Hydrology controls the carbon mass balance of a mountain lake in the eastern European Alps

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Abstract

Lakes and streams in mountain regions are important contributors to carbon (C) fluxes. However, detailed carbon balances of the stream-lake continuum are rare. Combining eddy covariance (EC) measurements of lake-atmosphere net ecosystem CO2 exchange with measurements of fluvial C fluxes (dissolved organic C, DOC; particulate organic C, POC; dissolved inorganic C, DIC), and in-lake sedimentation, we here present a detailed annual C balance of an oligotrophic clearwater lake in the eastern European Alps. The C flux into the lake was 1522 Mg C year\(^{-1}\) by DIC (93%), DOC (6%), and POC (0.7%). The largest C losses were fluvial exports (1595 Mg C year\(^{-1}\)) of DIC (93%), DOC (6%), and POC (0.8%), while sedimentation accounted for 7.3 Mg C year\(^{-1}\). The residual of all fluvial and sedimentation fluxes revealed the lake as a net sink of atmospheric CO2 of 77 Mg C year\(^{-1}\). The EC measurement confirmed a small positive or negative contribution of atmospheric exchange to the lake C balance. In-lake transfer among C pools was only significant for the flux from DIC to POC (8.4 Mg C year\(^{-1}\)), which, following our model, is the transfer through primary production in summer. Fluvial DOC and DIC fluxes were controlled by discharge; POC retention and sedimentation depended on the meteorological season and in-lake residence time. Following our findings, we conclude that hydrology acted as the most important control for the C balance of this clearwater mountain lake by controlling inflow, outflow, and sedimentation fluxes.

Lakes represent a significant component of the global carbon (C) cycle (Mendonca et al. 2017; Raymond et al. 2013; Sobek et al. 2005; Tranvik et al. 2009). They receive organic and inorganic C from various terrestrial sources within the catchment and from in-lake primary production (PP). Some of this C may be stored in lake biota and/or sediments (Cole et al. 2007; Mendonca et al. 2017), is released as gaseous C (i.e., CO\(_2\) and CH\(_4\)) to the atmosphere (Tranvik et al. 2009; Raymond et al. 2013), or leaves the lake through its outlet. The lake net balance of gross primary production (GPP) and community respiration (ER) defines its role as net-heterotrophic or net-autotrophic, while lake sedimentation, mineralization and evasion, and PP define the status of a lake as C sink or source along the aquatic continuum. Overall, lake ecosystems are considered as dynamic and sensitive players within the global C cycle (Tranvik et al. 2018).

Streams are the main source of organic C (OC) in the form of dissolved OC (DOC) and particulate OC (POC), and dissolved inorganic C (DIC) to lakes from the catchment (Schindler et al. 1997; Jonsson et al. 2001; Solomon et al. 2015), with increased C supply during high-flow events (McKnight et al. 1997; Likens 2009; Johnson et al. 2018). In addition to streams, rainfall and groundwater can also provide direct C inputs to lakes, with high DIC inputs from groundwater dominating the DIC pool in some boreal lakes (Weyhenmeyer et al. 2015). Overall the fluvial inputs link the C cycle of lakes to the terrestrial C balance and to the hydrological processes within the catchment.

Terrestrial OC may reside over varying times in the water column of the lake. This OC becomes engaged in biogeochemical cycling, that can alter the quantity and quality of DOC and POC (Meyers and Ishiwatari 1995). Specifically, lake transfer has been shown to modify the DOC composition dependent on season and residence time (Ejarque et al. 2018), while considerable proportions of inflowing DOC can also be...
respired (Algesten et al. 2004). Chemical flocculation and microbial uptake convert DOC into POC (Allgaier and Grossart 2006), while, at the same time, microorganisms transform POC back to DOC. This renders microorganisms to important players for large and rapid transformations between the POC and DOC stocks in lakes (Weisse et al. 1990). It should be noted that GPP-derived DOC is commonly more labile than terrestrial DOC and high GPP may thus enhance lake respiration (Ask et al., 2012; Brett et al. 2017).

Inflowing terrestrial and internally produced OC, as well as DOC precipitation contribute considerably to sedimentation (Gudasz et al. 2017; Guillemette et al. 2017). Thereby high PP can induce rapid precipitation of CaCO₃ and its subsequent sedimentation in hard-water lakes (Müller et al. 2016). As lake sediment decomposition rates are substantially lower than those of OC in the water column (Sobek et al. 2009; Gudasz et al. 2010), lake sediments sequester C (Downing et al. 2008; Tranvik et al. 2009).

Recent studies have highlighted the sensitivity of mountain lakes to climate change. For example, in high-mountain lakes, the duration of ice cover and the volume of snowmelt water determined the variation in summer epilimnetic temperatures (Sadro et al. 2019; Smits et al. 2020). Further, changes in stream flow altered the deliveries of terrestrial C into lakes (Schindler et al. 1997; Erlandsson et al. 2008; Fasching et al. 2016), with implications for lake ecosystem structure and functioning (Solomon et al. 2015). Finally, variations in stream flow also drive the water residence times in lakes and hence C transformations (Tranvik et al. 2009; Weyhenmeyer et al. 2012; Ejarque et al. 2018).

Modeling work has suggested that in clearwater lakes that are low in DOC, GPP and ER remain largely balanced with increasing water temperatures, whereas in lakes with high DOC from allochthonous sources, ER will dominate over GPP increasing CO₂ evasion (Hanson et al. 2003). This notion is supported by empirical findings that demonstrated a negative relationship between epilimnetic net heterotrophy and DOC concentration during the summer across lowland lakes in eastern Canada (Prairie et al. 2002). In addition, high input of presumably recalcitrant terrestrial DOC to lakes may also decrease lake productivity, as stained lakes enhance light attenuation (Carpenter et al. 2001; Karlsson et al. 2015).

With air temperatures increasing twice as fast in alpine regions since the industrial revolution compared to the global average (Böhm et al. 2001), mountain lakes around the world are substantially affected by climate change (Moser et al. 2019). A hydrological regime shift from glacial to a snow-dominated regime has been reported in high elevation catchments of the European Alps as glaciers retreat (Paul et al. 2004; Bavay et al. 2013). Similarly, lower elevation catchments shifted from snow to a rain-dominated regime (Paul et al. 2004; Bavay et al. 2013). Further alterations of lake catchments following an alpine temperature increase include changes in vegetation cover and soils (Dirnböck and Grabherr 2000) that will likely result in a modification of the soil water balance, as well as a potentially enhanced DOC mobilization from soils with higher temperatures (Freeman et al. 2001; Schelker et al. 2013).

Despite the notion that mountain lakes are subject to ongoing change, there remain substantial knowledge gaps regarding the controls and integrated effects of climate change on the C balance of clearwater mountain lakes. The overarching aim of this study was thus to examine how current hydrological variability affects the C balance of a mountain lake in the eastern European Alps. We established a full C balance of Lake Lunz, Austria that currently undergoes temperature changes (Kainz et al. 2017), over the course of 1 year. By quantifying major aquatic, sediment, and atmospheric C fluxes during different seasons and hydrological conditions, we tested the following hypotheses. First, hydrology acts as the major determinant of the lake C balance by delivering, and removing the main fractions of DOC, POC, and DIC, respectively, and second, C sequestration in sediments is linked to hydrological events with high POC inflows and/or high in lake POC production in summer.

Materials and methods

Study site

Lake Lunz is a mountain lake of glacial origin located in Lower Austria (47°51'N, 15°03'E; 609 m.a.s.l.). The lake is characterized by oligotrophic transparent waters with a mean total phosphorous concentration of 3.21 μg L⁻¹, a mean total nitrogen concentration of 1.14 mg L⁻¹ and a mean Chlorophyll a concentration of 1.4 μg L⁻¹ (Horváth et al. 2017). The Secchi depth varies between 10.5 and ~ 7 m during normal years, but can be reduced to values below 5 m during dry and hot summer conditions (Rasconi et al. 2018). The lake mixing pattern is dimictic with the length of summer stratification depending on temperature and the amount of discharge (Ejarque et al. 2018). The average water residence time is typically short (~0.3 years at median flow) due to the elongated shape and straight connection between inlet and outlet. The lake morphometry is steep and deep (average and maximum depth, 20 and 34 m, respectively), with few shallow littoral areas. The lake has a surface area of 68 ha and it is located in a mostly pristine limestone catchment of 23.4 km². The catchment is mainly forested with spruce (Picea abies) and larch (Larix decidua) and covered with shallow, humic-rich soils.

The Oberer Seebach (OSB) stream is the main lake inlet, draining 79% of the lake catchment. It is a second-order stream recharging the lake through alluvial deposits underlain by a low-permeability layer of fine lake sediment and calcareous rock (Battin, 1999). The riparian vegetation is characterized by common ash (Fraxinus excelsior), sycamore (Acer pseudoplatanus), common beech (Fagus sylvatica) and goat willow (Salix caprea) (Bretschko, 1990). The lake discharges into
one single outlet, the Unterer Seebach (USB). The hydrograph of the USB closely follows that of OSB with lag times of less than 1 day (Ejarque et al. 2018). The hydrological regimes of the streams in the region are nival or nivo-pluvial with low flows in winter, high flows during the spring freshet, and frequent storm events throughout summer and autumn.

