Plants or bacteria? 130 years of mixed imprints in Lake Baldegg sediments (Switzerland), as revealed by compound-specific isotope analysis (CSIA) and biomarker analysis

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Abstract. Soil erosion and associated sediment transfer are among the major causes of aquatic ecosystem and surface water quality impairment. Through land-use and agricultural practices, human activities modify the soil erosive risk and the catchment connectivity, becoming a key factor of sediment dynamics. Hence, restoration and management plans of water bodies can only be efficient if the sediment sources and the proportion attributable to different land-uses are identified. To this aim, we applied two approaches, namely compound-specific isotope analysis (CSIA) of long-chain fatty acids (FA) and triterpenoid biomarker analysis, to the eutrophic Lake Baldegg and its agriculturally used catchment (Switzerland). Soils reflecting the five main land-uses of the catchment (arable lands, temporary and permanent grasslands, mixed forests, orchards) were subjected to CSIA. The compound-specific stable isotope $\delta^{13}C$ signatures clearly discriminate between grasslands (permanent and temporary) and forests. Signatures of agricultural land and orchards fall in-between. The soil signal was then compared to the isotopic signature of a lake sediment sequence covering ca. 130 years (before 1885 to 2009). Most of the lake sediment samples lie out of the source soils polygon, most likely as a result of carbon exchanges with highly depleted material related to methanotrophic bacterial activity. The recent lake samples falling into the soil polygon indicate an important contribution of the forests, which can be explained by (1) the location of the forests on steep slopes, resulting in a higher connectivity of the forests to the lake, and (2) potential direct inputs of trees and shrubs growing along the rivers feeding the lake and around the lake. Despite the strong bacterial overprint on the isotopic signal, land-use and catchment history are clearly reflected in the CSIA results, with isotopic shifts being consistent with catchment, land-use and eutrophication history. While present in the soils, the investigated highly specific biomarkers were not detected in the lake sediment. Two trimethyltetrahydrochrysenes (TTHCs), natural diagenetic products of pentacyclic triterpenoids, were found in the lake sediments. Their origin is attributed to the in-situ microbial degradation of some of the triterpenoids. While the need to apportion sediment sources is especially crucial in eutrophic systems, our study stresses the importance of using caution with CSIA and triterpenoid biomarkers in such environments, where the presence of methanotrophic bacterial biomass might overprint original isotopic signals.

1 Introduction

While it is known that pollutant inputs have a severe impact on aquatic ecosystems, especially in agriculturally used catchments (Malaj et al., 2014; Allan, 2004; Liess et al. 2001), the influence of sediment input and sediment dynamics on biological quality and recovery of rivers remains highly uncertain (Scheurer et al., 2009; Matthaei et al., 2010). Sediment loads to freshwaters are increasing worldwide, often being related to anthropogenic activities (Scheurer et al. 2009). Sediment pollution has been identified as one of the most relevant pressures to water bodies (Borja et al., 2006), and sediments are among the top ten causes

of biological impairment in freshwater ecosystems (US EPA, 2009). Land-uses and agricultural practices modify the soils erosive risk and the catchments sedimentary connectivity, becoming a key factor of sediment dynamics and aquatic ecosystems health. Restoration and management plans of water bodies can only be efficient if the sediment sources and their respective contributions, i.e. the proportion attributable to different land uses are identified (Wasson et al. 2010; Sundermann et al. 2013).

5 The compound-specific isotope analysis (CSIA) technique, based on the compound specific stable isotope signatures of inherent organic biomarkers in the soil, was developed and applied to discriminate and apportion the source soil contribution from different land-uses (Gibbs, 2008; Blake et al., 2012; Hancock and Revill, 2013; Upadhayay et al., 2017). The FAs being transferable from plants to soils, stable, persistent in soils, mobile with sediments during flow events and easily isolatable from the other compounds in lipid mixtures, they are especially well suited for CSIA (Reiffarth et al., 2016). While FAs assemblages
10 are not variable enough among plant species to discriminate them, their $\delta^{13}C$ signature differs among plant species (Tolosa et al., 2013). The $\delta^{13}C$ signature of biomarkers is assumed to be more preserved than concentration during degradation and transport processes (e.g. Marseille et al., 1999; Gibbs, 2008), allowing to discriminate sources in various studies in lake sediment and catchment studies (e.g. Galy et al., 2011; Fang et al., 2014), even dominated by C3 vegetation only (Alewell et al., 2016).

15 In addition to the CSIA, attention was given to some cyclic compounds as specific tracers for source identification. A large part of the cyclic compounds is synthesized by more restricted plant groups than linear alkyl lipids. Among the cyclic compounds, some triterpenes were validated as family- or even species-specific (e.g. some triterpenyl acetates for Asteraceae, some sesqui-, di- and triterpenoids for conifers, methoxyserratenes for Pinaceae; Lavrieux et al., 2011; Otto and Wilde, 2001; Le Milbeau et al., 2013; respectively). Mostly developed and successfully used for paleo-environmental studies (e.g. Jacob et
20 al., 2008; Lavrieux, 2011; Guillemot et al., 2017), the high potential of these highly specific biomarkers (HSB) for tracking sediment sources and evaluating the soil vulnerability remains under-exploited.

The need to precisely identify sediment sources is especially important in eutrophic systems to enable efficient and targeted restoration measures. For this reason, we chose to use a mixed CSIA and HSB approach to the Lake Baldegg catchment (Central Switzerland). The eutrophic Lake Baldegg is a typical but also extreme example of a European freshwater body, as it
25 suffered substantially from nutrient input (mainly phosphorus, P) during the second half of the 20th century. Studies have been carried out on the P source attribution into the lake but the origin of sediments remains unclear. While the eutrophication history of the Lake Baldegg has extensively been studied (e.g. Niessen and Sturm, 1982; Lotter et al., 1997; Lotter, 1998; Teranes and Bernasconi, 2005), an in-depth confrontation of the lake evolution with the recent history of the catchment (including land-use and agricultural practices changes) has not yet been performed.

30 Our project aimed at filling these gaps. In this paper, the soil isotopic signatures of FAs characterizing the main land-uses of Lake Baldegg catchment are quantified and confronted to the evolution of the CSIA imprint of a 130-yrs long lake sediment sequence. This study is, to our knowledge, the first sediment fingerprinting CSIA concerning a lake sediment core covering more than a century.

