



Petrogenic organic carbon retention in terrestrial basins: A case study from perialpine Lake Constance

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ABSTRACT

Inland waters play a major role in the global carbon cycle, with particulate organic carbon (POC) burial in terrestrial wetlands surpassing that in ocean sediments. Lake Constance, the second largest lake at the periphery of the European Alps, receives POC sourced from both aquatic and terrestrial productivity as well as petrogenic OC (OC_{petro}) from bedrock erosion. Distinguishing POC inputs to lake sediments is key to assessing carbon flux and fate as reworked OC_{petro} represents neither a net sink of atmospheric CO₂ nor source of O₂. New stable and radiocarbon isotopic data indicate that 11 (9–12) Gg/yr of OC_{petro} is buried in Lake Constance with underlying sediments on average containing 0.3 (0.25–0.33) wt% OC_{petro}. Extrapolation of these results suggests that 27 TgOC_{petro}/yr (12–54 TgOC/yr) could be subject to temporary geological storage in lakes globally, which is comparable to estimates of 43⁺⁶¹₋₂₅ TgOC_{petro}/yr delivered to the ocean by rivers (Galy et al., 2015). More studies are needed to quantify OC_{petro} burial in inland sedimentary reservoirs in order to accurately account for atmospheric carbon sequestration in terrestrial basins.

1. Introduction

Particulate organic carbon (POC) burial in lakes and wetlands surpasses organic carbon (OC) burial in ocean sediments, positioning inland water bodies as major actors in the global carbon cycle (Tranvik et al., 2009). Discriminating between the allochthonous and autochthonous origin of POC retained in freshwater aquatic systems is key for understanding the net effect of terrestrial wetlands on carbon sequestration in the global carbon cycle (Tranvik et al., 2009), and is a fundamental prerequisite for accurate interpretation of Earth history manifested in the geological record. OC_{petro}, referring to POC of rock origin present in the form of kerogen (Durand, 1980), has emerged as an important contributor to OM in both modern river and ocean sediments (Dickens et al., 2004; Kao and Liu, 1996). OC_{petro} comprises over 99.9% of all reduced carbon present in the Earth's crust, totaling 15,000,000 PgOC, 3800-times larger than marine and terrestrial biota, soil, surface ocean sediments, and marine dissolved OC combined (Hedges and Oades, 1997). OC_{petro} is in part intrinsically resistant to degradation (Blair et al., 2003; Galy et al., 2008) and its mobilization from the bedrock and re-burial in recent sediments has no net effect on atmospheric CO₂ or O₂ (Hedges, 1992). In contrast, OC_{petro} which is

remineralized during weathering (Hemingway et al., 2018; Schillawski and Petsch, 2008) or along its transport pathway (Bouchez et al., 2010), contributes to atmospheric CO₂, thereby counterbalancing the effect of weathering of silicates and carbonates (Hilton et al., 2014), as well as burial of modern biospheric OC (Galy et al., 2008). In effect, the recalcitrant OC_{petro} fraction, such as graphitic carbon, is entrained in a simple carbon cycle where it bypasses the more complicated Earth surface carbon cycle upon its mobilization from bedrock and re-deposition in sediments (Sauramo, 1938). To date, much research focus has centered on constraining land-ocean transfer of OC_{petro}, with estimated fluxes (ca. 43 TgOC/a) corresponding to ~20% of overall land-ocean POC export globally (Galy et al., 2015). While attention has been focused on the export of OC_{petro} from the continents (Galy et al., 2015) and its occurrence in marine sediments (Dickens et al., 2004), little is known about its cycling and sequestration within terrestrial sedimentary basins. Currently, global carbon budgets do not consider contributions of OC_{petro} to the overall burial of POC in lake sediments (Cole et al., 2007; Einsele et al., 2001; IPCC, 2013; Tranvik et al., 2009), yet given its CO₂-neutral footprint, it is important to quantify OC_{petro} burial in order to accurately constrain CO₂ removal from the atmosphere via biospheric carbon burial (Galy et al., 2008).

