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Interactive comment on "Sediment source attribution from multiple land use systems with CSIA" *by* C. Alewell et al.

Anonymous Referee #1

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General comments :

The study aims in using Fatty-Acids CSIA to better constraint the contribution of several terrestrial sources to sediment lowland river for management cathment purpose. The first general comment is that litterature is missing, misquoted and/or not relevant . It leads to surprising "recommendations" and "discussions" in the "results-discussion and conclusion" sections (e.g see specific comments below). I listed several articles about the use of FAs as tracers of terrigenous sources in sediments that might help authors. Secondly, the introduction is very confuse and it is not clear why the Authors did such tremendous analytical effort. The study of schindler et al., 2012, published in biogeosciences, succefully answered to the rationale of the apportion of terrestrial sources to sediments of the same experimental site (the same set of samples were

used in both studies), using δ13Ctot, δ 15N, δ 13Corg and C/N ratio. The objectives of the study should be revised. Finally, I totally agree with recommendations of previous reviewers. The manuscript is not acceptable in its current form for publication and doesn't match with the standard level of pubilcations in Biogeosciences. I hope that comments will help the authors to rework the manuscript for latter publication. The manuscript deserves to be published in Biogeosciences but not in its current form.

Specific Comments :

Introduction:

L34 &38: The use of the word impairment remains unclear "Biological impairment in freshwater" vs "Restoration of rivers from sediment impairment" . Could the authors specify what "impairment " means exactly.

L40-44: "Geochemical fingerprinting has been used to discriminate between sources of sediments and was successful in discriminating between subsoil and surface soils (Collins et al., 1997; Walling, 2013) but the technique is limited in providing significant differences between sources of different land use types and vegetation cover in complex landscapes (Alewell et al., 2008; Mabit et al., 2013; Mabit et al., 2014; Hancock and Revill, 2013. . .)" References are misquoted: In the paper of Walling, 2013, CSIA is included into the geochemical fingerprint. Alewell et al 2008 deals with carbon mineralization during the soil detachment from the upland to the wheatland. Hancock and Revill 2013, was a paper using CSIA to discriminate land use and vegetation sources. I think that the terminology "Geochemical fingerprint" have to be define to clarify what was its meaning for the authors.

L45: "If tracer signatures fail to be significantly different sources": Could authors be more explicit. "Tracer signatures" includes a large panel of "geochemical fingerprints" including CSIA that allowed for complex sources determination.

L45-49: the paragraph is confused.

L50-56: For “CSSI” the right abbreviation is CSSIs for Compound-Specific Stable Isotopes. The CSSIs being the result of the CSIA= Compound-Specific Isotopes Analysis and not “L54: Compound specific stable isotope analysis”. Then the authors should dissociate the “technique” and the fields of applications.

(1) The use of biomarkers such as fatty acids to identify the contribution of organic matter sources to soils and sediments was intensely studied (Colombo et al., 1997; Eglinton et al., 1968; Eglinton & Eglinton, 2008; Jandl et al., 2005; Jandl et al., 2002; Jeng & Huh, 2004; Madan et al., 2002; Marseille et al., 1999; Meyers & Ishiwatari, 1993; Meyers & Takeuchi, 1979; Naafs et al., 2004a; Naafs et al., 2004b; Nierop et al., 2005; Nierop et al., 2001; Perry et al., 1979; Sanchez-Garcia et al., 2008; van Dongen et al., 2000).

(2) The combinaison of biomarkers with stable isotope analysis also called CSIA was also widely used to determine the sources and the fate of organic matter in soils and sediments. (Drenzek et al., 2007; Eglinton & Eglinton, 2008; Ficken et al., 2000; Ficken et al., 2002; Glaser, 2005; Huang et al., 1996; Lichtfouse et al., 1995; Quénéa et al., 2006; Wiesenberg et al., 2004).

(3) The use of CSIA for erosion and catchment management purposes is more recent. I suggest two additional publications on the use of biomarkers and CSIA in suspended sediments (Seki et al., 2010; Shi et al., 2001). Furthermore, the first publication cited by the authors related to the use of CSIA for identifying “soil sources” in estuarine sediment dates back to 2008. We are in 2015. I suggest replacing “New technique” by “recent advances”.

I recommend completing the bibliography of the manuscript with some of the publications cited above. The Authors could select the most relevant for their study.

