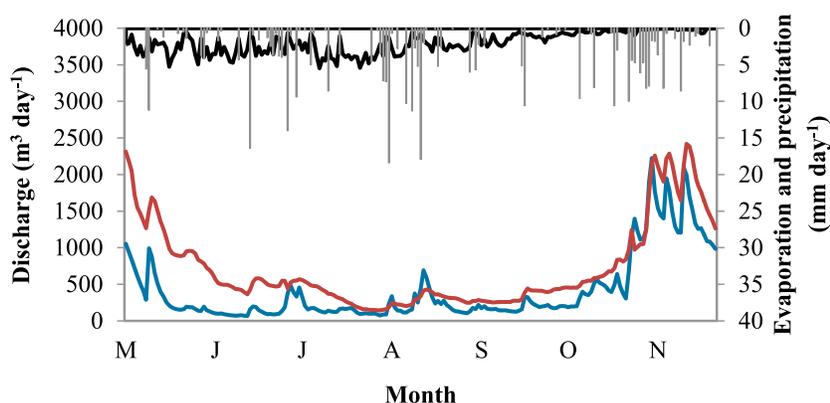
where  $U_{10}$  is the wind speed in m s<sup>-1</sup> at 10 m height. Daily wind data from SMHI was used to calculate the daily CO<sub>2</sub> emission.

## 2.6. DOC Reactivity Experiment

To test if the reactivity upon exposure to surface water conditions was higher for groundwater-derived than surface water-derived DOC, a laboratory experiment was conducted to determine the extent of DOC loss due to mineralization and flocculation. The experiments tested the effect of surface water conditions, using a light and a dark treatment, both at oxygenated conditions. Since there are no anoxic surface waters, this effect was not tested. Light exposure consisted of UV-A light, since short-wavelength light has strong effects on DOC mineralization and flocculation [Molot and Dillon, 1997; von Wachenfeldt et al., 2008]. DOC mineralization was determined as a decrease in DOC concentration, and flocculation was determined as formation of particles larger than 1.2 μm during the experiment [von Wachenfeldt et al., 2008]. All DOC that was lost from a sample during the incubation and could not be explained by flocculation (production of POC) was assumed to be lost via mineralization.

A 1.5 L of water was collected for incubation from three groundwater tubes (Gr3, Gr6, and Gr9), the lake, and Inlet 1 in October 2013. The samples were immediately put dark and cool (4°C) until the experiment start. The samples were filtered using precombusted 45 mm diameter glass fiber filter (GF/C Whatman). During filtration, all samples were oxygenated. A 200 mL of the filtrate was carefully filled into acid-washed UV-transparent polypropylene (PP) bags (9 cm × 21 cm). Water was sampled from the PP bags for initial DOC analysis. The bags were sealed headspace and bubble free with a plastic bag sealer. All plastic and glass equipment that were used in the experiment were acid washed over night, either in 10% HCl or 10% HNO<sub>3</sub> and rinsed in MQ for 1 day before use. In addition, all glassware was combusted at 450°C for 4 h prior to use.

Three replicates of each water sample were incubated under UV light and in darkness, except for site Gr6 (two dark treatment replicates) and site Gr9 (one dark treatment replicate) due to lack of water at the sampling occasion. The UV light treatment bags were put into a water bath at 20°C, and UV-A (320–400 nm) lamps were placed about 30 cm above it. Dark controls were put in a box and covered with thick black plastic and incubated at same temperature as the UV bags. All bags were incubated for 3 days. The measured irradiance during the UV light treatment was 5 W/m<sup>2</sup>. After incubation, the bags were opened and the water was drawn into a 60 mL syringe filtered through combusted glass filters (25 mm diameter Whatman GF/C). The filtrate was analyzed on a Shimadzu TC analyzer for DOC concentration. Filters were dried, put in tin capsules, and combusted in an Elemental Analyzer (Costech Instruments) to measure the mass of particulate organic carbon (POC) on the filter.



**Figure 2.** Water fluxes during the study period. (left axis) Daily discharge of the outlet stream (red line) and Inlet 1 (blue line). (right axis) Daily evaporation (black line) and precipitation (grey bars).

