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Quantitative sediment source attribution with compound-specific isotope analysis in a C3 plant-dominated catchment (central Switzerland)

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Abstract. As sediment loads impact freshwater systems and infrastructure, their origin in complex landscape systems is of crucial importance for sustainable management of agricultural catchments. We differentiated the sediment source contribution to a lowland river in central Switzerland by using compound-specific isotope analysis (CSIA). We found a clear distinction of sediment sources originating from forest and agricultural land use. Our results demonstrate that it is possible to reduce the uncertainty of sediment source attribution in: (i) using compound content (in our case, long-chain fatty acids; FAs) rather than soil organic matter content to transfer $\delta^{13}C$ signal of FAs to soil contribution and (ii) restricting the investigation to the long-chain FAs ($>C22:0$) not to introduce errors due to aquatic contributions from algae and microorganisms. Results showed unambiguously that during base flow, agricultural land contributed up to 65 % of the suspended sediments, while forest was the dominant sediment source during high flow. This indicates that connectivity of sediment source areas within the river changes between base and high flow conditions. Uncertainty, which might occur in complex, large-scale studies due to undetected source attribution and/or CSSI signature degradation, is low because of limited data complexity in our study (i.e., two–three sources and two tracers).

Our findings are the first published results highlighting (i) significant differences in compound-specific stable isotope (CSSI) signature of sediment sources from land uses dominated by C3 plant cultivation and (ii) the use of these differences to quantify sediment contribution to a small river.

1 Introduction

Sediment input to rivers causes clogging of river bed, eutrophication of waters, direct harmful effects of sediments on the biota and destruction of river infrastructure. The United States Environmental Protection Agency has identified sediments among the top 10 causes of biological impairment in freshwater ecosystems (US EPA, 2009), and at the European level, sediment pollution has been identified as one of the most relevant pressures to water bodies which impeded the aims of the water framework directive by the year 2015 (Borja et al., 2006). Restoration of rivers from sediment impact and associated management strategies can only be efficient if the origin of sediment loads, contribution of sources and their connection to different land uses and management strategies are identified. Geochemical (e.g., the use of elemental composition of source soils and sediments to track sediment origin) or isotopic fingerprinting has been used to discriminate between sources of sediments. However, successful discrimination between different sediment sources was often restricted to specific catchment settings having: (i) well-differentiated geological formation (at least

two) and/or (ii) significant temporal shifts from C3 to C4 vegetation.

Using the compound-specific stable isotope (CSSI) signatures of inherent soil organic biomarkers, allows to discriminate and apportion the source soil contribution from different land uses, and the knowledge gained from CSSI can reinforce the effectiveness of soil conservation measures (Gibbs, 2008; Blake et al., 2012; Guzman et al., 2013; Hancock and Revill, 2013; Ponton et al., 2014; Cooper et al., 2015a). The compound-specific isotope analysis (CSIA) measures the δ^{13}C or δ^{2}H isotope signature of specific organic compounds associated with the organic matter bound to the soil and/or sediment. In contrast to using the concentration of biomarkers as sediment tracers, the specific δ^{13}C signature of biomarkers is assumed to be preserved during degradation and transport processes (Marseille et al., 1999; Hughen et al., 2004; Wiesenberg et al., 2004; Drenzek et al., 2007; Gibbs, 2008). As such, the CSIA method has already been successfully applied to link organic matter of sediments in estuarine or lake deposits and to differentiate qualitatively between sources from algae, bacteria, zooplankton and higher plants and thus from terrestrial and aquatic sources (Galy et al., 2011; Tolosa et al., 2013; Fang et al., 2014; Ponton et al., 2014). In quantitative sediment source attribution approaches, the precision of the method was constrained by the nonsignificant differences in the isotope signals between the different sources (Gibbs, 2008; Blake et al., 2012), especially if organic matter in sediment sources was dominated by C3 plant vegetation (Blake et al., 2012; Cooper et al., 2015a). The difficulty to distinguish sediment sources from soils of C3 vegetation land cover by CSIA of δ^{13}C in biomarkers implied (i) a restriction to sources with vegetation shifts from C3 plants to C4 grasses, which are considerably higher in δ^{13}C values (Ficken et al., 2002; Quenea et al., 2006; Gibbs, 2008; Hancock and Revill, 2013; Cooper et al., 2015a); (ii) achieving more effective discrimination by including information on δ^{2}H of *n*-alkanes (Cooper et al., 2015a); or (iii) including additional geochemical mineral tracers for the fingerprinting (Blake et al., 2012), which is useful with obvious shifts in geologic bedrock of the soils. The above approaches restrict the application of biomarkers as sediment tracers either to specific landscape settings (shift in geologic bedrock, shift from C3 to C4 plant cultivation) and/or complicate the analytical procedures (additional analysis of complex geochemical patterns or additional laborious analytical investigations on CSIA of biomarkers).