2 Study site

35 Lake Baldegg (N47°12' 0", E8°15'40"; 463 m a.s.l.) is a eutrophic lake of glacial origin located on the central Swiss Plateau (Fig. 1). It has a maximum depth of 66 m, a surface area of 5.2 km^2 and a water volume of 0.173 km^3. The lake is fed by 15 streams and has a mean residence time of 4.3 years (Wehrli et al., 1997). The outflow is located at its northern end. Its North-South catchment, having an area of 67.8 km^2, has hillslopes of 700-800 m a.s.l. elevation. The catchment is today intensively

used for agriculture: 77% is used as agricultural land, 12% as forest (mostly on the slopes), 5% as urbanized areas (Wehrli et al., 1997). In 2015, one third of the agricultural land was devoted to permanent grassland, 40% to cereals and arable lands (including 10% of maize), 24% to temporary grasslands, while fruit production (small trees, mainly apples and pears) covered ca. 1% of the agricultural land (Federal Statistical Office, 2015). Intensive chicken farming and pig breeding are other

5   important farming activities.

Previous studies have provided extensive information about the lake eutrophication history (e.g. Lotter et al., 1997, 1998; Wehrli et al., 1997). Briefly, this eutrophication, starting in 1885, translated into annually laminated (varved) sediments in a context of constant anoxic lake bottom until the 1980s (anoxia below 60 m depth between 1885-1940; below 40 m between 1940-1970; below 10 m between 1970-1982; Niessen and Sturm, 1987; Lotter et al., 1997). Along the 20th century, a severe

10   increase in phosphorus loads stemming from the intensification of land-use, population and industrial activities, supported an increase in the eutrophication. The almost exponentially increasing phosphorus concentration in the lake water (up to > 500 µg.l⁻¹; Wehrli et al., 1997), leading to hypereutrophic conditions with dramatic fish kills and algal blooms, was curbed after the introduction of wastewater treatment plants and several restoration efforts. Despite the introduction of an artificial oxygenation system into the lake water column in 1982 (Stadelmann et al., 2002), which lead to the disappearance of the

15   varves from 1995, and strong decrease of P concentrations in the lake to below 30 µg.l⁻¹ as the result of lake external and internal measures, the lake has not yet fully recovered from eutrophication (Müller et al, 2014).

3 Materials and methods

3.1 Connectivity index

With the purpose to sample the source soils most likely contributing to the recovered lake sediment, a connectivity index

20   model and a connectivity map were built. Connectivity patterns in the catchment were identified using a modified sediment connectivity index (IC) based on the approach by Borselli et al. (2008) and modified by Cavalli et al. (2013) (Fig. 2). This index, calculating surface roughness from a high resolution digital elevation model (2m resolution, swissALTI3D), indicates the degree of linkage controlling sediment fluxes throughout landscape, and, in particular, between sediment sources and downstream areas and finally the freshwater system.

25   ### 3.2 Sampling

3.2.1 Soils

Soil sampling locations were chosen according to the abovementioned connectivity model approach, the land-use map (Fig. 2) and aerial photographs. The focus of this study was set on areas with high connectivity. Soil samples representing each main land-use type (arable lands, permanent grasslands, temporary grasslands, mixed forests, orchards) were taken. Five sites

30   were selected for orchards and forests, four sites for arable lands and temporary grasslands, and three sites for permanent grasslands. Within each site, four soil cores were sampled and mixed into a composite sample. For the forest soils, the humus layer was removed prior to sampling. For the orchards, samples were taken at the base of the trees, where no herbaceous vegetation was growing. Distinction between temporary and permanent grasslands was made from the vegetation diversity observed on the field, and the presence of a tilled horizon was checked with a Pürckhauer auger system. The 5 uppermost

35   centimeters of the soil were sampled with a 5-cm high cylindrical steel ring (98.2 cm³) and stored in aluminum foil in the fridge until drying.

3.2.2 Lake sediment core

We subsampled in January 2016 a sediment core (Ba-09-03) retrieved in autumn 2009 in the deepest part of Lake Baldegg, which was stored in a refrigerated storage room since then. The varved sediment allows dating of the cores at a seasonal resolution back to 1885 CE. Detailed retrieving and sediment core information, as well as the age-depth model, is documented

5 in van Raden (2012) and Kind (2012). The upper 45 cm of the core, covering the last 130 years, were sampled in 3 yrs slices. The 9-mm-thick turbidite of 1956 CE was sampled apart. Every second sample between 1885 and 2009 CE, as well as one sample older than 1885 CE, i.e. before eutrophication start, were further analyzed. The oldest sample was dated to ca. 1870 CE by extrapolating the sedimentation rate of the well-dated last 19th century varved part.

3.3 Sample preparation

10 After freeze-drying (lake sediments) or oven-drying (soils; 40°C, 72 hours), the sediment samples were carefully crushed with a pestle and mortar. Soils were dry sieved at 2 mm, which was not necessary for the fine-grained lake sediment. The macroscopic elements (vegetal remains, stones) were hand-picked from all the samples. 2-4 g of samples (soils and lake sediments) were processed for the lipid extraction, using a mixture of CH_2Cl_2:MeOH (9:1 v/v) in an Accelerated Solvent Extractor (Dionex ASE 200 for the lake sediments, Dionex ASE 350 for the soils). Lipid extracts were subsequently separated

15 into neutral, acidic and polar fractions using solid-phase extraction on aminopropyl-bonded silica as described in Jacob et al. (2005).

3.3.1 Fatty acid preparation for CSIA

The acidic fraction (including the free fatty acids) was methylated at 60°C for 1h using 1 mL of 12–14% BF_3 in MeOH. Fatty acid methyl esters (FAMEs) were extracted from the solution by agitating four times with ca. 2 mL hexane in the presence of

20 1 mL of 0.1 M KCl. The final extract was stored in the freezer until analysis.