### 2.7. Statistics and Calculations

Errors in water fluxes and C loads were calculated based on the standard error of the mean of the parameters entering into the calculations, using error propagation. Differences of C species concentration between groundwater, inlet streams, and the lake were tested by analysis of variance, followed by Tukey-Kramer HSD post hoc test to identify differences between groups. For this purpose, data from all measurement occasions of all seven groundwater wells, two inlet stream sites, and the lake/outlet sites were pooled into the groundwater, inlet, and lake categories. In addition, differences of C species concentrations between groundwater originating from wetland (four wells) and mineral soil (three wells) were tested by Student's *t* test. Data were log transformed to approach normal distribution and homogeneity of variances when needed. For the experiment data, we tested for differences of DOC loss between dark and light treatments by using the nonparametric Wilcoxon Rank Sums test. For testing DOC loss differences between different origins of water (groundwater, stream, and lake), we used the nonparametric Kruskal-Wallis test. All statistical analyses were performed in JMP 13.

## 3. Results

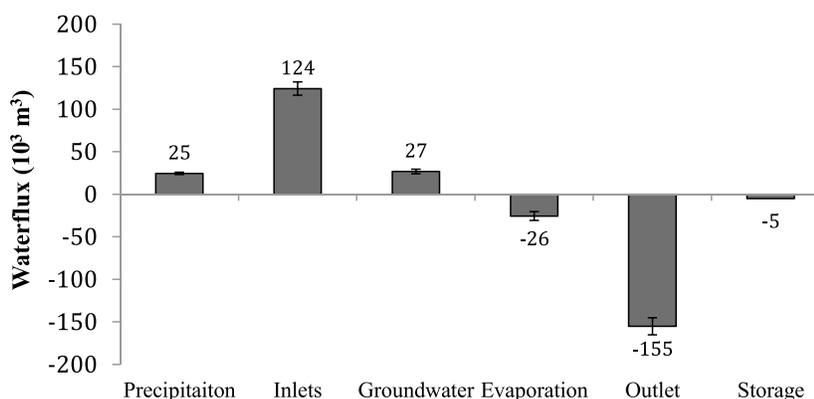
### 3.1. Hydrology

The study period was relatively dry compared to the long-term average, with low precipitation, high evaporation, and low stream discharge. The discharge of the outlet and Inlet 1 ranged from 1.6 to 28.3 L s<sup>-1</sup> and 0.8 to 30.9 L s<sup>-1</sup>, respectively (Figure 2). Discharge patterns were similar in the outlet and Inlet 1, but during May–June, the outlet discharge was higher than the inlet discharge as a consequence of ice-out occurring only a few days before the measurements started.

The water budget of Lake Gäddtjärn for the study period was close to balanced (Figure 3). Total water input was  $176 \pm 9 \times 10^3 \text{ m}^3$  (inlet streams  $124 \pm 8$ , groundwater  $27 \pm 3$ , and precipitation onto lake  $25 \pm 1 \times 10^3 \text{ m}^3$ , respectively) and very similar to the total water output of  $181 \pm 11 \times 10^3 \text{ m}^3$  (outlet stream  $155 \pm 10$  and evaporation  $26 \pm 5 \times 10^3 \text{ m}^3$ , respectively; mean  $\pm$  standard error). The water output being  $5 \times 10^3 \text{ m}^3$  higher than water input is probably related to a decrease in lake water storage, since the lake water level decreased by about 7 cm over the study period, corresponding to about  $5 \times 10^3 \text{ m}^3$  (data not shown). As the estimated water volume of the lake is about  $260 \times 10^3 \text{ m}^3$ , the lake water was not completely renewed during the study period.

### 3.2. Temporal and Spatial Variation in Carbon Concentrations

Both the magnitude and the spatiotemporal variability of all C species concentrations were higher in the groundwater than in the surface water (Table 1). Concentrations of DOC, DIC, and CH<sub>4</sub> were significantly ( $p < 0.001$ ) higher in groundwater (mean 27.7 mg L<sup>-1</sup>, 9.6 mg L<sup>-1</sup>, and 571 μg CL<sup>-1</sup>, respectively) than in the inlet streams (mean 16.5 mg L<sup>-1</sup>, 1.2 mg L<sup>-1</sup>, and 5.2 μg CL<sup>-1</sup>, respectively; analysis of variance (ANOVA), see supporting information). DOC and CH<sub>4</sub> concentrations were also significantly higher ( $p < 0.0001$ ) in the



**Figure 3.** The hydrological budget of Lake Gäddtjärn from the beginning of May until the end of November 2013. The input is shown as positive values (precipitation, inlet streams, and groundwater), and the output is shown as negative values (evaporation and outlet stream) along with changes in the lake water storage. Error bars show the standard error.

groundwater than the lake and its outlet (mean  $10.5 \text{ mg L}^{-1}$  and  $7.6 \mu\text{g C L}^{-1}$ , respectively). DIC did not significantly vary between groundwater ( $6.2 \text{ mg L}^{-1}$ ) and the lake and its outlet ( $4.3 \text{ mg L}^{-1}$ ;  $p = 0.44$ ; ANOVA; see supporting information).