Model of lake C mass balance

We conceptualized the lake as a control volume of ∼1.3 × 10^7 m^3 receiving and exporting C from and to the surrounding landscape (Fig. 1, Table 1). C was categorized into three main species: DOC, POC, and DIC. For each of these pools, we identified the main fluxes in and out of the lake. These included surface- and groundwater flows, sedimentation, and lake-atmosphere exchange (Table 1, Eqs. 1–3). Using mass conservation principles, we assumed that any imbalance among C species would correspond to a net-transformation in the lake; that is, C mass transfer from one pool to another due to biogeochemical cycling. Namely, carbon can be transferred from DOC to DIC through bacterial respiration and photo-mineralization; or to POC through bacterial production and flocculation. DIC can be transferred to DOC through metabolic loss of GPP via exudates or to POC via GPP, for example as algal biomass. Finally, POC can become DOC following bacterial degradation, or consequently DIC due to heterotrophic respiration (Table 1, Eqs. 4–6). We note that this conceptualization does not explicitly include two potentially relevant fluxes: the removal of DIC by calcite precipitation (Müller et al. 2016) and the release of CO2 to the water column from sediment respiration (Algesten et al. 2005).

Sampling design and analytical methods

In this study, we present data for a 1-year period (15 February 2016–15 February 2017). OSB and USB were sampled as the main lake inlet and outlet of DOC, POC and DIC, respectively, in surface water. OSB was sampled 450 m upstream of the inlet into Lake Lunz (Fig. 1) and USB was sampled directly at the lake outlet. At both sites, grab water samples were collected three times a week (Monday, Wednesday, and Friday) for DOC, DIC, and POC analysis. At OSB, streamwater was additionally sampled every 6 h using an automated sampler (Teledyne ISCO, model 3700) for DOC analysis to account for sub-daily variability due to a strong covariation with discharge. Samples collected by the autosampler were returned to the lab three times a week. Water samples for DOC concentration were filtered using pre-combusted GF/F filters (0.7 μm diameter pore size) and collected in pre-combusted, acid-rinsed (0.1 N HCl), 30 mL glass vials. POC was collected in triplicates by filtering 1 to 2 L of stream water using pre-combusted GF/F filters (0.7 μm diameter pore size). Filters were weighed before and after filtration (previous drying at 60°C for 24 h) to obtain the mass of suspended solids per water volume. Filters were stored at −80°C until C content analysis. DIC was determined by calculation from pH and total alkalinity (TA), following Butler (1991). For the TA analysis, 250 mL of water were collected at each site in headspace-free glass bottles. pH, TDS, water temperature, and atmospheric pressure were measured in-situ using portable probes (WTW pH 3310, Xylem Analytics Germany Sales GmbH & Co. KG, Weilheim, Germany). During a subset of sampling dates (n = 24) we additionally sampled streamwater in headspace-free 40 mL glass vials for direct DIC measurements. These were used to determine a linear regression function between estimated and measured DIC values (DIC_{measured} = 0.944*DIC_{calculated} − 0.015, df = 23, RMSE = 0.214 mg L⁻¹, adj R² = 0.93, p < 0.0001) in order to correct calculated DIC values for possible overestimation (Abril et al., 2015). Table 2 presents the results of the chemical analysis at the OSB and USB used to estimate aquatic C fluxes. TDS was used as a conservative tracer of water flows.

POC sedimentation in the lake was measured using sediment traps deployed at the deepest location of the lake (lat 15.056°,
Table 1. Equations for the C mass balance in Lake Lunz, as conceptualized in Fig. 1a.

| Eq. No. | Lake mass balance (fluxes through system boundary) |
|---------|--------------------------------------------------|
| (1)    | \( \frac{dDOC}{dt} = f_1 + f_2 \)               |
| (1a)   | \( f_1 = f_{DOC_{OSB}} + f_{DOC_{ung}} \)       |
| (1b)   | \( f_2 = f_{DOC_{USB}} + f_{DOC_{extr}} \)      |
| (2)    | \( \frac{dPOC}{dt} = f_3 + f_4 + f_5 \)        |
| (2a)   | \( f_3 = f_{POC_{OSB}} + f_{POC_{ung}} \)       |
| (2b)   | \( f_4 = f_{POC_{USB}} \)                       |
| (2c)   | \( f_5 = f_{POC_{sedim}} \)                     |
| (3)    | \( \frac{dDIC}{dt} = f_6 + f_7 + f_8 \)        |
| (3a)   | \( f_6 = f_{DIC_{OSB}} + f_{DIC_{ung}} \)       |
| (3b)   | \( f_7 = f_{DIC_{USB}} + f_{DIC_{extr}} \)      |
| (3c)   | \( f_8 = f_{DIC_{atm}} \)                       |

where
- \( f_{DOC_{OSB}}, f_{POC_{OSB}}, f_{DIC_{OSB}} \): inflowing loads through OSB.
- \( f_{DOC_{ung}}, f_{POC_{ung}}, f_{DIC_{ung}} \): inflowing loads from ungauged catchments.
- \( f_{DOC_{USB}}, f_{POC_{USB}}, f_{DIC_{USB}} \): outflowing loads through USB.
- \( f_{DOC_{extr}}, f_{POC_{extr}}, f_{DIC_{extr}} \): outflowing loads via extrfiltration.

\( f_{POC_{sedim}} \): loss of POC through sedimentation.

\( f_{DIC_{atm}} \): lake-atmosphere CO2 exchange.

**Internal lake cycling (fluxes within system boundary)**

| (4) | \( \frac{dDOC}{dt} = fa + fb + fc + fd \) |
| (5) | \( \frac{dPOC}{dt} = fc + fd + fe + ff \)  |
| (6) | \( \frac{dDIC}{dt} = fa + fb + fe + ff \)  |

where
- \( fa = \) bacterial respiration + photomineralization
- \( fb = \) metabolic loss of gross primary production (GPP) via exudates
- \( fc = \) bacterial degradation
- \( fd = \) bacterial production + flocculation
- \( fe = \) NPP

\( ff = \) ecosystem respiration

The organic C load to the lake sediment was quantified by the data of the lower sediment traps and the lake sediment accumulation area. The sediment accumulation area, defined as the lake bottom area in which continuous particle sedimentation takes place (Håkanson and Jansson 2002) was assumed to be 34 ha (50% of the total lake area), based on the lake trough-shaped morphometry.

DOC, DIC, and TA analyses were conducted on the same day, 1–4 h after sampling. A total organic C analyzer (GE-Sievers 900) was used to measure both DOC (with an inorganic carbon removal unit) and DIC concentration. TA was determined by titration (Metrohm 702 SM Titrino) of 50 mL water sample aliquots to an end point pH of 4.32 using 0.05 N HCl as a titrator. C content on GF/F filters was determined using an elemental analyzer (Flash 2000 HT Plus) coupled to a mass spectrometer (Delta V Advantage, Thermo Scientific). All analytical measurements were performed in triplicates.

We measured water-atmosphere CO2 exchange using the eddy covariance (EC) method. During summer (22 March 2016–24 October 2016), EC measurements were conducted on a floating platform anchored close to the deepest location of the lake (Fig. 1). The rest of the time, an EC tower was set up at the eastern shore of the lake. The platform/tower was equipped with an enclosed infrared gas analyzer (Li-7200, Li-Cor Inc., Lincoln, NE, USA) to measure CO2 and H2O dry mole fractions and a 3-D sonic anemometer (R3, Gill Instruments, Lymington, UK) to measure the three orthogonal wind components and the sonic temperature. The instruments were mounted at 2 and 3.9 m above the lake surface during summer and winter, respectively. Data were collected at 20 Hz. Additionally, half-hourly mean air temperature and relative humidity sampled once per minute were recorded.

CO2 fluxes were calculated using the software EddyPro (Li-Cor Inc., Lincoln, NE) according to commonly accepted procedures (Aubinet et al. 2012). Raw data processing prior to flux calculation included de-spiking, a double rotation of the wind data, as well as the detection and compensation of time delays in the CO2 signal by use of the covariance maximization method. Half-hourly CO2 fluxes were then derived from the covariance of the CO2 dry mole fraction \( c \) and the vertical wind speed \( w \); \( f8 = w'c' \), where primes denote fluctuations around the mean and the overbar a time average (30 min in our case). We corrected spectral losses in the low frequency range according to Moncrieff et al. (2005); corrections for spectral losses in the high frequency range was performed using the method by Moncrieff et al. (1997).

