Point by point reply to reviewer comments

Reviewer comments in bold text.

Anonymous Referee #1
Received and published: 27 July 2018

The authors state in P3 L 31-32. For the forest soils, the humus layer was removed prior to sampling.
I find this counter intuitive - as this layer contain most (recent) organic matter and in term of connectivity is most likely to contribute material (thus lipid markers) to the lake. It be useful for the authors to provide an reasoning why they think this removal was valid in the context of the paper and its aims.

In the case of the humus layer of the Lake Baldegg forest soils we find for four out of five locations humus profiles with partly degraded (Oe) and intact plant material (Oi), and only one location with a fully fermented Oa horizon (fine humus material which might be eroded with the soil sediments). Lake sediments were carefully prepared and all recognizable plant residues were picked out prior to lipid extraction. Thus, we think, that with this method we are able to minimize the influence of the forest humus layer (e.g., in this case non-fermented plant input) on the lake sediments.

We added a more detailed description of the humus constitution of the forest soils on
P 3 L33-36 in the marked manuscript
For all the sites the humus layer was removed prior to sampling.
At four of five investigated forest sites no Oa layer was present (only partly degraded material (Oe) and intact plant material (Oi)). Only at one site (Norwegian spruce and Thuidium tamariscinum moss) an Oa layer had built up. For all the sites the humus layer was removed prior to sampling.

In an ongoing study we analysed the isotopic composition of the FAs in the different humus horizons of the Lake Baldegg forest soil with the Oa horizon. The values of the Oa horizon FAs were slightly depleted in $\delta^{13}C$ compared to the Ah horizon, but also the depleted values lie within the area of the forest isoplot, and wouldn't be separable as a discrete source.

We added a section in the reworked results section on
P 7 L13-23 in the marked manuscript
The input of organics from humus material and mixing into the lake sediments might be discussed as a potential additional source. However, great care was paid to remove any macroscopic organic material from the sieved soil and lake sediment samples. Even if we missed some highly decomposed Oa material, a study about fractionation processes of FAs in the humus layer of forest soils at Baldegg Lake catchment recorded no or only slight changes in the isotopic signal from Oa to Ah horizon (unpublished data). For our site with the Oa horizon, C28:0 and C30:0 FA were only slightly depleted by 0.2 - 0.3‰ compared to the Ah horizon. C24:0 and C26:0 were depleted by 0.8 and 1‰ respectively. But these humus $\delta^{13}C$ values are -33.8‰ for C26:0 FA and -34.6‰ for C28:0 FA and can thus not explain shifts of C26:0/C28:0 to values more negative than -36‰ (compare Fig. 4). Further, these humus $\delta^{13}C$ values still lie in the isotopic range of the five analyzed forest locations (Fig. 4) and would not be separable as a discrete source. Also, as today's isotopic signals of lake sediment samples plot within the polygon of the source soil signals, we rather expect a source or process different from today's conditions being the cause for the deviation of isotopic signals.

Anonymous Referee #2
Received and published: 7 August 2018

Comments and over view: The manuscript is well written and describes a study of the sedimentation changes in a hypertrophic freshwater lake over a period of 130 y before

present. Most of the techniques used in this study were appropriate and it is good to see a study trying to use an alternative biomarker to the CSIA of fatty acids as a cross check to validate those results. However, there are some issues in this manuscript that I feel need addressing. My comments are therefore on the overall concept presented in the manuscript and are intended to be helpful. I focus on 1) the need to apply known corrections to data and 2) the three hypotheses raised by the authors to interpret their results.

1) It has been documented (Verburg 2007) that samples from lake sediment cores going back in time to when the isotopic value of _13C in the atmospheric CO2 was less depleted than at present, need to be corrected for this Suess effect. This is because plants assimilate atmospheric CO2 during photosynthesis to produce the fatty acids. Those isotopic values on that day are transferred to the fatty acids which bind to the soil and which are measured in the CSIA tracer study. Consequently, to use present day land use samples as the reference sources for the sediment in the core samples over time, the core data must be corrected for the Suess effect. The authors argue that, compared with isotopic depletion of the tracers in the deeper sections of the core, the Suess effect is "considered as negligible" and was not done. My understanding is that the main objective of science is find the truth from the limited resources and knowledge available. The Suess effect is a known truth and needs to be applied to the core data. It doesn't matter that effect is small relative to other unknowns, I believe that the authors should apply the correction to the data. This will save the authors a page of text arguing that it is not needed.
My contention is that, if everyone picks and chooses which corrections to apply to specific types of data, the supplementary data provided with each manuscript will be worthless.

We did a correction for the Suess Effect of lake sediments and catchment soils and calculated their corresponding values for 1840. With that method it was possible to compare all the sediments and soils at the same time. Assuming a very high incorporation rate of organic matter into the soil and the even more distinct depletion curve of straw by Zhao et al. (2001), the maximum depletion with time was 0.22‰ for the soils and 0.16‰ for the lake sediments. These values are smaller than the analytical uncertainty and since these values are based on the estimation of paramaters (e.g. soil incorporation rate), which in our case were actually chosen to rather overestimate the effect (high incorporation rate, depletion curve of straw) we choose only to show the corrected values and compare them with the original ones.

We added a new section "4.2.1 The Suess effect as a possible influence on CSSI of lake sediments" on **P6 L14 – P7 L 5** in the marked manuscript
And we added table **S4** in the supplementary material.