In this study, we used the δ^{13}C of fatty acids (FAs) to discriminate between soil sources of different land-use types (forest, pasture and arable land). Plants generally produce a set of similar FAs, however the abundance and the carbon stable isotopic signature (δ^{13}C) of those biomarkers have been reported to be different not only between aquatic organisms compared to terrestrial organisms but also between different taxa of terrestrial C3 plants, such as angiosperms and gymnosperms, or between trees and herbs (Chikaraishi and Naraoka, 2007; Pedentchouk et al., 2008; Tolosa et al., 2013). Because of their polar nature, FAs are easily leached from the plant – or from the decaying plant material – and become tightly bound to soil particles. If source soils from differing land cover fail to have significantly different CSSI signatures, this might be due to one or a combination of the following reasons: measurement imprecision of CSIA (procedural error), soil heterogeneity and low sample numbers, and/or changes in land use (former forests might now be grasslands or grasslands might now be arable soils, and as such, today's source soils might have mixed signals).

In contrast to previous studies, we selected a relatively simple setting with only three land-use types to evaluate whether or not sediment origin from soils with C3 plant cover can solely be differentiated by CSSI signature. The constrained setting will allow evaluation of the validity of the assumption that CSSI signature is preserved during degradation and transport. Further, results may be verified against Schindler Wildhaber et al. (2012a) who attributed sediment source origins using bulk isotopic signatures (δ^{13}C and δ^{15}N) in the same study area. The latter was possible due to a shift from calcareous to siliceous bedrock that coincided with a shift in land cover. Forests in the study area are on calcareous bedrock with a pronounced topography which makes a previous land use as grassland or arable soil very unlikely.

Our aim was sediment source attribution from three different land-use types within the Enziwigger catchment (Canton Lucerne, Switzerland) to: (i) evaluate differences of δ^{13}C signature in FAs of soil samples from possible sediment source areas dominated by C3 vegetation land-use types, (ii) compare the CSSI source signatures to the signals of suspended sediments captured in the river during a previous 2-year study (2009–2010), and (iii) attribute suspended sediments quantitatively to their sources.

2 Materials and methods

2.1 Site description

The river Enziwigger is a small and canalized river located in the Canton Lucerne, Switzerland, near Willisau, with a watershed size of 31 km^2. The flow regime at the sampling sites is not affected by any hydropower or waste water treatment plants. The ecomorphology of the river has been strongly modified and currently only 5 % is close to natural. Terraces have been installed to prevent deep channel erosion and scouring of the bed during flood events. Three experimental sites A, B and C (from upstream to downstream, see Fig. 1) were installed at altitudes of 757, 625 and 583 m above sea level, respectively. For complete experimental setup and additional study site information, please see Schindler Wildhaber et al. (2012b).

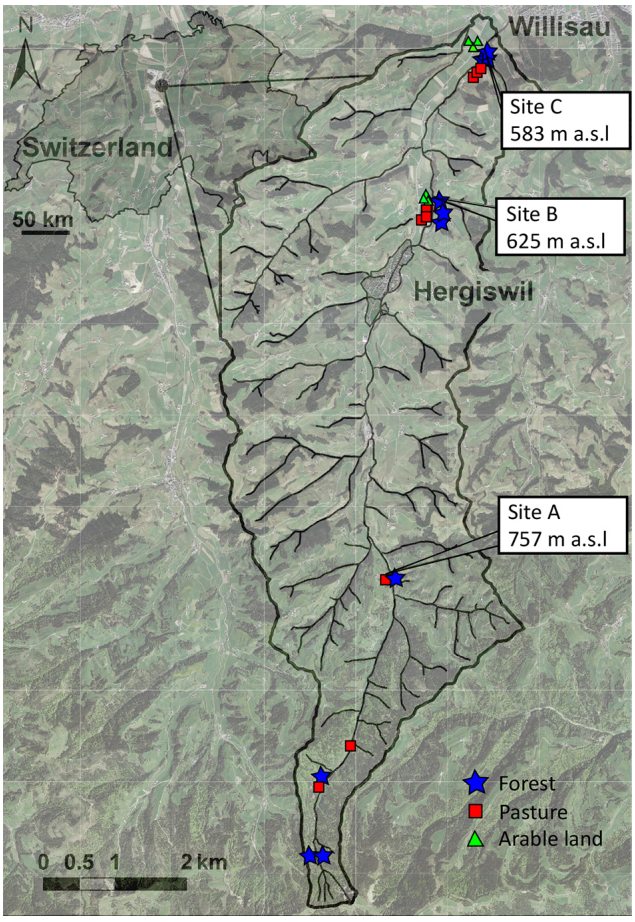

Figure 1. The Enziwigger catchment (Canton Lucerne, Switzerland) with the three suspended sediment sampling sites A, B, C and location of the source soil sampling spots forest, pasture and arable land.