Only data when wind was blowing from the lake and with a quality flag of 0 or 1 (Foken et al., 2005) were considered. Moreover, data were excluded when the infrared gas analyzer or anemometer malfunctioned because of weather conditions or technical problems. Data coverage was approximate 20%, which appears low when compared to terrestrial EC applications, but corresponds to typical data coverages of other lentic EC studies in complex terrain (Huotari et al. 2011; Mammarella et al. 2016). The average CO2 flux from all data with high quality was used to derive the annual budget for
Table 2. Seasonal variation in water chemical variables (mean values ± standard deviation) in the inflow and outflow of Lake Lunz.

| Date         | Inflow | Outflow |
|--------------|--------|---------|
|              | DIC* (ppm) | Alkalinity (meq L⁻¹) | pH (–) | Temp. (°C) | DIC* (ppm) | Alkalinity (meq L⁻¹) | pH (–) | Temp. (°C) |
| 21 Feb 2016  | 2.18 (±0.04) | 2.27 (±0.03) | 7.66 (±0.2) | 8.1 (±0.3) | 2.41 (±0.02) | 2.32 (±0.03) | 8.4 (±0.3) | 2.27 (±0.03) |
| 21 Mar 2016  | 2.08 (±0.06) | 2.04 (±0.03) | 7.39 (±0.4) | 8.0 (±0.7) | 2.27 (±0.01) | 2.27 (±0.01) | 8.4 (±0.3) | 2.27 (±0.03) |
| 21 Apr 2016  | 2.14 (±0.05) | 2.14 (±0.05) | 7.37 (±0.7) | 8.0 (±0.7) | 2.33 (±0.07) | 2.35 (±0.07) | 8.4 (±0.5) | 2.50 (±0.05) |
| 21 May 2016  | 2.36 (±0.09) | 2.36 (±0.09) | 7.82 (±0.4) | 8.4 (±0.6) | 2.33 (±0.05) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Jun 2016  | 2.36 (±0.09) | 2.36 (±0.09) | 7.82 (±0.4) | 8.4 (±0.6) | 2.33 (±0.05) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Jul 2016  | 2.36 (±0.09) | 2.36 (±0.09) | 7.82 (±0.4) | 8.4 (±0.6) | 2.33 (±0.05) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Aug 2016  | 2.46 (±0.04) | 2.46 (±0.04) | 8.02 (±0.1) | 8.3 (±0.4) | 2.36 (±0.04) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Sep 2016  | 2.64 (±0.05) | 2.64 (±0.05) | 8.2 (±0.4) | 8.3 (±0.4) | 2.36 (±0.04) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Oct 2016  | 2.93 (±0.6) | 2.93 (±0.6) | 8.2 (±0.4) | 8.3 (±0.4) | 2.36 (±0.04) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Nov 2016  | 3.03 (±0.5) | 3.03 (±0.5) | 8.2 (±0.4) | 8.3 (±0.4) | 2.36 (±0.04) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Dec 2016  | 3.03 (±0.5) | 3.03 (±0.5) | 8.2 (±0.4) | 8.3 (±0.4) | 2.36 (±0.04) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Jan 2017  | 3.03 (±0.5) | 3.03 (±0.5) | 8.2 (±0.4) | 8.3 (±0.4) | 2.36 (±0.04) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |
| 21 Feb 2017  | 3.03 (±0.5) | 3.03 (±0.5) | 8.2 (±0.4) | 8.3 (±0.4) | 2.36 (±0.04) | 2.36 (±0.04) | 8.4 (±0.3) | 2.35 (±0.05) |

*Corrected values (section Materials and methods).
†Calculated values based on Alkalinity, Temp. and pH.

Water balance and characterization of hydrological events

The annual hydrographs of OSB and USB were divided into individual events. For OSB, storm events were operationally categorized into “high flows” (peakflow > 6 m³ s⁻¹), “moderate flows” (peaking between 2 and 6 m³ s⁻¹) and “low flows” (peakflow ≤ 2 m³ s⁻¹). Two specific events were additionally discriminated: “snowmelt,” and “landslide,” with the latter being an event that occurred on May 28, 2016, when 53.4 mm of precipitation were registered within 1 h. This event caused several small to medium sized landslides within the OSB catchment. To put our records into context, we compared the hydrological conditions during our study year with long-term records using a data set of daily discharge in USB measured by the Biological Station Lunz (1931–1978) and the Hydrological Service of Lower Austria (1979–2017).

To calculate the lake water balance, OSB and USB discharges (Q_{OSB} and Q_{USB}), as well as direct rainfall, snowfall, and evaporation at the lake surface, were transformed into total volume equivalent per day (m³ d⁻¹). For this, pan evaporation rather than EC water flux data was used, because of the low data coverage of EC water flux estimates during warm and low-wind summer conditions, when open water evaporation is high. The residual term of the water balance (Q_{res}, Eq. 7) was considered to correspond to diffuse water inputs from the entire lake surface. As high quality data was reasonably well distributed across seasons and different times of day, and did not show clear diurnal variation, we expect no systematic bias from this approach.

Discharge was continuously measured at the lake inlet (OSB) and outlet (USB). In OSB, water levels were recorded at 10-min interval (Logger model: GPRS Datalogger type 255, HT Hydrotechnik GmbH, Obergünzburg, Germany) and converted into discharge according to the rating curve: Q = 0.00001503 wt⁻⁰·⁰⁰⁰⁴⁰⁷⁷¹¹ wt² + 0.02244630 wt - 0.36658727, r² = 0.99, with wt being the water table in cm. The rating curve included 16 manual discharge measurement covering the range from 0.1 to 12.1 m³ s⁻¹. Higher discharges were extrapolated from the fitted curve. Manual discharge was measured by salt slug additions and velocity profiling using an electromagnetic flow meter (Flo-Mate Modell 2000, Marsh-McBirney Inc., Frederick, MD). Additional 12 manual discharge measurement were excluded due to questionable data quality. Discharge at USB (5-min interval) was provided by the Hydrological Service of Lower Austria (www.noel.gv.at; Station #214262). This station is located in the first free flowing section of the USB, approximately 100 m downstream of the USB sampling site. Daily rainfall, snowfall (as snow water equivalents, using a heated precipitation gage), and evaporation (GGI 3000 evaporation pan) were regularly measured at the official Meteorological Station “Lunz am See,” located at the north-eastern shore of the lake, which is operated by the Zentralanstalt für Meteorologie und Geodynamik (ZAMG), Austria.
groundwater and ungauged catchments ($Q_{\text{ung}}$ when $Q_{\text{res}} > 0$) or diffusive groundwater outflows, that is, exfiltration ($Q_{\text{exfiltr}}$ when $Q_{\text{res}} < 0$). We note that this approach is not capable to represent diffusive inflows that are directly compensated by exfiltration, that is, when $Q_{\text{exfiltr}} > 0$ and $Q_{\text{ung}} > 0$.

$$Q_{\text{res}} = (Q_{\text{USB}} + \text{Evaporation}) - (Q_{\text{OSB}} + \text{Precipitation}) \left( \text{m}^3 \text{d}^{-1} \right)$$

(7)

Water and C flux calculations

DOC, DIC, and POC concentrations in OSB and USB were transformed into daily mass flows ($f_{\text{OSB}}, f_{\text{USB}}$, Table 1) as follows. Data from grab samples (frequency: three times a week) were interpolated to daily values using linear interpolation. The resulting daily concentrations (mg L$^{-1}$) were subsequently multiplied by the total daily water flows (m$^3$ d$^{-1}$), thereby obtaining the total daily flow of DOC, DIC, and POC (gC d$^{-1}$). Specifically, DOC mass flows in OSB were obtained from automatically sampled DOC concentration data (frequency: 6 h). These DOC concentrations were corrected for potential residual contamination by the plastic tubing and bottles of the ISCO automated water sampler system using a linear regression with manually sampled DOC tubing and bottles of the ISCO automated water sampler system. The resulting instanta- neous mass flows were interpolated onto a continuous cubic spline function, which was integrated to obtain the total daily DOC mass flows (gC d$^{-1}$).

We estimated additional C flows through diffuse inputs, that is, the contribution from ungauged catchments and groundwater infiltration and outputs (groundwater exfiltration, $f_{\text{exfiltr}}$, Table 1). For this, we attributed the same C concentrations (i.e., DOC, DIC, and POC) as the OSB to all ungauged inflows ($Q_{\text{ung}}$). Exfiltrating water ($Q_{\text{exfiltr}}$) was assumed to have the same C concentrations as the USB. We propose that these assumptions are reasonable for Lake Lunz. Most diffuse inflows originated from ungauged catchments (representing 21% of the lake catchment area; $f_{\text{ung}}$, Table 1) rather than groundwater. These smaller streams have DOC concentrations in the same range as the OSB (Caillon and Schelker 2020). Similarly, and given the specific morphology of Lake Lunz, diffuse groundwater outflows will likely only occur at high water levels and near the surface.

Mass balance calculations

The C influxes ($f_1$, $f_3$, and $f_6$; Fig. 1) were calculated as the sum of fluxes from OSB and those estimated from small, ungauged catchments (Eqs. 1a, 2a, and 3a, Table 1). Outflowing DOC and DIC fluxes ($f_2$ and $f_7$, Fig. 1) were calculated as the sum of fluxes from USB and those estimated to be lost through exfiltration (Eqs. 1b and 3b). Outflowing POC fluxes ($f_4$ and $f_5$, Fig. 1) were calculated as the sum of fluxes from USB and sedimentation (Eqs. 2b and 2c). The difference between mass inflows and outflows (Eqs. 1–3, Table 1) corresponded to the mass of DOC, DIC, and POC generated (dC/dt > 0) or retained (dC/dt < 0) in-lake. Following mass conservation, we assumed that dDOC/dt + dDIC/dt + dPOC/ dt = 0, meaning that any in-lake generation or retention of a C species (DOC, DIC, and POC) is to be offset by a change in another species. Lake-atmosphere CO$_2$ exchange ($f_8$, Fig. 1) was calculated as a residual term in the mass balance. This approach allowed us to compare the results from the mass balance to the independent estimate of annual net CO$_2$ exchange obtained by EC measurements.