2) The most important finding in this study is that there is increasing isotopic depletion in the FAs with depth and the authors have correctly associated this effect with methanogenesis by bacteria in the anaerobic sediments. This isotopic depletion, however, causes a problem where the sediment sample isotopic values do not plot within the source polygons, as in this study. The authors raise three hypotheses suggesting that "either (1) that values have to be corrected for the atmospheric 13C-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."
Simply applying the Suess correction removes hypothesis 1.
Hypothesis 3) violates the primary assumption of the CSSI sediment tracing technique (Gibbs 2008) that the isotopic signatures of FAs bound to the soil particles do not

change over time. The discussion around this point is speculative and then assumed to be correct without supporting evidence. The authors need to provide irrefutable evidence for the alteration in the isotopic signature of a soil-bound FA after it has been deposited in the sediment or acknowledge the basis for using FAs as tracers as correct, which removes this hypothesis.

We removed this argumentation from the manuscript and only left one last speculation about a potential alteration, but were admitting, that there were so far no studies showing such a process.
P10 L36 in the marked manuscript
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 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. And so far, no cases of such a diagenetic transformation have been described.

This leaves hypothesis 2) "that the major contributors to most of the lake FA isotopic signal are not the main source soils of the catchment". This is a realistic hypothesis, which the authors need to investigate further. Internal cycling is common in most lakes. Expanding on this concept, the 'other' sources need to be able to consume a food that is isotopically depleted and the consumer must be able to produce long-chain, even-carbon number FAs that can bind to the sediment particles rendering them stable against decomposition and fractionation to short-chain molecules. Methanotrophic bacteria assimilate the methane and produce odd-carbon chain lengths mostly in the C15, C17 and C19 chain lengths. Consequently, the bacteria are not the source of the even-carbon FAs, but they are the food source for chironomid larvae living in the anoxic sediment. Work by Jones and Grey (2004: Boreal Environment Research 9: 17–23), Deines et al (2007: Aquatic Microbial Ecology 46: 273–282), and others, indicate that chironomid larvae can take up the depleted isotopic signature from the bacteria and acquire highly depleted isotopic signatures. They may leave their skins and head capsules in the sediment when they hatch or the unseived sediment samples may have contained whole organisms. In severely hypertrophic lakes, chironomid populations can reach very large numbers. And yes, chironomids produce FAs (e.g., Makhutova et al 2017: Contemporary Problems of Ecology, 10: 230–239).

My colleague, experienced with chironomid larvae was doing the sample preparation and is convinced that there were no complete organisms or residues of chironomid larvae present in the sediments in relevant amounts. But we took up this interesting point and added a section in the completely reworked results part.
P8 L5-9 in the marked manuscript
One potential missed source might be the influence of complete organisms or residues of e.g. chironomid larvae on the $\delta^{13}C$ signal of the lake sediment. Fatty acids produced by these larvae might be depleted in $\delta^{13}C$ (Makhutova et al., 2017) and could act as a potential depleted source. However, sample preparation was done in paying attention to the possible occurrence of chironomid larvae, and we can thus exclude the presence of these organisms in relevant amounts. Moreover, no literature was found stating the production of FAs longer than C22:0 by these larvae.

A further issue around the selection of the fatty acid tracers, the authors have chosen to use only C24:0, C26:0 and C28:0 and wonder why they cannot discriminate grasses. Grasses produce very low levels of these long-chain FAs but high levels of C18:0 and C18:1 fatty acids.

We added an explanation in the method section why we choose the above-mentioned FAs.

P4 L33 - P5 L2 in the marked manuscript
Only long-chain FAs ≥C24:0 were investigated. These are characteristic for the higher plant input into the soil (Eglinton and Eglinton, 2008). Short- or mid-chain FAs can also be produced by bacteria or aquatic plants and would bias our approach to trace back the terrestrial input into the lake.

There is also no bulk _13C data. Including these tracers may help sort out some of the source identification problems in this manuscript. If all the tracers are not included in the isotopic inputs to the mixing model, they cannot be seen in the model output.

In the same study also suspended sediments (Filter) were sampled and the sample amount was not enough to do additional analysis for bulk carbon. Due to the high temporal resolution, also all material of the lake sediments was used for lipid extraction.
Moreover, by comparing concentration of bulk C and FAs through the humus profile to the upper soil horizon, it was obvious that the FAs are the more recalcitrant/stable biomarker. Concentration per g TOC in the upper soil horizon is up to factor 10 enriched compared to the humus layer. This makes them a much more suitable tracer for terrestrial input than the more labile bulk C.

In the conclusions, the authors have reiterated a statement "strongly overprinted by carbon exchanges". As stated above, this is an unsupported hypothesis which cannot be correct. It is more likely that the FA signatures from the terrestrial sources have been overprinted by an in-lake source that has not been sampled and more work is required to identify that source.

As pointed out above, we removed the unsupported hypothesis.
Regarding the 2nd part of the comment and the new comment of the reviewer, which we received with the Editors decision letter (see below in green), we completely revised the "Results and discussion" part. We are providing two new hypotheses, in-situ production of FAs by algae, or lateral transport from wetlands/peat with depleted $\delta^{13}C$ signature. The possible production by methanotrophic bacteria is also part of the "Results and Discussion" section. We did not, as suggested by the reviewer, use the most negative sediment sample as source signal of bacterial contribution. If it is produced by methanotroph bacteria, then the FAs would probably be even more depleted. And since we assume, as stated in the new manuscript, that C28:0 FA is mainly produced by terrestrial higher plants, and the concentrations of the FAs C24:0 and C26:0 (2 new concentration graphs Fig S1 and S2 are added in the supplementary material) in the sediments do not differ much from concentration pattern in the soils, the missing source would have to be more depleted than the lake sediment from 1908-1910 to cause this negative isotopic shift.
We added the two new sections ***"4.2.2 The likelihood of missing an additional terrestrial source to the isotopical FA signal of lake sediments"*** on **P7 L6** and ***"4.2.3 The likelihood of missing an in-situ source to the isotopical FA signal of lake sediments"*** on **P8 L4**. And we revised the "Conclusions" and give an outlook how it would be possible to identify the missing source, as you can see in the marked manuscript. Mainly **P12 L21-36** and **P13 L13-L20**. And we added **Fig. S1** and **Fig. S2** in the supplementary material