2.2 Suspended sediment sampling

Suspended sediments were sampled at three sites A, B and C along the river (Fig. 1); the site A being near the headwaters of the catchment is under forested and pastured land covers, while river sections at site B and C are potentially influenced by pastures (C3 grasses only), forest (mainly coniferous) and arable land (mainly wheat production, some maize in single years but with no detectable effect on stable isotope signature of soils; Schindler Wildhaber et al., 2012a). The riverbanks have not been considered as original separate sources to river sediments since there is either a continuum of forest or grassland soils down to the riverbanks or small grassland riverbanks act as intermediate deposits to sediments from source soils. Further, we did not include riverbed in our analysis, since riverbed sediments themselves (e.g., the underlying bedrock) should not influence the CSSI signal as the fraction of petrogenic organic carbon is expected to be low with no significant contribution of FAs to the sediments. The latter might be a source of error during storm flow events but most likely not for base flow conditions with low sediment contribution (Galy et al., 2015). If riverbed material contains biospheric FAs, these should be either originating from terrestrial sources, which will be attributed in our analysis to the original source, or should be of aquatic origin which requires the identification of riverine FA production not connected to sediment transport (see below).

Suspended sediments (SS) were collected weekly at the three investigated sites with time-integrated SS samplers, according to Phillips et al. (2000). For more detailed information, see Schindler Wildhaber et al. (2012b).

Water level at the three sites was measured in 15 s intervals with pressure transmitter probes (STS, Sensor Technik Sirnach, Switzerland). Average values were logged every 10 min. For detailed experimental setup, see Schindler Wildhaber et al. (2012b).

2.3 Soil sampling

Upstream of each of the three sites A, B and C, representative soil samples of each land-use type (i.e., forest, pasture and arable land) were taken. Each soil sample represents a composite sample of three cores. In addition, each site was sampled in triplicates (see Fig. 1 for the location of the source area sampling sites). For the forest sites, the humus layer was removed prior to sampling. The upper 5 cm of the topsoil were sampled with a cylindrical steel ring (98.2 cm^3) and then stored in plastic bags.

After collection, soil samples were stored in a fridge at 4 °C. For analysis of carbon and nitrogen contents in the soil and SS, the samples were oven dried at 40 °C for at least 48 h, roughly ground in a mortar, and stones as well as root material were removed. The samples were ground with a ball mill (Retsch MM400, Retsch GmbH, 42781 Haan, Germany) for 90 sec at a frequency of 24 s.

2.4 Carbon and nitrogen analysis

The milled samples were analyzed for organic and inorganic carbon as well as for nitrogen contents. Total nitrogen was measured with a LECO CN628. Total organic carbon (TOC) and total inorganic carbon (TIC) were analyzed on a LECO RC612 (LECO, St. Joseph, Michigan 40985, USA).

2.5 Lipid extraction and preparation

Soil samples (11–21 g) and suspended sediments (4.5–25 g) were extracted using the method of Elvert et al. (2003). For quality and quantification control purposes, an internal standard (i.e., nonadecanoic acid) with known concentration and $\delta^{13}C$ isotopic value was added to the samples prior to extraction.

Extraction was performed by ultrasonication of the soil and sediment samples, which were put in PTFE centrifuge tubes, using solvent mixtures of declining polarity. First, 25 mL of methanol (MeOH)–dichloromethane (DCM; 2 : 1,

v/v), followed by MeOH–DCM (1 : 1, v/v) and two steps with pure DCM were used for the ultrasonic extraction. In between the ultrasonication steps, the PTFE tubes were centrifuged (5 min at 4000 rpm, 0 °C). The supernatant was pooled in a separation funnel and partitioned against pre-extracted 0.05 M KCl solution. The organic phase at the bottom of the funnel was collected and evaporated under a stream of nitrogen. This resulted in the total lipid extract (TLE). Half of the TLE was removed and stored as backup in the freezer at −20 °C. The other half was transferred to a 5 mL reaction vial and 1 mL of 12 % KOH in MeOH for saponification was added. Saponification was maintained at 80 °C for 3 h. After cooling down, 1 mL of 0.1 M KCl was added. The neutral lipid fraction was then extracted from the basic solution by agitating four times with ca. 2 mL hexane, dried under a stream of nitrogen and stored in the freezer at −20 °C. The remaining solution was set to pH 1 with concentrated HCl. Free FAs were extracted by again agitating four times with ca. 2 mL hexane. The extract was evaporated almost to the point of dryness under a stream of nitrogen, and then 1 mL of 12–14 % BF_3 in MeOH was added. Methylation reaction of free FAs to FA methyl esters (FAMEs) took place at 60 °C for 1 h. The last hexane extraction step (see above) in the presence of 1 mL 0.1 M KCl was performed. The final extract was dried under a stream of nitrogen and stored in the freezer at −20 °C. Samples were extracted in three different extraction batches. To monitor the quality of lipid extraction batches and the analysis performance, one control sample (pasture at site C) was extracted in each extraction batch (in triplicate) and included in the further analysis.