The purity of the extract and the concentration of the FAMEs were checked using a Trace Ultra gas chromatograph (GC) with a flame ionization detector (FID; Thermo Scientific, Walthalm, MA 02451, USA) as described in Alewell et al. (2016). Lake sediments FAMEs stable carbon isotopic composition was measured as described in Alewell et al. (2016) using a Trace Ultra GC, coupled via combustion interface GC Isolink and Conflo IV with a Delta V Advantage isotope ratio mass spectrometer

25 (Thermo Scientific). Soils FAMEs stable carbon isotopic composition was measured using a Trace 1310 GC instrument interfaced on-line via a GC-Isolink II to a Conflo IV and Delta V Plus isotope ratio mass spectrometer (Thermo Fisher Scientific). A DB 5ms column (J & W DB-5MS, 50 m × 0.2 mm i.d., 0.33 μm film thickness) was used. The GC temperature program was 70 °C (held 4 min) to 150°C at 20°C/min and afterwards to 320 °C (held 40 min) at 5 °C/min. He was used as carrier gas at a constant 1 ml/min. CO_2 of known $\delta^{13}C$ composition was automatically introduced via Conflo IV into the isotopic

30 ratio mass spectrometer in a series of 5 pulses at the beginning and 4 pulses the end of each analysis, respectively, and used as reference gas during every measurement. The comparability of soils and lake sediment results was ensured by triplicate measurements of 3 lake samples realized on both instruments. Each sample was measured at least 3 times. Carbon stable isotope ratios were reported in delta notation, per mil deviation from Vienna Pee Dee Belemnite (VPDB). The instruments performance was routinely checked with an external isotopically characterized fatty acids mixture (F8-3) obtained from Arndt

35 Schimmelmann (see http://pages.iu.edu/~aschimme/hc.html), to which a mixture of isotopically characterized C24:0, C26:0, C28:0 and C30:0 FAMEs was added. Performance was controlled with a C19:0 FA internal standard. The reported $\delta^{13}C$ values were corrected for the additional carbon atom introduced during methylation. Mean values of at least triplicate measurements, as well as their corresponding standard deviation, were calculated. The analytical uncertainty is lower than ±0.5 ‰.

3.3.2 Triterpenoids

The neutral fraction (including the cyclic biomarkers considered in this study) was further separated into aliphatics, aromatics, ethers and esters, ketones and acetates, and alcohols by flash chromatography on a Pasteur pipette filled with activated silica (24 h at 120 °C, then deactivated with 5% H_2O) and using a sequence of solvents of increasing polarity. The alcohol fraction

5   was silylated before injection by reaction with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane and pyridine for approximately 1 h at 60°C. 5α-cholestane, which was used as an internal standard, was added to all fractions, prior to analysis by gas chromatography-mass spectrometry (GC-MS) with a Trace GC Ultra coupled to a DSQII mass spectrometer (Thermo Fisher Scientific). The GC instrument was fitted with a Restek Rxi-5ms column (60m x 0,25mm i.d., 0.25µm film thickness). Samples were injected in splitless mode, with the injector temperature set at 300 °C.

10   He was the carrier gas at a constant flow of 1.2 ml.min^{-1}. The GC temperature program was 50 °C (held 2 min) to 140 °C (held 1 min) at 10 °C/min, then to 300°C (held 63 min) at 4°C/min. The transfer line to MS detector was operated at 260°C. The mass spectrometer was operated in the electron ionization (EI) mode at 70eV and scanned from m/z 40 to 1000. Component identification was based on comparison with literature data.

15   ## 4 Results and discussion

4.1 CSIA of soils

Among the FAs detected in soils (C17:0 to C32:0), only the longer chains, i.e. longer than C24:0, were further considered for this study to limit errors due to aquatic organisms contribution (Alewell et al., 2016). Though present in soils, C30:0 and C32:0 were not further considered here as their too low concentration (C30:0) or absence (C32:0) in the lake sediments hampers their

20   use for fingerprinting. Fig. 3 displays the CSIA isoplots for the C24:0 vs. C26:0, C26:0 vs. C28:0, and C24:0 vs. C28:0. Data are provided in Table S1. The C26:0 vs. C28:0 show the best discrimination between the different land-uses.

All the samples align along a line, which ends are the grasslands and the forests. Halfway between them, orchard signature probably holds a mix between the inputs of the fruit trees, which signature can be supposed to be comparable to forest trees one, and of the underlying grass. One orchard sample plots within the forest pool. Being covered of the same tree species as

25   the other orchards (apple trees), and the age of the orchard having no influence on the measured imprint (Table S3), it is most probable that the corresponding sample was taken nearer from the trees than the other ones. CSIA signatures of arable lands plot near the orchards. The good separation between grasslands and forest pools confirm the results published on the Enziwigger catchment (ca. 30 km West of Lake Baldegg; Alewell et al., 2016), but our results show a better distinction between arable lands and grasslands – which could not be separated in this previous study. This can be either due to the greatest surface

30   covered with maize in Lake Baldegg catchment (ca. 10% of agricultural land in 2015; Federal Statistical Office) compared to Enziwigger catchment, where the low maize production does not produce any detectable effect on the stable isotope signature of soils (Schindler Wildhaber et al., 2012) or to more frequent rotation of grasslands and arable crops in the Enziwigger study. Temporary grasslands being generally part of crop rotations including cereals, we expected temporary grasslands to plot near arable lands at Lake Baldegg. But CSIA signatures cannot distinguish between non-permanent and permanent grasslands. As

35   turnover times of one to several decades were reported for lipid fractions in croplands, permanent grasslands and forests (Wiesenberg et al., 2004; Wiesenberg et al., 2008; Griepentrog et al., 2015, respectively), the rapid loss of an arable land imprint after rotation to grassland seems unlikely. Most probably, the corresponding non-permanent grasslands are, even though regularly ploughed and the vegetation regularly re-sowed, used mostly as grasslands since years, resulting in an imprint comparable to the permanent grasslands one.

4.2 CSIA of lake sediments

Because of the very low concentration of the C30:0 FA in the lake sediment, only the C24:0, C26:0 and C28:0 homologues were considered here to avoid any concentration effect (Fig. 4). Data are provided in Table S2. The isotopic signature of most of the samples fall out of the source soils mixing polygon, making the use of an mixing model to quantify the contribution of

5 different land-uses to sediment inputs impossible. This mismatch between soil and most of the lake sediment signals indicates either (1) that values have to be corrected for the atmospheric ^{13}C-depletion of the industrial era (Suess effect; Suess, 1955; Keeling, 1979) (2) that the major contributors to most of the lake FA isotopic signal are not the main source soils of the catchment, or (3) that the signal, originating from catchment soils, was altered after its introduction into the lake. These three hypotheses are discussed below.