2nd comment of Reviewer2 with the Editors decision letter

Their comment that the discussion will not change their conclusion is also rather dogmatic. The missing information such as bulk delta13C data could have helped their cause. The use of the polygon is to define the sources contributing to the sediment in the mixture. If the mixture values lie outside the polygon, there is a source missing. In this case rather than look for the missing source, the authors have put forward a hypothesis which has the potential to destroy the integrity of the compound specific stable isotope source tracing technique. The most obvious missing source not modelled in their paper is the methanogenic bacteria in the sediment. If the CSIA data from the 1908-1910 sediment depth is used as the bacteria signature, that closes the polygon and all the rest of the sediment samples fall within the new polygon. This is a realistic solution to the

author's problem. They are already postulating an effect caused by these bacteria and I agree that that is the most likely solution. I do not believe that any bacteria has sufficient energy to break the ionic bond between the terrigenous FA and the clay soil particle - in many other studies this bond has remained intact over thousands of years.
Conversely, for fatty acids to bind to the soil, they have to be produced insitu and apparently these methanogenic bacteria can do that. If they are producing the long chain FAs and the terrigenous signatures are not being replaced (as they won't be at that depth in the sediment), the new FA signatures will overwrite them and they will be below detection limit. This is not that "activity of bacteria would alter our isotope signals", which implies breaking the ionic bonds of the terrestrial FA, but simply overwhelming the terrestrial FA signatures with the new bacterial signatures. Expressed in this way, the research is providing new information about the effects of hypereutrophic lake sediments.

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 potential grasslands (permanent and temporary) and forest sources. Signatures of agricultural land and orchards fall in-between. The soil signal was compared to the isotopic signature of a lake sediment sequence covering ca. 130 years (before 1885 to 2009). The recent lake samples (1940 – 2009, with the exception of 1964-1972) fall into the soil isotopic signature polygon and indicate an important contribution of the forests, which might 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. However, the lake sediment samples older than 1940 lie outside the source soils polygon, most likely as a result of FA contribution from a not yet identified source, potentially produced by an in-situ aquatic source or by lateral transport from historical formerly drained wetlands. Despite the overprint of the yet unknown source on the isotopic signal of the lake sediments, land-use and catchment history are clearly reflected in the CSIA results, with isotopic shifts being consistent with catchment, land-use and eutrophication history. The investigated highly specific biomarkers were not detected in the lake sediment even though they were present in the soils. However, 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 active metabolism of bacteria might overprint the original terrestrial 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

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[2] nach oben verschoben: 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.
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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).

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; Alewell et al., 2016). 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 are not variable enough among plant species to discriminate them, their $\delta^{13}C$ signature differs among groups of plant species (Tolosa et al., 2013). The $\delta^{13}C$ signature of biomarkers is assumed to be more preserved than their 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).

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 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 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.

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

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

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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 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 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 $\mu g.l^{-1}$; 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 varves from 1995, and strong decrease of P concentrations in the lake to below 30 $\mu g.l^{-1}$ 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 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.

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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 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 all forest sites the humus layer was removed prior to sampling. At four of five investigated forest sites no Oa layer was present (only partly degraded material (Oe) and intact plant material (Oi)). Only at one site (Norwegian spruce and *Thuidium tamariscinum* moss) an Oa layer had built up. 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 centimeters of the soil were sampled with a 5-cm high cylindrical steel ring (98.2 cm^3) and stored in aluminum foil in the fridge until drying.

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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 in van Raden (2012) and Kind (2012). The upper 45 cm of the core, covering the last 130 years, were sampled in 3 years 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

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

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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 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 (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 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 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 ‰. Only long-chain FAs ≥ C24:0 were investigated. These are characteristic for the higher plant input into the soil (Eglinton and Eglinton,

2008). Short- or mid-chain FAs can also be produced by bacteria or aquatic plants and would bias our approach to trace back the terrestrial input into the lake.

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 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. 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.

4 Results and discussion

4.1 CSIA of potential source 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 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-use types.

All the samples align along a line, which ends are the isotopic signals of the grasslands and the forests soils. Halfway between them, orchard signature probably holds a mix between the inputs of the fruit trees, which signature might be supposed to be comparable to forest trees, and of the underlying grass. One orchard sample plots within the forest pool. Being covered of the same tree species as 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 greater surface 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. As we cannot exclude for temporary grasslands to be 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 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,

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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. Further inquiries with local farmers confirmed, that most temporary grasslands were just plowed and reseeded to control for homogenous and highly productive species distribution.

4.2 CSIA of lake sediments

Considering 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 biases due to concentration effect (Fig. 4). Data are provided in Table S2. The isotopic signature of the samples older than 1940 and from 1964 - 1972 fall out of the source soils mixing polygon, making the use of a mixing model to quantify the contribution of 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 we did not catch all contributors to the lake FA isotopic signal.

4.2.1 The Suess effect as a possible influence on CSSI of lake sediments

The $\delta^{13}C$ value of atmospheric CO_2 has decreased by approximately 1.5‰ since the beginning of the industrial era in response to fossil fuel combustion (atmospheric $\delta^{13}C$ = -6.5‰ in the preindustrial era vs. -8‰ today; Rubino et al., 2013; Keeling et al., 2005, respectively). Therefore, we would expect older lake sediment samples to be relatively enriched (less depleted) in $\delta^{13}C$ compared to our todays source soils or sediments. But actually, the lake sediments older than 1940 are depleted compared to the recent sediments and source soils. Therefore the Suess effect can be excluded as explanation for the negative $\delta^{13}C$ shift of C26:0 FA for the sediments older than 1940.