2.6 Gas chromatography and isotope ratio mass spectrometry

Concentrations of FAMEs were determined by using a Trace Ultra gas chromatograph (GC) with a flame ionization detector (FID; Thermo Scientific, Walthalm, MA 02451, USA). GC oven temperature started at 50 °C and was increased to 150 °C at a rate of 10 °C min^{-1}, held for 1 min, increased to 300 °C at a rate of 4 °C min^{-1} and held for 63 min. The carrier gas helium was set to a constant flow of 1 mL min^{-1}. Injector temperature was set to 300 °C and the detector temperature to 320 °C. Concentrations of FAMEs were calculated relative to the internal nonadecanoic acid standard, which was added prior to the extraction. For error estimation, triplicates from the control soil (see above) were analyzed. Standard deviation was < 5 % for all FA concentrations (see Sect. 2.7.).

The FAMEs were identified using the same Trace Ultra GC as above, coupled to a DSQ mass spectrometer (Thermo Scientific). The GC-MS is equipped with the same injector and capillary column and uses the same method as described above. Transfer line temperature to MS was set to 260 °C. Stable carbon isotope compositions of the FAMEs were analyzed 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). The system is equipped with a split–splitless injector, operated in splitless mode. The combustion oven was set to 1000 °C. GC oven temperature started at 50 °C and was increased to 140 °C at a rate of 10 °C min^{-1}. Temperature was held for 2 min and increased to 300 °C at a rate of 4 °C min^{-1} and held for 35 min. The carrier gas helium was set to a constant flow of 1.2 mL min^{-1}. Injector temperature was set to 300 °C. Carbon stable isotope ratios were reported in delta notation, per mil deviation from Vienna Pee Dee Belemnite (VPDB). The system was externally calibrated with an isotopically characterized n-alkane mixture (B3) obtained by Arndt Schimmelmann (see http://pages.iu.edu/~aschimme/hc.html). 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 and had an analytical uncertainty lower than ±0.5 ‰.

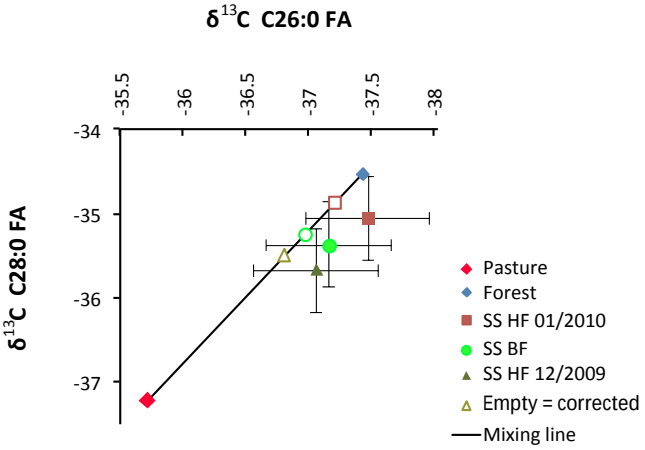

Figure 2. $\delta^{13}C$ of the FAs C26 : 0 and C28 : 0 in suspended sediments (SS) of two high flow (HF) and one base flow (BF) events and the two possible sediment sources from the land-use types pasture and forest at site A. Considering measurement uncertainty, $\delta^{13}C$ were corrected to the mixing line. Error bars of SS display the measurement error of 0.5 ‰.

2.7 Procedural error and measurement precision

Measurement precision of the GC-IRMS is 0.5 ‰. However, considering the analytical uncertainty only (e.g., checking an externally added standard) might neglect uncertainties, which bias the interpretation of isotope data. We recommend analyzing single samples of the source soils repeatedly as procedural controls to estimate the reproducibility within the analysis procedure (from taking the soil sample out of the sample bag, via the lipid extraction, methylation, identification and quantification of FAs up to the final determination of the CSSI) as well as the heterogeneity in one sample bag. We analyzed three samples out of the same sample bag (control soil), including lipid extraction (pasture, site C), which

resulted in an overall procedural standard deviation of 0.13, 0.84 and 0.26 ‰ δ^{13}C for C14 : 0, C26 : 0 and C28 : 0 FAs, respectively.