Uncertainty analysis

For aquatic C concentrations, three relevant sources of uncertainty were considered: (1) analytical variability, (2) uncertainty from gap filling, and (3) uncertainty from data corrections using regression models. The uncertainty caused by analytical variability was quantified as the average standard deviation of triplicate measurements. Uncertainty of interpolated missing values was estimated for each gap length using the following procedure. First, we created artificial gaps in the interpolated data record. For gaps longer than 3 days, we imposed the condition that at least 2/3 of the data values should correspond to original data. Then, the artificial gaps were filled using linear interpolation. Finally, the error was estimated as the average difference between the estimated and the original data. To obtain an average error, this process was iterated for all possible gaps throughout the data set and the error averaged. The error associated with data transformation using regression models was considered to be the root of mean squared error (RMSE) of the fitted regression model. For discharge, we assumed a constant relative error of 10%, a common value for established gauging stations at natural streams (Harmel et al. 2006). We note that this assumption is a simplification and does not account for unsteady conditions, such as “out-of-bank” high flow events or similar. Assuming the three uncertainties to be independent, the overall uncertainty for each C species was derived by a Gaussian error propagation.

Furthermore, the uncertainty associated to the overall mass balance model was quantified using TDS as a conservative reference tracer of water flows. We inferred that any imbalances between inputs and outputs for C species can only be attributed to in-lake reactive processes if the imbalance in C were greater than the observed variation in TDS. For this, we assume that TDS is not significantly altered by carbonate precipitation or dissolution.

Statistical analyses

We analyzed the responsiveness of C inflow ($f_1$, Fig. 1; Eq. 1a, Table 1) to hydrological events using the following methods. First, we calculated the flow-weighted average (FWA) concentrations of each C species $i$ (DOC, DIC, and POC) as
\[ \sum C_i Q_i / \sum Q_i \] where \( C \) is concentration and \( Q \) is discharge. FWA values were then compared among different event types. Second, we fitted a generalized least squares (GLS) model to predict the inflowing mass of each C species per event, as a function of event magnitude (total water volume exported per event), and season. Third, we compared how the response of C fluxes during hydrological events changed from lake inflow to outflow. For this, we performed an analysis of covariance (ANCOVA), that is, for each season and C pool, we fitted a GLS model predicting the total mass of exported C as a function of event magnitude, flux (inflow, outflow), and their interaction.

In both statistical models, the significant predictors were selected using fivefold cross-validation and the AIC criterion. In the ANCOVA approach, we interpreted the model selection analysis as follows. If the sampling site factor was significant, both individually and as an interaction term with event magnitude, it would indicate that the lake had a significant effect on the slope of the relationship between C mass export and event magnitude. If the sampling site factor was only significant as an individual term, then it would indicate that the lake had an effect only on the intercept. Finally, if sampling site was not significant at all, it would indicate that the lake had no relevant effect on the responsiveness of C mass export to hydrological events.

In all models, the variance of the residuals was allowed to vary by meteorological season (spring, March to end of May; summer, June to end of August; fall, September to end of November; winter, December to end of February). Non-factor variables were mean-centered and normalized by their standard deviation to obtain standardized slopes, comparable among C pools. The explanatory power of the model (\( R^2 \)) was obtained by correlating the observed and fitted data using ordinary least squares. GLS models were fitted with the mgcv package (Wood et al., 2015) for R (R Core Team, 2018).

Results

Hydrology

Hydrological analysis showed that the study year (2016) represented average hydrological conditions for the region with a pluvio-nival flow regime with high flows in spring and summer. Flow percentiles in USB during 2016 (P25 and P75, 2.09 and 0.64 m³ s⁻¹, respectively) were only slightly higher than those of long-term (1913–2017) data records (1.87 and 0.64 m³ s⁻¹ for P25 and P75, respectively). Discharge in OSB and USB ranged between 0.24 and 13.9 m³ s⁻¹ with frequent events. We registered a total of 35 events (Fig. 2) 2016. In OSB, high-flow events \((n = 9)\) exported 13.4 × 10⁶ m³, representing 41.0% of the total annual water flows. Moderate- \((n = 11)\) and low-flows \((n = 12)\) delivered 8.6 × 10⁶ and 4.8 × 10⁶ m³, representing 26.3 and 14.6% of the total annual flow. The spring freshet began in April and lasted for 34 d with two distinct snowmelt events, overall contributing 13.1% to the annual water flow. Finally, the landslide event was the one individual event with the highest discharge (1.56 × 10⁶ m³; peakflow 13.9 m³ s⁻¹ at OSB) and represented 4.9% of the total annual discharge, despite its short duration of only 44 h. The USB hydrograph mimicked that of OSB with peak lag times of less than 1 day.

On an annual basis, the OSB provided most water to the lake (62.5%) with diffuse water sources from ungauged catchments representing 35.4%. Direct inputs from precipitation to the lake surface accounted for 2.1% of total water inputs. 95.7% of water outputs occurred through USB outflow, whereas exfiltration and evaporation (normalized to lake area) represented only 3.9% and 0.4% of the total, respectively.

Aquatic C inflows

On average, lake inflow (OSB streamwater and ungauged catchments; that is, f1, f3, and f6, Table 1, Fig. 1) had

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**Fig 2.** Stream discharge at OSB and classification of hydrological events during the study period.
2.96 ± 0.55, 0.20 ± 0.38, and 43.33 ± 2.70 mg C L\(^{-1}\) (FWA ± SD) of DOC, POC, and DIC, respectively. Therefore, DIC was the dominant species of inflowing C. Because high-flow events delivered, on average, the largest amounts of water (1.49 ± 0.48 × 10\(^6\) m\(^3\)), these were also responsible for the largest loads of DOC (4.84 ± 1.04 Mg C), POC (0.21 ± 0.70 Mg C) and DIC (61.53 ± 13.20 Mg C) per event. During moderate and low-flow events, lower water flows resulted in reduced C inputs. C deliveries were 0.92 ± 0.38, 0.12 ± 0.09, and 19.56 ± 8.63 Mg C per low flow event for DOC, POC, and DIC, respectively. Snowmelt events, despite their moderate discharge (1.46 ± 0.71 m\(^3\) s\(^{-1}\) average, 3.84 m\(^3\) s\(^{-1}\) maximum), exported similar amounts of water as high-flow events due to their extended duration. This resulted in similar contents of exported DOC (4.26 ± 0.77 Mg C), POC (0.39 ± 0.08 Mg C), and DIC (67.22 ± 9.21 Mg C) as high-flow events. The landslide event, amounting to 1.56 × 10\(^6\) m\(^3\) of water volume, exported similar contents of DOC (5.45 Mg C) and DIC (62.80 Mg C) as other high-flow events, but delivered twice as much POC (0.48 Mg C).

Overall, these results indicated that the total content of C delivered during an event was positively related to the volume of exported water. However, the FWA concentrations differed among event types, and among C species (Fig. 3). For DOC, the FWA concentrations tended to decrease from landslide and high-flow to low-flow and snowmelt events (Fig. 3a) reflecting a flushing effect where higher discharge increased DOC concentration in OSB streamwater. DIC followed the opposite trend with FWA concentrations increasing from landslide and high-flows to low-flow events (Fig. 3b). This reflected a dilution effect, where higher discharge is associated with decreased DIC concentration. During snowmelt, however, FWA concentration was lowest. POC results also suggested a dilution effect; yet, patterns were less evident due to an overall high variability (Fig. 3c). The FWA POC concentrations for moderate and low-flow events were higher than for high-flow events, however, data variability was also higher. During the landslide event, FWA POC concentration was higher than the average for all other event types. Yet, some individual moderate and low-flow events exceeded the landslide FWA POC concentrations.

The relationships between hydrology and C export to the lake was further explored by correlating the C mass export per event with event magnitude (water volume exported per event) and season (Fig. 4). GLS modeling revealed that, for DOC and DIC, the total C mass exported per event was significantly dependent not only on event magnitude, but also on season. During summer and autumn, normalized slopes were higher than those of winter and spring, indicating a higher response of C export to event magnitude during these seasons. Models had a high goodness-of-fit, explaining up to 91.2% (DOC) and 96.2% (DIC) of total variance. In contrast, we found no seasonal effect for POC and the only significant predictor for POC export per event was event magnitude. The POC standardized slope (0.735) was similar to the slopes of DOC and DIC during winter (0.760 and 0.812, respectively). However, the model had a much lower explanatory power (54.7%), indicating a less predictable response of POC to hydrological events.