However, because long-term experiments have shown that a depletion due to the Suess effect with time is well recorded in plants (e.g. Zhao et al., 2001), 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 degradation and metabolism was identified as 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‰, like observed in the atmosphere, or 2.5‰, taking the dataset of Zhao et al. (2001) for straw from 1845 until 1997 into account. And it might only have an influence in the case of a soil having a very fast (and unrealistic) turnover time of the overall soil organic matter 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 in $\delta^{13}C$ of only 0.2-0.3‰ (i.e. in the range of the measurement precision) was calculated for an arable temperate soil between 1960s and 2000s, i.e. during the period when the Suess effect would be most relevant (Wiesenberg, 2004). These results are comparable to the 0.1-0.3‰ shift related to the Suess effect in a tropical soil with a <10 years turnover rate estimated by Bird et al. (2003). Furthermore, the ploughing of arable soils or non-permanent grasslands results in a mix of young and old organic matter, mitigating all the more the recording of the Suess effect in such soils. However, to avoid potential bias or errors we did a correction of the Suess effect for the soils and lake sediments (please see the corrected $\delta^{13}C$ values of the FAs for the Lake Baldegg catchment soils and lake sediments in Table S4). We assumed a rather unrealistic high incorporation rate of 3% of new organic material into the soil per year and as "Suess factor" the calculated $\delta^{13}C$ depletion curve of straw from Zhao et al. (2001), who recorded a shift of -2.5‰ in $\delta^{13}C$ of straw over the period between preindustrial era to 2000 and thus a stronger effect as in the atmospheric CO_2. For a better comparability, both, soils and sediments were Suess-effect corrected to "before industrialization" values (1840).

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Gelöscht: , or (3) that the signal, originating from catchment soils, was altered after its introduction into the lake. These three hypotheses are discussed below.

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Gelöscht: Thus, although the effect of atmospheric $\delta^{13}C$ depletion may play a role on the long-chain FAs $\delta^{13}C$ signal at the time scale considered in this study, this effect can here be considered as negligible. Moreover, most of the samples being shifted of more than 1.5‰ from the soils polygon, (an)other factor(s) must play a ... [10]

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The resulting maximum effect is a depletion of 0.22‰ from 1840 until 2016 for the soils. For the lake sediments the maximum depletion is 0.16‰ between 1840 to 2010. The older the sediments the smaller is the Suess effect on them. In 1965 the calculated Suess effect on the lake sediments is only 0.01‰. If we assume the calculated effect on the soils to be uniform and take into account that it is smaller than the analytical uncertainty, and further is based on the estimation of parameters like soil incorporation rate and actual effect of the Suess effect on the plants, we think that in our case it can be neglected.

4.2.2 The likelihood of missing an additional terrestrial source to the isotopical FA signal of lake sediments

Land use and land use change is exceptionally well documented in this Swiss catchment. Vegetation composition did not dramatically change during the last century and to our knowledge there are no plausible additional land use types as soil sources to the lake sediments 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 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).

The input of organics from humus material and mixing into the lake sediments might be discussed as a potential additional source. However, great care was paid to remove any macroscopic organic material from the sieved soil and lake sediment samples. Even if we missed some highly decomposed Oa material, a study about fractionation processes of FAs in the humus layer of forest soils at Baldegg Lake catchment recorded no or only slight changes in the isotopic signal from Oa to Ah horizon (unpublished data). For our site with the Oa horizon, C28:0 and C30:0 FA were only slightly depleted by 0.2 - 0.3‰ compared to the Ah horizon. C24:0 and C26:0 were depleted by 0.8 and 1‰ respectively. But these humus $\delta^{13}C$ values are -33.8‰ for C26:0 FA and -34.6‰ for C28:0 FA and can thus not explain shifts of C26:0/C28:0 to values more negative than -36‰ (compare Fig. 4). Further, these humus $\delta^{13}C$ values still lie in the isotopic range of the five analyzed forest locations (Fig. 4) and would not be separable as a discrete source. Also, as today's isotopic signals of lake sediment samples plot within the polygon of the source soil signals, we rather expect a source or process different from today's conditions being the cause for the deviation of isotopic signals.

Historical research (Kopp, 1962) has revealed that the lake level was lowered by 30-40 cm at the beginning of the 19th century. This lake level change has changed the hydrology of riparian zones and wetlands, which have drained into the lake and were drained by the farmers to use the fertile riparian area. As such, organic material might have been leached and eroded due to the change in hydrological regime and/or drainage of sites due to adapted land use. Furthermore, established reedlands, with *phragmites australis*, next to the main inflow at the southern end of the catchment have been cut starting in 1944 and in 1955 they completely drained this reedland. Today this area is a small lake with small surrounding wetlands, still containing *phragmites australis* (Rezbanyai, 1981). As such, another possible explanation for the negative values of the FAs C24:0 and C26:0 could be a larger contribution of wetland organic matter derived from e.g. *phragmites australis* or *sphagnum* species, to the eroded sediments. Especially *sphagnum* species comprise high concentrations of C24:0 and C26:0 FAs (Baas et al., 2000, Pancost et al., 2002). Photosynthesis of *Phragmites* or mosses like *sphagnum* in the riparian zone or in peats respectively with CO_2 derived from oxidized methane could be an optional source for depleted long-chain fatty acids (cf. Alewell et al. 2011, $d^{13}C$ depletion of mosses, induced by photosynthesis with methane derived CO_2, effected the bulk carbon $d^{13}C$ in Scottish bog). However, $\delta^{13}C$ values of long-chain FAs from a Scottish peat core are not depleted and range between -29.5‰ and -32.8‰ (Ficken et al., 1998) and would not be an adequate explanation for our missing source. Nevertheless, a depleted $\delta^{13}C$ of C24:0 and C26:0 FAs from wetlands or peat could explain the deviation for most of our lake sediment samples. Even more so, if we consider the relatively low C28:0 FA concentration in Sphagnum (Baas et al., 2000, Pancost et al., 2002) compared to C24:0 and C26:0 FAs. The larger proportions of C24:0 and C26:0 FA would clearly dominate over the C28:0 FA signal and

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could explain the stronger shift of the lake sediments to more depleted C24:0 and C26:0 FA $\delta^{13}C$ values compared to a C28:0 FA $\delta^{13}C$ signal, dominated by the other land-use types.