10 δ^{13}C value of atmospheric CO_2 has decreased of ca. 1.5‰ since the beginning of industrial era in response to fossil fuel combustion (-6.5‰ in the preindustrial era vs. less than -8‰ today; Rubino et al., 2013; Keeling et al., 2005, respectively). Long-term experiments have shown that this depletion is well recorded in plants (e.g. Zhao et al., 2001). Accordingly, this effect should also be recorded in soils, and consequently also in organic terrestrial markers archived in lake sediments, such as FAs. While numerous studies have revealed ^{13}C-enrichment with depth in soil profiles, microbial biomass was identified as

15 the key factor of such changes, the Suess effect being a minor contribution only (see discussion in Krull et al., 2005, and references therein). Besides, the Suess effect can only account for a maximum decrease of ca. 1.5‰, and only in the case of a soil having a very fast (and unrealistic) turnover time of one to a few years (Garten et al., 2000). Longer turnover times imply necessarily a time lag in the recording of the Suess effect in soils. Accordingly, a shift of only ca. 0.2-0.3‰ (i.e. in the range of the measurement precision) was calculated in an arable temperate soil δ^{13}C between 1960s and 2000s, i.e. during the period

20 when most of the atmospheric isotopic shift is recorded, by Wiesenberg (2004). These results are comparable to the 0.1-0.3‰ estimated by Bird et al. (2003) in a tropical soil with a <10 years turnover rate. Furthermore, the ploughing of soils, such as in arable lands and grasslands in the case of Lake Baldegg catchment, results in a mix of young and old organic matter, mitigating all the more the recording of the Suess effect in such soils. Thus, although the effect of atmospheric δ^{13}C depletion may play a role on the long-chain FAs δ^{13}C signal at the time scale considered in this study, this effect can here be considered as

25 negligible. Moreover, most of the samples being shifted of more than 1.5‰ from the soils polygon, (an)other factor(s) must play a role.

Vegetation composition did not dramatically change during the last century and to our knowledge there are no plausible additional sources we might have missed over the last decades. Any input from sewage sludge or from pig faeces originating from the intensive farming attested since the mid-1960's around the lake can be excluded, even before the introduction of

30 wastewater treatment plants in the late 1960's, since both are not known as sources of long-chain saturated FAs (Cummings, 1981; Jørgensen et al., 1993; Jardé et al., 2005; Réveillé et al., 2003, respectively).

Other sources for long-chain FAs can be hypothesized. Some lacustrine macrophytes and microbial organisms are reputed producing long-chain FAs (e.g. Volkmann et al., 1988; Volkmann et al., 1998; Bovee and Pearson, 2014; Schouten et al., 1998), but no reference to the production of long-chain FAs by organisms known to live in the Lake Baldegg could be found:

35 the algae responsible for the blooms (toxic blue algae *Aphanizomenon* and *Anabaena* during the 1960's, green algae *Pediastrum* especially between 1965-1970; Stadelmann et al, 2002; van der Knaap et al., 2000) are indeed not reputed producing long-chain saturated FAs (Gugger et al., 2002; Caudales and Wells, 1992; Parker et al., 1967; Blokker et al, 1998). Other unidentified autochthonous organisms might still produce some.

Interestingly, the shorter the homologue is, the more deviated from the soils polygon its isotopic values are: while the soils values have a range of 3.5‰ for C24:0, 2.6‰ for C26:0, and 3.2‰ for C28:0, the lake values have a range of 9, 5 and 5, respectively. For long-chain FAs of close chain-length, the δ^{13}C values are generally comprised in a range of a few permil because of their common biosynthesis pathway (Hayes, 1993; Wiesenberg et al., 2004). However, we observe considerable

5 differences between isotopic signatures of the long-chain FAs. Both, the greater variation of the CSIA values in the lake compared to the soils as well as the discrepancies of up to 7 permil between C24:0 and C28:0, as observed here in lake sediments, suggest that a process affected the isotopic signatures after their production in the soils. Literature shows that much depleted δ^{13}C values are linked to bacterially assimilated carbon, associated to anoxic conditions in the water column (Summons et al., 1994; Teranes and Bernasconi, 2005). Biogenic methane carbon typically shows δ^{13}C values of -50 to -70‰

10 (Whiticar, 1999), leading to a much depleted methanotrophic bacteria biomass (e.g. Summons et al., 1994; Lehmann et al, 2004). The influence of the methanotrophic bacterial communities in the Lake Baldegg was already underlined by the study of Teranes and Bernasconi (2005). Furthermore, the production of these long-chain *n*-fatty acids by lake bacteria is unlikely here, since to our knowledge, reports about the production of long-chain *n*-fatty acids by bacteria are rare and constrained to extreme environments (e.g. Antarctic Ace Lake, Volkman et al., 1988; Volkman et al., 1998). Hence, our data suggest that

15 carbon exchanges took place between the long-chain *n*-FAs and a much depleted, methanotrophic bacteria-related material. Such a hypothesis also explains why the C24:0 is more affected than the C26:0 and the C28:0: a supposed exchange of the same number of carbon in these 3 homologues would indeed result in a stronger depletion of the isotopic composition for the shorter homologues relative to the longer ones. Such a carbon exchange makes it impossible to assess to what extent the isotopic signal is biased, and thus renders any correction to the data to retrieve the original signal impossible. Once again, the

20 role of the Suess effect can be evoked, as it is well documented that it also bias the lake sediment signal (e.g. Schelske and Hodell, 1995; Verburg, 2007). It could indeed affect the methanogenic bacterial biomass, and thus consequently impact the FAs δ^{13}C through the carbon exchanges. In such a case, it would count as a part of the inestimable bias of the FAs δ^{13}C signal expanded above – a part which could certainly here again be considered as minor, a maximal 1.5 permil effect being negligible compared to the much depleted methanotrophic bacterial biomass. This is confirmed by the temporal pattern observed in CSIA,

25 which consistency with lake history reconstructions led in previous studies (see below, section 4.2.1) would not be observed if the CSIA signal was too biased by the Suess effect.

Although the influence of other sources, as expanded above, cannot be fully excluded, the fact that the C28:0 lake isotopic values fall in the same range as the soils tends to indicate (1) that the soils are most probably the main sources and (2) that the C28:0 δ^{13}C values have been relatively little affected by carbon exchanges with highly depleted material. As the data indicate

30 that the C24:0 signal is the most affected of the 3 considered homologues, the following discussion will focus on the C26:0 vs. C28:0 signals (Fig. 4), which were also the homologues allowing the best distinction between the land-uses in the source soils (Sect. 4.1.).

4.2.1 Eutrophication, lake and catchment history, in the light of the CSIA

The C26:0 vs. C28:0 CSIA allows the clear distinction of different units (Fig. 4): before 1900; 1900 to 1940's; 1940's to early

35 1960's, early 1960's to early 1970's, early 1970's to today. These units confirm the changes along different time periods discussed in previous studies led in the lake (e.g. based on diatoms succession, bulk carbon isotopes, eutrophication history; Lotter, 1998; Teranes and Bernasconi, 2005; Stadelmann et al, 2002, respectively), which attests to the reliability of the CSIA signal to discuss the lake and catchment history.