**Aquatic C outflow and sedimentation**

FWA DOC and POC concentrations in the outflow were 1.91 ± 0.26 and 0.24 ± 0.08 mg L\(^{-1}\), respectively (f2 and f4 in Table 1 and Fig. 1, respectively). These fluxes were not statistically different from inflowing fluxes (weighted t-test, p > 0.05).
However, FWA DIC concentration \((29.67 \pm 1.82 \text{ mg L}^{-1})\) was significantly lower (weighted \(t\)-test \(p < 0.05\)) than the inflow. Further, the FWA concentrations varied between inflow and outflow among hydrological events (Fig. 3). For DOC and DIC, FWA concentrations were similar among event types and remained at lower average values than inflows for all types of event (Fig. 3a,b). Also, data variability was reduced in the outflows. At the outlet, POC had a similar variability as the inflow, but POC FWA concentrations tended to decrease from high-flow to low-flow events (Fig. 3c). This variability (range of 0.07–0.37 mg L\(^{-1}\)) was one and two orders of magnitude lower than that of DOC (1.51–2.37 mg L\(^{-1}\)) and DIC (26.05–32.74 mg L\(^{-1}\)), respectively.

The ANCOVA analysis revealed that the relationship between C mass export per event and event magnitude was not significantly different in inflow and outflow. This indicates that the lake does not have a significant effect on C export during hydrological events. Exceptions were found as a significant increase in the intercept during winter for DOC (\(\Delta\text{intercept} = +0.386 \text{ gC}\)) and DIC (\(\Delta\text{intercept} = +0.412 \text{ gC}\)), and during summer for POC (\(\Delta\text{intercept} = +0.489 \text{ gC}\)). In autumn, a significant decrease in the slope was found for DIC (\(\Delta\text{slope} = -0.407 \text{ gC m}^{-3}\)).

The POC sedimentation flux varied by season and followed a bell shaped curve, peaking in summer (Fig. 5). This contrasted with lower and temporally stable amounts of inflowing...

**Fig 4.** ANCOVA analysis of the relationship between inflowing C mass to the lake and event magnitude for DOC (panel a), DIC (panel b), and POC (panel c). Data have been mean-centered and normalized to allow for comparison among C species. The gray line in panel c indicates that slope and intercept were not significantly different among seasons.

**Fig 5.** Monthly fluxes of POC in the lake inflow (OSB and small ungauged catchments), outflow (USB and exfiltration), and sedimentation. February 2016 and February 2017 include only half a month of data.
The highest in-lake POC sedimentation (13.1 ± 0.3 Mg C) was measured in June. This deviated from the overall seasonal pattern as represented by the bell-shaped curve and corresponded to the occurrence of the landslide event at the end of May.

Annual mass balance and EC-based net ecosystem CO2 exchange

Annually, up to 1600 Mg C were transferred through Lake Lunz. Among the inputs, 93% of the C was in the form of DIC, whereas DOC and POC were only minor fluxes (6 and 0.6%, respectively) in comparison. DOC mass transfer was balanced (Table 3). The difference between DOC inputs and outputs (+3.23%) was lower than the estimated uncertainty (TDS = +4.60%), indicating no significant change of DOC quantity between in and outflow. According to that, the fluxes \( f_\text{w} \) to \( f_\text{d} \) of our mass balance model (Fig. 1a) were negligible in 2016 in terms of the total C mass losses or gains.

Contrastingly, POC had a 76.71% imbalance between inputs and outputs, indicating an in-lake production of 8.4 ± 0.4 Mg C. The even mass balance for DOC between inflow and outflow implied that the main internal cycling pathway for the observed POC production had to be net primary production, NPP. Further, this also purported that for DIC the reduction through NPP was the only relevant internal C-cycling pathway of the lake. Therefore, we could calculate the CO2 exchange across the lake-atmosphere interface simply as the residual term in the DIC mass balance. According to this estimate, the lake was a net sink of 76.5 ± 2.1 Mg C. Interestingly, this flux represented only 5.13% of DIC inputs to the lake.

Lake-atmosphere EC measurements registered, on average, a CO2 emission flux of 0.8 ± 2.9 g C m\(^{-2}\) d\(^{-1}\) from the lake to the atmosphere throughout the study year. This evasion was highest in August and lowest in May and January (Fig. 6), with the latter coinciding with a fully developed ice cover on the

**Table 3. Annual lake C mass balance.**

|              | DOC |      | DIC |      | POC |      | TDS |      |
|--------------|-----|------|-----|------|-----|------|-----|------|
|              | Mg C | %    | Mg C | %    | Mg C | %    | Mg C | %    |
| Inflow       |      |      |      |      |      |      |      |      |
| OSB          | 62.4 ±0.1 | 64.57 | 895.3 ±1.1 | 60.01 | 7.5 ±0.3 | 68.68 | 7620.8 ±9.4 | 63.5 |
| Diffuse inflow | 34.2 ±0.1 | 35.43 | 520.1 ±1.1 | 34.86 | 3.4 ±0.2 | 31.32 | 4383.6 ±9.5 | 36.5 |
| Total        |      |      |      |      |      |      |      |      |
|   | 96.6 ±0.1 | 100.00 | 1491.9 ±2.6 | 100.00 | 10.9 ±0.3 | 100.00 | 12,004.4 ±13.4 | 100.00 |
| Outflow      |      |      |      |      |      |      |      |      |
| USB          | 96.0 ±0.1 | 96.23 | 1424.4 ±1.3 | 96.01 | 11.9 ±0.1 | 61.99 | 12,059.8 ±13.3 | 96.04 |
| Exfiltration | 3.8 ±0.0 | 3.77 | 59.1 ±0.5 | 3.99 | NA    |      | 496.6 ±4.6 | 3.96 |
| Sedimentation | NA  | NA    | NA   | NA   | NA    |      | NA   |      |
| Total        | 99.7 ±0.1 | 100.00 | 1483.6 ±1.4 | 100.00 | 19.3 ±0.2 | 100.00 | 12,556.4 ±14.1 | 100.00 |
| Mass         |      |      |      |      |      |      |      |      |
| \( C_{\text{out}} - C_{\text{in}} \) (Mg C) | +3.1 ±0.1 | -8.4 ±2.9 | +8.4 ±0.4 | +552.0 ±19.4 |
| Balance      |      |      |      |      |      |      |      |      |
| \( C_{\text{out}} - C_{\text{in}} \) (%) | +3.23 | -0.56 | +76.71 | +4.60 |

*Estimated as a residual term.
†Positive numbers denote in-lake C production, whereas negative numbers indicate a loss.

**Fig 6.** Monthly net ecosystem CO2 exchange of the lake surface as quantified by EC measurements. Positive numbers indicate a net flux from the water column to the atmosphere (error bars represent one standard deviation of means).
lake that is likely to have limited gas exchange. This variation was similar in preceding years (data not shown). There was nearly no gas exchange recorded in January for years where an ice cover was present (2015 and 2017, but not 2016), followed by intermediate emissions during spring (range 0.2–0.8 g C m$^{-2}$ d$^{-1}$; February to April) and a second minimum (<0.2 g C m$^{-2}$ d$^{-1}$) in late spring/early summer (April/May). Summertime emissions were intermediate to high and highly variable; emissions peaked between 1.1–1.6 g C m$^{-2}$ d$^{-1}$ in August (2015, 2016) or September (2017). Fall and winter emissions were intermediate again, ranging from 0.3–1.0 g C m$^{-2}$ d$^{-1}$.

Extrapolating the net ecosystem CO2 exchange measured by EC to the entire lake surface for the full study year resulted in a total emission of 190 Mg C, with a range (95% confidence intervals) of +1496 Mg C (lake as source) to −1116 Mg C (lake as sink). This range consistently overlapped with our previous calculation as the mass balance residual (sink of 76.5 ± 2.1 Mg C). The resulting annual C balance is portrayed in Fig. 7.

**Discussion**

**Contemporary C balance of Lake Lunz**

This study presents a 1-year C mass balance of a clearwater mountain lake. The overall finding of this analysis was that the lake mass balance is dominated by fluvial fluxes of DIC, DOC, and POC. The fluvial fluxes were much larger than the atmospheric exchange, as well as the sedimentation. Sedimentation represented only ~0.5% of the fluvial C input to the lake, while atmospheric CO2 exchange following the residual approach accounted for ~5%, respectively. Even the EC-based estimate of atmospheric CO2 exchange, although subject to substantial uncertainty, represented only ~12% of the combined inflowing DIC, POC, and DOC on an annual basis. These findings demonstrate the fundamental relevance of fluvial C fluxes for mountain lake C budgets.

Several previous studies have reported C budgets for lake ecosystems in different climates, but few quantified all incoming and outgoing DOC, POC, and DIC fluxes over a duration of at least 1 year (Dillon and Molot 1997; Jonsson et al. 2001; Andersson and Kumblad 2006; Sobek et al. 2006; Stets et al. 2010; Cremona et al. 2014; Hanson et al. 2015; Einarsdottir et al. 2017). Overall, these studies present a wide range of fluvial contributions to the lake C mass balance. For example, Andersson and Kumblad 2006 quantified a sedimentation rate of 187% of the C influx, meaning that the sedimentation was a much larger flux than the fluvial C inflow. This high sedimentation was caused by high C fixation and POC production in this small and shallow, high DOC lake in central Sweden. At the contrary, Cremona et al. (2014) estimated the sedimentation flux to be ~8% of the total C inflow, while atmospheric exchange represented 9.3% of the inflowing C. This eutrophic lake is large (270 km$^2$) and shallow, with intermediate DOC concentrations (2–8 mg L$^{-1}$).