4.2.3 The likelihood of missing an in-situ source to the isotopical FA signal of lake sediments

One potential missed source might be the influence of complete organisms or residues of e.g. chironomid larvae on the $\delta^{13}C$ signal of the lake sediment. Fatty acids produced by these larvae might be depleted in $\delta^{13}C$ (Makhutova et al., 2017) and could act as a potential depleted source. However, sample preparation was done in paying attention to the possible occurrence of chironomid larvae, and we can thus exclude the presence of these organisms in relevant amounts. Moreover, no literature was found stating the production of FAs longer than C22:0 by these larvae.

Other sources for long-chain FAs might be lacustrine macrophytes and microbial organisms (e.g. Volkmann et al., 1988; Volkmann et al., 1998; Bovee and Pearson, 2014; Schouten et al., 1998; van Bree et al., 2018), but no reference to the production of long-chain FAs by organisms known to live in the Lake Baldegg could be found: 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). Very recently van Bree et al. (2018) were suggesting production of long-chain FAs, mainly C28:0, in the water column, while studying suspended particulate matter (SPM) from Lake Chala (Kenya/Tanzania). They draw their conclusions from a very strong seasonal variability in the SPM, different timing of the maximum concentrations of long-chain *n*-alkanes and long-chain fatty acids, and very negative $\delta^{13}C$ values down to -46.3‰ for C28:0 FA and -41.9‰ for C26:0 FA. One possible explanation for the very depleted $\delta^{13}C$ values of the FAs might be the CO_2 uptake of the lake surface water. During times of under saturation with CO_2 and high pH values (8.3-9) atmospheric CO_2 is reacting with OH^- to HCO_3^- (Hydroxilation of CO_2). This reaction results in a strong carbon isotopic fractionation of -12‰. This highly depleted HCO_3^- can heavily influence the isotopic signal of FAs produced by aquatic organisms (van Bree et al., 2018 and references therein; Terranes et al., 1999 and reference therein, describing the same process for depleted $\delta^{18}O$ in Lake Baldegg).

As we have conditions of CO_2 undersaturation beginning at the end of April when stratification is starting and epilimnic primary production is increasing (Müller et al., 2016) in Lake Baldegg, this might be a possible explanation. Also pH values during that time of the year are above 8.3 and reach 8.6 during June (Terranes et al., 1999) and hydroxilation of CO_2 will be the dominant process.

Interestingly in our study, the shorter the homologue is, the more deviated from the soils polygon its isotopic values are: while the soil 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 $\delta^{13}C$ 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 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 an aquatic process might have affected the terrestrial isotopic signatures. Maybe similar to Lake Chala (van Bree et al., 2018), in Lake Baldegg the FAs C24:0 and C26:0 are primarily produced by an aquatic source whereas C28:0 reflects still the signal of the terrestrial vegetation. However, we do not see any increase in concentration of C24:0 or C26:0 FA in the lake sediments until 1940 compared to today's soils (compare Fig. S1 and S2 in the supplementary material).

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Some of the depleted $\delta^{13}C$ values might also be 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 $\delta^{13}C$ values of -50 to -70‰ (Whiticar, 1999), leading to a very 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). A $\delta^{13}C$ value of -70+- 15‰ for methanotrophic bacteria using biogenic methane can be assumed (Lehmann et al., 2004 and references therein). In this case only little bacterial biomass would be needed to cause depletion effects like we observe in the Lake Baldegg sediments. But the presence of these long-chain *n*-fatty acids produced by lake bacteria seems to be 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). Gong and Hollander (1997) were suspecting marine bacteria contributing depleted long-chain FAs to the formerly assumed terrestrial long-chain FA pool in marine sediments. Also Feakins et al. (2007) described the in-situ production of long-chain FAs in a lacustrine environment by algae or bacteria as very likely. In their study not the depletion of the FAs was leading to this conclusion but the ratios between *n*-alkanes and FAs. Taking all this into account the production of long chain FAs by methanotroph bacteria seems, also if unlikely, to be given.

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

As the data indicate 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.).

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 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) 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.

