Associate Editor Decision: Publish subject to minor revisions (review by editor) (25 Mar 2019) by Koji Suzuki

Comments to the Author:

Dear Dr. Birkholz,

The Referee #2 was very pleased to see your modifications, but this expert has still some concerns on your manuscript. So we would appreciate it very much if you could revise your manuscript following the suggestions from Referee #2 (see below), and send us the revised paper with your point-by-point responses.

Thank you again for your patience and nice efforts to improve the manuscript.

Kind regards,

Koji Suzuki
Associate Editor

Dear Prof Suzuki, dear reviewer,

Thanks a lot for this very positive response and for your further efforts to improve the present manuscript. We did our best to meet the reviewers concerns and hope and think we were successful with it. Please find below our point by point reply. But we wanted to emphasize here that we are glad, that the reviewer and us are now in complete agreement in the most important questions about the manuscript, namely that the Suess effect is not the cause for the isotopic deviation of the older sediments, and that there is an autochthonous source producing long chain FAs. Further we would like to point out that the whole section in the manuscript, discussing the Suess effect, arose from the reviewers request to correct the data for this effect, which is not a trivial task as we were trying to explain to the reviewer and to the public with the last revised manuscript. Thus, and because we believe that a lot of readers will wonder about the influence of the Suess effect on our data, we would like to leave this section in the new revised version of the manuscript. Lastly we wanted to emphasize, that we didn’t do the modelling of the recent sediments due to the inability to use a model like MixSIAR, but we didn’t want to overload the already very complex manuscript. In a next step we want to model the different contributions to the recent lake sediment but also for the contributing streams, for which we have a complete set of suspended sediments, sampled during every high flow event over the course of two years.

We hope, that we were able with this revision to bring the manuscript to a level where it can be published in Biogeosciences.

Kind regards,

Axel Birkholz

in the name of all Co-authors.

Referee 2, revised manuscript 2018_288-version 3

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

Authors: Marlène Lavrieux, Axel Birkholz, Katrin Meusburger, Guido L.B. Wiesenberg, Adrian Gilli, Christian Stamm, Christine Alewell

Comments and over view:

The authors have largely answered the referee's comments. There is obviously a missing source in the polygons and this has been discussed with suggested sources, both allochthonous and autochthonous being raised as possibilities. It is Okay to state that there is an unknown source.

Thanks for these overall positive comments.

The only remaining contentious issue is the question of the Suess effect, what it means to this study and how it should be calculated.

Please see below for our detailed answers.

There is also some confusion in the authors understanding of how the CSIA data is incorporated into the soil and thus how it is corrected.

It seems we have differing understanding of how organic matter is incorporated into the soil and then bound to soil particles. Thanks for the interesting discussion and please see below for more detailed answers.

Referring to section 4.2.3 The necessity of "Suess effect" correction for terrestrial lipids in lake sediments"

Definitions: Terrestrial lipids are allochthonous, i.e., produced outside the lake. Autochthonous lipids are those produced, by whatever mechanism, in the lake water column or lake sediment.

The lipids of concern are the polar fatty acids, which exude from plant roots and bind ionically to the soil particles. They are sufficiently soluble that they can be moved by infiltration rainwater though the surface soils until they bind to the soil particles. Once they attach to the soil particle, they cannot be removed by natural processes, with the exception of bacterial consumption.

We totally agree up to this point, may be with the slight exception that we would not exclude that organic matter bound to soil particles might be desorbed again, even from the relatively stable mineral clay-humus-complexes (please see works by Kalbitz et al, Kögel-Knaber et al., Guggenberger et al., Kaiser et al. etc.).

Under those conditions the concentration of the FA will decrease BUT the isotopic signature of that FA pool remains unchained.

Yes, sure, we agree that concentrations of dissolved organic carbon (DOC) and thus also dissolved fatty acids decrease if organic matter is bound to soil particles and clay minerals and that at least according to today's knowledge no isotope fractionation is accompanied by this process.

As a consequence of this binding, the FAs attached to the soil particles do not have a turnover time, which would imply that they can be exchanged from the soil particles.

Well, here we clearly have to disagree. Soil organic matter can sorb and desorb to soil particles, they might even desorb from clay minerals, even though, of course the latter binding might be considered pretty stable. Please see publication by Wiesenberg et al. (2004), where they determine turnover times in soils by using d13C of the FAs. We were wondering if the term "turnover time" led to misunderstandings, and we thus replaced it with "mean residence time" in the new revised manuscript.

The FAs are not waxes. Waxes, including n-alkanes, are non-polar and do not bind to the soil particles. They are generally not soluble in water but form part of the soil humus.

Well, macromolecular non-polar substances will be part of the colloids in soils and will thus be part of the complex colloid dynamic in soils, soil solutions and waters. They might be hold back in soils, if we have elluvial and illuvial processes, like e.g., podsolization or clay migration.

When the soil is washed off the land, the soil particles labelled with the FAs are carried to the downstream deposition zone, in this case, Lake Baldegg. During that transport mode, the light humic/organic component is separated from the original bulk soil and will eventually settle on top of the heavier soil particles in the lake.

Well, we think that most of the time the binding between soil particles and FAs are pretty stable, especially as fines are washed of preferentially. If generally or dominantly the FAs, would be separated from the soil particles during detachment and transport, the whole concept of using them as tracer would not work. And we do not think that there is any scientific evidence for this theory.

Because that material is organic it will be decomposed rapidly by allochthonous bacteria. In contrast, the FA labelled soil particles will remain isotopically unchanged although the concentration may reduce over time as they are consumed by bacteria.

Again, sorry, to disagree. As long as the FAs are bound to soil/ mineral particles, they will not be degraded. However, IF they are desorbed and degraded, we have to assume that we will have at least some slight isotopic fractionation (unpublished data from our group, will be submitted this month, we are willing to share the data with the reviewer, if he/she is interested).

The application of the Suess correction can only be applied to the allochthonous FAs, because they are in contact with the atmosphere, which is experiencing the Suess effect. The autochthonous FAs may experience some of the atmospheric Suess effects, but they will also experience the biogenically altered CO2 from sediment decomposition processes and plant respiration.

Well, as plants as well as algae respire the CO2 from the atmosphere, and most organic material in the lake or in the soil has its origin from plant material, all organic molecules younger than 1840 will be affected by the Suess effect. But we agree, that this potential Suess effect will then be overprinted by the described possible effects in our lake system (P14L12-15).

This effect has been correctly discussed by the authors. Since these latter processes have not been assessed or documented, the authors have correctly not attempted to model the allochthonous sources in the historical sediments.

Thanks, we are glad you agree.

(There is no reason why they couldn't model the contemporary sediment in the lake surficial sediments, but they haven't.)

Please see our detailed comments below, why a modelling of the recent sediments was not done within this publication.

With these basic facts as a starting point, the description of how the Suess effect affects the CSIA values and how the correction for this effect should be calculated is misleading at best and is misinformation, which should not be in this manuscript or any other.

Of particular concern is the lumping of the FA component bound to the soil particles with the organic carbon from leaf litter and crop debris. When these are mixed in the soil they will have a turnover time associated with the natural carbon cycle, as described by the authors. However, the authors have combined the two distinctly different forms of soil carbon into a supposed soil label, and that is wrong. Only the FAs bound to the soil particles act as labels. The leaf litter could have been blown into the landscape from anywhere, thus contaminating the isotopic signature of the defined land use. Most importantly, because this organic debris is non-polar, it cannot bind to the soil as a label, as explained above.

Sorry, but here we disagree. FA components bound to the soil particles originate from plants the same way leaf litter or crop debris does. So all these substances will be prone to the Suess effect.

Yes, the organic debris will breakdown and yes, there are FAs in the organic debris. The difference is that those FAs are already ionically bound to other organic debris and are not able to bind to the soil particles. If bacterial decomposition does release a free FA, it will be a shorter chain length than the FA labels being measured and will not affect the CSIA values of the long chain length FAs being used as labels.

Yes, sure, we agree. This is why we only consider LCFA. Furthermore, from another study we were conducting on intact leaves/needles, debris, humus and organic soil horizons we know that there are plenty of free long chain fatty acids available in all fractions. This study will be submitted this April.

The use of the Feng 1998 equation is not appropriate for the Suess correction. The equation published by Verburg (2007) should be used. The use of the Verburg equation needs to be promoted as the standard method for Suess correction rather than using older equations that do not have the level of sophistication of the Verburg equation. The Verburg equation shows a present day isotopic depletion of the CO2 in the atmosphere of just over 2.5‰ since the beginning of the industrial revolution, which is generally accepted as 1700AD.

It does not make a big difference, but we changed in the text accordingly and used Verburg (2007) for correcting the data.

The authors are correctly trying to eliminate the Suess effect as the cause of the much larger isotopic depletion of some of the sediment FA tracers in the lake.

We are glad that we agree with the reviewer in this really important point. And we think this is the most important point within the whole discussion: that the Suess effect is not the cause of the deviation in isotopic signatures of sources and sediments.

This can be done with a simple statement just like that: e.g., "The isotopic depletion due to the Suess effect is estimated to be about -2.5‰ since 1700AD (Verburg 2007) and is, therefore, unlikely to have a substantial effect on the autochthonous production of FAs by lacustrine processes. Consequently, the large isotopic depletion observed is most likely from an unknown autochthonous source or associated with draining wetlands etc, etc . . ." Write it how you want. This is all that is needed in this manuscript.
I strongly recommend that the misinformation in section 4.2.3 is removed by deleting everything from page 9, line 23 starting "We thus want to discuss ".to." speculative" on page 10, line 28, and rewriting the text in a form similar to that suggested above. Figure S4-7 and Table S4-5 may need to be revised to match this textual change, if they are still needed.
The reason for the deletion is that the Suess effect can quickly be eliminated as a causal influence, as suggested above, and is, therefore, not a significant component of the manuscript. As it is written, it is a distraction and the reader would be justified in asking "Why did the authors put this in, it adds nothing to the manuscript and is very confusing."