The oldest sediment samples are deposited prior to the eutrophication start, which beginning was dated from 1885 from (1)

40 phosphorus concentrations inferred from the diatom assemblages and (2) the appearance of varves in the sediment sequence

(Lotter et al., 1997; Lotter, 1998). At the onset of the 20th century, a deviation in the C26:0 CSIA data towards lower values is recorded (Fig. 4a) while simultaneously a first important step in eutrophication is reached. Indeed, at that time, the microbial biomass increases (Teranes and Bernasconi, 2005) and a change in diatoms assemblage is recorded (Lotter, 1998), in response to the important industrial development of the catchment and the associated massive wastewater inputs into the lake.

5   In the early 1940's, a strong shift towards higher values is recorded in the C26:0 CSIA data signal (Fig. 4a). The lake then enters in a severe eutrophication period, marked by an increased influence of the bacterial communities (Neunlist et al., 2002; Teranes and Bernasconi, 2005). Lake water is anoxic below 40 m depth (Niessen and Sturm, 1987). The influence of the land-use changes on the lake response deserves consideration. Indeed, as a result of the Wahlen Plan, a Swiss food self-sufficiency program launched at the beginning of the Second World War, arable lands expand at the country scale (Popp, 2001). In Lake

10   Baldegg catchment, surfaces dedicated to open lands are multiplied by a factor of 3.6 between 1934 and 1945; they even increase by a factor of 4.1 for the cereals (Federal Statistical Office, 1949). Maize is introduced in the catchment during the 1940s, but its dedicated surface is under 3 ha in the mid-1940's and remains small until the 1980s (Federal Statistical Office, 1949; Lotter, 2010). No other cereal is introduced, but the relative proportion of winter wheat strongly increases (Federal Statistical Office, 1949). The agricultural intensification is reflected in the decline of grassland species, the decrease of ruderals

15   of poor soils, the increase of *Urtica* and the appearance of *Ambrosia*, the latter testifying to soil destructuration (pollen analyses of van der Knaap, 2000; Ducerf, 2017). According to air photographs, forest composition also changes to include more coniferous trees, and forest roads develop. Besides, agricultural intensification leads to intense river corrections: for instance, on the Western part of the catchment, 4 small rivers are buried in the 1940s. Such corrections, accompanied by the development of drainage system, will continue until the 1960s.

20   The isotopic excursion begins in the early 1960's (Fig. 4a), as the lake tends towards its most severe hypertrophic conditions, with a hypolimnion anoxia from 10 m depth (Niessen and Sturm, 1987). The strongly increasing phosphorus concentration fosters the development of photoautotrophic biomass, while the chemautotrophic bacterial biomass is still largely present in the lake, though declining (Teranes and Bernasconi, 2005). This anoxic phase is synchronous to increased sewage sludge inputs, as well as to a strong intensification of pig breeding in the catchment.

25   This isotopic excursion ends with the introduction of wastewater treatment plants in the catchment (Stadelmann et al., 2002). Later, the artificial oxygenation system set up in the lake in 1982 allows the return to oxic conditions at the bottom of the lake. This favors the development of phytoplanktonic producers, at the expense of the chemautotrophic biomass (Teranes and Bernasconi, 2005).

It is worth noting that from the mid-1940's, all the lake samples (except the early 1960's to early 1970's isotopic excursion)

30   fall into the source soil polygon (Fig. 4a), suggesting that these samples are not, or very little affected by carbon exchanges with highly depleted material. All the CSIA data of these samples from the forest / arable land / orchard areas fall into the polygon of the source soils signatures. While the sediment contribution from the arable lands can be explained by its associated discontinuous land cover and the agricultural practices (ploughing), the contribution of the forest pool is more surprising. However, most of the forests develop on steep slopes in the catchment, favoring the export of forest soil material

35   towards the lake. Besides, sedimentary inputs into the Lake Baldegg occur mainly during high flow events, which CSIA imprints were also shown to be dominated by forest contribution in a nearby catchment (Enziwigger catchment; Alewell et al., 2016). Furthermore, the development of trees and shrubs along the streams and on the shores of the lake since the 1940s (air photographs, pollen analysis; van der Knaap, 2000; field observation) may contribute directly to the signal.

4.2.2 General considerations

While the units defined with the CSIA match well with the eutrophication and the catchment history, it is remarkable that the oldest sediments (older than 1940) seem to be more affected by carbon exchanges with depleted material than the younger ones (except the isotopic excursion of the mid-1960's to mid-1970's). Indeed, the maximal extent of the chemautotrophic

5 biomass activity takes place during the most severe eutrophication periods of the lake, i.e. after 1940. It is also worth noting that while C24:0 and C26:0 are more depleted than C28:0 for the oldest lake sediments, the opposite is observed for the mid-1960's to mid-1970's excursion. Changes in the microbial biomass composition, resulting in contrasted effects on the n-FAs isotopic signature, can be suspected though no available data can support this hypothesis. A diagenetic transformation of the FAs isotopic signal can also be speculated for the sediments older than 1940. Such an assumption would mean that these

10 sediments would have been affected by carbon exchanges years to decades after their deposition, during the most severe eutrophic phases of the lake history. Why these exchanges would not have affected the younger sediments remains unexplained.

4.3 Triterpenoid biomarkers

The occurrence of cyclic highly specific biomarkers was checked both in soils and lake sediments. Pentacyclic triterpenes such

15 as some triterpenyl acetates, tricyclic diterpenes and methoxyserratenes (biomarkers of Asteraceae, conifers, Pinaceae, respectively; Lavrieux et al., 2011; Otto and Wilde, 2001; Le Milbeau et al., 2013) were investigated. While some non-specific molecules of these families have been identified in soils under the expected land-uses, and some triterpenoids were detected in the lake sediment, the most specific of them were totally absent from the latter. The concentration of these HSB in sediments is usually lower than the more common linear compounds such as n-fatty acids (e.g. Lavrieux, 2011). Accordingly, their non-

20 detection in the Lake Baldegg archive can be due to small undetectable inputs from the catchment or a signal dilution into autochthonous (lake organisms) contribution. Besides, a possible degradation of these pentacyclic triterpenes after their deposition can be hypothesized although the successful use of these molecules for palaeoenvironmental studies suggest their high preservation potential (e.g. Lavrieux, 2011; Guillemot et al., 2017 for triterpenyl acetates; Simoneit, 1986; Stefanova et al., 2002 for tricyclic diterpenes).