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 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,

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Gelöscht: Historical research (Kopp, 1961) has revealed that at the lake level was lowered by 30-40 cm at the beginning of the 19th century. This lake level change could have lead to a broader riparian area with wetlands, which have drained themselves into the lake over time or where drained by the farmers to use the fertile riparian area. A lot of organic material would have been transported during such a process. Furthermore, there were reedlands, with *phragmites australis*, until 1944 next to the main inflow at the southern end of the catchment. From 1944 they started cutting of peat and in 1955 they completely drained this reedland. Today it is a small lake, Siedeweiher, with wetlands, still containing *phragmites australis*, surrounding it. Taking only these two informationthese two information into account, another possible explanation for the negative values of the FAs C24:0 and C26:0 could be a larger contribution of wetlands organic matter derived from e.g. *phragmites australis* or sphagnum species, to the eroded sediments. Especially sphagnum species comprise C24:0 and C26:0 FAs as most concentrated fatty acids (Baas et al., 2000, Pancost et al., 2002). Photosynthesis of Phragmites or mosses in the riparian zone or in peats respectively with CO_2 derived from oxidized methane could be an optional source for depleted long-chain fatty acids (cf. Alewell et al. 2011, $d^{13}C$ depletion of mosses, induced by photosynthesis with methane derived CO_2, effected the bulk carbon $d^{13}C$ in Scottish bog). In the plant-humus study mentioned above (Hirave et al., 2018), we found $\delta^{13}C$ values for *Thuidium tamariscinum*sphagnum moss FAs, -38‰ - -39.4‰, which were depleted up to 6 ‰ permil compared to Norwegian spruce organic material. However, $\delta^{13}C$ values of long-chain FAs from a Scottish peat core show are not depleted and range between -29.5‰ and -32.8‰ (Ficken et al., 1998) and would not be an adequate solution for our missing source. However to proveFor visualizing a possible wetland signalcontribution we choose to use the *Thuidium tamariscinum* mosssphagnum $\delta^{13}C$ values from the Baldegger lakeLake Baldegg catchment to simulate the missing source (see Figure 4neu5). Apparently this signal could explain our most of our lake sediment samples. Even more if we take into account the relative low C28:0 FA concentration in Sphagnum (Baas et al., 2000, Pancost et al., 2002) compared to C24:0 and C26:0 FAs. Also for *Thuidium tamariscinum* moss we observed C24:0 dominating over C26:0 and C28:0 having the least concentration of the three (Hirave et al., 2018 in prep). The larger proportions of C24:0 and Sphagnum C26:0 FA would clearly dominate over the the Sphagnum C28:0 FA signal and could explain the stronger shift of the lake sediments to more depleted C24:0 and C26:0 FA $\delta^{13}C$ values withcompared to a rather grassland dominated C28:0 FA $\delta^{13}C$ valuessignal.¶
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Gelöscht: 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 carbon exchanges took place between the long-chain *n*-FAs and a much depleted, methanotrophic bacteria-related material. [27]
Gelöscht: Although thee influence of other not yet identified sources to our lake sediments, as expanded above, cannot be fully excludedmight be, 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 [28]
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[3] nach unten verschoben: As the data indicate 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.
[3] verschoben (Einfügung)

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 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.

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.

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) fall into the source soil polygon (Fig. 4a), suggesting that these samples are not, or very little affected by depleted organic material from the unknown source. 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 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.

Gelöscht: carbon exchanges with highly depleted material

Gelöscht: additional

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 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 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. Here the example of van Bree et al. (2018) can be consulted, as they found a compound-specific enrichment of mostly C28:0 FA in the water column. Also the accompanying depletion of, in their case, C28:0 FA compared to the terrestrial C28:0 FA signal is hinting into the direction of an aquatic source. 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 sediments would have been affected by carbon exchanges years to decades after their deposition, during the most severe eutrophic phases of the lake

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history. Why these exchanges would not have affected the younger sediments remains unexplained. And so far, no cases of such a diagenetic transformation have been described.

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4.3 Triterpenoid biomarkers

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

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 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. 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 δ^{13}C FAs (δ^{13}C C24:0/δ^{13}C C26:0; δ^{13}C C26:0/δ^{13}C C28:0; δ^{13}C C24:0/δ^{13}C C28:0). 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.), δ^{13}C C26:0/δ^{13}C C28:0 and δ^{13}C C24:0/δ^{13}C C28:0 ratios are taken as more reliable than the δ^{13}C C24:0/δ^{13}C C26:0 ratio.

Interestingly, the TTHCs concentration evolution is highly similar to the δ^{13}FAs ratios trend, even more for the δ^{13}C C24:0/δ^{13}C C28:0 than for the δ^{13}C C26:0/δ^{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 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 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 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 from mid-1960's to mid-1970's actually fall out of the polygon of the source soils signatures.

Although the influence of not yet identified sources to our lake sediments, as expanded above, might be likely, 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 of C28:0 FA and (2) would hint into the direction of an additional source with low C28:0 FA concentrations compared to C24:0 and C26:0 FAs. This could be true for example for a larger contribution of Sphagnum/moss derived organic matter released from historical peat bogs or the riparian zone as described above or (3) due to in-situ FA production of C24/26:0 FA by either algae or other microorganisms with depleted δ^{13}C values due to described effects of hydoxilation reaction of CO_2 combined with high pH values in the epilimnion and CO_2 undersaturation, or by methanotroph bacteria.

The reason for the occurrence of the depletion effects only before 1940, and during the invervall in the 1960s and 1970s is so far unclear. Potentially the algae or other microorganism responsible for the production of the long-chain FAs was not present anymore after 1940. Following the hypothesis with organic material originated from the riparian zone and/or wetlands, the explanation could be that with time, wetlands, evolved after the lake level changes drained themselves or were drained by the farmers until 1940 for the intensification of agricultural practices. The 1960s and 70s excursion could be explained similarly as for the pre 1940 time interval. The temporary occurrence of an algae or microorganism, mainly producing C28:0 FA could be the explanation for this time interval. Alternatively, the reedland close to the southern inlet of the lake could have transported a lot of depleted, peat derived organic material into the lake, when it was drained after 1955 and being responsible for the isotopic excursion during the 1960s and 70s.

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, bacteria and microbial organisms were previously

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shown to produce also long-chain FAs, and our study highlights that an interference of the terrestrial isotopic signal linked to such an activity should not be underestimated. CSIA was proven to be unusable quantitatively unmix terrestrial sources from the Lake Baldegg sediments, and thus to apportion the relative contribution of different land-uses to the sedimentary archive as long as the missing source is not known.