Well, sorry, we feel that in combination with a correction for this effect, it is important to include the discussion on the Suess effect, because even though the deviation we are observing is in the opposite direction of the Suess effect and the Suess effect can thus not be an explanation at all, we show in the graphs describing the Suess effect as a function of component mean residence time, that the effect can have significant consequences and a correction for it should be discussed. Especially if we have an aquatic source, which would make a valid correction almost impossible. And as far as we know the Suess effect was never discussed for terrestrial biomarkers in lake sediments.

The whole section in the manuscript, discussing the Suess effect, arose from the Reviewers request to correct the data for this effect, which is not a trivial task as we were trying to explain to the reviewer and to the public with the last revised manuscript.

Already in the last revised manuscript we excluded the Suess effect as explanation for our negative deviation with a simple statement. Please see P9L23-25 "Therefore, we would expect older lake sediment samples to be relatively enriched (less depleted) in δ^{13}C compared to our todays source soils or sediments. As such, the Suess effect cannot explain our deviation of the isotopic signals between source soils polygon and lake sediments."

General comments:
Throughout the manuscript, the range between two values has been either a dash "-" or the word "to". Because some of the numbers have negative values (e.g., -40.0 - -43.3‰), the word "to" should be used consistently throughout the manuscript.

we changed it accordingly.

The abbreviation "FA" has been defined as "fatty acid" in the abstract only. This definition must be repeated in the manuscript text at the first occurrence of FA. The abbreviation should then be used *consistently throughout the manuscript.*

We changed it accordingly.

The author's proof reading of their manuscript is not good. There are nine references which are not cited in the text and two references that have no year. See "references section below".
Extremely sorry for this. It happened due to the deletion of whole sections in this paragraph during the revisions. We corrected for that in the revised manuscript.

Specific points:
Page 6, Line 12: I disagree with the general statement that "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. Certainly, before 1972, source proportion modelling would be inappropriate until the missing source has been found. However, where the more recent sediment CSIA data falls within the mixing polygon, those data can be modelled, and should be for the completeness of this manuscript. I can recommend the use of MixSIAR, without including concentration or any other "priors".

You are totally right and we have to admit, that this might be one weak point of our manuscript. However, we have a whole data set of river sediments from 5 rivers of the Baldegg Lake including storm events and we would like to do the sediment source attribution with MixSIAR for the recent lake sediments together with the river sediment data. To include all of this in the current manuscript would certainly overload this current study and would make the manuscript much too long and confusing. Even more so, as the uncertainty connected to the distribution of the source soil isotopic signatures (e.g. not a clear spread polygon, but all signals on a more or less straight line), will need a complex and in depth evaluation, interpretation and discussion.

Page 8, Line 19: Why would you expect higher fatty acid concentrations in lake sediments compared to source soils? Unless the autochthonous fatty acids are produced in the sediment, where they can bind to the sediment particles, they will deposit on the sediment surface where they can be rapidly destroyed by bacterial decomposition processes. This means that the concentrations in the lake will decrease. Recommend that this sentence and the next are deleted as unnecessary and speculative.

If there would be an aquatic source producing FAs, preferentially C26:0 and C24:0FA, and masking the corresponding terrestrial FA signal in the lake sediment, we would expect higher concentrations of these 2 FAs compared to C28:0FA (not absolute concentrations but relations between the concentrations) which is obviously not as much affected as the two shorter ones. We will change the wording in the manuscript for a better understanding (please see P8L18-21).

Page 8, line 24: Change "-70+-15‰" to "-70 ±15‰"
Changed accordingly.

Page 8, lines 29 and 30 (and elsewhere): Where did the "n-fatty acids" expression come from. Please remove the "n-" and just use "FAs" consistently throughout the manuscript.

Changed accordingly.

Page 13, Line 11: The sentence "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." No it doesn't point to degradation. It probably points to a variable amount of the unknown source or other sources in the FA mixture in the sediment. The isotopic signal will only change through fractionation, and fractionation will destroy the original long chain FAs producing shorter chain FAs, which are not measured or included in the data.

Yes, you are right, this was a relict of the original manuscript. Thanks a lot for pointing that out.

We changed accordingly P13L11-14

But there seems to be a major misunderstanding how isotope fractionation works. If bacteria/enzymes preferentially use the lighter isotope, the remaining fraction of intact FAs will increase in its stable isotope signal.

Since part of section 4.2. should have been deleted, this sentence and the following sentences need to be checked against the rewrite of section 4.2.3 for consistency. As written, this appears to be an example of where earlier speculation and misinformation has been treated as fact, thereby perpetuating misinterpretation of the otherwise good data.

Please see above comment and changes.

Page 9, Line 23: (Verburgh 2007) incorrect spelling of 'Verburg'

We corrected accordingly.

Page 13, line 29: The sentence "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 samples lying between grasslands and forests end-members." They don't always plot in the same positions with the different isotopic tracers, therefore discrimination should be possible. Have you tried to model the data using a stable isotopic mixing model, such as "MixSIAR", just using the contemporary surface lake sediment as the lake endmember? The surficial sediment will have received negligible effect from any possible autochthonous source. Just looking at the isotopic signatures gives an indication of which sources are present. Modelling the isotopic signatures gives a robust assessment of the isotopic proportions. Using an isotope-to-soil proportion converter, as presented in Gibbs 2008, gives the proportional contribution of each source soil to the sediment mixture. These calculations will be valid to a date/depth of about 1970 and would add greatly to the usefulness of this manuscript.

Please see line 211-220 why we would prefer not to do the sediment source attribution in this manuscript. Of course, using a model like MixSIAR might provide you with results and probabilities, but if the underlying data is not rigorously discriminating between the sources, the results of this modelling exercise might be rather questionable. As such, this will for sure be a complex discussion and needs careful and in-depth evaluations and interpretation and is thus, in our opinion, beyond the possibilities of this current manuscript. We think that a combination of the lake sediment data with the river suspended sediments will yield better and more justified results.

Page 14, line 3: The text "(2) would hint into the direction of an additional source with low C28:0 FA concentrations . . .". The interpretation of the data doesn't "hint in the direction of" it 'indicates an additional source'. That source doesn't have "low C28:0 FA concentrations" it has 'a depleted C28:0 FA isotopic signature'. Since concentration is not a factor when dealing with isotopic signatures, the relationship between C28:0 and C24:0 and C26:0 FAs should be checked in the text statements and discussion.

If the additional source would have depleted isotopic d13C values of C28:0 FA, as the reviewer is suggesting in his above comment, we would expect a deviation from the source soils as we do see for C26:0 and C24:0FA. But, since the C28:0FA values all lie within the isotopic range of the sources we conclude that the aquatic source isn't producing C28:0 FAs at all, or just in small amounts. We will more clearly formulate it in the manuscript (please see P14L3-4).

Page 14, line 8: "(iii) algae with depleted δ13C values due to described effects of hydoxilation reaction of CO2 combined with high pH values in the epilimnion and CO2 undersaturation, . ."
This paragraph does not fit what you are describing and should be deleted.
Explanation: The high pH by itself does not alter the isotopic signature of C. High pH in the water column is most likely due to consumption of dissolved CO2 by algae during photosynthesis, which is what you are alluding to. The algal species that cause the highest pH are cyanobacteria, which are bicarbonate adapted so that they can utilise bicarbonate (HCO3) when all the CO2 has been used. Thus, they outcompete non-bicarbonate adapted algae such as greens and diatoms. However, cyanobacteria are buoyant and tend to stay near the surface for high light and, since the majority of the CO2 and HCO3 at the lake surface water will be of atmospheric origin, their isotopic signatures will mostly reflect the atmospheric value -12‰ for fractionation. The cyanobacteria can come into contact with isotopically depleted CO2 when the lake mixes in autumn releasing the nutrients (especially P) and the methanogenically-derived isotopically depleted CO2 that have accumulated in the bottom waters. (Aquatic macrophytes can also raise the pH if they are bicarbonate adapted).

We are not sure if we understand the reviewers comment correctly. As described in van Bree et al. (2018) (and Teranes et al. (1999) for oxygen in Lake Baldegg), during times of CO2 undersaturation and high pH values in the lake water (as we find in Lake Baldegg) atmospheric CO2 might dissolve in water and react with OH^- to form $HCO3^-$ (Hydroxilation of CO2), which is strongly depleted in d13C (-15‰ compared to +8‰ during the reaction with H_2O). Aquatic microorganisms using this HCO3- would be able to produce depleted FAs.

We will reformulate in the revised manuscript to avoid misunderstanding.

We rephrased P14L8-10 and P7L36-40.

Page 14, line 14: The text "CSIA was proven to be not suitable to quantitatively unmix terrestrial sources from the Lake Baldegg historic sediments, and thus to apportion the relative contribution of different land-uses to the sedimentary archive as long as the isotopic signal of the missing source is not known."

This is not strictly correct. It was not ‘proven’ that CSIA was not suitable to quantitatively unmix terrestrial sources from Lake Baldegg historic sediment, the authors have stated that, because the isotopic data from the historic sediments did not fall inside the mixing polygon, they would not model them. That is a valid approach but does not constitute proof that CSIA was not suitable to quantitatively unmix, it means that the data was unsuitable to be modelled using CSIA to quantitatively unmix. Very important difference.

You are right, we will re-formulate this sentence. Thanks for pointing this out.

We rephrased m P14L14-15.

In this respect, there is no evidence in the manuscript that the authors have attempted to model any isotopic data, including the data that did fall inside the polygon. This is a missing element that could improve the paper.

Please see above for our reasons, why we suggest not to include the modelling in this study.

Notwithstanding this, the conclusion that the authors see the imprints of plants AND bacteria in the Lake Baldegg sediments is an important finding and that conclusion can be drawn from the data presented without modelling.

Thanks.

References:

Sorry for having missed to check references in the latest version. After the deletion of entire sections during the review process, this slipped our attention. We removed references which were not cited in the text and added publication dates which were where missing (please see below for the list).