Hanson et al. (2015) show in their summary, that the fate of inflowing C (and especially OC) depends, in addition to trophic status and the water residence time, on the degree of brownification. Of the studies mentioned above, only two studies investigated clearwater lakes with mean DOC concentrations <2 mg L$^{-1}$ (Dillon and Molot 1997; Hanson et al. 2015). Similarly, only one study focused on a lake with a mean depth equal or greater to Lake Lunz (mean depth Lake Örträsk, Sweden ~23 m, see Jonsson et al. 2001 vs. mean depth Lake Lunz ~20 m).

In brown-water lakes, heterotrophic microbial uptake and much of the entire aquatic food web is sustained by autochthonous DOC (Brett et al. 2017), while allochthonous DOC additionally supports secondary production and respiration (Pace et al. 2004; Kritzberg et al. 2005; Bade et al. 2007). In contrast, in clearwater lakes, DOC availability is lower resulting in a reduced contribution of terrestrial DOC to heterotrophic microbial metabolism (Hanson et al. 2015). Thus, increases in autochthonous DOC from high PP during summer fuels both enhanced microbial uptake and respiration leading to a coupling of ER and GPP (Prairie et al. 2002; Hanson et al. 2003). This coupling then results in a largely balanced C-budget of clearwater lakes at an annual timescale.

We found substantial seasonal variation in lake C fluxes, concerning most C species at the inflow and outflow. The dynamic DOC and POC inflow patterns were strongly linked to hydrological variation and event type. Large runoff events during spring and summer provided most DOC and POC (Fasching et al. 2016). However our study system was largely balanced, while dominated by DIC loads. Overall, this would also support the proposed coupling of ER and GPP to be relevant in Lake Lunz. We note, however, that we did not explicitly quantify these ecosystem fluxes.

The EC measurements indicated that the CO2 exchange derived from our mass balance calculations as a residual were within a plausible range. We note, however, that the EC
measurements were subject to substantial methodological difficulties. For example, the location of the EC-system on the floating platform was limited from spring to late fall due to lake ice, while in wintertime the EC systems had to be operated from the shore. Next, low wind speeds, often found in mountain valleys, caused a substantial reduction of high-quality data and thus a low data coverage. We propose that these challenges in quantifying atmospheric exchange with EC methods are common for mountain lakes. As a result, the estimated confidence intervals of EC measurement are large and would allow the lake to be either a CO₂ sink or source to the atmosphere during the study period.

Overall, we conclude that Lake Lunz, in accordance with other clearwater lakes, cannot be considered as a defined sink or source of CO₂ to the atmosphere under present conditions. These findings are also in broad agreement with recent work suggesting that carbon dioxide supersaturation may be abundant in high-elevation mountain lakes, while their annual atmospheric CO₂ exchange remains small compared to other freshwater ecosystems (Cohen and Melack 2020).

In this study, the respiration of the lake sediments contributing to DIC in the water column (Algesten et al. 2005; Gudasz et al. 2010) was not measured. Assuming a mean sediment temperature of 4°C in Lake Lunz, one can derive an approximate sediment respiration rate of ~62 mg C m⁻² d⁻¹ (Equation given in Fig. 1a; Gudasz et al. 2010). Considering a lake sediment accumulation area of 34 ha, this would result in an approximate gain of 7.6 Mg C of DIC in the water column per year. It is worth noting that this flux would exceed our uncertainty estimate for the annual DIC influx of ±2.6 Mg C (Table 3), whereas it would only represent 0.51% of the annual inflow of DIC (1492 Mg C). With this, the contribution of sediment respiration would also stay well below the overall flux uncertainty estimate according to the TDS mass balance of +4.60% between inflow and outflow.

Climate sensitivity of the lake C-balance

With Lake Lunz not being a significant source or sink of atmospheric CO₂ during the study period, the question which factors may shift this balance in the future is of ecological importance. Specifically, we are attentive to what may modify the fluxes and storage of C in a mountain lake, given altered environmental conditions. In the following, we use our results as a framework to investigate potential implications of some climate change scenarios on mountain lake C-cycling.

Hydrological regime shift

A change of mountain stream runoff regimes from snow governed to a rain-dominated regime is predicted to result in profound hydrological changes. More runoff is expected in winter, while the spring freshet will be reduced or may even be absent (Ziel and Bugmann 2005; Gobiet et al. 2014). This change will likely enhance the influx of DOC and nutrients into lakes during winter (Likens 2009), while springtime DOC loads are reduced (Stottlemeyer and Toczydlowski 1991). The lake water residence time in spring will also be enhanced due to lower stream discharge, while water temperatures in summer may increase (Sadro et al. 2019; Smits et al. 2020).

Following our analysis of event types and GLS modeling, we predict that this change may result in some alterations of the lake C-balance. For DOC, we predict minor changes, as the dynamics of the inflow and outflow remain approximately the same for snowmelt, as compared to other low and moderate flow events (Fig. 3), while DOC dilution is higher during snowmelt. Although GLS results showed some seasonal DOC dynamics, the slopes of C export vs. event magnitude were similar in winter and spring, suggesting only minor changes if the spring freshet is replaced by mid-winter flow events. For POC, a strong increase of the load during snowmelt was observed (Fig. 3). This was also similar to other high flow events, while moderate and low flows resulted in lower POC loads. Further, the GLS model suggested no sensitivity of POC loads to seasonal variation. This points towards a likely increase of POC sedimentation if the number of mid-winter high flows increases.

Increased occurrence of hydrological extreme events

An increase in the occurrence and intensity of hydrological extreme events has been proposed for alpine catchments (Gobiet et al. 2014). European extreme droughts, such as the events in 2003 and 2015 may become common by the end of the 21st century (Gobiet et al. 2014; Laaha et al. 2017). Similarly, the occurrence and intensity of floods is predicted to rise. Blöschl et al. (2019) estimated that for the northern side of the central and eastern European Alps, future floods will increase by ~2.5-12% in water volume per decade.

Following our results for different event types on C-transport and storage, we suggest the following possible implications of these changes: An increased occurrence of droughts will potentially result in enhanced DOM transformation during lake transit. This pattern has already been observed during the exceptional summer of 2015 as compared to 2016 in Lake Lunz (Ejarque et al. 2018). However, as inflows and outflow remained largely stable regarding DOC and POC masses during the observed drought, we propose that no major change of the lake C-balance is to be expected from more frequent drought events. An increased occurrence of floods will likely enhance supply of terrestrial DOC (Schindler et al. 1997; Erlandsson et al. 2008) and POC (Johnson et al. 2018) to mountain lakes. Our previous analysis on DOC dynamics during different flow conditions (Ejarque et al. 2018) attested little sensitivity of DOC retention to more frequent moderate and regularly occurring high flows (recurrence interval, R < 1 yr), as during these conditions the lake mainly transits solutes. Similarly, the ANCOVA results indicated that the lake has no significant effect on DOC and POC export during such hydrological events (no significant difference in the relationship of event C export and event magnitude between USB and OSB).
However, the data from the landslide event suggest that large hydrological events (with $R_i > 1$ to $R_i >> 1$) that also cause strong erosion in the catchment will likely result in substantially increased sedimentation fluxes (Figs. 4, 5) (Johnson et al. 2018). Further, they can transiently increase water turbidity, thereby limiting PP and favoring heterotrophy (Sadro and Melack 2018). Thus, we propose that more frequent large floods, as explicitly predicted for the Lunz region (Blöschl et al. 2019), will likely result in an enhancement of future C sedimentation. Also, these events may contribute to transiently shifting the C balance towards an atmospheric CO$_2$ source in clearwater mountain lakes.

**Conclusions**

This study quantified all major C fluxes of the mountain Lake Lunz for 1 year, with the overall result that the contemporary C budget is well balanced and has a low atmospheric exchange. That is, C inputs largely matched C outputs, with only minor internal net-transfer among C pools. The hydrological connectivity of the lake with the catchment was a major control of the C balance, as inflowing and outflowing waters dominated the main loads of DOC, POC, and DIC. In light of these results, we suggest that the most relevant implications of climate change are the increased occurrence of floods, that affect lake C input and subsequent C sedimentation, while factors such as hydrological regime shift will likely have less effect on the lake C balance.