While the isotopic signal, especially C24:0 and C26:0 FAs until 1940 and C28:0 FA during the 1960s and 1970s, is clearly influenced by unknown sources, land-use and catchment history are still surprisingly accurate reflected in the background patterns: 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 molecule 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 activity is known or suspected.

While our study revealed missing sources of FAs to our isotopic signal, this should be investigated for other families otherwise used in CSIA, such as *n*-alkanes. To find the responsible sources of the bias in our isotopic data and thus allow source apportionment, soil, plant and sediment samples from the riparian zone, reedlands and peat bogs (e.g. *Phragmites australis*, *Sphagnum species*) around Baldegger Lake should be studied to verify their potential contribution to the depleted $\delta^{13}C$ values of the FAs in the lake sediments. Another approach could be to analyze DOC from the contributing rivers and from different depth intervals of the Baldegger Lake water column, to compare changes in the FA abundance and prove the presence or absence of in-situ producers in the water column. Further it would be interesting to analyze the FAs from the suspended organic matter in the water column to see whether FAs produced by methanotrophs are present. Furthermore, 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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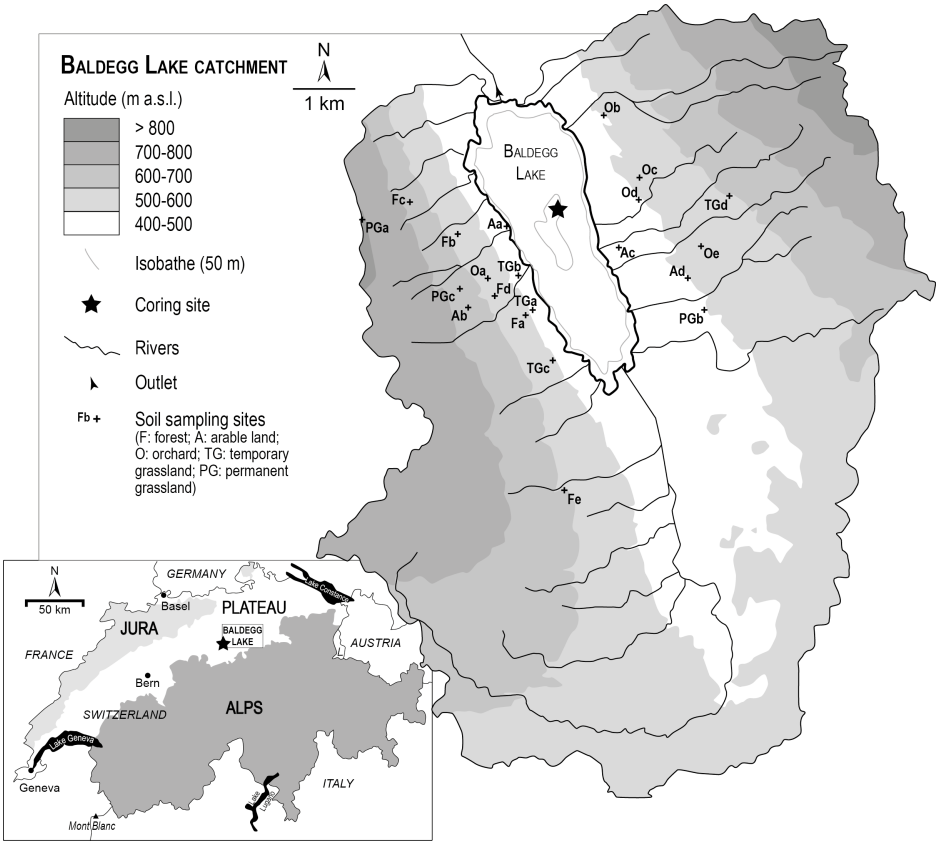

Figure 1: Catchment of Lake Baldegg with sampling sites.

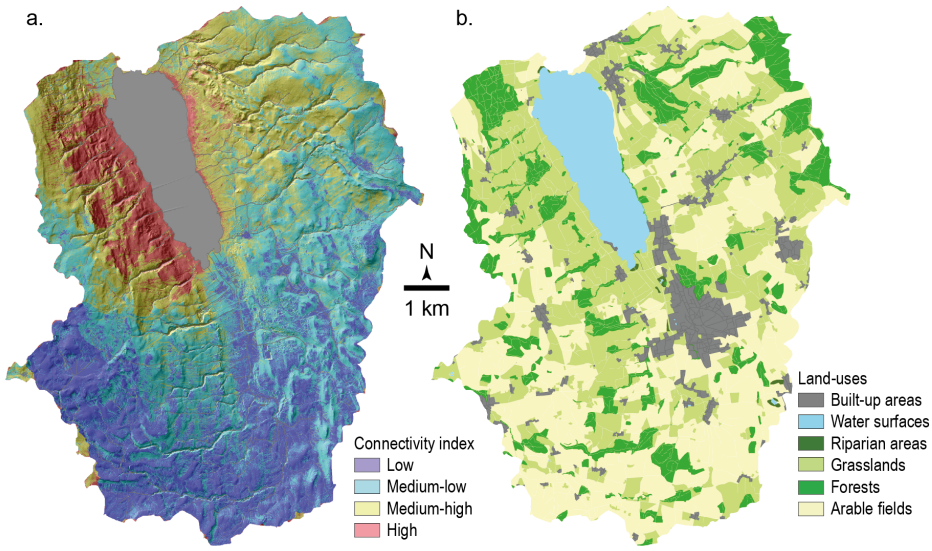

Figure 2: a. Connectivity index for the Lake Baldegg catchment, with a topographic map underlying. The lake is indicated in grey. b. Land-use map.