Jansen, B., van Loon, E.E., Hooghiemstra, H. and Verstraten, J.M., Improved reconstruction of palaeo-environments through unravelling of preserved vegetation biomarker patterns, Palaeogeogr. Palaeocl., 285, 119-130.

Reference has no date and is not cited in the text. Added date

Jansen, B., de Boer, E.J., Cleef, A.M., Hooghiemstra, H., Moscol-Olivera, M., Tonneijck, F.H. and Verstraten, J.M., Reconstruction of late Holocene forest dynamics in northern Ecuador from biomarkers and pollen in soil cores, 25 Palaeogeogr. Palaeocl., 386, 607-619, 2013.

Reference not cited in text. deleted

Keeling, C.D., The Suess effect: 13Carbon–14Carbon interrelations, Environ. Int., 2, 229–300, 1979

Reference not cited in text. deleted

Krull, E.S., Skjemstad, J.O., Burrows, W.H., Bray, S.G., Wynn, J.G., Bol, R., Spouncer, L., and Harms, B., Recent vegetation changes in central Queensland, Australia: Evidence from d13C and 14C analyses of soil organic matter, Geoderma, 126, 241-259, 2005.

Reference not cited in text. deleted

Réveillé, V., Mansuy, L., Jardé, E. and Garnier-Sillam, E.: Characterisation of sewage sludge-derived organic matter: lipids and humic acids, Org. Geochem., 34, 615-627.

Reference has no date. Added date

Schelske, C.L., and Hodell, D.A., Using carbon isotopes of bulk sedimentary organic matter to

reconstruct the history of nutrient loading and eutrophication in Lake Erie, Limnol. Oceanogr., 40, 918-929, 1995.

Reference not cited in text. deleted

Steger, K., Premke, K., Gudasz, C., Boschker, H & Tranvik, L.: Comparative study on bacterial carbon sources in lake sediments: The role of methanotrophy. Aquat. Microb. Ecol., 76, 39-47, 2015

Reference not cited in text. deleted

Suess, H.E., Radiocarbon concentration in modern wood, Science, 122, 415–417, 1955

Reference not cited in text. deleted

Upadhayay, H.R., Bodé, S., Griepentrog, M., Huygens, D., Bajracharya, R.M., Blake, W.H., Dercon, G., Mabit, L., Gibbs, M., Semmens, B.X., Stock, B.C., Cornelis, W. and Boeckx, P.: Methodological perspectives on the application of compound specific stable isotope fingerprinting for sediment source apportionment. Journal of Soils and Sediments, 17, 1537–1553, 2017.

Reference not cited in text. deleted

van Bergen, P.F., Bull, I.D., Poulton, P.R. and Evershed, R.P.: Organic geochemical studies of soils from the Rothamsted classical experiments. I - Total lipid extracts, solvent insoluble residues and humic acids from Broadbalk wilderness, Org. Geochem., 26, 117-135, 1997.

Reference not cited in text. deleted

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

Gelöscht: analysis

Marlène Lavrieux[1]*, Axel Birkholz[1]*, Katrin Meusburger[1,2], Guido L.B. Wiesenberg[3], Adrian Gilli[4], Christian Stamm[5], Christine Alewell[1]

[1]Environmental Geosciences, Department Environmental Sciences, University of Basel, Basel, Switzerland
[2]Swiss Federal Institute for Forest, Snow and Landscape Research, Birmensdorf, Switzerland
[3]University of Zurich, Department of Geography, Zurich, Switzerland
[4]Geological Institute, ETH Zurich, Zurich, Switzerland
[5]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland
* These authors contributed equally to this work.

Correspondence to: Axel Birkholz (axel.birkholz@unibas.ch)

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 to 2009, with the exception of 1964 to 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/or (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, as a result of FA contribution from a not yet identified source, most likely produced by an *in-situ* aquatic source, either algae, bacteria or other microorganisms or an ex-site historic source from wetland soils and plants (e.g. Sphagnum spec.). Despite the overprint of the yet unknown source on the historic isotopic signal of the lake sediments, land-use and catchment history are clearly reflected in the CSIA results, with isotopic shifts being synchronous with changes in 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 mask the original terrestrial isotopic signals.

Gelöscht: –

Gelöscht: -

Formatiert: Schriftart: Kursiv

Gelöscht:

Formatiert: Schriftart: Kursiv

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).

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 δ^{13}C signature differs among groups of plant species (Tolosa et al., 2013). The δ^{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, 1987; 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.

Gelöscht: 1982

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 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 to 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.

Gelöscht: -

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 to 1940; below 40 m between 1940 to 1970; below 10 m between 1970 to 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 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. The introduction of an artificial oxygenation system into the lake water column in 1982 (Stadelmann et al., 2002) lead to the disappearance of the varves from 1995. Despite the accompanying 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).

Gelöscht: -

Gelöscht: -

Gelöscht: -

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.

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.

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 to 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).

Gelöscht: -

3.3.1 Fatty acid preparation for CSIA

The acidic fraction, including the free fatty acids (FA), 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.

Gelöscht: (

Gelöscht: fatty acids

Gelöscht:)

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 FA 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,

Gelöscht: fatty acids

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 mean residence 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 for many 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.

Gelöscht: turnover times

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 to 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 that we did not catch all contributing sources to the lake sediment FA isotopic signal.

Gelöscht: -

Gelöscht:

4.2.1 The likelihood of missing an additional terrestrial source to the isotopic 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 to 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.

Gelöscht: -

Historical research (Kopp, 1962) has revealed that the lake level was lowered by 30 to 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 from wetland soils (e.g., fens, riparian zones) might have been leached and eroded due to the change in hydrological regime and/or drainage of sites due to adapted

Gelöscht: -

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 FAs (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, δ^{13}C values of long-chain FAs from a Scottish peat core were 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 δ^{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 could explain the stronger shift of the lake sediments to more depleted C24:0 and C26:0 FA δ^{13}C values compared to a C28:0 FA δ^{13}C signal, dominated by the other land-use types. This hypothesis cannot be tested in retrospect, as these reedlands/wetlands disappeared 50 – 75 years ago, but seems one possible explanation for the isotopic depletion of the FAs before 1940, especially if we consider the high concentration of C24:0 in sphagnum (cf. Baas et al., 2000, Pancost et al., 2002).

4.2.2 The likelihood of missing an *in-situ* source to the isotopic 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 δ^{13}C signal of the lake sediment. FAs produced by these larvae might be depleted in δ^{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 to 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 by algae or bacteria, 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 FAs, and very negative δ^{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 δ^{13}C values of the FAs was the dissolution of CO_2 into undersaturated lake water. During times of undersaturation with CO_2 and high pH values (8.3 to 9) the dissolution of atmospheric CO_2 into the lake water is enhanced and the CO_2 is, instead with H_2O, reacting with OH^- to form HCO_3^- (Hydroxilation of CO_2). This reaction results in a strong carbon isotopic fractionation of -15‰, compared to +8‰ during the reaction with H_2O. This highly depleted HCO_3^- can be taken up as carbon

Gelöscht: fatty acids

Gelöscht:

Gelöscht:

Formatiert: Schriftart: Kursiv

Gelöscht: Fatty acids

Gelöscht: -

Gelöscht: fatty acids

Gelöscht: might be

Gelöscht: uptake of the

Gelöscht: lake

Gelöscht: surface

Gelöscht:

Gelöscht: -

Formatiert: Tiefgestellt

Formatiert: Tiefgestellt

Gelöscht: 2

Formatiert: Tiefgestellt

source and can thus heavily influence the isotopic signal of FAs produced by aquatic organisms (van Bree et al., 2018 and references therein; Teranes et al., 1999 and reference therein, describing the same process for depleted δ^{18}O in Lake Baldegg).

As we have generally conditions of CO$_2$ undersaturation in Lake Baldegg beginning at the end of April when stratification is starting and epilimnic primary production is increasing (Müller et al., 2016), the above described incorporation of atmospheric CO$_2$ into FAs might also serve as a possible explanation for the depleted values of C24:0 and C26:0. Also pH values during that time of the year are above 8.3 and reach 8.6 during June (Teranes et al., 1999) and hydroxilation of CO$_2$ will be a dominant process.

We noted that 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 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 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 masked 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 algal or bacterial source whereas C28:0 still reflects 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). As a result of an enhanced *in-situ* production of long chain FAs, masking the terrestrial FA isotopic signal, we would expect higher concentrations of the concerned FAs in the lake sediment, namely C24:0 FA and C26:0 FA, compared to the non-effected C28:0 FA. But since the FA concentration patterns (e.g. relation to each other) of the sediments is not significantly different from the soils (Fig. S2) this expectation is not fulfilled. However, we do not know the historic FA content of source soils.

The depleted δ^{13}C values might also be linked to bacterially assimilated carbon, associated to anoxic conditions in the water column, sediments or wetland soils (Summons et al., 1994; Teranes and Bernasconi, 2005). Biogenic methane carbon typically shows δ^{13}C values of -50 to -70‰ (Whiticar, 1999), leading to a very depleted methanotrophic bacterial 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 δ^{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. As well, δ^{13}C depleted CO$_2$ produced by methane-oxidizing bacteria (MOB) would result in the depleted long-chain FAs. Algae or Cyanobacteria could take up this depleted CO$_2$ and produce on their part depleted FAs (Naeher et al., 2014). But the presence of these long-chain FAs produced in the lake seemed so far to be unlikely here, since to our knowledge, reports about the production of long-chain FAs by bacteria or algae are rare and constrained to extreme environments (e.g. Antarctic Ace Lake, Volkman et al., 1988; Volkman et al., 1998; van Bree et al., 2018). 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.

In a recent publication, Petrisic et al, (2017) were reporting δ^{13}C values of -40.0 to -43.3‰ for C26:0 FA from surface sediments from Lake Bled, Slovenia. They suspected either methanotroph bacteria or cyano bacteria as the producers of C26:0

Gelöscht: for ??? photosynthesis?? And

Gelöscht: r

Gelöscht:

Gelöscht: r

Formatiert: Schriftart: Kursiv

Gelöscht: to

Gelöscht: We would expect higher FA concentrations in lake sediments compared to source soils with a significant enhanced *in-situ* production in the lake water column.