For assessment of the source heterogeneity, we report the standard deviation of the different sampling spots within our source areas (see the Supplement; Table S1). To establish mixing lines for sediment source attribution, we calculated mean values of source areas (Figs. 2 and 3). Deviation of CSSI of suspended sediments from the mixing line should not be greater than the procedural error or the measurement precision otherwise contribution of additional sources and/or isotope fractionation during degradation cannot be excluded. For unmixing of the suspended sediment signature we decided to use the measurement uncertainty of 0.5 ‰ rather than the FA specific procedural error because the latter was even smaller for the C14 : 0 and the C28 : 0 FAs. In case of the C26 : 0 FA, a smaller value of the measurement uncertainty is tightening our requirements in respect to the sediment source attribution to the SS (e.g., the even larger error of 0.84 ‰ would allow a larger correction to the mixing line than we actually needed to do).

2.8 Unmixing of suspended sediment signatures

Deducing from mathematical constraints, it is possible to find unique algebraic solutions for the sediment source attribution with n tracers for $n+1$ sources resulting in an equation system with $n+1$ equations and $n+1$ unknown variables. Mixing models such as IsoSource (Phillips and Gregg, 2003) or, more recently, Bayesian mixing modeling (e.g., Smith and Blake, 2014; Cooper et al., 2015b) have been employed to establish confidence intervals around the estimates. IsoSource (Phillips and Gregg, 2003) relaxes the strictly linear system and allows for multiple solutions, but without explicit incorporation of source and suspended sediment variability. The multiple valid solutions to the linear system produced by IsoSource can be plotted in a histogram-like fashion, although unlike Bayesian models, they do not represent probability distributions, but rather simply the range of values that might be plausible given the geometry of the system.

In this study, we have a limited number of sources (two for site A and three for sites B and C). For site A, the forest as well as the pasture value was calculated as average from three sample areas. Since site B includes subcatchment A and B, and catchment C includes A, B and C, these values include three forest and/or pasture areas from each site A and B and C, respectively. Accordingly, the arable land value consists of three areas for site B and six for site C. The averaged agricultural land value at site B consists of six pasture areas (A, B) and three arable land areas (B), and at site C, nine pasture areas (A, B, C) and six arable land areas (B, C). Standard deviations of the averaged values are given in Table S1. Due to the linear arrangement of the problem, we prefer the calculation of a unique algebraic solution that includes the uncertainty ranges resulting from the measurement uncertainty.

In case deviations from the mixing line occur that lie within the measurement uncertainty of 0.5 ‰, we consider it valid to correct the measured isotope signals to the mixing line. The corrected value corresponds to the intersect of the mixing line and a normal through the measured value. We applied IsoSource with a tolerance value equivalent to the measurement uncertainty, only if a unique algebraic solution was not possible due to the nonsignificant differences between the sources.

2.9 Weighting sediment source attribution according to FA content

The CSIA rather traces the FAs which bind to the soil particles as part of the organic matter than the mineral soil sediment itself. Therefore, results need to be adjusted to account for the different amounts of the FAs in each of the soil sources and to transfer signature contribution into soil contribution to suspended sediments:

$$\%\text{Soilsource}_n = \frac{(P_n/\text{FA}_n)}{\sum_n (P_n/\text{FA}_n)} \times 100,$$

where P_n is the proportion of soil n resulting from the unmixing of FA signatures, and FA_n is the sum of concentrations of FAs used for discrimination in the soil.

3 Results and discussion

3.1 CSSI signatures of terrestrial soil sources

From all FAs analyzed (even numbered from C14 : 0 to C30 : 0), the C18 : 0, C22 : 0, C26 : 0 and C28 : 0 FAs showed significant differences between the sources forest and pasture soil as well as forest and arable soil (see Tables S1 and S2). The C26 : 0 and C28 : 0 FAs resulted in greatest differences with highest significances between forest and agricultural land use (see Tables S1 and S2). For the difference between pasture and arable land, only the CSSI of the C14 : 0 FA was significantly different ($p < 0.043$). Thus, we found four tracers to differentiate between sediment sources from forest and agricultural land use (pasture and arable land) but only one tracer (C14 : 0) to distinguish pasture and arable land sediment contribution. In our study, with a maximum of three different land-use types (forest, grassland and arable land), we should be able to separate the source attribution at all our sites with two tracers without the use of mixing models.