25 However, in all lake sediment samples, two trimethytetrahydrochrysenes (TTHCs) were detected: 3, 4, 7-trimethyl-1, 2, 3, 4-tetrahydrochrysene (TTHC2) and 3, 3, 7-trimethyl-1,2,3,4-tetrahydrochrysene (TTHC3). These polycyclic aromatic hydrocarbons (PAH) of natural origin derive from the rapid diagenesis of ubiquitous pentacyclic triterpenoids of the oleanane- and ursane series synthesized by upper plants (e.g. Wakeham et al., 1980). These TTHCs were reported during the last decades in recent lakes sediments (e.g. Wakeham et al., 1980; Yunker and MacDonald, 1995; Jacob et al., 2008), as well as in deltaic

30 environment (Bouloubassi and Saliot, 1993). Their formation in anaerobic conditions via microbial activity (Wakeham et al., 1980) was confirmed by the laboratory experiment of anaerobic transformation of triterpenes into PAH by Lohmann et al. (1990). Despite their production conditions are known, it is still under debate where this transformation takes place and would depend on the study site context: the TTHCs would be synthesized either in leaf litter or in deep soils (Wakeham et al., 1980; Jacob et al., 2008), during transport (Bouloubassi and Saliot, 1993), or produced *in-situ* in the lake sediment column (e.g.

35 Bouloubassi et al., 2001; Yunker and MacDonald, 2003).

While our investigations revealed the occurrence of these TTHCs in lake core sediments, they were neither detected in the upper soils, nor in river suspended sediments from Lake Baldegg catchment (unpublished results). Hence, the formation of TTHCs in soils and during transport appears here very unlikely, although their presence in deep soils (as reported by Wakeham et al., 1980) and their subsequent transport through deep soil erosion cannot be fully excluded.

The temporal evolution of TTHCs concentration is provided in Fig. 5. The lowest concentrations are recorded in the earliest part of the archive, before the onset of the eutrophication, and increase as the latter start. The maximal concentration is reached in the middle of the 1960's, i.e. synchronously to the isotopic excursion recorded in CSIA. The evolution of TTHCs concentration was confronted to ratios of $\delta^{13}C$ FAs ($\delta^{13}C$ C24:0/$\delta^{13}C$ C26:0; $\delta^{13}C$ C26:0/$\delta^{13}C$ C28:0; $\delta^{13}C$ C24:0/$\delta^{13}C$ C28:0).

5 As expanded above (Sect. 4.2.), a high discrepancy in isotopic values between long-chain FAs of close chain-length points to a degradation of the isotopic signal. Then, the more the values differ (i.e. the more the ratio of their isotopic values is >1 or <1), the more the isotopic signal of one of the FAs can be considered as degraded. Keeping in mind that such a ratio is not an absolute indicator because of some variability results from the biosynthesis pathway, one can still consider the overall evolution of the ratio along the core. C28:0 being considered as only little affected by the carbon exchanges (Sect. 4.2.), $\delta^{13}C$

10 C26:0/$\delta^{13}C$ C28:0 and $\delta^{13}C$ C24:0/$\delta^{13}C$ C28:0 ratios are taken as more reliable than the $\delta^{13}C$ C24:0/$\delta^{13}C$ C26:0 ratio.

Interestingly, the TTHCs concentration evolution is highly similar to the δ^{13}FAs ratios trend, even more for the $\delta^{13}C$ C24:0/$\delta^{13}C$ C28:0 than for the $\delta^{13}C$ C26:0/$\delta^{13}C$ C28:0. This suggests a TTHCs concentration under the control of the lake bacterial activity, similarly as the CSIA signal. In other words, the TTHCs signal archived in the Lake Baldegg sediments most probably testifies to an in-situ degradation of pentacyclic triterpenes, consequent to the bacterial activity favored by the anoxic conditions in the

15 water column (Wakeham and Canuel, 2016). While these compounds have successfully been used in many contexts for palaeoenvironmental reconstructions (e.g. Lavrieux, 2011; Dubois and Jacob, 2016; Guillemot et al., 2017), our results show the impossibility to use them to decipher the terrestrial inputs in the case of the highly eutrophic and microorganism-dominated Lake Baldegg environment.

Thus, the microbial activity overprints to a large extent the terrestrial molecular inputs in the Lake Baldegg, and affects the

20 linear compounds (as shown by the CSIA) as well as the cyclic ones (as shown by the HSB).

5 Conclusions

The aim of this study was to apply a mixed CSIA and HSB approach to the highly eutrophic context of Lake Baldegg catchment. The main land-uses were successfully discriminated with the CSIA and align along a line. The CSIA signals of arable lands as well as orchards plot halfway between grasslands and forests, which may render difficult to correctly attribute

25 the sources of sediment sample lying between grasslands and forests end-members. Most of the recent lake sediments plot within the forest soil pool, underlining the potential important contribution either of the steeply sloping and loosely structured forest soils or to tree lines growing along the streams and around the lake, which could contribute directly to the signal transported to the lake sediment archive. Further studies are required to investigate the extent of this potential contribution. However, all lake sediments older than 1940's, as well as those dating from mid-1960's to mid-1970's, actually fall out of the

30 polygon of the source soils signatures. While the long-chain fatty acids are becoming widely used for CSIA as markers of the terrestrial contribution only, our results underline the need to temper this standpoint. Some lacustrine macrophytes and microbial organisms were previously shown to produce also long-chain FAs, and our study highlights that a degradation of the isotopic signal linked to bacterial activity should not be underestimated. CSIA was proven to be unusable to trace and unmix terrestrial sources from the Lake Baldegg sediments, and thus to apportion the relative contribution of different land-

35 uses to the sedimentary archive. While the isotopic signal is strongly overprinted by carbon exchanges, land-use and catchment history are still to some extent reflected in the background: human activities and land-uses directly impacted the trophic level of the lake and its accompanying biomass, imprinting its mark on the FAs isotopic signal. The main phases of land-uses and catchment history over the last 150 years are thus still visible in the CSIA results. More than affecting just linear compounds, it is highly probable that the microbial activity also affected the more specific cyclic molecules assemblages, as testified by

the presence of TTHCs, which in-situ origin seems here clear. Special care should thus be taken for further studies on eutrophic systems, where a strong bacterial and methanotrophic activity is known or suspected. To overcome this carbon exchange bias and allow source apportionment, other approaches could be tested. While our study revealed the susceptibility of FAs to isotopic signal alteration, this should be investigated for other families otherwise used in CSIA, such as *n*-alkanes. Besides,

5   biomarker modelling approaches such as the VERHIB model (Jansen et al., 2010, 2013) could also be tested. Using plant-specific groups of biomarkers (including linear compounds), this linear regression model, developed to identify the plant-sources composing peat sequences, has yet to be applied for lake sediment cores. Efficient and reliable approaches have to be identified for Lake Baldegg and other similar contexts, where the sediment source apportionment is crucial to initiate efficient and targeted restoration measures.