Formatiert: Schriftart: Kursiv

Gelöscht:

Formatiert: Schriftart: Nicht Kursiv

Gelöscht: +-

Gelöscht: *n*-

Gelöscht: fatty acids

Gelöscht: n-fatty acids

Formatiert: Schriftart: Nicht Kursiv

Gelöscht:

Formatiert: Schriftart: Nicht Kursiv

Formatiert: Schriftart: Kursiv

Gelöscht: -

FA. Pertrisics findings from Lake Bled are giving strong evidence that bacteria can play an important role for *in-situ* production of long chain FAs also in lakes beyond extreme environments. This leaves the open question why C24:0 FA in the Lake Bled sediments is not, or only slightly depleted with δ^{13}C values ranging from -36.3 to -37.7‰. Unfortunately, no data for C28:0 FA from Lake Bled is available (Petrisic et al., 2017). As explained above, the influence of the unknown source in Lake Baldegg sediments is increasing from C26:0 to C24:0 FA. However, Neunlist et al. (2002) presented isotopic data for C24:0 – C28:0 FA from Lake Bled and Lake Baldegg sediment samples. Interestingly, in the two more recent sediment samples from Lake Bled, 1993 to 1996 and 1984 to 1990, no depletion of the δ^{13}C values was observed, whereas the two older sample from 1967 to 1976 and 1943 to 1956 show a clear isotopic depletion. The Authors were suggesting a continuous change in the isotopic composition of the carbon source of the producing organisms. For Lake Baldegg, four sediment samples from different depths were analyzed, but in contrast to our study, no significant depletion of the FA δ^{13}C values was observed. However, none of the investigated samples originated from a time where we observed the strong isotopic depletion of C26:0 and C24:0 FA in Lake Baldegg. Neunlist et al. (2002) concluded, that there were constant stable sources for the linear compounds and a higher plant origin very likely.

Taking all this into account the likelihood of an *in-situ* production of long chain FAs by aquatic organisms like algae or bacteria is given. The most likely were algal (phytoplankton) production caused by uptake of depleted HCO_3^- due to undersaturation of CO_2 in the surface water, high pH values and associated hydroxylation of CO_2 (van Bree et al., 2018) or production by methanotroph bacteria and/or by algae or Cyanobacteria which used CO_2 depleted in δ^{13}C, formerly produced by MOB (Naeher et al., 2014; Petrisic et al., 2017).

4.2.3 The necessity of "Suess effect" correction for terrestrial lipids in lake sediments

The δ^{13}C value of atmospheric CO_2 has decreased by approximately 2‰ since the beginning of the industrial era in response to fossil fuel combustion (atmospheric δ^{13}C = -6.5‰ in the preindustrial era vs. -8.5‰ today; Rubino et al., 2013; Keeling et al., 2005, Verburg, 2007, respectively). Therefore, we would expect older lake sediment samples to be relatively enriched (less depleted) in δ^{13}C compared to our todays source soils or sediments. As such, the Suess effect cannot explain our deviation of the isotopic signals between source soils polygon and lake sediments. However, it is widely recognized as necessary to correct for the Suess effect in autochthonous organic matter (Verburg 2007). We thus want to discuss in the following the application of this correction for terrestrial derived organic matter in lake sediments (in our study long-chain FAs as biomarker for higher plants (Eglinton and Eglinton, 2008)).

Long-term experiments have shown that because a depletion due to the Suess effect 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. However, the Suess effect can only account for a maximum decrease of ca. 2‰ in the atmosphere, or taking the dataset of Zhao et al. (2001) for straw from 1845 until 1997 into account, an enhanced depletion of 2.5‰ in the biomass compared to 1.5‰ depletion in the atmosphere at the end of the 1990s. And it might only have an influence in the case of a soil comprising short mean residence time of the overall soil organic matter of one to a few years (Garten et al., 2000). Longer mean residence times imply necessarily a time lag in the recording of the Suess effect in soils accompanied with a strong dampening of the incoming isotopic signal.

Formatiert: Schriftart: Kursiv

Gelöscht: -

Gelöscht: -

Gelöscht: -

Gelöscht: -

Gelöscht: -

Gelöscht:

Formatiert: Schriftart: Kursiv

Gelöscht: 1

Gelöscht: .5

Gelöscht:

Gelöscht:

Gelöscht: h

Gelöscht: 1.5

Gelöscht: for a maximum of 2.5‰

Gelöscht: having

Gelöscht: a fast turnover

Gelöscht: turnover

Gelöscht:

To estimate the Suess effect on our soils and sediments we did a correction based on the atmospheric CO_2 curve of Verburg (2007). We applied the following equation (1) to calculate the Suess effect induced changes from year to year with 1840 as the starting point.

$$\delta^{13}C_{Soil\,(t+1)} = (1-1/R)\ {}^{13}C_{Soil\,(t)} + 1/R\ (\delta^{13}C_{Soil\,(t0)} + (\delta^{13}C_{Atm\,(t+1)} - \delta^{13}C_{Atm\,(t0)})) \qquad (1)$$

Where t is the year of observation with t=0 equal to 1840, and R is the mean residence time for the FAs in years. Further we assumed no changes in $\delta^{13}C$ of atmospheric CO_2 before 1840 and calculated the changes afterwards following the values of atmospheric CO_2 of Verburg (2007). The soil organic carbon pool size was assumed to be stable over the time and no changes in isotope fractionation during photosynthesis due to a concentration increase in CO_2 were considered.

We assumed three different mean residence times for organic material in the soil of 10, 30 and 100 years, which are discussed in soil science (Lichtfouse, 1997; Six and Jastrow, 2002; Wiesenberg et al., 2004). For a better comparability, both, soils and sediments were Suess-effect corrected, following equation 1, to "before industrialization" values (1840) like it was also done when correcting tree rings for the Suess effect (McCarroll et al., 2009) (for the results please see Fig. S4-7 and Table S4-5). For the shortest mean residence time the resulting maximum effect is a depletion of -1.82‰ from 1840 until 2015 for the soils. For the lake sediments the maximum depletion is -1.63‰ between 1840 and 2010. The older the sediments the smaller the Suess effect. For 100 years mean residence time we observe smaller changes for the soils and sediments, of -0.65‰ and -0.58‰, respectively. Despite all uncertainties and simplifications, we can expect that the Suess effect will also affect the FAs deposited in the lake sediments. Thus, it is important to apply this correction also to the sediments, since the terrestrial derived long-chain FAs in the sediment express the $\delta^{13}C$ status of the soil in the year of deposition and have therefore to be corrected in parallel to the soils.

Our results in calculating the Suess effect are considerably higher than previously discussed in the literature from measurements of archived soil samples. A shift of 0.2 to 0.3‰ in $\delta^{13}C$ (i.e. in the range of the measurement precision) was measured in arable temperate soil samples from 1960s compared to 2000s, i.e. during the period when the Suess effect would be most relevant (Wiesenberg, 2004). Congruently, a 0.1 to 0.3‰ shift related to the Suess effect was measured for a tropical soil with an estimated mean residence time for soil organic carbon of <10 years by Bird et al. (2003). The considerably lower measured effects of the Suess effect compared to our calculated effects might be due to either (i) the ploughing of arable soils or non-permanent grasslands which results in a mix of young and old organic matter, or (ii) considerably longer mean residence times in soils than we assumed for our calculations.

However, with the new findings in our study and others (Petrisic et al., 2017; van Bree et al., 2018) the production of long-chain FAs within the lake has to be considered (see above for discussion). In this case, the Suess effect has a direct link to the autochthonous produced FAs and a correction for the resulting growing depletion with time should be carried out if the ratio between autochthonous produced and soil derived organic matter would be known. Since the responsible algae, bacteria or microorganisms are not yet identified and the $\delta^{13}C$ source signal is not yet known, a serious correction for the Suess effect is not possible. Therefore a correction for the Suess effect in this study would be very speculative (please note that we document the Suess effect corrected values in the supporting information Figure S4-7 and Table S4-5).

Gelöscht: Feng (1998)
Gelöscht: turnover time
Gelöscht: Feng (1998)
Gelöscht: taken into account
Gelöscht: turnover
Gelöscht: disccused
Gelöscht: .
Gelöscht: highest turnover rate
Gelöscht: 91
Gelöscht: 71
Gelöscht: turnover
Gelöscht: 7
Gelöscht: 63
Gelöscht:
Gelöscht: -
Gelöscht:
Gelöscht: -
Gelöscht: turnover rate
Gelöscht: lower turnover rates
Gelöscht:
Gelöscht:
Gelöscht: is

4.2.4 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 a 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 land use 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, 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.

4.2.5 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. But this could also be explained by a change of the presence or in abundance of the *in-situ* producers of long-chain FAs accompanying with the change of the lakes trophic status. 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 FAs isotopic signature, can be suspected. Here the example of van Bree et al. (2018) can be consulted, as they found a compound-specific concentration increase of mostly C28:0 FA in the water column. Also, the accompanying isotopic depletion of, in their case, C28:0 FA compared to the terrestrial C28:0 FA signal is giving strong evidence for an aquatic source. However, we conclude, that the modelling of the different source contributions for the lake sediments cannot be conducted in this study. Any approach to deduce the isotopic signal from the data, without identifying the actual sources and their isotopic signature would be very speculative (see Fig. S3) and would not lead to serious and concise results. Therefore, future research should focus on identification of the aquatic producers of long-chain FAs in lacustrine environments and its isotopic composition.

Formatiert: Schriftart: Kursiv

Gelöscht: *n*-

Gelöscht: enrichment

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 FAs (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).

Gelöscht: n-fatty acids

Formatiert: Schriftart: Nicht Kursiv

Formatiert: Schriftart: Nicht Kursiv

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). A high discrepancy in isotopic values between long-chain FAs of close chain-length points to different major origins of the single FAs, namely isotopically depleted aquatic contribution in addition to the expected terrestrial origin. 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 influenced by different sources. 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 authochtonous production, 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.