3.2 Unmixing of suspended sediment signatures

Following the theoretical concept of n tracers with $n+1$ sources, we only need one tracer for site A where sediments might originate from only two different land-use types. However, using only one tracer, no mixing line can be established and deviations from mixing lines either due to the influence of an additional source or due to degradation during

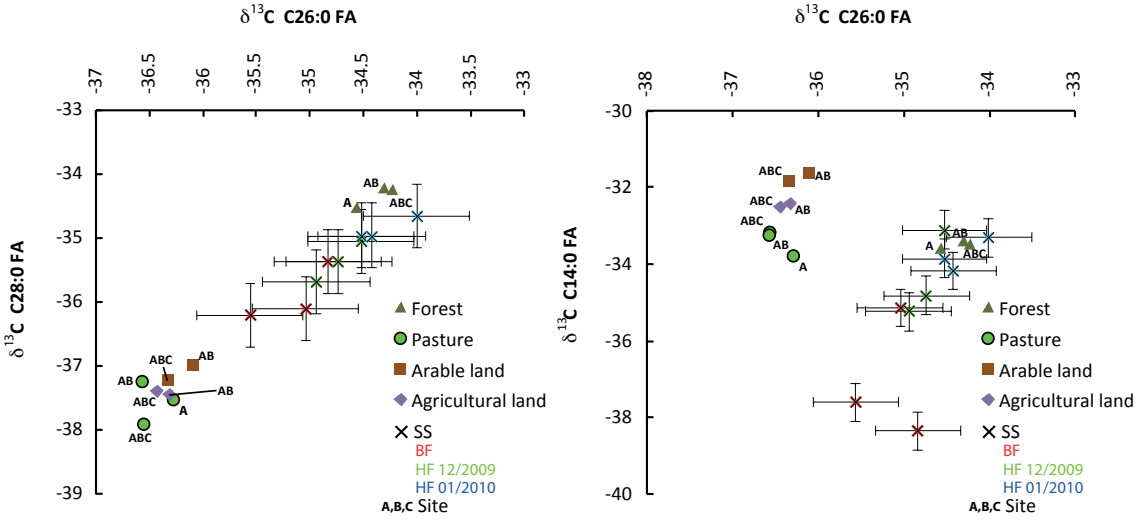

Figure 3. δ^{13}C isotopic signatures of FAs C26 : 0 vs. C28 : 0 (left) and C26 : 0 vs. C14 : 0 (right) of sediment sources and suspended sediments at the three sites (A, B and C) in the Enziwigger catchment. Error bars of SS display the measurement error of 0.5 ‰.

Table 1. Contribution of the different sediment source areas to the suspended sediment, calculated with the different methods and using two or three sources and two FAs as tracers (i.e., C26 : 0 and C28 : 0). Values in brackets represent the uncertainty ranges of the estimates.

		2 Tracer/2 Sources				2 Tracer/3 Sources (IsoSource)					
Site	Event	% Forest		% Agriculture		% Forest		% Pasture		% Arable	
A	BF	70.2	(40–100)	29.8	(0–47)						
A	HF 2010	85.0	(54–100)	15.0	(0–37)						
A	HF 2009	59.7	(31–92)	40.3	(12–55)						
B	BF	36.7	(12–60)	63.3	(51–72)	28.2*	(25–48)	16.6*	(0–56)	55.2*	(0–75)
B	HF 2010	93.5	(76–100)	6.5	(0–24)	92.1	(90–100)	2.4	(0–8)	5.5	(0–10)
B	HF 2009	78.1	(59–100)	21.9	(0–41)	69.5	(61–93)	9.4	(0–31)	21.1	(0–39)
C	BF	34.3	(15–57)	65.7	(33–79)	31.8	(38–58)	23.6	(0–56)	44.6	(0–62)
C	HF 2010	71.5	(53–100)	28.5	(0–37)	64.7	(67–93)	12.3	(0–29)	23.0	(0–33)
C	HF 2009	54.7	(35–85)	45.3	(10–55)	49.2	(52–80)	17.7	(0–42)	33.1	(0–48)

HF = High flow; BF = Base flow. * For BF sediment contribution at site B a unique solution was possible.

transport will not be recognized. The latter can be overcome due to the fact that several significantly different tracer signals should result in the same calculated source attribution. This is the case if the suspended sediments plot exactly on the mixing line between the two different tracers. In general, whether or not using a mixing model, the isotopic values of the sediment mixture being evaluated must be within the isotopic values of the source endmembers (Phillips and Gregg, 2003). In our case, suspended sediments are not exactly on the mixing line between the two source soils (Fig. 2), which resulted in differences of up to 15 % for source attribution at site A using either the C26 : 0 or the C28 : 0 FA. Since the deviation from the mixing line is within the uncertainty associated with the measurement precision of 0.5 ‰, we consider it valid to correct the measured isotope signals in forcing them on to the mixing line for sediment source apportionment (Fig. 2). When using the stable isotope signals which were corrected to the value at the intersect of the mixing line and a normal through the measured value, sediment source attribution results in the same source attribution for both tracer applications (Table 1). The question whether the CSSI signature is preserved during degradation and transport cannot be answered with absolute certainty. We observe a small but systematic deviation of the SS signal from the mixing line (Fig. 2), which could be due to a small contribution from an additional source and/or a slight degradation of the signal during transport processes. Nevertheless, the effect is very small and lies within the magnitude of the measurement uncertainty.