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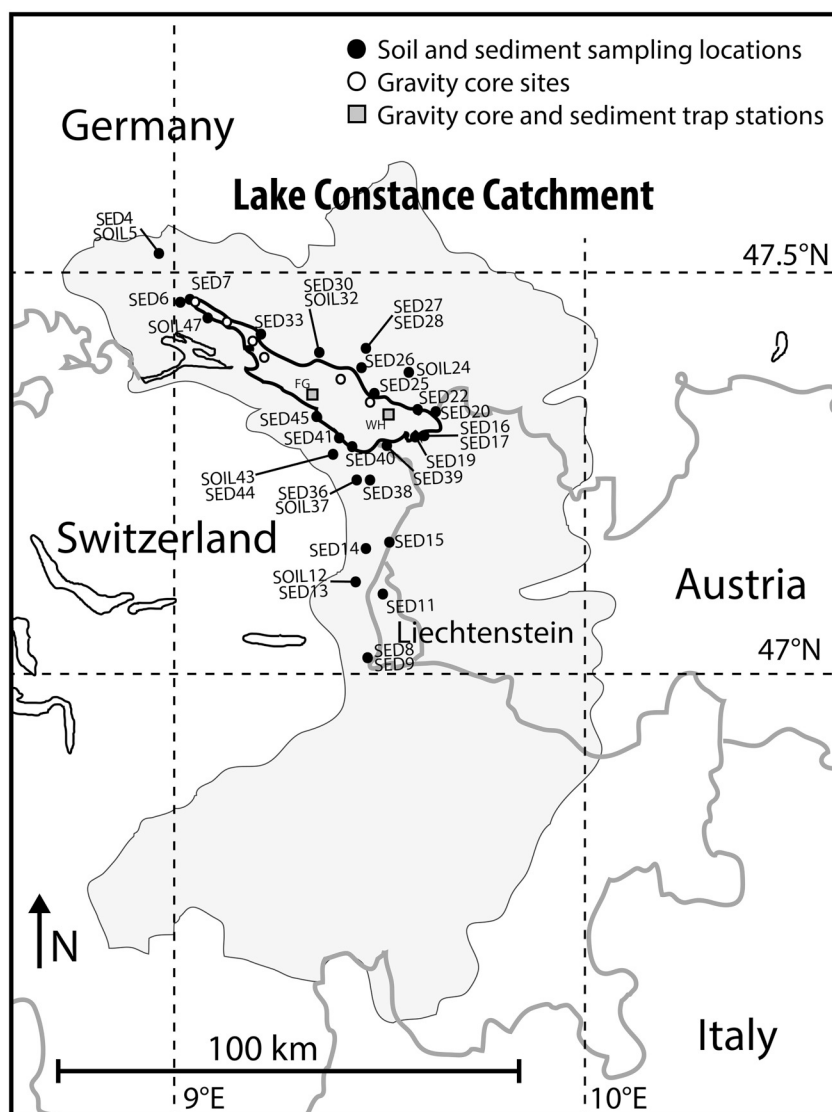


Fig. 1. Geographic overview of Lake Constance catchment showing land, river, and lake-based sampling locations in Upper Lake Constance. The Rhine-distal and Rhine-proximal sediment trap deployment sites are indicated by FG and WH, respectively.

Here we use a stable and radiocarbon isotope source apportionment approach to study carbon cycling in Lake Constance and its drainage basin in order to assess OC_{petro} fluxes in a modern coupled watershed-lake system and to shed light on the fate of OC_{petro} in terrestrial basins. We extrapolate our findings to derive first-order estimates on the retention of OC_{petro} in lakes globally.

2. Materials and methods

2.1. Study site

Lake Constance, the subject of this investigation, borders Germany, Switzerland, and Austria (see Fig. 1). During the Last Glacial Maximum (LGM, ca. 25,000 y BP), the area occupied by the present-day lake was covered by hundreds of meters of glacial ice. Upon glacial retreat, an erosional base lying 100–200 m below sea level was formed, and Lake Constance evolved in a landscape of drumlins, erratic blocks, moraines, and proto-lakes (Müller and Gees, 1968; Wessels, 1998). Since the LGM, ca. 10.7 km^3 of sediment are estimated to have accumulated in the lake basin, with an additional $> 140 \text{ km}^3$ deposited within the glacially overdeepened Alpine Rhine Valley that is filled with lacustrine, deltaic, and fluvial sediments (Eberle, 1987; Hinderer, 2003). Within this

valley, lacustrine deposits extend back to the city of Chur, around 80 km upstream of the present-day outflow of the Rhine River into Lake Constance (Eberle, 1987; Steudel, 1874). Already in the 19th Century, the significant role that perialpine lakes, such as Lake Constance, play in trapping sediments sourced from the Alps was recognized (Bischof, 1852). Lake Constance is composed of two basins - the Upper Lake Constance and the Lower Lake Constance basins. Upper Lake Constance, covering an area of 472 km^2 , receives the brunt of Alpine erosional products and is the subject of this investigation. Upper Lake Constance stands at 395 m above sea level and holds 47.6 km^3 of water with a maximum and average depth of 251 m and 101 m, respectively, as reported by the Internationale Gewässerschutzkommission für den Bodensee (IGKB) (IGKB, 2009; IGKB, 2016). The corresponding watershed rises to a maximum elevation at Tödi with 3614 m above sea level and encompasses an area of $11,438 \text{ km}^2$, of which 6119 km^2 is drained by the Alpine Rhine (IGKB, 2009).

2.2. Sample collection

Soil, river sediment, and lake samples were collected in 2012 and 2013 and frozen and freeze-dried. Surface exposed rock, soil material, overbank deposits, and river sediments were sampled in the catchment



Fig. 2. Lake Constance sediment cores. From left to right: BO12-110 (Mooring WH), BO12-111 (Mooring FG), BO12-112, BO12-113, BO13-09, BO13-10, BO13-11, and BO13-12.

using a shovel and van Veen grab sampler. In the lake, eight gravity cores (< 1 m length, 63 mm diameter) were collected. “Core top” and “core bottom” samples encompassed the uppermost 0.5 to 2 cm and lowermost 5 to 20 cm of the core, respectively. See Figs. 1 and 2 and Supplementary data set S1 for details on locations and descriptions of samples. See Supplementary data set S2 for details on core samples. See Supplementary data set S3 for details on rock samples.