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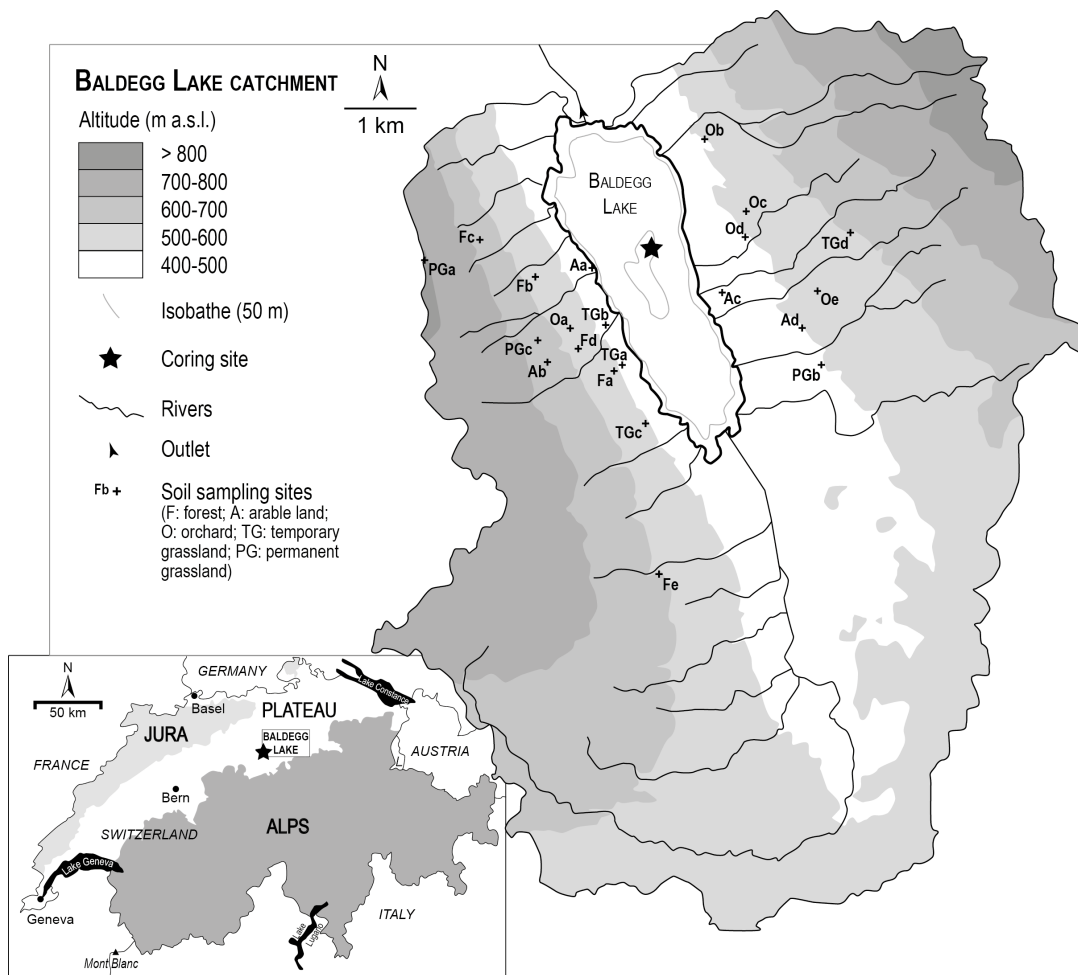
Figure 1: Catchment of Lake Baldegg with sampling sites.
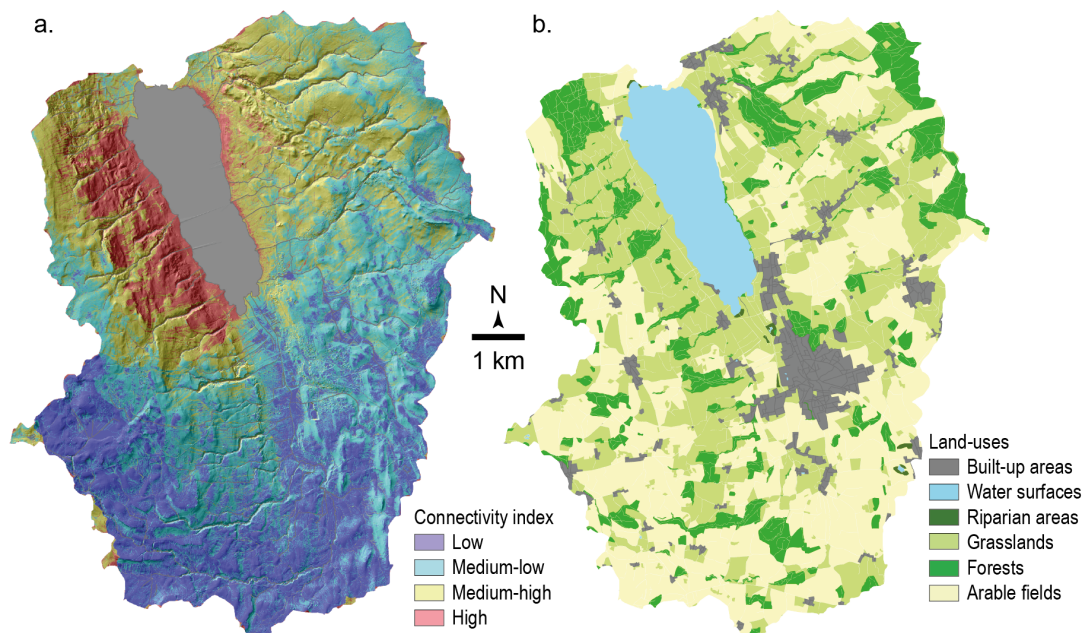
Figure 2: a. Connectivity index for the Lake Baldegg catchment, with a topographic map underlying. The lake is indicated in grey. b. Land-use map.
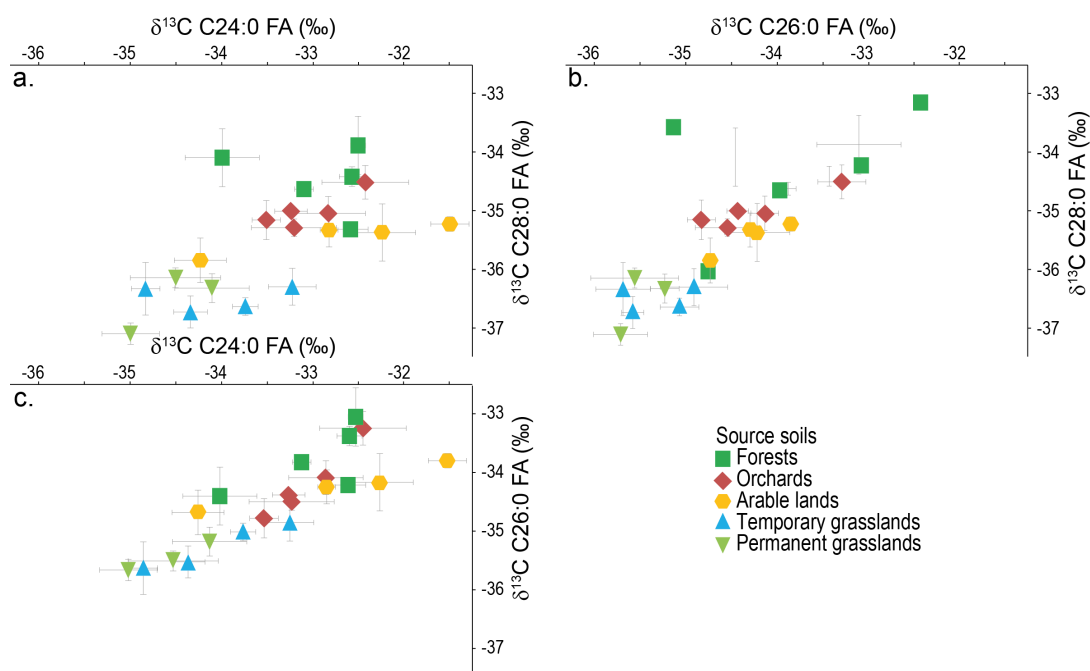
Figure 3: δ¹³C of the FAs (a.) C24:0 vs. C28:0, (b.) C26:0 vs. C28:0, (c.) C24:0 vs. C26:0 in soils. Error bars: standard deviation of the triplicate measurements.