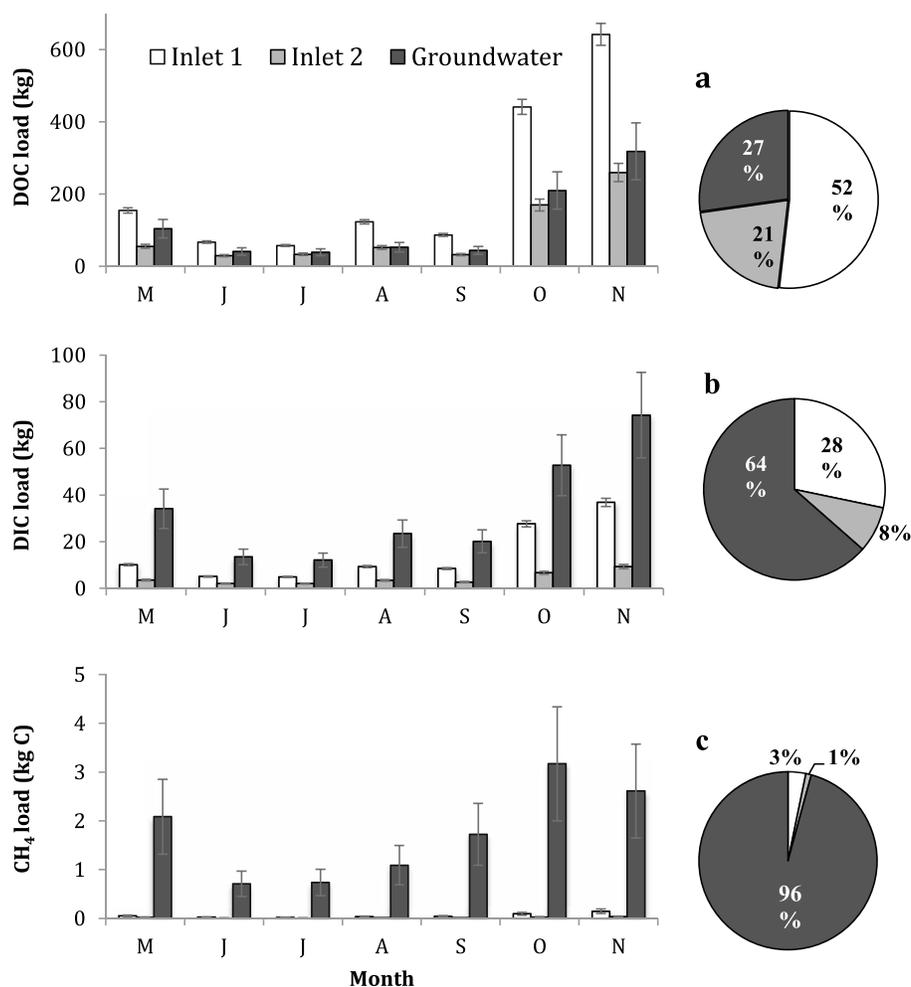
The difference in C concentrations between groundwater tubes was substantial at all occasions (as indicated by  $\pm$  SE (standard error) in Table 1). DOC concentration varied between groundwater wells with factor of 2–10 (maximum range:  $7.9$  to  $93.4 \text{ mg L}^{-1}$  in October), DIC concentration with a factor of 3–10 (maximum range:  $1.7$ – $16.0 \text{ mg L}^{-1}$  in November), and  $\text{CH}_4$  concentration with a factor of 20–200 (maximum range:  $5.9$ – $1410 \mu\text{g C L}^{-1}$  in October). The DOC concentration in groundwater was significantly higher in mineral soil versus wetland (mean  $38.2 \text{ mg L}$  versus  $23.2 \text{ mg L}$ , respectively; Student  $t$  test,  $t_{(46)} = -3.2$ ;  $p = 0.0025$ ). Both  $\text{CH}_4$  and DIC concentration did not substantially vary between the two soil types (Student  $t$ ;  $t_{(32)} = -0.33$ ,  $p = 0.74$  and  $t_{(41)} = 1.21$ ,  $p = 0.88$ ). While DOC concentrations in groundwater were not showing a distinct temporal pattern, DIC concentration was peaking in August and September, and  $\text{CH}_4$  concentration was peaking in September and October (Table 1).