Settling particulate material was collected in 2012 from time-series sediment trap deployments at a “Rhine-proximal” (WH) and “Rhine-distal” (FG) station (Fig. 1; see Supplementary data set S4), in a setup described elsewhere (Fuentes et al., 2013; Gilfedder et al., 2010). A water column profile of suspended POC samples (see Supplementary data set S5) was collected from location FG using a Niskin rosette sampler on combusted 47 mm diameter Whatman GF/F filters. Filters were folded into pre-combusted aluminum envelopes and stored frozen.

2.3. Laboratory analyses

2.3.1. Carbonate removal and stable carbon isotope measurements

Prior to all OC isotope analyses, samples were vapor-acidified in an

evacuated (10–15 in. Hg) glass desiccator (60–65 °C, 72 h) in the presence of 12 M HCl (Komada et al., 2008; Whiteside et al., 2010). Vapor acidification was chosen over the traditional rinse method as the procedure yields more accurate OC quantifications and isotopic compositions (Komada et al., 2008). Solid and on-filter POC samples were vapor acidified in silver capsules/boats and petri dishes, respectively. Prior to acidification, weights of dry samples were noted to later normalize OC contents to sample weight in order to calculate weight percent OC. After carbonate removal, samples were neutralized in the presence of NaOH pellets in a desiccator at 60–65 °C until dry for 3–5 days. After neutralization, samples were folded into tin capsules/boats for analysis with a ThermoFisher Flash EA coupled to a ThermoFisher Delta V PLUS mass spectrometer or on an Elementar varioMICRO Cube coupled to an Isoprime VISION isotope ratio mass spectrometer. In-house standards atropine and peptone were run in parallel to samples to calibrate %C and to correct stable carbon isotope data. The reproducibility of atropine was used for the measurement error of respective runs. Stable carbon isotopes are reported in per mil units (‰ VPDB) (Craig, 1957).

2.3.2. Radiocarbon measurements

For the preparation of samples for radiocarbon analysis, decarbonated samples were inserted into quartz tubes with cupric oxide, evacuated on a vacuum line, flame sealed, and combusted at 850 °C for 5 h. Evolved CO₂ was then barometrically quantified, cryogenically isolated and purified, and flame sealed in Pyrex ampules. Radiocarbon measurements were then made on a Mini Carbon Dating System (MICADAS) at the Laboratory of Ion Beam Physics at ETH Zurich by direct injection of sample CO₂ into the gas ion source (Ruff et al., 2007; Snyal et al., 2007). Anthracite coal and oxalic acid (NIST SRM 4990C) were used as the normalizing standard and for background correction and were used to assess procedural contamination stemming from sample treatment including acidification, neutralization, and sealed-tube combustion by preparing them in parallel to all samples. Blank filters were also prepared for assessing and correcting for extraneous carbon associated with on-filter POC samples. Measurements were corrected for constant contamination and errors were propagated (Wacker and Christl, 2011). Radiocarbon data are reported in units fraction modern (Fm) (Reimer et al., 2004; Stuiver and Polach, 1977).

2.4. Calculations

A radiocarbon decay correction and ternary mass balance was used for quantitatively interpreting provenance of Lake Constance POC as described in below. These source apportionment assessments are reported in Figs. 3, 4, and 5. Corresponding uncertainties centered on a sensitivity analysis of the soil end member are projected in Fig. 3.

2.4.1. Radiocarbon decay correction

The radiocarbon data of downcore sediments was decay corrected (Stenström et al., 2011) and reported in decay corrected fraction modern units (see Supplementary data set S2) in order to take natural aging of sediment since deposition into account for accurate POC source apportionment using constant sedimentation rate age models by applying Eq. (1).

$$Fm_{\text{decay corrected}} = Fm * e^{\ln(2) * t / 5730 \text{ yr}} \quad (1)$$

Here, the variable t represents time in years since deposition. This is calculated by dividing sediment depth (mm) by sedimentation rate (mm/yr). Sedimentation rates were estimated by using flood layers

from the Alpine Rhine marking discrete historical events and marker horizons reflecting encroaching 20th Century eutrophication and reaching its zenith in 1979 (Müller, 1997; Wessels, 1995; Wessels et al., 1995). Sedimentation rates ranged from 1.7–3.1 mm/year for the sites where decay corrections could be applied (see Supplementary data set S2). In the case of the gravity core sediments from Lake Constance, the depositional ages of the sediments were < 500 calendar years and had minor effects on the decay corrected radiocarbon values and on the final source apportionment, with the conclusions drawn in this study unaffected even if decay is left uncorrected.