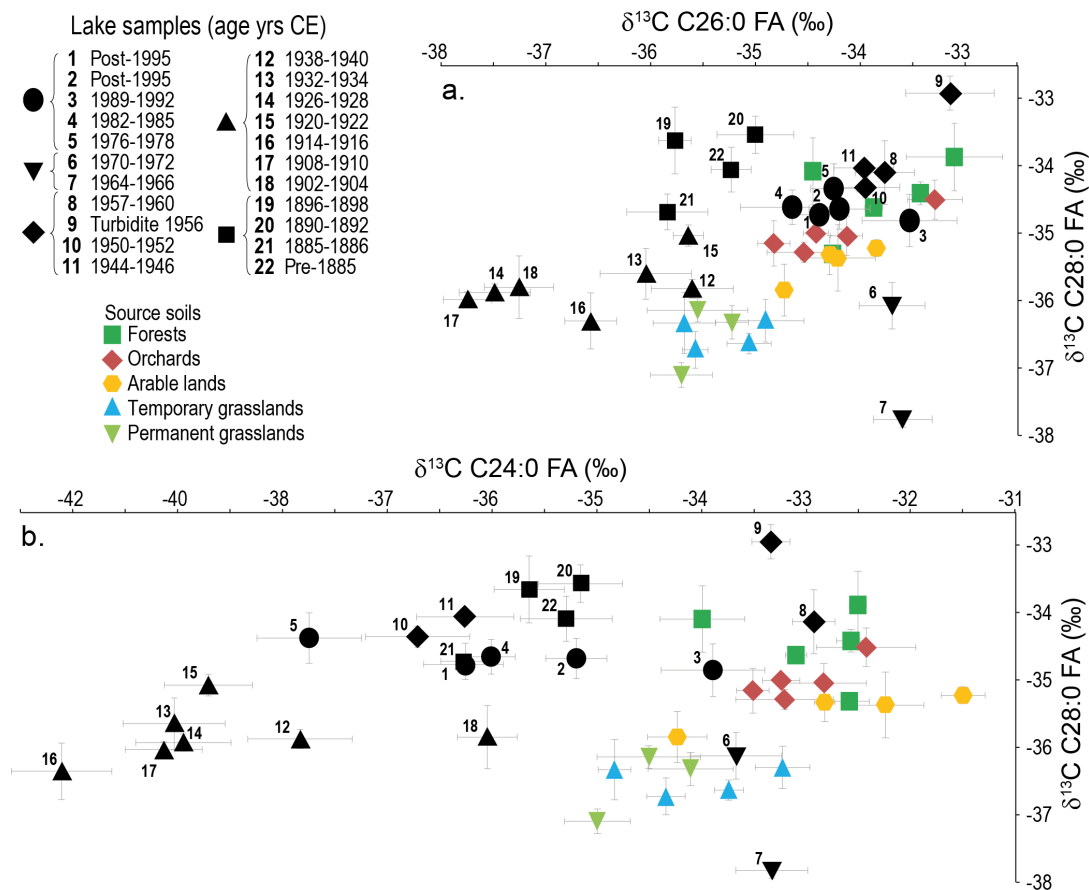
Figure 4: δ¹³C of the FAs (a.) C26:0 vs. C28:0, (b.) C24:0 vs. C28:0, in lake sediments, compared to soils. Note the different scale for the x axis between (a.) and (b.). Error bars: standard deviation of the triplicate measurements.
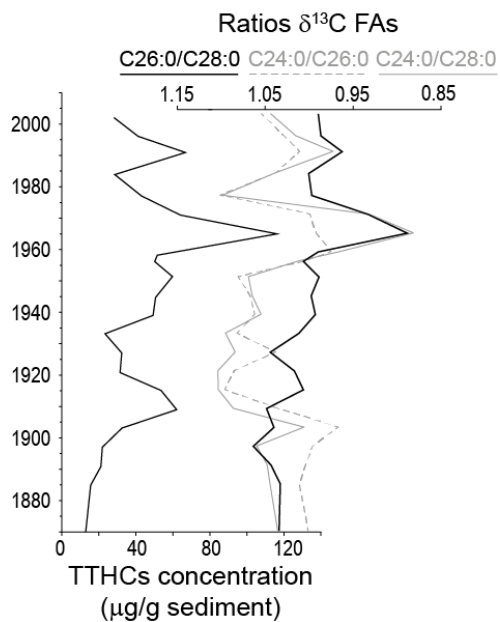
Figure 5: Evolution of the TTHCs concentration (sum of TTHC2 and TTHC3) along the sediment core, compared to evolution of the ratios of δ¹³C of FAs.