Gelöscht: As expanded above (Sect. 4.2.), a

Gelöscht: a degradation of the

Gelöscht: isotopic signal

Gelöscht: Then, the

Gelöscht: degraded

Gelöscht: (Sect. 4.2.)

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 masks 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 but 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 samples 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 today's source soils signatures.

Although the influence of not yet identified sources to our lake sediments, as expanded above, is very 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 but (2) indicates an additional source with depleted $\delta^{13}C$ values for C24:0 and C26:0 FAs and, compared to the source soils, a lower concentration of C28:0 FA. This leaves a number of potential additional sources, namely, (i) a larger contribution of Sphagnum/moss derived organic matter released from historical peat bogs or the riparian zone as described above, or, during time periods of hypereutrophic status of the lake, *in-situ* FA production of preferably C24/26:0 FA. The latter might be produced by (i) methanotroph bacteria or other bacteria which were using $\delta^{13}C$ depleted CO_2 derived from methane-oxizing bacteria (MOB), (ii) *in-situ* production by algae, which were using depleted $\delta^{13}C$ from HCO_3^- due to described effects of hydoxilation reaction of CO_2 during times of high pH values in the epilimnion and CO_2 undersaturation, or (iii) due to algal uptake of MOB derived CO_2 depleted in $\delta^{13}C$ analogous to the bacteria mentioned before.

While the long-chain FAs are becoming widely used for CSIA as markers of the terrestrial sediment contribution to rivers and lakes, our results underline the need to temper this standpoint for lake sediments. Some lacustrine macrophytes, bacteria and microbial organisms were previously shown to produce also long-chain FAs, and also our study highlights that an interference of the terrestrial isotopic signal linked to aquatic activity might be underestimated. In the case of Lake Baldegg it was shown, that, as long as the isotopic signal of the missing source is not known, it is impossible to quantitatively unmix terrestrial sources from the Lake Baldegg historic sediments, and thus to apportion the relative contribution of different land-uses to the sedimentary archive.

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, but most likely aquatic sources, land-use and catchment historical development are still surprisingly accurately 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 microbial activity also affected the more specific cyclic molecule assemblages, as testified by the presence of *in-situ* produced TTHCs. Special care should thus be taken for further studies on eutrophic systems, where a strong bacterial activity is known or suspected.

To conclude, we see the imprints of plants AND bacteria in the Lake Baldegg sediments: the influence of terrestrial derived compounds and their changes with land use management are very precisely documented, but at the same time the influence of *in-situ* produced FAs is very likely and has an impact on the overall isotopic composition of long chain FAs.

Acknowledgements. This study was funded by the European COST Action ES1306, "Connecting European connectivity research" and was finalized in the framework of the IAEA Coordinated Research Project (CRP) "Nuclear techniques for a better understanding of the impact of climate change on soil erosion in upland agro-ecosystems" (D1.50.17). Core recovery was financially supported by an ETH research grant (CH1-02-08-2). We wish to thank Dr. Stefano Bernasconi (ETH Zurich) for granting access to the ASE, and Judith Kobler-Waldis, Thomas Kuhn, Simon Imhof, Oliver Rehmann and Lukas Burgdorfer for their help in the laboratory. We thank Robert Lovas, Pius Stadelmann and Franz Stadelmann (Canton Lucerne)

Gelöscht:

Gelöscht: and

Gelöscht: would hint into the direction of an

Gelöscht: a

Gelöscht: low

Gelöscht: concentrations compared to C24:0 and C26:0 FAs

Gelöscht: (ii)

Gelöscht:

Gelöscht: either

Gelöscht: i

Gelöscht: or

Formatiert: Schriftart: Kursiv

Gelöscht: with

Gelöscht: values

Formatiert: Tiefgestellt

Formatiert: Hochgestellt

Gelöscht: combined with

Gelöscht: iv

Gelöscht: the

Gelöscht: fatty acids

Gelöscht: CSIA

Gelöscht: was proven to be not suitable to

Gelöscht: as long as the isotopic signal of the missing source is not known.

Gelöscht:

Gelöscht: .

for providing helpful information about the catchment. Further we thank Stefano Crema and Marco Cavalli for their support to calculate the connectivity index. Our acknowledgements are also addressed to the land owners for sampling permissions and their curiosity about our work.

References

Alewell, C., Giesler, R., Klaminder, J. Leifeld, J., Rollog, M., Stable carbon isotopes as indicators for micro-geomorphic changes in palsa peats. Biogeosciences, 8, 1769-1778, 2011.

Alewell, C., Birkholz, A., Meusburger, K., Wildhaber, Y. S. and Mabit, L.: Quantitative sediment source attribution with compound-specific isotope analysis in a C3 plant-dominated catchment (central Switzerland), Biogeosciences, 13, 1587-1596, 2016.

Allan, J.D.: Landscapes and riverscapes: the influence of landuse on stream ecosystems, Annu. Rev. Ecol. Evol. S., 35, 257-284, 2004.

Baas, M., Pancost, R., van Geel, B., Sinninghe-Damste, J. S.: A comparative study of lipids in Sphagnum species, Org. Geochem., 31 (6), 535-541, 2000.

Bird, M., Kracht, O., Derrien, D., and Zhou, Y., The effect of soil texture and roots on the stable carbon isotope composition of soil organic carbon, Aust. J. Soil Res., 41, 77– 94, 2003.

Blake, W. H., Ficken, K. J., Taylor, P., Russell, M. A., and Walling, D. E.: Tracing crop-specific sediment sources in agricultural catchments, Geomorphology, 139, 322–329, 2012.

Blokker, P., Schouten, S., van den Ende, H., de Leeuw, J., Hatcher, P.G. and Damsté, J.S.S.: Chemical structure of algaenans from the fresh water algae *Tetraedron minimum*, *Scenedesmus communis* and *Pediastrum boryanum*, Org. Geochem., 29, 1453-1468, 1998.

Borja, Á., Galparsoro, I., Solaun, O., Muxika, I., Tello, E.M., Uriarte, A. and Valencia, V.: The European Water Framework Directive and the DPSIR, a methodological approach to assess the risk of failing to achieve good ecological status, Estuar. Coast. Shelf S., 66, 84-96, 2006.

Borselli, L., Cassi, P. and Torri, D.: Prolegomena to sediment and flow connectivity in the landscape: A GIS and field numerical assessment, CATENA, 75, 268-277, 2008.

Bouloubassi, I. and Saliot, A. Dissolved, particulate and sedimentary naturally derived polycyclic aromatic hydrocarbons in a coastal environment: geochemical significance, Mar. Chem. 42, 127-143, 1993.

Bouloubassi, I., Fillaux, J. and Saliot, A.: Hydrocarbons in surface sediments from the Changjiang (Yangtze River) estuary, East China Sea, Mar. Pollut. Bull., 42. 1335-1346, 2001.

Bovee, R.J. and Pearson, A.: Strong influence of the littoral zone on sedimentary lipid biomarkers in a meromictic lake, Geobiology, 12, 529–541, 2014.

Caudales, R. and Wells, J.M.: Differentiation of free-living *Anabaena* and *Nostoc* cyanobacteria on the basis of fatty acid composition, Int. J. Syst. Bacteriol., 42, 246-251, 1992.

Cavalli, M., Trevisani, S., Comiti, F. and Marchi, L.: Geomorphometric assessment of spatial sediment connectivity in small Alpine catchments, Geomorphology, 188, 31-41, 2013.

Cummings, J.H.: Short chain fatty acids in the human colon, Gut, 22, 763-779, 1981.

Dubois, N. and Jacob, J.: Molecular biomarkers of anthropic impacts in natural archives: A review, Front. Ecol. Evol., 4, 92, 2016.

Ducerf, G.: L'encyclopédie des plantes bio-indicatrices alimentaires et médicinales. Guide de diagnostic des sols, 4th edition, Promonature editions, France, 352 pp, 2017.

Eglinton, T. I. and Eglinton G.: Molecular proxies for palaeoclimatology, Earth Planet. Sci. Lett., 275 (1), 1-6, 2008.

Fang, J., Wu, F., Xiong, Y., Li, F., Du, X., An, D., and Wang, L.: Source characterization of sedimentary organic matter using molecular and stable carbon isotopic composition of *n*-alkanes and fatty acids in sediment core from Lake Dianchi, China, Sci. Total Environ., 473, 410–421, 2014.

Feakins, S.J., Eglinton, T.I., deMenocal, P.B., 2007. A comparison of biomarker recordsof northeast African vegetation from lacustrine and marine sediments (ca. 3.40 Ma). Org. Geochem. 38, 1607-1624, 2007.

Federal Statistical Office: Surface Agricole Utile 1975-2015, Neuchâtel (Switzerland), 2015.

Federal Statistical Office: Der Schweizerische Ackerbau in der Kriegszeit, Eidgenössische Anbauerhebungen 1939-1947, Bern, Switzerland, 360 pp, 1949.

Feng, X.: Long-term c_i/c_a responses of trees in Western North America to atmospheric CO_2 concentration derived from carbon isotope chronologies. Oecologia, 117, 19-25, 1998.

Ficken, K. J., Barber, K. E., Eglinton, G., Lipid biomarker, δ13C and plant macrofossil stratigraphy of a Scottish montane peat bog over the last two millennia, Org. Geochem., 28, 217-237, 1998.

Galy, V., Eglinton, T., France-Lanord, C., and Sylya, S.: The provenance of vegetation and environmental signatures encoded in vascular plant biomarkers carried by the Ganges-Brahmaputra rivers, Earth Planet. Sci. Lett., 304, 1–12, 2011.

Garten, C.T., Cooper, L.W., Post, W.M., and Hanson, P.J., Climate controls on forest soil C isotope ratios in the Southern Appalachian Mountains, Ecology, 81, 1108– 1119, 2000.

Gibbs, M. M.: Identifying source soils in contemporary estuarine sediments: A new compound-specific isotope method, Estuar. Coast., 31, 344-359, 2008.