Fig. 2 shows the cores that were collected in this study and their sedimentation rates are discussed in this paragraph. For core BO12-111, visible dark grey layers indicate some flood events, which constrains deposition time to depth 25.5 cm to the 1880s (Müller, 1997). This yields an estimated sedimentation rate of 1.9 mm/year. For core BO12-112, sedimentation rates can be estimated from flood horizons in 1999 (3–4 cm interval), 1987 (10–10.5 cm interval), and 1893 (37–37.25 cm interval) (Wessels, 2003; Wessels et al., 1995), with sedimentation rate estimates yielding 3.1 mm/year, 4.2 mm/year, and 3.1 mm/year, respectively. The sedimentation rate estimate of 3.1 mm/year integrating over the longest time interval was taken to as the more representative estimate and was used for correcting ¹⁴C-decay. For core BO13-09, based on the last occurrence of steam boat slag (21–22 cm) a sedimentation rate of 2.6 mm/year is estimated. Steamboats disappear from lake sediments around 1927 (Wessels, 1995). A turbidite layer at 30–31.5 cm deposited circa 1885 suggests a sedimentation rate of 2.5 mm/year, which was taken to as the more robust estimate and was used for correcting ¹⁴C-decay. Increasingly dark lamination and a transition into black sediment give first order time constraint of the eutrophication history (Müller, 1966a; von Gunten et al., 1987; Wessels et al., 1999). Based on these age models based on event horizons, the onset of iron sulfide-rich laminated deposits for BO12-111, BO12-112, and BO13-09 at 11 cm, 20 cm, and 16 cm begins between the late 1940s and mid 1950s, which fits remarkably well with first changes in diatom assemblages (Wessels et al., 1999). Observations from the 1960s recording the widespread occurrence of this deposit type on the sediment-water interface across large swaths of the lake bottom in connection with lake-wide eutrophication (Müller, 1966a; Müller, 1966b; Wagner, 1971) reveal an approximate level of isochronicity in the occurrence of this sediment type. On the premise that the onset of these prominent

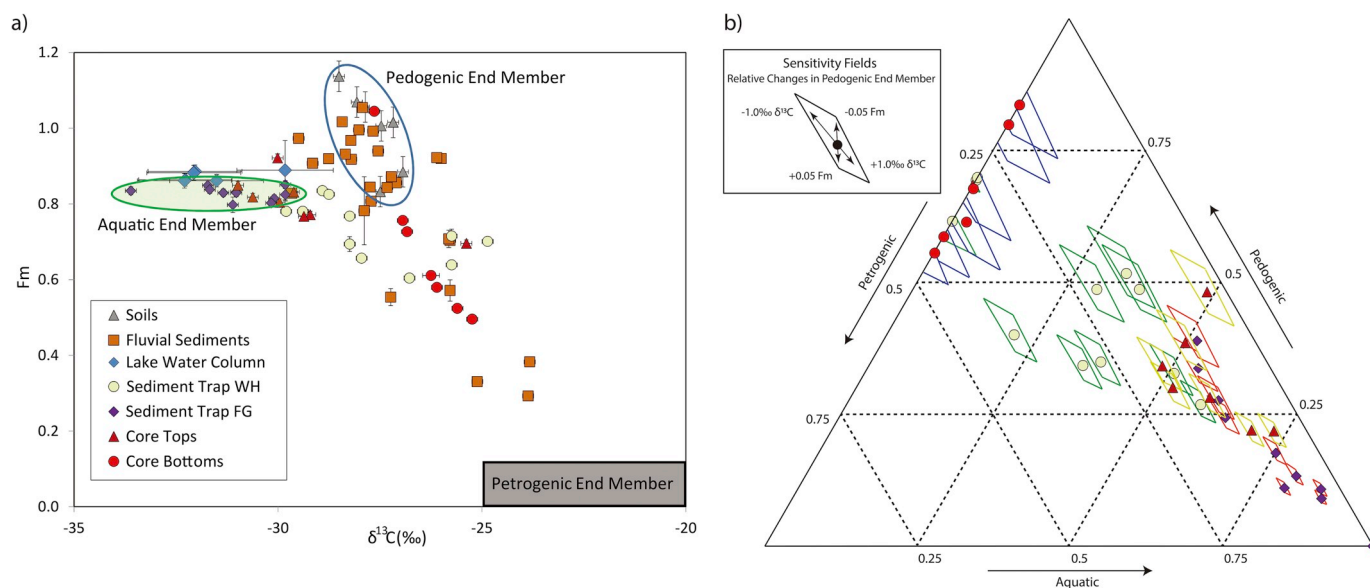


Fig. 3. a) Fraction modern versus stable carbon isotopic composition of bulk POC from different settings in and around Lake Constance. Three end members emerge from the plot: aquatic, pedogenic, and petrogenic POC, which lay the framework for the ternary mixing model. b) Relative abundance of POC type based on ternary mixing model with uncertainties.