We also observed differences in C concentrations between surface waters. The DOC concentration of the inlet streams (Inlets 1 and 2) varied from  $11.4$  to  $22.7 \text{ mg L}^{-1}$  and was consistently higher ( $p = 0.0059$ ) than in the lake and its outlet stream (range:  $9.2$  to  $13.6 \text{ mg L}^{-1}$ ; Table 1), without clear patterns over time. Conversely, DIC concentration was higher in the lake and its outlet (range:  $0.7$ – $5.8 \text{ mg L}^{-1}$ ) than in the inlet streams (range:  $0.8$ – $1.6 \text{ mg L}^{-1}$ ) ( $p = 0.0026$ ; see supporting information).  $\text{CH}_4$  concentrations were not significantly higher in the lake and its outlet (range:  $4.0$ – $10.4 \mu\text{g C L}^{-1}$ ) than in the inlet streams (range:  $2.1$ – $7.7 \mu\text{g C L}^{-1}$ ; Table 1) ( $p = 0.88$ ; see supporting information). In the inlet streams, DOC and DIC concentration did not show any seasonal pattern, while  $\text{CH}_4$  concentration was elevated during August–October. In the lake and its outlet, DOC was comparatively low during July–October, DIC was increased between May and July, and  $\text{CH}_4$  was elevated during September and October.

### 3.3. C Inputs and Outputs

The load of C to the lake varied seasonally, mainly related to variability in discharge. Highest C load was during peak discharge in November, and relatively low C load prevailed during low discharge in spring and summer (Figure 4). The total C load to the lake over the study period was  $3.5 \pm 0.4 \text{ t C}$ . Direct groundwater inflow into the lake contributed to almost one third of the total C load ( $1.1 \pm 0.3 \text{ t C}$ ). Of the total C load to the lake, 89% was as DOC, 11% as DIC, and less than 0.5% as  $\text{CH}_4$ -C.

DOC entered the lake mainly via Inlet 1 (52% of total DOC load), followed by groundwater load (27%) and Inlet 2 (21%) (Figure 4a). Concerning DIC, groundwater was the most important pathway of loading to the lake (64% of total DIC load), while Inlets 1 and 2 contributed with 28% and 8% to the total DIC load, respectively (Figure 4b).  $\text{CH}_4$  load to the lake was greatly dominated by groundwater inflow (96% of total load), and only 4% of the  $\text{CH}_4$  load entered the lake via the inlet streams (Figure 4c).



**Figure 4.** The load of (a) DOC, (b) DIC, and (c) CH<sub>4</sub> from land to Lake Gäddtjärn via Inlet 1, Inlet 2, and direct groundwater inflow, expressed both on a monthly basis (bar graphs) and as contribution to total load over the study period (pie charts). Error margins are propagated standard errors.

The area-normalized load of C (DOC + DIC, as CH<sub>4</sub> was negligible) over the entire study period was about two times larger from the subcatchment draining directly to the lake via groundwater inflow (26.7 kg C ha<sup>-1</sup>) than from the subcatchments of Inlets 1 and 2 (12.1 and 14.7 kg C ha<sup>-1</sup>, respectively; Table 2).

Lake DOC import exceeded DOC export. Downstream DOC export through the lake outlet was 1.8 ± 0.2 t C, while DOC input to the lake from the catchment was 3.0 ± 0.4 t C (Figure 5). Conversely, lake DIC import was much smaller than IC export. The emission of CO<sub>2</sub> from the lake to the atmosphere during the study period was estimated at 4.6 ± 0.3 t C (Figure 5). Downstream DIC export from the lake through the outlet was 0.6 ± 0.1 t C, such that the total IC export from the lake was 5.2 ± 0.3 t C. Catchment import of DIC summed up to 0.3 ± 0.1 t C, corresponding to 6% of total lake IC export.