**References**

Abril G., and others. 2015. Technical Note: Large over-estimation of $p$CO$_2$ calculated from pH and alkalinity in acidic, organic-rich freshwaters. Biogeoosciences **12**: 67–78. doi:10.5194/bg-12-67-2015

Algesten, G., S. Sobek, A. K. Bergström, A. Agren, L. J. Tranvik, and M. Jansson. 2004. Role of lakes for organic carbon cycling in the boreal zone. Glob. Chang. Biol. **10**: 141–147. doi:10.1111/j.1365-2486.2003.00721.x

Algesten, G., S. Sobek, A. K. Bergström, A. Jonsson, L. J. Tranvik, and M. Jansson. 2005. Contribution of sediment respiration to summer CO$_2$ emission from low productive boreal and subarctic lakes. Microb. Ecol. **50**: 529–535. doi:10.1007/s00248-005-5007-x

Allgaier, M., and H.-P. Grossart. 2006. Seasonal dynamics and phylogenetic diversity of free-living and particle-associated bacterial communities in four lakes in northeastern Germany. Aquat. Microb. Ecol. **45**: 115–128. doi:10.3354/ame045115

Andersson, E., and L. Kumblad. 2006. A carbon budget for an oligotrophic clearwater lake in mid-Sweden. Aquat. Sci. **68**: 52–64. doi:10.1007/s00027-005-0807-0

Ask, J., J. Karlsson, and M. Jansson. 2012. Net ecosystem production in clear-water and brown-water lakes. Global Biogeochemical Cycles **26**: GB1017. doi:10.1029/2010gb003951

Aubinet, M., T. Vesala, and D. Papale. 2012. Eddy Covariance: A Practical Guide to Measurement and Data Analysis. And Springer. Dordrecht, Netherlands. doi:10.1007/978-94-007-2351-1.

Bade, D. L., et al. 2007. Sources and fates of dissolved organic carbon in lakes as determined by whole-lake carbon isotope additions. Biogeochemistry **84**: 115–129. doi:10.1007/s10533-006-9013-y

Battin, T. J. 1999. Hydrologic flow paths control dissolved organic carbon fluxes and metabolism in an Alpine stream hyporheic zone. Water Resources Research **35**: 3159–3169. doi:10.1029/1999wr900144

Bavay, M., T. Grünewald, and M. Lehning. 2013. Response of snow cover and runoff to climate change in high Alpine catchments of Eastern Switzerland. Adv. Water Resour. **55**: 4–16. doi:10.1016/j.advwatres.2012.12.009

Blöschl, G., and others. 2019. Changing climate both increases and decreases European river floods. Nature **573**: 108–111. doi:10.1038/s41586-019-1495-6

Böhm, R., I. Auer, M. Brunetti, M. Maugeti, T. Nanni, and W. Schöner. 2001. Regional temperature variability in the European Alps: 1760–1998 from homogenized instrumental time series. Int. J. Climatol. **21**: 1779–1801. doi:10.1002/joc.689

Brett, M. T., and others. 2017. How important are terrestrial organic carbon inputs for secondary production in freshwater ecosystems? Freshwat. Biol. **62**: 833–853. doi:10.1111/fwb.12909

Bretschko, G. 1990. The dynamic aspect of coarse particulate organic matter (CPOM) on the sediment surface of a second order stream free of debris dams (RITRODAT-LUNZ study area). Hydrobiologia **203**: 15–28. doi:10.1007/bf00005609

Butler, J. N. 1991. Carbon dioxide equilibria. Chelsea, MI: Lewis Publishers.

Caillon, F., and J. Schelker. 2020. Dynamic transfer of soil bacteria and dissolved organic carbon into small streams during hydrological events. Aquat. Sci. **82**: 41. doi:10.1007/s00227-020-0714-4

Carpenter, S., and others. 2001. Trophic cascades, nutrients, and Lake productivity: Whole-Lake experiments. Ecol. Monogr. **71**: 163–186 doi:10.1890/0012-9615(2001)071[0163:tcnamp]2.0.co;2

Cohen, A. P., and J. M. Melack. 2020. Carbon dioxide supersaturation in high-elevation oligotrophic lakes and reservoirs in the Sierra Nevada, California. Limnol. Oceanogr. **65**: 612–626. doi:10.1002/lno.11330

Cole, J. J., and others. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems **10**: 171–184. doi:10.1007/s10021-006-9013-8

Cremona, F., and others. 2014. Dynamic carbon budget of a large shallow lake assessed by a mass balance approach.
Hydrobiologia 731: 109–123. doi:10.1007/s10750-013-1686-3

Dillon, P. J., and L. A. Molot. 1997. Dissolved organic and inorganic carbon mass balances in Central Ontario lakes. Biogeochemistry 36: 29–42. doi:10.1023/A:1005731828660

Dirnbock, T., and G. Grubherr. 2000. GIS assessment of vegetation and hydrological change in a high mountain catchment of the Northern Limestone Alps. Mt. Res. Dev. 20: 172–179 doi:10.1659/0276-4741(2000)020[0172:gaovah].2.0.co;2

Downing, J. A., and others. 2008. Sediment organic carbon burial in agriculturally eutrophic impoundments over the last century. Global Biogeochemical Cycles 22: GB1018. http://dx.doi.org/10.1029/2006gb002854

Einarsson, K., M. B. Wallin, and S. Sobek. 2017. High terrestrial carbon load via groundwater to a boreal lake dominated by surface water inflow. J. Geophys. Res.-Biogeosci. 122: 15–29. doi:10.1002/2016jg003495

Ejarque, E., S. Khan, G. Steniczka, J. Schelker, J. Kainz Martin, and J. Battin Tom. 2018. Climate-induced hydrological variation controls the transformation of dissolved organic matter in a subalpine lake. Limnol. Oceanogr. 63: 1355–1371. doi:10.1002/lo.10777

Erlandsson, M., and others. 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Glob. Chang. Biol. 14: 1191–1198. doi:10.1111/j.1365-2486.2008.01551.x

Fasching, C., A. J. Ulseth, J. Schelker, G. Steniczka, and T. J. Battin. 2016. Hydrology controls dissolved organic matter export and composition in an Alpine stream and its hyporheic zone. Limnol. Oceanogr. 61: 558–571. doi:10.1002/lo.10232

Freeman, C., C. D. Evans, D. T. Monteith, B. Reynolds, and N. Fenner. 2001. Export of organic carbon from peat soils. Nature 412: 785–785. doi:10.1038/35090628

Foken, T., M. Göckede, M. Maeder, L. Mahrt, B. Amiro, and W. Munger. 2005. Post-Field Data Quality Control, X. LeeW. Masson and B. Law Handbook of Micrometeorology: A Guide for Surface Flux Measurement and Analysis. Springer. Dodrecht, Netherlands. 181–208. doi:10.1007/1-4020-2265-4_9

Gobiet, A., S. Kotlarski, M. Beniston, G. Heinrich, J. Rajczak, and M. Stoffel. 2014. 21st century climate change in the European Alps—A review. Sci. Total Environ. 493: 1138–1151. doi:10.1016/j.scitotenv.2013.07.050

Gudasz, C., D. Bastviken, K. Steger, K. Premke, S. Sobek, and L. J. Tranvik. 2010. Temperature-controlled organic carbon mineralization in lake sediments. Nature 466: 478–U473. doi:10.1038/nature09186

Gudasz, C., and others. 2017. Contributions of terrestrial organic carbon to northern lake sediments. Limnol. Oceanogr. Lett. 2: 218–227. doi:10.1002/ol2.10051

Guillemette, F., E. von Wachenfeldt, D. N. Kothawala, D. Bastviken, and L. J. Tranvik. 2017. Preferential sequestration of terrestrial organic matter in boreal lake sediments. J. Geophys. Res. Biogeogr. 122: 863–874. doi:10.1002/2016jg003735

Håkanson, L., and M. Jansson. 2002. Principles of lake sedimentology. The Blackbrun Press. New Jersey. doi:10.1007/978-3-642-69274-1

Hanson, P. C., D. L. Bade, S. R. Carpenter, and T. K. Kratz. 2003. Lake metabolism: Relationships with dissolved organic carbon and phosphorus. Limnol. Oceanogr. 48: 1112–1119. doi:10.4319/lo.2003.48.3.1112

Hanson, P. C., M. L. Pace, S. R. Carpenter, J. J. Cole, and E. H. Stanley. 2015. Integrating landscape carbon cycling: Research needs for resolving organic carbon budgets of lakes. Ecosystems 18: 363–375. doi:10.1002/1095-4850.1122

Hamel, R. D., R. J. Cooper, R. M. Slade, R. L. Haney, and J. G. Arnold. 2006. Cumulative uncertainty in measured streamflow and water quality data for small watersheds. Trans. ASABE 49: 689–701, http://pubs.er.usgs.gov/publication/70030364,

Horváth, Z., et al. 2017. Zooplankton communities and Bythotrephes longimanus in lakes of the montane region of the northern Alps. Inland Waters 7: 3–13. doi:10.1080/20442041.2017.1294317

Huotari, J., and others. 2011. Long-term direct CO2 flux measurements over a boreal lake: Five years of eddy covariance data. Geophys. Res. Lett. 38: L18401. doi:10.1029/2011GL048753

Johnson, E. R., S. Inamdar, J. Kan, and R. Vargas. 2018. Particulate organic material composition in stream runoff following large storms: Role of POM sources, particle size, and event characteristics. J. Geophys. Res. Biogeogr. 123: 660–675. doi:10.1002/2017JG004249

Jonsson, A., M. Meili, A. K. Bergström, and M. Jansson. 2001. Whole-lake mineralization of allochthonous and autochthonous organic carbon in a large humic lake (Örtrasket, N. Sweden). Limnol. Oceanogr. 46: 1691–1700. doi:10.4319/lo.2001.46.7.1691

Kainz, M. J., R. Ptacnik, S. Rasconi, and H. H. Hager. 2017. Irregular changes in Lake surface water temperature and ice cover in subalpine Lake Lunz, Austria. Inland Waters 7: 27–33. doi:10.1080/20442041.2017.1294332

Karlsson, J., A.-K. Bergström, P. Byström, C. Gudasz, P. Rodríguez, and C. L. Hein. 2015. Terrestrial organic matter input suppresses biomass production in lake ecosystems. Ecology 96: 2870–2876. doi:10.1890/15-0515.1

Kritzberg, E. S., J. J. Cole, M. M. Pace, and W. Granéli. 2005. Does autochthonous primary production drive variability in bacterial metabolism and growth efficiency in lakes dominated by terrestrial C inputs? Aquat. Microb. Ecol. 38: 103–111. doi:10.3354/ame038103

Laaha, G., et al. 2017. The European 2015 drought from a hydrological perspective. Hydrol. Earth Syst. Sci. 21: 3001–3024. doi:10.5194/hess-21-3001-2017
Ejarque et al.