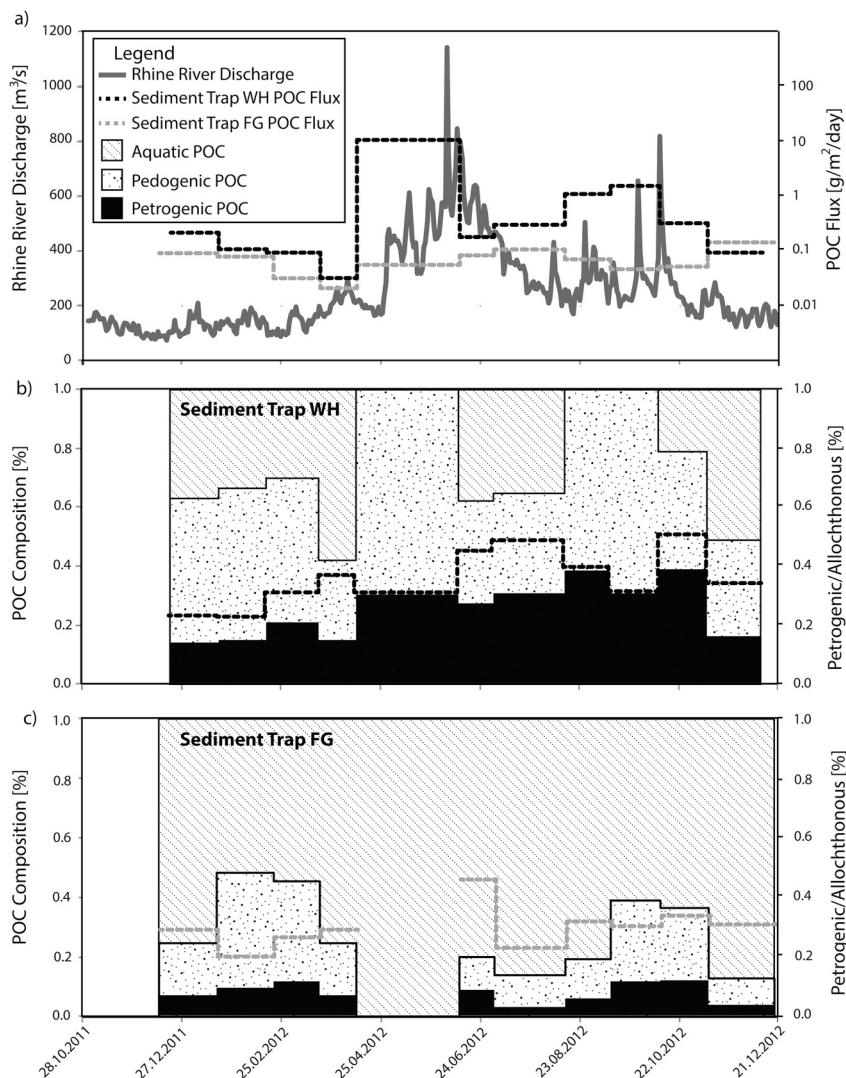


Fig. 4. Time-series records spanning the time period from 2011 and 2012 with (a) water discharge of the Rhine at Diepoldsau (measured by NADUF) with sediment trap POC fluxes. Source apportionment of POC at stations from radiocarbon and stable carbon isotopic compositions are shown for sediment traps (b) WH and (c) FG.

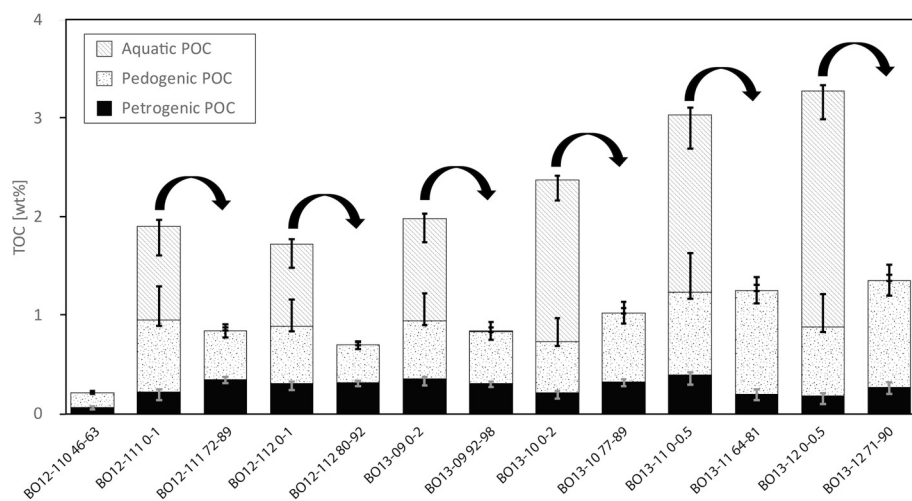


Fig. 5. POC provenance calculated using the ternary mixing model for core tops and core bottoms using the carbon isotopic end members of modern-day and pre-bomb pools, respectively. Arrows indicate paired core tops and bottoms.

deposits is approximated by the year 1950, representing the average from the aforementioned three cores using independent age models, the sedimentation rates for BO13-10, BO13-11, and BO13-12 can be approximated to 1.7, 1.7, and 2.1 mm/year, respectively. Significant uncertainty in the sedimentation rates of these cores can be expected. In order to account for this uncertainty, a generous relative error of 50% is applied for all sedimentation rates for propagating error uncertainty in the decay correction of downcore radiocarbon values. No ^{14}C -decay corrections and source apportionments were applied for downcore sediments of sites BO12-110 and BO12-113 due to very high sedimentation rates.