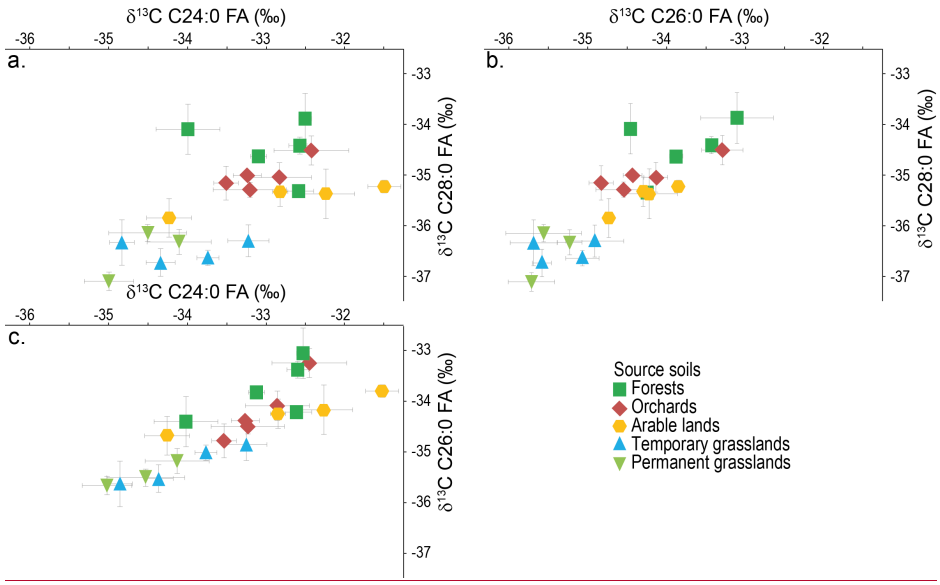

Figure 3: $\delta^{13}C$ of the FAs (a.) C24:0 vs. C28:0, (b.) C26:0 vs. C28:0, (c.) C24:0 vs. C26:0 in soils. Error bars: standard deviation of the triplicate measurements.

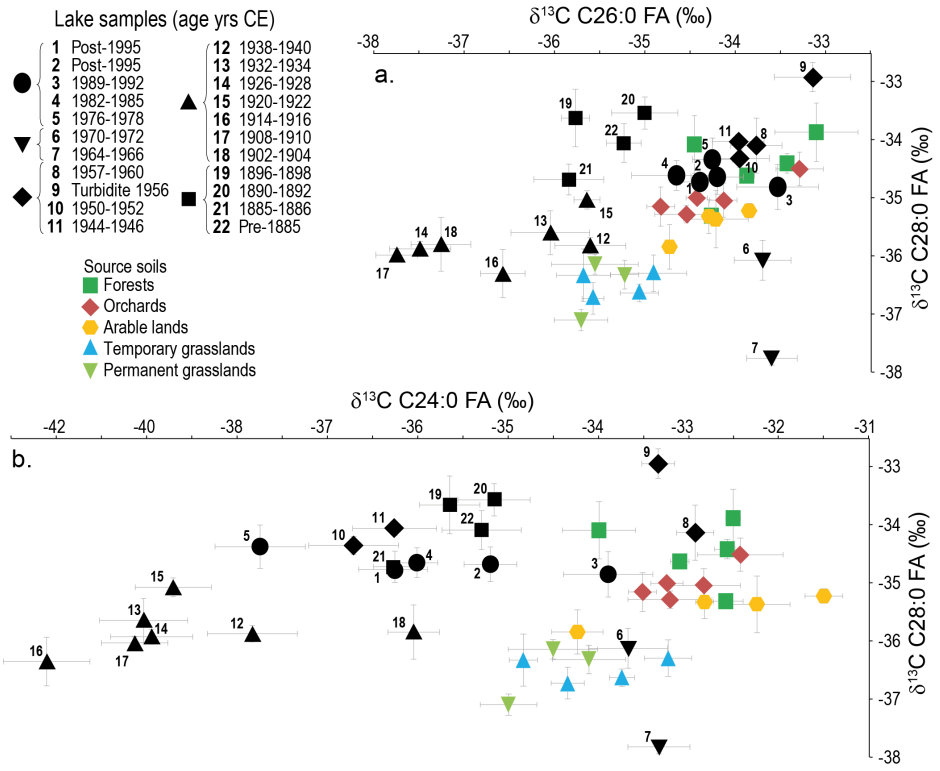

Figure 4: $\delta^{13}C$ of the FAs (a.) C26:0 vs. C28:0, (b.) C24:0 vs. C28:0, in lake sediments, compared to soils. Note the different scale for the x axis between (a.) and (b.). Error bars: standard deviation of the triplicate measurements.

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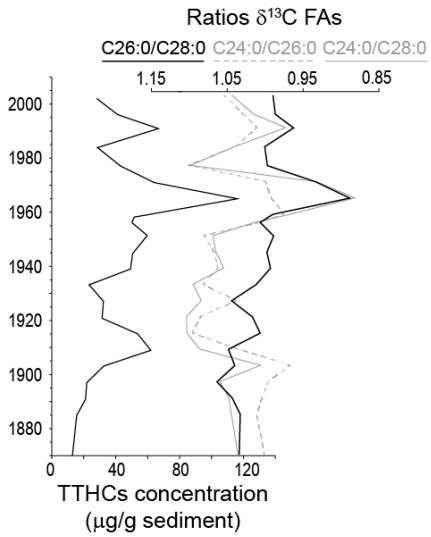

Figure 8: Evolution of the TTHCs concentration (sum of TTHC2 and TTHC3) along the sediment core, compared to evolution of the ratios of $\delta^{13}C$ of FAs.

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