The only FA resulting in significant differences between tracer signals of soils from the two land-use types pasture and arable land was the C14 : 0 FA (see Tables S1 and S2). However, using this FA as a tracer did not lead to meaningful solutions (e.g., negative sediment source contributions), because

the isotopic values of the sediment mixture (suspended sediments) were not within the isotopic values of the source endmembers (Fig. 3, right). No set of source proportions is possible if the isotope mixture of the suspended sediments is outside the convex polygon bounded by the sources (Phillips and Gregg, 2003). Short-chain and medium-chain FAs (C12 : 0 to C16 : 0) are not only produced by higher plants but also by microorganisms and algae, mainly by aquatic algae (Lichtfouse et al., 1995; Huang et al., 1996; Hughen et al., 2004; Eglinton and Eglinton, 2008; Freeman and Pancost, 2014). As such, the C14 : 0 FA signals we determined in the suspended sediments were most likely influenced by aquatic contribution as an additional source. The latter is confirmed by the generally higher concentrations of C14 : 0 FAs in our SS compared to source soils, as well as in base flow SS compared to high flow SS (Table S1), which indicated the potential riverine origin. Thus, even though short-chain and medium-chain FAs have been used to track terrestrial sediment contribution to rivers (Gibbs, 2008; Blake et al., 2012; Hancock and Revill, 2013), we would highly suggest constraining the concept of tracking terrestrial sediments to the long-chain FAs (C24 : 0 to C30 : 0).

Because of the nonsignificant differences between the CSSI signatures of long-chain FAs of pasture and arable land (Fig. 3), we can solve the sediment contribution at sites B and C only for two different sources: forest vs. agricultural land (the latter averaging the signals from pasture and arable land). The algebraic solution was also used for site A, correcting suspended sediment isotope signals of both FAs to the mixing line of sediment sources.

Aggregating the data from the land-use types pasture and arable land is useful, not only because of the nonsignificant difference between the sources but also because the combined source group has a functional significance (agricultural vs. forest land use). However, a separation between pasture and arable soil sources might seem desirable from catchment management perspectives. If we want to distinguish between pasture and arable land using the nonsignificant source signal differences of C26 : 0 and C28 : 0 as tracers, the mixing model IsoSource is useful. IsoSource constrains the relative proportions of the various sources in the mixture by evaluating all possible combinations of each source contribution (from 0 to 100 %). Even though we used the model to calculate sediment source contribution from all three sources (Table 1), we are fully aware that the separation between pasture and arable land cannot be considered statistically sound.

Because we trace with CSIA the FAs rather than the soil itself, the results given by the unmixing of the δ^{13}C signals of FAs need to be adjusted to account for the different FA contents of each of the soil sources. Based on the available literature, the percentage of carbon content at each source was used to weight sediment source attribution (Gibbs, 2008; Blake et al., 2012; Hancock and Revill, 2013). However, the relative carbon distribution in each source might be very different to the relative distribution of the specific tracer FA

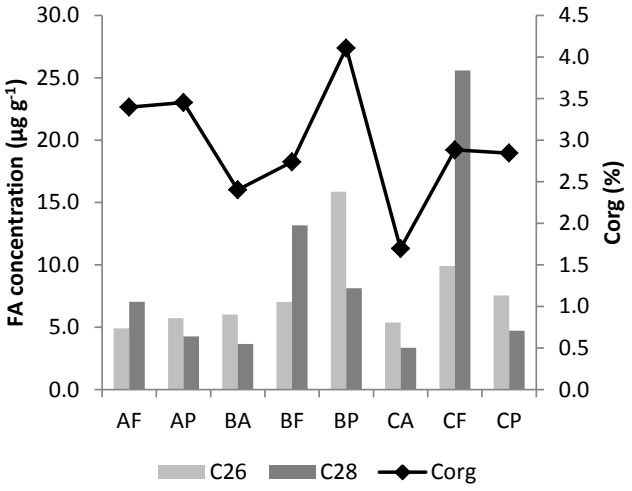

Figure 4. FA concentration compared to % C_{org} at the source sites. The first letter gives the site notation (sites A, B, C) while the second letter indicates the land-use type (F is forest, P is pasture, A is arable land).