L66-72: “In quantitative sediment attribution approaches, the precision of the method was impeded by the non-significant differences in the isotope signals between the different sources (Gibbs, 2008; Blake et al., 2012), especially if organic matter in sed-

iment sources was dominated by C3 plant vegetation (Blake et al., 2012; Cooper et al., 2015b). The latter implied a restriction to (i) differ between sources with vegetation shifts from C3 plants to the warm-climate C4 grasses, which are considerably higher in δ13C values. . .” Why non-significant differences in the isotope signals when C3 plant vegetation dominated implied a restriction to differ between sources with vegetation shifts from C3 plants to the warm-climate C4 grasses, which are considerably higher in δ13C values. The sentence is confused.

L91: “reducing method uncertainty in reducing the complexity of the unmixing procedure.” It is the first time the authors introduce “the unmixing procedure”. The sentence is difficult to understand, and we don’t know “the unmixing procedure” refers to.

The introduction part is very confused. If I resume:

1-Conventional tracers used as geochemical fingerprint failed in differentiating sediment sources when it is too complex (for example several land use types for one catchment). 2- But a new technique, the CSIA allowed for this type of discrimination. 3- Nevertheless, the technique have some limitations: If vegetation coverage have the same phytosynthetically pathway (e.g. C3) the isotopic signal is not significantly different. 4- Finally, to achieve more effective discrimination it is better to include information on D/H of n-alkanes (???) (Question: why did the authors choose to work on FAs), and geochemical tracers for the fingerprint (that corresponds to the (1) of the introduction,) Authors go round in circles.

Materials and methods.

L176-177: Could the authors precise analitical uncertainties on concentrations. L194-196: “However, considering the analytical uncertainty only (e.g., checking an externally added standard) might neglect uncertainties, which bias the interpretation of isotope data” I don’t understand the meaning of the sentence.

L192: “We recommend analyzing single samples in multiplicities. . .” I suggest removing

the sentence. GC-C-IRMS analyses are always performed in replicate as conventional procedure in all serious laboratories.

Results and discussion

The discussion on multiple sources of fatty acids in sediments is very week. Your suggestion to constrain the track of terrestrial sediments to n-alkanoic acids > n-C22, is already largely recognize, See (Meyers & Takeuchi, 1979; Pearson & Eglinton, 2000; Shi et al., 2001, Galy et al., 2011), and references cited above. Furthemore, Authors cited Galy et al. 2011, and in this paper, it could be notice that only the FAs from C24 to C32 were used to track terrestrial sources in sediments. Short chain alkanoic acids are characteristics for algae, bacteria, aquatic microflora and microorganisms (Boon et al. 1975; Perry et al. 1979; van Vleet and Quinn 1979; Volkman 1986, Banowetz et al. 2006). I think that there is a confusion between the use of FAME microbial soil profiles as soil geochemical fingerprints in surface waters and the use of terrigenous FAs as tracers of vegetation and land use in sediments for erosion purpose. I also observed this confusion in Gibbs, 2008 and Blake et al., 2012.

These are the reasons that lead previous reviewers to reject the manuscript. When they asked "why authors did not consider alkanes but only FAs", authors answered "if we can do the attribution with FAs why increase analytical effort and use alkanes in addition?" This answer is surprising, because in Schindler et al 2012, authors analyzed the same set of samples for their δ13Ctot, δ 15N, δ 13Corg contents and C/N ratio, with the same rationale than in the present work. And they successfully answered to the initial scientific question. Why did Authors spend time consuming and expensive cost analysis, if isotopic analyses on bulk sediments,(which are less expensive analysis (in time and cost)) were shown to be sufficient. Indeed, long chain n-alkanes are more reliable than FAs concerning terrestrial sources attribution in sediments.

Colombo, J.C., Silverberg, N., Gearing, J.N., (1997) Lipid biogeochemistry in the Laurentian Trough–II. Changes in composition of fatty acids, sterols and aliphatic hydro-