### 3.4. Reactivity of DOC Exposed to Surface Water Conditions

A consistent loss of DOC was observed in all samples exposed to UV-A irradiation and also in dark incubations of two groundwater samples (Figure 6). The loss of DOC was significantly higher in light treatments than in dark treatments (Wilcoxon test;  $z = -3.86$ , and  $p < 0.0001$ ), and there was a substantial difference in DOC loss between water origins (Kruskal-Wallis test;  $\chi^2_{(4)} = 11.75$ ;  $p = 0.02$ ). The lake water showed smaller DOC loss as compared to stream water or groundwater (Figure 6). The largest DOC loss (55%) was detected in the stream water. The loss from the groundwater varied from 25 to 42%, and the DOC loss from the lake water was 16%. The majority of DOC loss was via mineralization, except in Gr9 where more than half of the DOC

**Table 2.** Subcatchment Specific DOC and DIC Load to Lake Gäddtjärn<sup>a</sup>

	Inlet 1		Inlet 2		Groundwater	
	DOC	DIC	DOC	DIC	DOC	DIC
	(kg ha <sup>-1</sup> )					
May	1.1	0.1	1.2	0.1	2.7	0.9
June	0.5	0.04	0.7	0.05	1.1	0.3
July	0.4	0.04	0.7	0.05	1	0.3
August	0.9	0.1	1.2	0.1	1.4	0.6
September	0.6	0.1	0.7	0.1	1.1	0.5
October	3.2	0.2	3.8	0.1	5.4	1.4
November	4.7	0.3	5.8	0.2	8.2	1.9
Total (kg ha <sup>-1</sup> )	11.4	0.7	14	0.7	20.8	5.9

<sup>a</sup>Subcatchment specific dissolved C load (kg C ha<sup>-1</sup> month<sup>-1</sup>), referring to the subcatchments drained by Inlet 1, Inlet 2, and groundwater discharge directly to the lake.

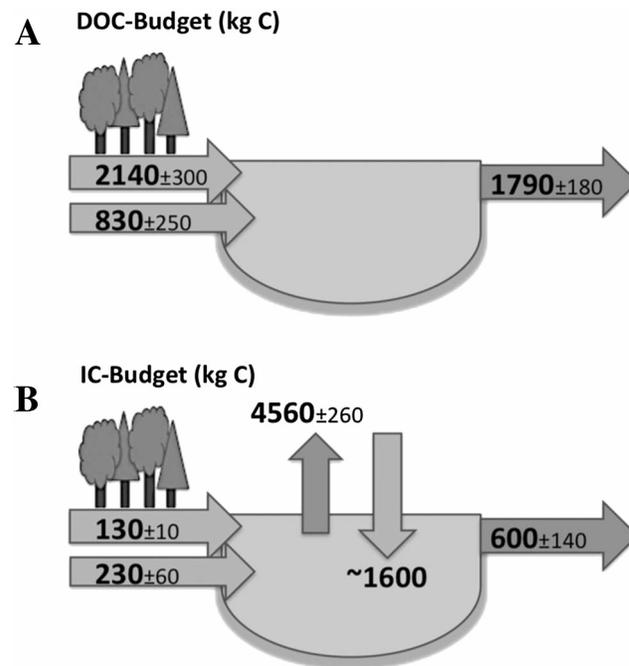
loss was via flocculation (Figure 6a). Results from dark incubations showed DOC loss in two groundwater samples (Gr6, 9% DOC loss; Gr9, 29% DOC loss). Two thirds of the DOC loss in Gr9 and one third of the loss in Gr6 were due to flocculation of DOC, with the remainder of DOC loss being ascribed to mineralization (Figure 6b).

#### 4. Discussion

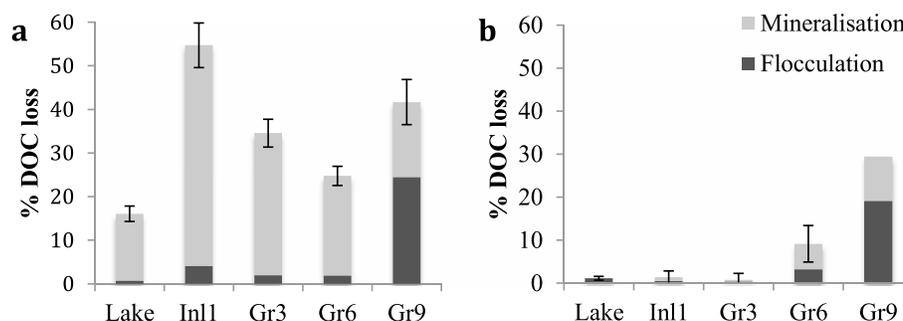
##### 4.1. Groundwater Contribution to the Terrestrial C Load