(Fig. 4). Since we used FAs as tracers and not the total soil organic carbon, we corrected with the concentration sum of the respective FAs (see Methods section). The difference between these two correction approaches might be considerable. In our study, a correction using the soil organic carbon content overestimates forest contribution and underestimates arable land up to 13 %. However, depending on the site-specific differences in the relation of soil organic carbon to specific FA content, the uncertainty introduced might be even higher at other study locations. Further, if quality and characteristics of bulk soil organic carbon (SOC) is variable between sources, degradability during detachment and transport might also be very different, which will increase uncertainty if correction is carried out with bulk SOC. Thus, we highly recommend for future CSIA studies to correct with the sum of FA content and not with the soil organic matter content.

3.3 Apportionment of suspended sediment during high and base flow

Following the above sediment source attribution approach, 30 and 70 % of sediments at site A originated from pastures and forests, respectively, during base flow (Table 1). Downstream, at sites B and C, sediments from agricultural sources increase considerably during base flow (65 % from agricultural sources and 35 % from forests) reflecting the contribution from more intensively used arable land and pasture. At the two investigated high flow events, sediment sources varied considerably at site A (between 15 and 40 % from pastures and between 60 and 85 % from forests) and site B and C (contribution between 6 to 45 % from agricultural land and

55 to 93 % from forests), with sediment contribution from forests clearly being dominant during high flow events.

Our findings are consistent with the outcome of Schindler Wildhaber et al. (2012a) where sediment source attribution was achieved with bulk isotope signals (the latter was feasible due to the change in geology from calcareous bedrock under forest soils and siliceous bedrock under agricultural soils).

The results of our study indicate that connectivity of sediment source areas with the river change from base to high flow regime. Management options to decrease sediment peaks during storm events should thus aim at adapted forest management (e.g., increasing soil and understory vegetation). The dominance of forest soil sources to sediment contribution during high flow is an important and surprising result since typically agricultural areas are in the focus of soil conservation management. The larger forest contribution is likely conditioned by the extremely steep slopes and loosely structured calcareous soils under forests compared to the flat arable land on siliceous bedrock in the Enziwigger catchment.

Separation between the agricultural land-use types pasture and arable soil with IsoSource pointed to the same direction as the unique algebraic solution regarding the high forest contributions during high flow (Table 1). The difference between the IsoSource results and our unique solutions regarding the forest contribution is between 3 and 15 % at sites B and C. Sediment source attributions according to the IsoSource modeling at sites B and C from pasture are 20–30 % during base flow and 5–20 % during high flow and from arable land 45 % during base flow and 10–30 % during high flow. However, these separations within the agricultural land uses should be considered with caution, as tracer signals of sources are not significantly different.

As rivers are slowly but progressively recovering from the effects of acidification, eutrophication and pollutant contamination (Alewell et al., 2000, 2001; Palmer et al., 2010; Layer et al., 2011), the expected increase of sediment input to rivers in the future is an unsolved problem (Scheurer et al., 2009; Matthaei et al., 2010). Without assessing sediment sources and their connection to different land-use types, catchment management will be impeded to make progress in sediment load reduction. Because of the work and cost-intensive analytical procedures, CSIA might be far from being used as a regular management tool. Nevertheless, it might give insight into sources of sediments in some selected study areas. Furthermore, with the rapid improvement of analytical tools in recent years, CSIA has all the potential to become a key decisional tool for investigating highly selective point measurements, where sediment origin and thus catchment management options are unclear. As such, research development targets should be directed towards biomarker tracer approaches with the least possible analytical effort, using low numbers of tracers set up for straightforward iso-space evaluations.

4 Conclusions

Our aim was a rigorous, quantitative sediment source attribution with CSIA of FAs from three different land-use types (forest, pasture and arable land) dominated by C3 vegetation only. We found significant differences between forest and agricultural soil sources for four of the investigated FAs (i.e., C18 : 0, C22 : 0, C26 : 0 and C28 : 0). Only one FA (C14 : 0) resulted in significant differences between pastures and arable land, but a discrimination within these two agricultural sources was not possible, because results indicated a likely influence of aquatic contribution to the CSSI of this short-chain FA. We recommend focusing on long-chain FAs (C24 : 0 to C30 : 0) only for sediment source attribution from terrestrial sources. We further would like to suggest using compound content – in our case long-chain FA content – rather than soil organic matter content when converting the δ^{13}C signal of FAs into soil contribution.

Sediment source attribution resulted in high sediment contribution from forests during high flow conditions. In contrast, during base flow sediment input mostly originated from agricultural sources. Thus, connectivity of sediment source areas with the river changed with flow regime changes.

Catchment managers are often requested to take soil conservation decisions on the basis of land use, as different land-use types are connected to differences in soil erosion severity. Assuming the CSIA develops further to a routine analysis in the future, it might become a valuable decision support tool as a sound and scientifically accepted "fingerprint" to track down sediment origin. Small-scale studies with well-defined sediment sources and significant differences in CSSI signature may help to verify the suitability of the CSIA as a sediment fingerprint technique in fluvial systems.

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