Gong, C.R., Hollander, D.J., Differential contribution of bacteria to sedimentary organic matter in oxic and anoxic environments, Santa Monica Basin, California, Org Geochem, 26, 545-563, 1997.

Griepentrog, M., Eglinton, T.I., Hagedorn, F., Schmidt, M.W.I. and Wiesenberg, G.L.B., Interactive effects of elevated CO_2 and nitrogen deposition on fatty acid molecular and isotope composition of above- and belowground tree biomass and forest soil fractions, Glob. Change Biol., 21, 473-486, 2015.

Gugger, M., Lyra, C., Suominen, I., Tsitko, I., Humbert, J.F., Salkinoja-Salonen, M.S. and Sivonen, K.: Cellular fatty acids as chemotaxonomic markers of the genera *Anabaena*, *Aphanizomenon*, *Microcystis*, *Nostoc* and *Planktothrix* (cyanobacteria), Int. J. Syst. Evol. Micr., 52, 1007–1015, 2002.

Guillemot, T., Bichet, V., Gauthier, E., Zocatelli, R., Massa, C. and Richard, H.: Environmental responses of past and recent agropastoral activities on south Greenlandic ecosystems through molecular biomarkers, Holocene, 27, 783-795, 2017.

Hancock, G.J. & Revill, A.T.: Erosion source discrimination in a rural Australian catchment using compound-specific isotope analysis (CSIA). Hydrological Processes, 27, 923–932, 2013.

Hayes, J.M.: Factors controlling ^{13}C contents of sedimentary organic compounds: Principles and evidence, Mar. Geol., 113, 111-125, 1993.

Jacob, J., Disnar, J.R., Boussafir, M., Sifeddine, A., Albuquerque, A.L.S., and Turcq, B.: Pentacyclic triterpene methyl ethers in recent lacustrine sediments (Lagoa do Caçó, Brazil), Org. Geochem., 36, 449–461, 2005.

Jacob, J., Disnar, J.R., Arnaud, F., Chapron, E., Debret, M., Lallier-Vergès, E., Desmet, M. and Revel-Rolland, M.: Millet cultivation history in the French Alps as evidenced by a sedimentary molecule, J. Archaeol. Sci., 35, 814-820, 2008.

Jardé, E., Mansuy, L. and Faure, P.: Organic markers in the lipidic fraction of sewage sludge, Water Res., 39, 1215-1232, 2005.

Gelöscht: Jansen, B., van Loon, E.E., Hooghiemstra, H. and Verstraten, J.M., Improved reconstruction of palaeo-environments through unravelling of preserved vegetation biomarker patterns, Palaeogeogr. Palaeocl., 285, 119-130.
Jansen, B., de Boer, E.J., Cleef, A.M., Hooghiemstra, H., Moscol-Olivera, M., Tonneijck, F.H. and Verstraten, J.M., Reconstruction of late Holocene forest dynamics in northern Ecuador from biomarkers and pollen in soil cores, Palaeogeogr. Palaeocl., 386, 607-619, 2013.

Jørgensen, H., Jakobsen, K. and Eggum, B.O.: Determination of endogeous fat and fatty acids at the terminal ileum and on faeces in growing pigs, Acta Agric. Scand., Sect. A., Animal Sci., 43, 101-106, 1993.

Keeling, C. D., S. C. Piper, R. B. Bacastow, M. Wahlen, T. P. Whorf, M. Heimann, and Meijer, H. A., Atmospheric CO_2 and $^{13}CO_2$ exchange with the terrestrial biosphere and oceans from 1978 to 2000: Observations and carbon cycle implications, in: A history of atmospheric CO_2 and its effects on plants, animals, and ecosystems, Springer, New York, USA, 83–113, 2005.

Gelöscht:
Keeling, C.D., The Suess effect: ^{13}Carbon–^{14}Carbon interrelations, Environ. Int., 2, 229–300, 1979.

Kind, J.: Ferromagnetic resonance spectroscopy and Holocene Earth's magnetic field variations in sediment from Swiss lakes, Ph.D. thesis, ETH Zurich (Switzerland), 2012.

Kopp, Joseph: Veränderungen von Seen und Flussläufen in der Zentralschweiz in interglazialer und postglazialer Zeit, Mitteilungen der naturforschenden Gesellschaft Luzern, 19, 155-167, 1962.

Lavrieux, M.: Biomarqueurs moléculaires d'occupation des sols, du sol au sédiment : exemple du bassin-versant et du lac d'Aydat (Puy-de-Dôme), Ph.D. thesis, University Tours (France), 2011.

Gelöscht: Krull, E.S., Skjemstad, J.O., Burrows, W.H., Bray, S.G., Wynn, J.G., Bol, R., Spouncer, L., and Harms, B., Recent vegetation changes in central Queensland, Australia: Evidence from $\delta^{13}C$ and ^{14}C analyses of soil organic matter, Geoderma, 126, 241-259, 2005.

Lavrieux, M., Jacob, J., Le Milbeau, C., Zocatelli, R., Masuda, K., Bréheret, J.G., and Disnar, J.R.: Occurrence of triterpenyl acetates in soil and their potential as chemotaxonomical markers of Asteraceae, Org. Geochem., 42, 2011.

Le Milbeau, C., Lavrieux, M., Jacob, J., Bréheret, J.G., Zocatelli, R., and Disnar, J.R.: Methoxy-serratenes in a soil under conifers and their potential use as biomarkers of Pinaceae, Org. Geochem., 55, 45-54, 2013.

Lehmann, M.F., Bernasconi, S.M., McKenzie, J.A., Barbieri, A., Simona, M., and Veronesi, M.: Seasonal variation of the $\delta^{13}C$ and $\delta^{15}N$ of particulate and dissolved carbon and nitrogen in Lake Lugano: Constraints on biogeochemical cycling in a eutrophic lake, Limnol. Oceanogr., 49, 415-429, 2004.

Lichtfouse, Eric: Heterogeneous turnover of molecular organic substances from crop soils as revealed by ^{13}C labeling at natural abundance with Zea mays. Die Naturwissenschaften, 84 (1), 23-25, 1997.

Liess, M., Schulz, R., Berenzen, N., Nanko-Drees, J. and Wogram, J.: Pflanzenschutzmittelbelastung und Lebensgemeinschaften in Fliessgewässern mit landwirtschaftlich genutztem Umland, UBA Texte 65-01, Berlin, 227 pp, 2001.

Lohmann, F., Trendel, M.L., Hetru, C. and Albrecht, P.: C-29 tritiated β-amyrin: chemical synthesis aiming at the study of aromatization processes in sediments, J. Label. Compd. Radiopharm., 28, 377–386, 1990.

Lotter, A.F., Sturm, M., Teranes, J.L. and Wehrli, B.: Varve formation since 1885 and high-resolution varve analyses in hypertrophic Baldeggersee (Switzerland), Aquat. Sci., 59, 304-325, 1997.

Lotter, A.F.: The recent eutrophication of Baldeggersee (Switzerland) as assessed by fossil diatom assemblages, Holocene, 8, 395-405, 1998.

Lotter, A.F.: Pollen profile BALDEGG, Baldeggersee, Switzerland. European Pollen Database (EPD), doi:10.1594/PANGAEA.738987, 2010.

Makhutova, O. N., Borisova, E. V., Shulepina, S. P., Kolmakova, A. A., Sushchik, N.N., Fatty acid composition and content in chironomid species at various life stages dominating in a saline Siberian lake, Cont. Probl. of Ecol., 10, 230-239, 2017.

Malaj, E., P. C. von der Ohe, M. Grote, R. Kühne, C. P. Mondy, P. Usseglio-Polatera, W. Brack and Schäfer, R. B.: Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale, P. Natl. A. Sci., 111, 9549-9554, 2014.

Marseille, F., Disnar, J.R., Guillet, B. and Noack, Y.: *n*-Alkanes and free fatty acids in humus and A1 horizons of soils under beech, spruce and grass in the Massif-Central (Mont-Lozère), France, Eur. J. Soil Sci., 50, 433-441, 1999.

Matthaei, C., Piggitt, J.J., and Townsend, C.R.: Multiple stressors in agricultural streams: interactions among sediment addition, nutrient enrichment and water abstraction, J. Applied Ecology, 47, 639-649, 2010.

Müller, B., Gächter, R. and Wüest, A., 2014, Accelerated Water Quality Improvement during Oligotrophication in Peri-Alpine Lakes, Environ. Sci. Tech., 48, 6671-6677, 2014.

Müller, B., Meyer, J. S., Gächter, R., Alkalinity regulation in calcium carbonate-buffered lakes, Limn. Oceanogr., 61, 341-352, 2016.

Naeher, S., Niemann, H., Peterse, F., Smittenberg, R. H., Zigah, P. Z., Schubert, C. J.: Tracing the methane cycle with lipid biomarkers in Lake Rotsee (Switzerland), Org. Geochem., 66, 174-181, 2014.

Gelöscht: 2004

Neunlist, S., Rodier, C. and Llopiz, P.: Isotopic biogeochemistry of the lipids in recent sediments of Lake Bled (Slovenia) and Baldeggersee (Switzerland), Org. Geochem., 33, 1183–1195, 2002.

Niessen, F. and Sturm, M.: Die Sedimente des Baldeggersees (Schweiz) – Ablagerungsraum und Eutrophierungsentwicklung während der letzten 100 Jahre, Arch. Hydrobiol., 108, 365–383, 1987.

Otto, A. and Wilde, V.: Sesqui-, di-, and triterpenoids as chemosystematic markers in extant conifers - a review, Bot. Rev., 67, 141-238, 2001.

Pancost, R., Baas, M., van Geel, B., Sinninghe-Damste, J. S.: Biomarkers as proxies for plant inputs to peats: an example from a sub-boreal ombrotrophic bog, Org. Geochem, 33, 675-690, 2002.

Parker, P.L., Van Baalen, C. and Maurer, L.: Fatty acids in eleven species of blue-green algae: geochemical significance, Science, 155, 707-708, 1967.