Despite only representing 17% of the total catchment, drainage of groundwater directly into the lake contributed about 30% of the total terrestrial load of dissolved C to Lake Gäddtjärn. For the different C species, direct

groundwater inflow into the lake contributed 27% of the DOC, 64% of the DIC, and 96% of the CH<sub>4</sub> loads from the catchment to the lake (Figure 4). While studies have shown that the contribution of dissolved C via shallow groundwater inflow is an important source of C to boreal streams [Öquist *et al.*, 2009; Grabs *et al.*, 2012; Leith *et al.*, 2015], evidence concerning the groundwater contribution to the C budget of lakes is more ambiguous, potentially related to regional difference in geology [Striegl and Michmerhuizen, 1998; Hanson *et al.*, 2003; Larmola *et al.*, 2003; Sobek *et al.*, 2006; Stets *et al.*, 2009]. Here we show that in a lake in boreal Sweden, where deep groundwater flow is limited by Precambrian bedrock and thin soils [Rodhe, 1987; Bishop *et al.*, 2004], shallow groundwater inflow through riparian soils could lead to high groundwater-mediated flux of land-derived C to the lake. Organic-rich riparian soils are common around the wet margins of boreal lakes, and similarly to streams, groundwater moving down-slope passes through riparian soils and acquires their C-rich soil solution chemistry (Table 1) before entering the lake



**Figure 5.** Illustration of the (a) DOC budget and (b) IC-budget of Lake Gäddtjärn during the study period. Vertical arrows indicate CO<sub>2</sub> emission and input of lime through the Swedish national liming program. Horizontal arrows indicate input with inlet streams (upper arrow), input with groundwater (lower arrow), and output with the outlet stream. The CH<sub>4</sub> load was negligible in terms of C mass and is therefore not included in these budgets. Numbers are expressed as the mean ± SE.



**Figure 6.** DOC loss in surface water (lake and Inl1) and shallow groundwater (Gr3, Gr6, and Gr9) via mineralization and flocculation during a 72 h incubation (a) with UV-A exposure and (b) in darkness. Error bars display the standard deviation (SD).

[Bishop *et al.*, 2004; Seibert *et al.*, 2009; Ledesma *et al.*, 2015]. Accordingly, the area-specific dissolved C load (DOC + DIC) from the subcatchment draining directly into Lake Gäddtjärn via groundwater discharge ( $26.7 \text{ kg ha}^{-1}$ ) was  $\sim 2$  times larger than the area-specific dissolved C load from the subcatchments drained by streams ( $12.1 \text{ kg ha}^{-1}$  for inlet 1 and  $14.7 \text{ kg ha}^{-1}$  for inlet 2, respectively; Table 2; see supporting information). Hence, it is likely that the part of a catchment that drains directly to a lake via groundwater discharge can be a disproportionately important source of land-derived dissolved C to boreal lakes.

#### 4.2. Significance of Groundwater Input to Lake C Budget

The large groundwater contribution to the terrestrial C load has important implications for our understanding of boreal lake ecosystems. This is illustrated by the C budget that, even though not being complete, contains the major C fluxes of this lake [Chmiel *et al.*, 2016]. For example, without accounting for groundwater DOC load, there was only a small difference between DOC input ( $2140 \pm 300 \text{ kg C}$ ; Figure 6a) and DOC output ( $1790 \pm 180 \text{ kg C}$ ), implying that the lake was only slightly heterotrophic (15% DOC loss in the lake). However, adding the groundwater input of  $830 \pm 250 \text{ kg DOC}$  results in a total input of  $2970 \pm 390 \text{ kg DOC}$  and implies a pronounced DOC loss of roughly 40% in the lake, indicative of a strongly net heterotrophic ecosystem. Hence, the DOC load via groundwater inflow can be highly important and should not be neglected when estimating the metabolic balance of small boreal lakes like Lake Gäddtjärn.

In accordance with the evidence of strong net heterotrophy, we found that the input of terrestrial DIC was a small contribution to the lake  $\text{CO}_2$  emission (8%), and groundwater-mediated DIC input constituted only 5% of lake  $\text{CO}_2$  emission (Figure 5b). Even if the DIC budget is complicated by the addition of lime to the lake (see supporting information), our data suggest that the majority of the  $\text{CO}_2$  emission was driven by mineralization of OC in the water column and in the sediments (Figure 5) [Chmiel *et al.*, 2016]. While this finding is in line with some previous studies [Jonsson *et al.*, 2001; Hanson *et al.*, 2003; Kortelainen *et al.*, 2006; Sobek *et al.*, 2006], it contrasts with other studies that suggested a strong terrestrial DIC supply of lake  $\text{CO}_2$  emission [McDonald *et al.*, 2013; Weyhenmeyer *et al.*, 2015; Wilkinson *et al.*, 2016]. These different observations may be related to regional-scale differences in, e.g., geology [Marce *et al.*, 2015], climate [Kosten *et al.*, 2010], topography, and land cover [Sobek *et al.*, 2007] affecting both catchment DOC and DIC load and in-lake processes. Also, weather conditions may play a role. For example, for the wetter year 2012, 22% of the  $\text{CO}_2$  emission from Lake Gäddtjärn was suggested to be derived from terrestrial DIC load [Chmiel *et al.*, 2016], in accordance with reports of elevated  $\text{CO}_2$  emission from boreal lakes during wet years [Rantakari *et al.*, 2015]. This suggests that depending on the hydrological conditions, terrestrial DIC load may contribute on the order of 10–25% to the  $\text{CO}_2$  emission of Lake Gäddtjärn.