2.4.2. Source apportionment

A ternary mass balance was established for quantitatively interpreting provenance of Lake Constance POC using Eqs. (2)–(4) and supplementary data presented in Supplementary data sets S2 and S4 (cf. Vonk et al., 2016). The sum of the three contributions of POC denoted by f_x including petrogenic, pedogenic, and aquatic is equal to one.

$$1 = \sum_x f_x \quad (2)$$

$$Fm_{\text{measured}} = \sum_x f_x * Fm_x \quad (3)$$

$$\delta^{13}\text{C}_{\text{measured}} = \sum_x f_x * \delta^{13}\text{C}_x \quad (4)$$

The quantitative interpretation of POC provenance, using Eqs. (2)–(4) and the isotopic end member compositions assigned in Section 3.1, is presented in Figs. 3 and 4. For downcore lake sediments, radiocarbon data is decay corrected prior to quantitative source apportionment to account for loss of since deposition (see previous section). In the case of compositions lying outside of the ternary mixing framework (i.e., negative calculated values for f_x), these were projected onto the ternary plot in the direction of the opposing end member and the negative variable was set to zero. To assess the sensitivity of mass balance results to the chosen end members (including for those outside the ternary mixing framework), sensitivity fields are plotted in Fig. 2 showing POC compositions as a function of changing pedogenic POC isotopic composition. Greater sensitivity (uncertainty) is seen for compositions lying closer to the pedogenic end member. These reveal variations of greater than $\pm 10\%$ in aquatic POC contributions for $\pm 1.0\%$ changes in $\delta^{13}\text{C}_{\text{org}}$.

3. Results and discussion

3.1. Carbon source apportionment

3.1.1. OC_{petro}

The majority of Lake Constance sediments are sourced from readily erodible claystones from the Bündnerschiefer formations and flysch in the Rhine catchment (Stuedel, 1874), which are of Mesozoic and early Cretaceous to Oligocene age, respectively (Hsü, 1995). The bedrock $\delta^{13}\text{C}_{\text{org}}$ values depend on the geologic age of the sediments and on the source and type of kerogen (Lewan, 1986) as well as on metamorphic overprint, the latter giving rise to higher (more ^{13}C -enriched) values (Hoefs and Frey, 1976). By definition, OC_{petro} is characterized by Fraction modern (Fm) = 0, meaning it is devoid of radiocarbon. Although there is marked variance in $\delta^{13}\text{C}_{\text{org}}$ values of rock samples from the Lake Constance catchment ($-21 \pm 4\%$; $n = 17$; ranging from -28 to -15% ; see Supplementary data set S3), within the Lake Constance system, $\delta^{13}\text{C}_{\text{OC}_{\text{petro}}}$ trends towards a value of -22.5% based on observations from the Alpine Rhine River (Fig. 3), which is adopted as the end-member value for OC_{petro} supplied to the lake. The quantification of OC_{petro} shows only minor sensitivity as a function of the choice of the stable carbon isotopic composition of the OC_{petro} end member (see Fig. 3b).

3.1.2. Pedogenic POC

Soil erosion leads to contributions of POC of pedogenic origin in Lake Constance sediments. Swiss alpine and sub-alpine soil OC of relative uniform radiocarbon isotopic compositions has been reported across a range of climatic, geologic conditions, and soil depth (van der Voort et al., 2016). Soils collected during the 1990s, show an average radiocarbon isotopic composition for topsoil and subsoil of 1.14 ± 0.03 and 1.08 ± 0.04 Fm, respectively (van der Voort et al., 2016), with topsoil radiocarbon values overlapping with those of 1990s atmospheric radiocarbon (Levin and Kromer, 2004). In light of these data, as well as radiocarbon data for eroding pedogenic OC determined in this study (see Fig. 2) that are close to modern-day atmospheric values, a value of 1.05 Fm is assigned to best represent the radiocarbon signature of current, pedogenic POC actively contributing to river and lake sediments. Previous observations from Lake Constance (Wessels, 1995) have shown discrepancies in depositional age ascertained by lamination counting and radiocarbon dating of wood fragments. In sediments deposited between 900 and 4000 years before present, the ages of the wood fragments are older by 480 ± 370 calendar years ($n = 4$) than the age of deposition (Wessels, 1995). Interpreting this time lag as the average age of terrestrial biospheric POC introduced to lake sediments prior to industrialization and bomb-derived carbon inputs, leads to an estimate of 0.95 ± 0.05 Fm to best describe the pre-bomb, pre-industrial radiocarbon signature of pedogenic POC delivered to Lake Constance covering the time span (< 500 years before present) of the downcore sediments investigated here. This assignment allows the carbon isotopic composition of bulk sedimentary POC found in downcore lake sediments to reside within a mixing triangle of the aquatic, OC_{petro} , and pedogenic POC end members. The carbon isotopic composition of POC in fluvial sediments, besides those of the Rhine, reflects POC sourced predominantly from soils.