Petrišič, M. G., Heath, E., Ogrinc, N.: Lipid Biomarkers and Their Stable Carbon Isotopes in Oxic and Anoxic Sediments of Lake Bled (NW Slovenia), Geomicrobiol. J., 34 (7), 606-617, 2017.

Popp, H. : Le siècle de la révolution agricole. L'agriculture et la politique agricole suisses au 20e siècle, Agri, Lausanne, Switzerland, 111 pp, 2001.

Reiffarth, D.G., Petticrew, E.L., Owens, P.N. and Lobb, D.A.: Sources of variability in fatty acid (FA) biomarkers in the application of compound-specific stable isotopes (CSSIs) to soil and sediment fingerprinting and tracing: A review. Sci. Total Environ., 565, 8–27, 2016.

Réveillé, V., Mansuy, L., Jardé, E. and Garnier-Sillam, E.: Characterisation of sewage sludge-derived organic matter: lipids and humic acids, Org. Geochem., 34, 615-627, 2003.

Rezbanyai, L.: Zur Insektenfauna des Siedereiteiches bei Hochdorf, Kanton Luzern, Entomologische Berichte Luzern, 5, 1981.

Rubino, M., D. Etheridge, C. Trudinger, C. Allison, M. Battle, R. Langenfelds, L. Steele, M. Curran, M. Bender, and White, J., A revised 1000 year atmospheric $\delta^{13}C$-CO_2 record from Law Dome and South Pole, Antarctica, J. Geophys. Res. Atmos., 118, 8482–8499, 2013.

Scheurer, K., Alewell, C., Bänninger, D. and Burkhardt-Holm, P.: Climate and land-use changes affecting river sediment and brown trout in alpine countries—a review, Environ. Sci. Pollut. R., 16, 232-242, 2009.

Gelöscht: Schelske, C.L., and Hodell, D.A., Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie, Limnol. Oceanogr., 40, 918-929, 1995.¶

Schindler Wildhaber, Y., Liechti, R. and Alewell, C.: Organic matter dynamics and stable isotope signature as tracers of the sources of suspended sediment, Biogeosciences 9, 1985–1996, 2012.

Schouten, S., Klein Breteler, W.C.M., Blokker, P., Schogt, N., Rijpstra, I.C., Grice, K., Baas, M. and Damsté, J.S.S.: Biosynthetic effects on the stable carbon isotopic compositions of algal lipids: Implications for deciphering the carbon isotopic biomarker record, Geochim. Cosmochim. Acta, 62, 1397–1406, 1998.

Simoneit, B.R.T.: Cyclic terpenoids of the geosphere, in: Biological markers in the Sedimentary Record, Johns, R.B. Elsevier, Amsterdam, Netherlands, 43-100, 1986.

Six, J & Jastrow, Julie: Organic Matter Turnover. Encyclopedia of Soil Science. 10.1201/NOE0849338304.ch252, 2002.

Stadelmann, P., Lovas, R. and Butscher, E.: 20 Jahre Sanierung und Überwachung des Baldeggersees, Mitteilungen der Naturforschenden Gesellschaft Luzern, Volume 37, 2002.

Stefanova, M., Oros, D.R., Otto, A. and Simoneit, B.R.T.: Polar aromatic biomarkers in the Miocene Maritza-East lignite, Bulgaria, Org. Geochem., 33, 1079-1091, 2002.

Summons, R.E., Jahnke, L.L. and Roksandic, Z.: Carbon isotopic fractionation in lipids from methanotrophic bacteria: Relevance for interpretation of the geochemical record of biomarkers, Geochim. Cosmochim. Acta, 58, 2853-2863, 1994.

Gelöscht: Steger, K., Premke, K., Gudasz, C., Boschker, H & Tranvik, L.: Comparative study on bacterial carbon sources in lake sediments: The role of methanotrophy. Aquat. Microb. Ecol., 76, 39-47, 2015¶
Suess, H.E., Radiocarbon concentration in modern wood, Science, 122, 415–417, 1955.¶

Sundermann, A., Gerhardt, M., Kappes, H. and Haase, P.: Stressor priorisation in riverine ecosystems: Which environmental factors shape benthic invertebrate assemblage metrics?, Ecol. Indic., 27, 83-96, 2013.

Teranes, J.L. and Bernasconi, S.M.: Factors controlling δ^{13}C values of sedimentary carbon in hypertrophic Baldeggersee, Switzerland, and implications for interpreting isotope excursions in lake sedimentary records, Limnol. Oceanogr., 50, 914–922, 2005.

Tolosa, I., Fiorini, S., Gasser, B., Martin, J. and Miquel, J.C.: Carbon sources in suspended particles and surface sediments from the Beaufort Sea revealed by molecular lipid biomarkers and compound-specific isotope analysis, Biogeosciences, 10, 2061-2087, 2013.

US EPA: National Water Quality Inventory: Report to Congress 2004, Reporting Cycle January 2009, United States Environmental Protection Agency Office of Water Washington, DC 20460 EPA 841-R-08-001, 2009.

Gelöscht: Upadhayay, H.R., Bodé, S., Griepentrog, M., Huygens, D., Bajracharya, R.M., Blake, W.H., Dercon, G., Mabit, L., Gibbs, M., Semmens, B.X., Stock, B.C., Cornelis, W. and Boeckx, P.: Methodological perspectives on the application of compound-specific stable isotope fingerprinting for sediment source apportionment. Journal of Soils and Sediments, 17, 1537–1553, 2017.¶

van Bree, L. G. J., Peterse, F., van der Meer, M. T. J., Middelburg, J.J., Negash, A. M. D., De Crop, W., Cocquyt, C., Wieringa, J.J., Verschuren, D., Sinninghe Damsté, J.S., Seasonal variability in the abundance and stable carbon-isotopic composition of lipid biomarkers in suspended particulate matter from a stratified equatorial lake (Lake Chala, Kenya/Tanzania): Implications for the sedimentary record, Quat. Sc. Rev., 192. 208-224, 2018.

Gelöscht: van Bergen, P.F., Bull, I.D., Poulton, P.R. and Evershed, R.P.: Organic geochemical studies of soils from the Rothamsted classical experiments. I - Total lipid extracts, solvent insoluble residues and humic acids from Broadbalk wilderness, Org. Geochem., 26, 117-135, 1997. ¶

van der Knaap, W.O., van Leeuwen, J.F.N., Fankhauser, A. and Ammann, B.: Palynostratigraphy of the last centuries in Switzerland based on 23 lake and mire deposits: chronostratigraphic pollen markers, regional patterns, and local histories, Rev. Palaeobot. Palyno., 108, 85–142, 2000.

van Raden, U.: High resolution Swiss lake records of climate change, Ph.D. Thesis, ETH Zurich (Switzerland), 2012.

Verburg, P., The need to correct for the Suess effect in the application of d13C in sediment of autotrophic Lake Tanganyika, as a productivity proxy in the Anthropocene, J. Paleolimnol., 37, 591-602, 2007.

Volkman, J.K., Burton, H.R., Everitt, D.A. and Allen, D.I.: Pigment and lipid compositions of algal and bacterial communities in Ace Lake, Vestfold Hills, Antarctica, Hydrobiologia, 165, 41-57, 1988.

Volkman, J.K., Barrett, S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L. and Gelin, F.: Microalgal biomarkers: A review of recent research developments, Org. Geochem., 29, 1163-1179, 1998.

Wakeham, S.G., Schaffner, C. and Giger, W.: Polycyclic aromatic hydrocarbons in Recent lake sediments - II. Compounds derived from biogenic precursorsduring early diagenesis, Geochim. Cosmochim. Acta, 44, 415-429, 1980.

Wakeham, S.G. and Canuel, E.A.: Biogenic polycyclic aromatic hydrocarbons in sediments of the San Joaquin River in California (USA), and current paradigms on their formation, Environ. Sci. Pollut. Res., 23, 10426–10442, 2016.

Wasson, J., Villeneuve, B., Iital, A., Murray-Bligh, J., Dobiasova, M., Bacikova, S., Timm, H., Pella, H., Mengin, N. and Chandesris, A.: Large-scale relationships between basin and riparian land cover and the ecological status of European rivers, Freshwater Biol., 55, 1465-1482, 2010.

Wehrli, B., Lotter, A.F., Schaller, T. and Sturm, M.: High-resolution varve studies in Baldeggersee (Switzerland): Project overview and limnological background data, Aquat. Sci., 59, 285–294, 1997.

Whiticar, M.J.: Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, Chem. Geol., 161, 291-314, 1999.

Wiesenberg, G.L.B., Input and turnover of plant-derived lipids in arable soils, Ph.D. thesis, University Cologne (Germany), 2004.

Wiesenberg, G.L.B., Schwarzbauer, J., Schmidt, M.W.I. and Schwark, L.: Source and turnover of organic matter in agricultural soils derived from *n*-alkane/*n*-carboxylic acid compositions and C-isotope signatures, Org. Geochem., 35, 1371–1393, 2004.

Wiesenberg, G.L.B., Schwarzbauer, J., Schmidt M.W.I., Schwark, L.: Plant and soil lipid modification under elevated atmospheric CO2 conditions: II. Stable carbon isotopic values (δ13C) and turnover, Org. Geochem., 39, 103-117, 2008.

Yunker, M.B. and MacDonald, R.W.: Composition and origins of polycyclic aromatic hydrocarbons in the Mackenzie River and on the Beaufort Sea shelf, Arctic, 48, 118-129, 1995.

Yunker, M.B. and MacDonald, R.W.: Alkane and PAH depositional history, sources and fluxes in sediments from the Fraser river basin and strait of Georgia, Canada, Org. Geochem., 34, 1429–1454, 2003.

Zhao, F.J., Spiro, B. and McGrath, S.P., Trends in ^{13}C/^{12}C ratios and C isotope discrimination of wheat since 1845, Oecologia, 128, 336-342, 2001.

Formatiert: Deutsch (Schweiz)

Gelöscht: a

Gelöscht: J.

Gelöscht: b

Gelöscht: M.W.I.

Gelöscht: cL.