We found that  $\text{CH}_4$  input via groundwater inflow was the dominant pathway of terrestrial loading to the lake. While we did not measure lake  $\text{CH}_4$  emission within this study, we can compare with measurements in 2008 of  $\text{CH}_4$  emission of Lake Gäddtjärn during the open water season, corresponding to  $110 \text{ kg C}$  [Chmiel *et al.*, 2016]. Terrestrial  $\text{CH}_4$  import was  $11.6 \text{ kg C}$  ( $11.1 \text{ kg C}$  via groundwater), and hence, we conclude that the main source of  $\text{CH}_4$  emission from the lake is internal production and congruent with a previous study of two northern temperate lakes [Striegl and Michmerhuizen, 1998].

### 4.3. Water Fluxes and Their Importance for C Loads

The hydrological budget of Lake Gäddtjärn for the open water season in 2013 showed only about 5000 m<sup>3</sup> difference between input and output of water (Figure 3), corresponding well to the observed 5–7 cm change in lake water level over the study period. This gives confidence to our approach of estimating groundwater flow by applying the area-specific discharge of the major inlet stream to the subcatchment that drains directly to the lake via groundwater discharge. While area-specific discharge has been observed to vary within mesoscale (70 km<sup>2</sup>) boreal catchments [Lyon *et al.*, 2012], the similarity of area-specific discharge of Inlets 1 and 2 corroborated the assumption of homogenous area-specific discharge across the Lake Gäddtjärn catchment. Being apparently successful for the studied catchment, this approach represents a relatively simple way to estimate groundwater flow into a lake.

The load C to the lake was proportional to discharge, with low C loads during the dry summer and high C load during high-discharge events in autumn (Figures 2 and 4). This observation indicates a strong hydrological control on the terrestrial C load, something that is commonly observed in boreal regions [Köhler *et al.*, 2008; Wallin *et al.*, 2015]. Therefore, it is important to consider that 2013 was a comparatively dry and warm year, with 30% lower precipitation and 2°C higher temperature than the long-term annual means of 1961–1990 (SMHI) and thus very low discharge. Terrestrial C load is consequently likely to be considerably higher in a wet year [Kokic *et al.*, 2015] (see supporting information). It seems plausible to assume that the interannual variation in groundwater C load to boreal lakes is proportional to the interannual variation in stream C load, since also the streams receive terrestrial C load via groundwater inflow through riparian soils. As a first approximation, applying groundwater DOC and DIC flow as a percentage of stream water DOC and DIC load may be used to estimate groundwater C load for different years [Chmiel *et al.*, 2016].

### 4.4. Spatial and Temporal Variability in C Concentrations

The concentrations of all C species were greater in groundwater than in the inlet or outlet streams and in the lake itself (Table 1). The large concentration difference between groundwater and surface water was especially pronounced for DIC and CH<sub>4</sub>. This was expected since much of the DIC (in the form of CO<sub>2</sub>) and CH<sub>4</sub> is rapidly degassed to the atmosphere [Kokic *et al.*, 2015]. Also, the high variability in C concentrations between groundwater sampling sites was expected since topography, soil type, vegetation composition, moisture, and position of groundwater table [Laudon *et al.*, 2011; Kelsey *et al.*, 2012] all affect accumulation, production and processing of C, and the locations of the groundwater tubes were chosen to reflect different soil types (wetland/mineral soil) and topographies (slope). Also seasonal changes, e.g., because of temperature changes, can affect groundwater C concentration [Kelsey *et al.*, 2012]. Possibly, the observation of elevated groundwater concentrations of both DIC, and particularly of CH<sub>4</sub> (Table 1), may be related to the temperature dependence of soil respiration and methane production [Davidson and Janssens, 2006; Yvon-Durocher *et al.*, 2014]. By stretching over a wide spatial and temporal gradients in groundwater C concentrations, we consider that C loads were calculated using representative means and standard errors of C concentrations. We also performed a sensitivity analysis on the influence of assuming the mean C concentrations when there was missing data (Table 1), but we could only see a small effect on C loads (see supporting information). This indicates that even if C concentrations vary, C load is primarily driven by discharge.