Hydrology controls mountain lake C-mass balance

Likens, G. E. 2009. Limnological introduction to Mirror Lake, p. 1–22. In T. C. Winter and G. E. Likens [eds.], Mirror Lake interactions among air, land, and water. University of California Press, http://www.jstor.org/stable/10.1525/j.ctt1ppvb5

Mammarella, I., O. Peltola, A. Nordbo, L. Järvi, and Ü. Rannik. 2016. Quantifying the uncertainty of eddy covariance fluxes due to the use of different software packages and combinations of processing steps in two contrasting ecosystems. Atmos. Meas. Tech. 9: 4915–4933. doi:10.5194/amt-9-4915-2016

McKnight, D. M., R. Harnish, R. L. Wershaw, J. S. Baron, and S. Schiff. 1997. Biogeochemistry 36: 99–124. doi:10.1023/a:1005783812730

Mendonça, R., and others. 2017. Organic carbon burial in global lakes and reservoirs. Nat. Commun. 8: 1694. doi:10.1038/s41467-017-01789-6

Meyers, P. A., and R. Ishiwatari. 1995. Organic matter accumulation in lake sediments, p. 279–328. In A. Lerman, D. M. Imboden, and J. R. Gat [eds.], Physics and chemistry of lakes. Berlin Heidelberg: Springer. doi:10.1007/978-3-642-85132-2_10

Moser, K. A., and others. 2019. Mountain lakes: Eyes on global environmental change. Global Planet. Change 178: 77–95. doi:10.1016/j.gloplacha.2019.04.001

Moncrieff, J. B., and others. 1997. A system to measure surface fluxes of momentum, sensible heat, water vapour and carbon dioxide. Journal of Hydrology 188-189: 589–611. doi:10.1016/s0022-1694(96)03194-0

Moncrieff, J. R, Clement, J. Finnigan, and T. Meyers. 2005. Averaging, Detrending, and Filtering of Eddy Covariance Time Series, X. Lee W. Massman and B. Law. Handbook of Micrometeorology: A Guide for Surface Flux Measurement and Analysis. 7–31. Springer. Dodrecht, Netherlands. doi:10.1007/1-4020-2265-4_2

Müller, B., J. S. Meyer, and R. Gächter. 2016. Alkalinity regulation in calcium carbonate-buffered lakes. Limnol. Oceanogr. 61: 341–352. doi:10.1002/lno.10213

Pace, M. L., and others. 2004. Whole-lake carbon-13 additions reveal terrestrial support of aquatic food webs. Nature 427: 240–243. doi:10.1038/nature02227

Paul, F., A. Kääb, M. Maisch, T. Kellenberger, and W. Haeberli. 2004. Rapid disintegration of Alpine glaciers observed with satellite data. Geophys. Res. Lett. 31: L21402. doi:10.1029/2004GL020816

Prairie, Y. T., D. F. Bird, and J. J. Cole. 2002. The summer metabolic balance in the epilimnion of southeastern Quebec lakes. Limnol. Oceanogr. 47: 316–321. doi:10.4319/lo.2002.47.1.0316

R Core Team, 2018. R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna. www.R-project.org

Rasconi, S., R. Ptacnik, and M. J. Kainz. 2018. Seston fatty acid responses to physicochemical changes in subalpine Lake Lunz, Austria. Water Resour. Res. 54: 8442–8455. doi:10.1029/2017wr020959

Raymond, P. A., and others. 2013. Global carbon dioxide emissions from inland waters. Nature 503: 355–359. doi:10.1038/nature12760

Sadro, S., and J. M. Melack. 2018. The effect of an extreme rain event on the biogeochemistry and ecosystem metabolism of an oligotrophic high-elevation lake. Arct. Antarct. Alp. Res. 44: 222–231. doi:10.1657/1938-4246-44.2.222

Sadro, S., J. M. Melack, J. O. Sickman, and K. Sleen. 2019. Climate warming response of mountain lakes affected by variations in snow. Limnol. Oceanogr. Lett. 4: 9–17. doi:10.1002/lo2.10099

Schelker, J., T. Grabs, K. Bishop, and H. Laudon. 2013. Drivers of increased organic carbon concentrations in stream water following forest disturbance: Separating effects of changes in flow pathways and soil warming. J. Geophys. Res. Bioge. 118: 1814–1827. doi:10.1002/2013jg002309

Schindler, D. W., P. J. Curtis, S. E. Bayley, B. R. Parker, K. G. Beaty, and M. P. Stainton. 1997. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochemistry 36: 9–28. doi:10.1023/a:1005792014547

Smits, A. P., S. MacIntyre, and S. Sadro. 2020. Snowpack determines relative importance of climate factors driving summer lake warming. Limnol. Oceanogr. Lett. 5: 271–279. doi:10.1002/lo2.10147

Sobek, S., L. J. Tranvik, and J. J. Cole. 2005. Temperature independence of carbon dioxide supersaturation in global lakes. Global Biogeochem. Cycles 19: GB2003. doi:10.1029/2004gb002264

Sobek, S., B. Soderback, S. Karlsson, E. Andersson, and A. K. Brunberg. 2006. A carbon budget of a small humic lake: An example of the importance of lakes for organic matter cycling in boreal catchments. Ambio 35: 469–475 doi:10.1579/0044-7447(2006)35[469:acoa]2.0.co;2

Sobek, S., and others. 2009. Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. Limnol. Oceanogr. 54: 2243–2254. doi:10.4319/lo.2009.54.6.2243

Solomon, C. T., and others. 2015. Ecosystem consequences of changing inputs of terrestrial dissolved organic matter to lakes: Current knowledge and future challenges. Ecosystems 18: 376–389. doi:10.1007/s10021-015-9848-y

Stets, E. G., T. C. Winter, D. O. Rosenberry, and R. G. Striegl. 2010. Quantification of surface water and groundwater flows to open- and closed-basin lakes in a headwaters watershed using a descriptive oxygen stable isotope model. Water Resour. Res. 46: W03515. doi:10.1029/2009WR007793

Stottlemeyer R., Toczydlowski D. 1991. Stream chemistry and hydrologic pathways during snowmelt in a small watershed
adjacent Lake Superior. Biogeochemistry **13**: 177–197. doi: 10.1007/bf00002941

Tranvik, L. J., and others. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. **54**: 2298–2314. doi:10.4319/lo.2009.54.6_part_2.2298

Tranvik, L. J., J. J. Cole, and Y. T. Prairie. 2018. The study of carbon in inland waters—From isolated ecosystems to players in the global carbon cycle. Limnol. Oceanogr. Lett. **3**: 41–48. doi:10.1002/lol2.10068

Weisse, T., H. Müller, R. M. Pinto-Coelho, A. Schweizer, D. Springmann, and G. Baldringer. 1990. Response of the microbial loop to the phytoplankton spring bloom in a large prealpine lake. Limnol. Oceanogr. **35**: 781–794. doi:10.4319/lo.1990.35.4.0781

Weyhenmeyer, G. A., and others. 2012. Selective decay of terrestrial organic carbon during transport from land to sea. Glob. Chang. Biol. **18**: 349–355. doi:10.1111/j.1365-2486.2011.02544.x

Weyhenmeyer, G. A., S. Kosten, M. B. Wallin, L. J. Tranvik, E. Jeppesen, and F. Roland. 2015. Significant fraction of CO2 emissions from boreal lakes derived from hydrologic inorganic carbon inputs. Nature Geosci. **8**: 933–936. doi:10.1038/ngeo2582

Wood, S. N., Y. Goude, and S. Shaw. 2015. Generalized additive models for large data sets. Journal of the Royal Statistical Society: Series C (Applied Statistics) **64**: 139–155. doi:10.1111/rssc.12068

Zierl, B., and H. Bugmann. 2005. Global change impacts on hydrological processes in alpine catchments. Water Resour. Res. **41**: W02028. doi:10.1029/2004WR003447

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Conflict of Interest

None declared.

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