3.1.3. Aquatic POC

The radiocarbon content of the aquatic end member is constrained by three different sample types at a location distal from fluvial inputs (station FG): settling POC intercepted by a bottom-tethered sediment trap at 100 m depth, water column dissolved inorganic carbon (DIC) samples, and water column suspended POC samples. Over the entire year, corresponding sediment trap intercepted POC yielded an average radiocarbon value of 0.83 ± 0.02 Fm ($n = 11$; Supplementary data set S4). DIC of the water column averaged 0.856 ± 0.005 Fm ($n = 6$) (Blattmann et al., 2018), and suspended POC collected from the same water column averaged 0.87 ± 0.01 Fm ($n = 6$; Supplementary data set S5). Given uncertainties associated with potential degradation of fresh (labile) aquatic OM or contributions of laterally-transported terrigenous OC to sediment trap samples, and relatively large blank corrections that were applied to suspended POC samples, the average DI^{14}C of the water column is considered the most reliable and representative metric of the aquatic end member (Broecker and Walton, 1959), and this value is adopted for subsequent quantitative provenance analysis. Based on the radiocarbon ratio of atmospheric carbon in lakewater DIC, pre-bomb Lake Constance DI^{14}C is estimated to be 0.84 Fm (Blattmann et al., 2018). Unlike DI^{13}C , DI^{14}C Fm values are fractionation-corrected, meaning that biological effects such as preferential uptake of isotopically-light carbon do not affect the Fm ratio (Stuiver and Polach, 1977). Over the deployment year, station FG sediment trap intercepted POC yielded an average $\delta^{13}\text{C}$ value of $-31.0 \pm 1.1\%$ ($n = 11$) with variability largely attributable to seasonal changes in both the concentration and stable carbon isotopic composition of DIC (Fuentes et al., 2013; Hirschfeld, 2003; Hollander and McKenzie, 1991). With station FG receiving minor amounts of allochthonous, land-derived sediment, measures of allochthony and autochthony, including chlorite abundance and chlorophyll concentrations, respectively, show correlations with $\delta^{13}\text{C}_{\text{POC}}$ and support the usage of -32.5% to best represent the end member for quantification of aquatic POC inputs into Lake Constance sediments (Fuentes et al., 2013). Potential

contributions to Lake Constance sediments of C_4 plant-derived POC characterized by heavy stable carbon isotopic compositions (-14 to -18‰) (Meyers, 1994) has been previously debated and considered negligible (Fuentes et al., 2013), agreeing with our observed carbon isotope patterns with neither river nor lake sediments receiving discernable C_4 contributions.

3.2. Organic carbon burial fluxes

3.2.1. Sediment trap observations

Marked variations in sedimentation rates occur locally within Lake Constance due to strong spatiotemporal variations in autochthonous and particularly allochthonous sediment deposition. For sediment trap WH proximal to the Rhine inflow, organic geochemical signatures reflect episodic fluvial sediment supply. Both Fm and $\delta^{13}C_{org}$ values plummet when upper Rhine discharge increases (see Fig. 3). During times of elevated flow, the Rhine POC flux in trap WH increases by approximately 10 to 100 fold (cf. Müller and Förstner, 1968). The event-driven mode of Rhine sediment delivery and deposition results in short oxygen exposure times during source-to-sink transfer, thus promoting POC burial (Sobek et al., 2009). The composition of POC delivered to sediment trap WH is strongly influenced by Rhine discharge and thus of the erosive power of the Rhine in the catchment. In contrast, for river-distal station FG, organic geochemical signatures mirror primary productivity in the surface water and pulses of allochthonous sediment input are greatly attenuated (Fig. 4).

3.2.2. Lake bottom sediments

A total average sediment flux of 3.70 Tg/yr into Lake Constance is estimated for all rivers combined with the Alpine Rhine River contributing over 90% (Gilfedder et al., 2010; Müller, 1971). On average, 1.0 wt% OC is preserved long term, which we here define as > 200 years, the minimum depositional age of core bottoms investigated (see Fig. 5 and Data Set S2). When comparing core top to core bottom, it becomes evident that pedogenic POC and OC_{petro} behave in a recalcitrant manner, undergoing little to no remineralization during early burial (200–450 years). This stands in contrast to aquatic POC, which in all locations undergoes extensive remineralization. Based on the ternary mixing model and the end member uncertainty shown in Fig. 3b, the weight percentage of preserved OC in downcore sediments breaks down into 0.002 wt% (0–0.10 wt%) aquatic POC, 0.3 wt% (0.25–0.33 wt%) OC_{petro} , and 0.7 wt% (0.61–0.75) soil-derived (pedogenic) POC. Using the total sediment flux of 3.70 Tg/yr into Lake Constance as representative of a long-term average flux and best available data for smaller rivers (Gilfedder et al., 2010) and multiplying these with percentage OC, we calculate a total of approximately 37 GgOC/yr is buried and sequestered in Lake Constance sediments. Based on the percentage of specific OC types, this partitions into 0.1 (0–3.8), 11 (9–12), and 26 (23–28) GgOC/yr of aquatic, petrogenic, and pedogenic origin, respectively.

3.3. Protracted storage of OC_{petro}

The burial of 11 Gg OC_{petro} /yr in Lake Constance sediments represents OC_{petro} retention within a terrestrial basin, hindering further transmission and ultimate discharge to the marine realm. The amount of OC_{petro} retained in other lakes remains unknown and therefore how global continent-ocean OC_{petro} fluxes are attenuated by this mechanism is unknown. Nonetheless, it is likely that OC_{petro} is present in many lake sediments as illustrated by radiocarbon content and complementary evidence in various other case studies (Donner and Jungner, 1974; Fowler et al., 1986; Olsson, 1979; Vonk et al., 2016). However, case studies on OC_{petro} fluxes in lake sediments remain too rare to rigorously account for continent-ocean OC_{petro} retention on a global scale. Taking the global-scale estimate of land-ocean OC_{petro} flux (Galy et al., 2015), the amount entrapped in Lake Constance represents about 0.03% of this