### 4.5. Reactivity of Lake, Stream, and Groundwater DOC

Our experimental data strongly suggest that DOC imported from the catchment via streams and groundwater was more photoreactive than the DOC of the lake water itself (Figure 6). Both samples of groundwater and of the Inlet 1 stream showed significantly greater DOC loss than the lake sample ( $p < 0.02$ ) upon UV-A irradiation, suggesting that up to half of the soil-derived DOC could be lost relatively rapidly in the lake. The in situ rate of DOC loss depends on solar irradiation and the depth of the surface mixed layer of the lake, and it is likely that the effective light exposure in the lake is much smaller than during the experiment. The experimental DOC loss rates should therefore not be interpreted as reflecting in situ rates but for comparison of reactivity of DOC from different sources. The DOC loss was somewhat higher in the stream than in the groundwater samples (Figure 6a), which may be related to that the water was sampled in October just after a rainstorm, when the stream had a higher concentration of DOC (Table 1) and likely contained more fresh and reactive DOC [Vidon *et al.*, 2014].

The DOC loss during the experiment was mainly due to photochemical degradation or sequential photochemical-microbial degradation [Bertilsson and Tranvik, 1998], since little mineralization was observed in the dark control (Figure 6). Flocculation was detectable in all light treatment samples, possibly indicating photoaggregation of DOC to POC [von Wachenfeldt et al., 2008; Moody et al., 2013]. In addition, DOC flocculation was detected in two of the groundwater samples in the dark treatment (groundwater of forested sites, Gr6, and Gr9; Figure 6). These two groundwater samples had very low oxygen concentration at sampling ( $1.33$  and  $0.28$  mg L<sup>-1</sup>, respectively), and it is likely that the oxygenation of the water samples caused oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> and thereby favored flocculation of DOC [Riedel et al., 2013]. Accordingly, the import of both dissolved reduced iron (Fe<sup>2+</sup>) and DOC from anoxic groundwater could flocculate upon mixing with oxygenated lake water, resulting in flocculation of groundwater-derived DOC and subsequent sedimentation. Additionally, oxygenation favors the microbial DOC degradation of previously anoxic water [Bastviken et al., 2004a], which may explain the high-DOC loss via mineralization in the dark treatment of the two reactive groundwater samples. We conclude that groundwater-derived DOC that enters the lake will only react not only to sunlight but also probably to oxygenation and to a significant extent be mineralized or flocculated to form sediment. Groundwater inflow thus not only adds a significant quantity of DOC to the lake but also adds DOC of comparatively high reactivity.

#### 4.6. Potential Applicability to Other Systems

Our study suggests that the magnitude of groundwater C inflow to a boreal lake strongly depends not only on the areal distribution of the catchment, i.e., size of the subcatchment area draining directly into the lake, in relation to the subcatchment drained by streams, but also on hydrological flow paths and riparian soil characteristics; i.e., in how far the groundwater that drains directly into the lake is flowing through shallow, organic-rich soils, or rather through mineral soil horizons. For our study lake, 17% of the catchment that is draining directly to the lake by groundwater contributed 30% of the total terrestrial C lake input. Importantly, these numbers are derived from the study of only one lake, and it remains to be seen in how far they are applicable to other boreal lakes.

It has further been shown that in the gentle topography of boreal Sweden, soils situated in depressions, such as close to lake shores, are often characterized by high water table and high organic content [Grabs et al., 2012]. Given that lateral groundwater flow dominantly occurs in superficial flow paths [Rodhe, 1987; Bishop et al., 2004] there is a high probability that it will pass through organic-rich riparian soils close to the lake shores. Nonnegligible quantities of groundwater C load is therefore likely to be a common feature in lakes of boreal Sweden, worth investigating also elsewhere. We propose that determining the proportion of catchment area draining directly to lakes via groundwater discharge, combined with data on riparian soil water chemistry, either measured or modeled [Grabs et al., 2012], may be a feasible approach for modeling groundwater C fluxes to boreal lakes at larger scales.

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