Gelöscht: akkkkk look

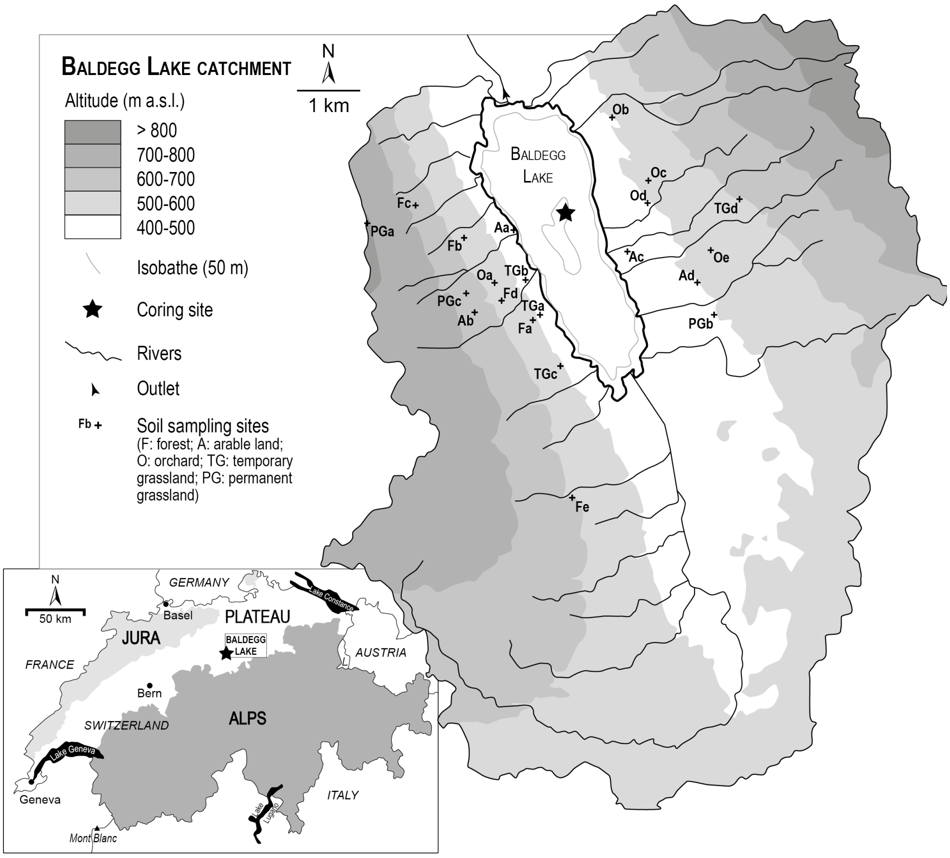


Figure 1: Catchment of Lake Baldegg with sampling sites.

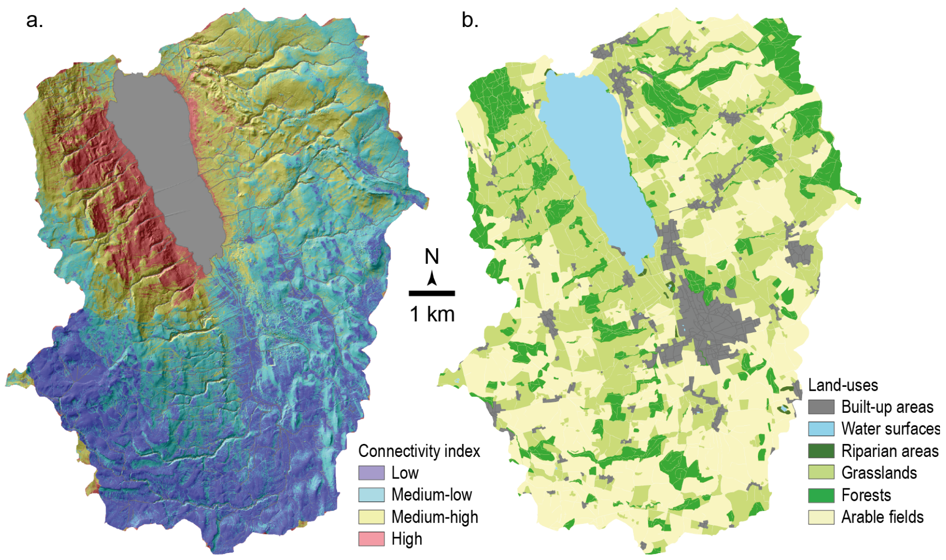
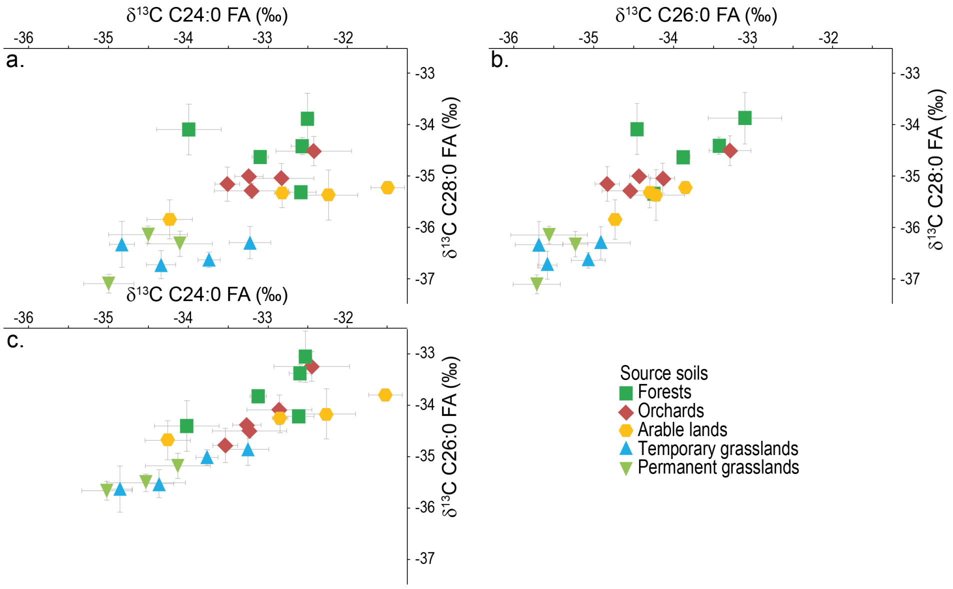


Figure 2: a. Connectivity index for the Lake Baldegg catchment, with a topographic map underlying. The lake is indicated in grey. b. Land-use map.



5

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.

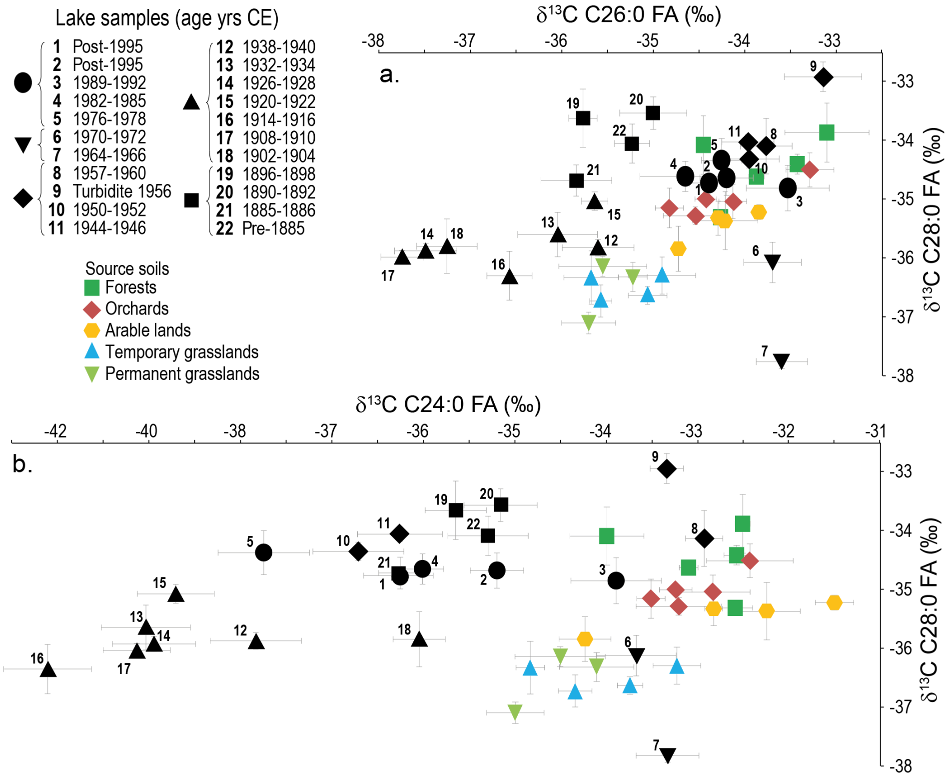


Figure 4: δ13C of the FAs (a.) C26:0 vs. C28:0, (b.) C24:0 vs. C28:0, in lake sediments, compared to soils. Note the different scale for the x axis between (a.) and (b.). Error bars: standard deviation of the triplicate measurements.

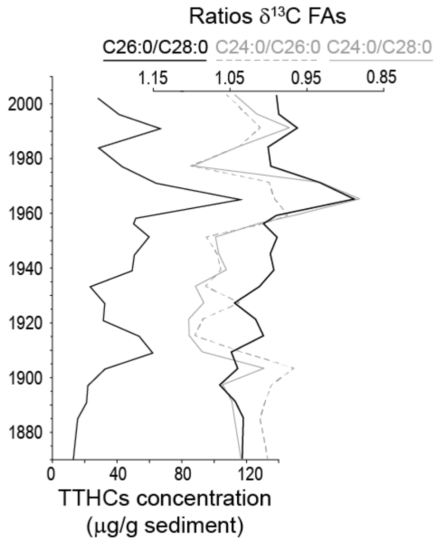


Figure 5: Evolution of the TTHCs concentration (sum of TTHC2 and TTHC3) along the sediment core, compared to evolution of the ratios of δ^{13}C of FAs,