global flux. From its watershed, Lake Constance also receives an equivalent of 0.03% of global land-ocean freshwater flux (Dai and Trenberth, 2002; Gilfedder et al., 2010), indicating that OC_{petro} delivery to Lake Constance is approximately within the global average expected from fluvial supply. In order to derive a first-order estimate, we scale our results to estimate an OC_{petro} burial flux for lakes globally. Given current estimates that 90 TgOC/yr (40–180 TgOC/yr) is sequestered in lakes annually (Mendonça et al., 2017), extrapolation of our OC_{petro} burial rates from Lake Constance (following geochemical evidence that approximately three-tenths of the total OC is of petrogenic origin) to lakes globally suggests that about 27 Tg OC_{petro} /yr (12–54 TgOC/yr) undergoes temporary geological storage in the terrestrial sphere. In a previous study that assumed 0.5 wt% of sediment consists of OC_{petro} , lacustrine burial of OC_{petro} was estimated to be 18 TgOC/yr globally (Meybeck, 1993). Although this prior study and the present study involved markedly different datasets and assumptions, the final global estimate for OC_{petro} flux is remarkably similar. Nevertheless, existing datasets remain sparse and prone to inherent biases, and therefore current estimates carry substantial uncertainty. Given the focus of the current investigation of a perialpine setting and glaciofluvial origin of Lake Constance (see next section), additional case studies spanning a range of geological and climatic settings would be required to further constrain global OC_{petro} burial fluxes in lacustrine deposits. In particular, studies of the small but numerous high latitude lakes that comprise a relatively large share of global total lake area (Verpoorter et al., 2014) represent key targets for improving this first-order estimate, particularly given available evidence for significant OC_{petro} contributions to their sediments (Vonk et al., 2016).

Today, in addition to natural lakes, manmade reservoirs are responsible for trapping and burying 60 TgOC/yr (20–110 TgOC/yr) globally (Mendonça et al., 2017) with the retention of the OC_{petro} portion possibly ephemeral, depending on the mode of human operation. Studies on the role of these impoundments on regional and carbon cycles are beginning to emerge (Li et al., 2015; Maavara et al., 2017; Ran et al., 2014) including their role in retaining OC_{petro} (Li et al., 2015). With fluxes of POC into such impoundments set to rise with increasing numbers of dams (Van Cappellen and Maavara, 2016), their, yet unstudied, importance for OC_{petro} cycling in terrestrial basins is set to increase.

3.4. Perspectives on perialpine OC_{petro} cycling

Glacial-interglacial cycles introduce a pattern of sediment production, mobilization, temporary storage in terrestrial basins with complex time lags of sediment delivery related to sediment routing, trapping, and remobilization (Hinderer, 2012). Anthropogenic activity has now also led to its own attenuation of sediment fluxes (Hinderer, 2012). From the many glacial lakes formed by retreating glaciers, we speculate that riverine OC_{petro} fluxes to the ocean drop in the wake of glacial periods with a slowly (possibly step-wise) increase in OC_{petro} export through interglacial periods as accommodation space in lakes reach capacity, enabling by-passing of these natural sediment traps. Geomorphologically, this carbon cascade is expressed in the (re)distribution of sediment observed in sedimentary valley infills in the Alpine Rhine Valley (Eberle, 1987; Hinderer, 2003; Steudel, 1874), perialpine sedimentary valley infills in central Europe (Hinderer, 2001; Preusser et al., 2010), and paraglacial environments in general (Ballantyne, 2002; Hinderer, 2012). Glacially overdeepened Lake Constance serves as a particularly efficient trap with nearly all inflowing particulate sediment deposited even during high flux events that carry high suspended sediment loads (Hinderer, 2001; Müller and Förstner, 1968). In addition to the remobilization and deposition loops in the modern, the presence of Triassic zircons in Cretaceous-age sandy Bündnerschiefer intervals in the catchment of Lake Constance have been interpreted as being sourced from a reworked Austro-Alpine nappe stack (Beltrán-Triviño et al., 2013). The orogenic reworking of sediments renders

likely the possibility that a fraction of the OC_{petro} entrained in the modern carbon cycle may have already embarked on this same voyage many millions of years ago.

4. Conclusions

Within Upper Lake Constance, 11 (9–12) Gg/yr of OC_{petro} is retained in sediments with average sedimentary OC_{petro} content of 0.3 wt %. Extrapolation of these results suggests that 27 Tg OC_{petro} /yr (12–54 Tg OC_{petro} /yr) could be subject temporary geological storage in lakes globally, however, robust constraints require acquisition of more comprehensive datasets. Retention of OC_{petro} in lakes results in a decrease in the overall OC_{petro} flux from land to ocean over geological timescales. Geologically short-term storage in lake sediments allows OC_{petro} to escape oxidation as long as the lake sediments are not reworked by advancing glaciers, tectonic uplift, and river incision, and in this context terrestrial basins may play a key role in retarding OC_{petro} remineralization on human timescales. Further studies are needed to quantify OC_{petro} sequestration in lake sediments in order to quantify their global effect on OC_{petro} entrapment, and also to disentangle and derive separate budgets for biospheric and petrogenic carbon sequestration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2018.10.021>.

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