carbons during early diagenesis. Organic Geochemistry, 26(3-4), 257-274. Drenzek, N.J., Montluçon, D.B., Yunker, M.B., Macdonald, R.W., Eglinton, T.I., (2007) Constraints on the origin of sedimentary organic carbon in the Beaufort Sea from coupled molecular 13C and 14C measurements. Marine Chemistry, 103(1-2), 146-162. Eglinton, G., Hunneman, D.H., Douraghi-Zadeh, K., (1968) Gas chromatographic-mass spectrometric studies of long chain hydroxy acids-Part II: The hydroxy acids and fatty acids of a 5000-year-old lacustrine sediment. Tetrahedron, 24(18), 5929-5941. Eglinton, T.I., Eglinton, G., (2008) Molecular proxies for paleoclimatology. Earth and Planetary Science Letters, 275(1-2), 1-16. Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., (2000) An n-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. Organic Geochemistry, 31(7-8), 745-749. Ficken, K.J., Wooller, M.J., Swain, D.L., Street-Perrott, F.A., Eglinton, G., (2002) Reconstruction of a subalpine grass-dominated ecosystem, Lake Rutundu, Mount Kenya: a novel multi-proxy approach. Palaeogeography, Palaeoclimatology, Palaeoecology, 177(1-2), 137-149. Glaser, B., (2005) Compound-specific stable-isotope δ13C analysis in soil science. Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde, 168(5), 633-648. Huang, Y., Lockheart, M.J., Logan, G.A., Eglinton, G., (1996) Isotope and molecular evidence for the diverse origins of carboxylic acids in leaf fossils and sediments from the Miocene Lake Clarkia deposit, Idaho, U.S.A. Organic Geochemistry, 24(3), 289-299. Jandl, G., Leinweber, P., Schulten, H.R., Ekschmitt, K., (2005) Contribution of primary organic matter to the fatty acid pool in agricultural soils. Soil Biology & Biochemistry, 37(6), 1033-1041. Jandl, G., Schulten, H.R., Leinweber, P., (2002) Quantification of long-chain fatty acids in dissolved organic matter and soils. Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde, 165(2), 133-139. Jeng, W.L., Huh, C.A., (2004) Lipids in suspended matter and sediments from the East China Sea shelf. Organic Geochemistry, 35(5), 647-660. Lichtfouse, E., Berthier, G., Houot, S., Barriuso, E., Bergheaud, V., Vallaeys, T., (1995) Stable carbon isotope evidence for the microbial origin of C14-C18 n-alkanoic acids in soils. Organic Geochemistry, 23(9), 849-852. Madan, R., Pankhurst, C., Hawke, B.,

Smith, S., (2002) Use of fatty acids for identification of AM fungi and estimation of the biomass of AM spores in soil. Soil Biology and Biochemistry, 34(1), 125-128. Marseille, F., Disnar, J.R., Guillet, B., Noack, Y., (1999) n-Alkanes and free fatty acids in humus and Al horizons of soils under beech, spruce and grass in the Massif-Central (Mont-Lozere), France. European Journal of Soil Science, 50(3), 433-441. Meyers, P.A., Ishiwatari, R., (1993) Lacustrine organic geochemistry-an overview of indicators of organic matter sources and diagenesis in lake sediments. Organic Geochemistry, 20(7), 867-900. Meyers, P.A., Takeuchi, N., (1979) Fatty acids and hydrocarbons in surficial sediments of Lake Huron. Organic Geochemistry, 1(3), 127-138. Naafs, D.F.W., van Bergen, P.F., Boogert, S.J., de Leeuw, J.W., (2004a) Solvent-extractable lipids in an acid andic forest soil; variations with depth and season. Soil Biology and Biochemistry, 36(2), 297-308. Naafs, D.F.W., van Bergen, P.F., de Jong, M.A., Oonincx, A., de Leeuw, J.W., (2004b) Total lipid extracts from characteristic soil horizons in a podzol profile. European Journal of Soil Science, 55(4), 657-669. Nierop, K.G.J., Naafs, D.F.W., van Bergen, P.F., (2005) Origin, occurrence and fate of extractable lipids in Dutch coastal dune soils along a pH gradient. Organic Geochemistry, 36(4), 555-566. Nierop, K.G.J., van Lagen, B., Buurman, P., (2001) Composition of plant tissues and soil organic matter in the first stages of a vegetation succession. Geoderma, 100(1-2), 1-24. Pearson, A., Eglinton, T.I., (2000) The origin of n-alkanes in Santa Monica Basin surface sediment: a model based on compound-specific [Delta]14C and [delta]13C data. Organic Geochemistry, 31(11), 1103-1116. Perry, G.J., Volkman, J.K., Johns, R.B., Bavor, H.J., (1979) Fatty-acids of bacterial origin in contemporary marine-sediments. Geochimica et Cosmochimica Acta, 43(11), 1715-1725. Quénéa, K., Largeau, C., Derenne, S., Spaccini, R., Bardoux, G., Mariotti, A., (2006) Molecular and isotopic study of lipids in particle size fractions of a sandy cultivated soil (Cestas cultivation sequence, south-west France): Sources, degradation, and comparison with Cestas forest soil. Organic Geochemistry, 37(1), 20-44. Sanchez-Garcia, L., de Andres, J.R., Martin-Rubi, J.A., González-Vila, F.-J., Polvillo, O., (2008) Use of lipid biomarker patterns as a proxy of environmental variability in the coastal sedimentary record from the Gulf of Cádiz

(SW Spain). Organic Geochemistry, 39(8), 958-964. Seki, O., Nakatsuka, T., Shibata, H., Kawamura, K., (2010) A compound-specific n-alkane delta C-13 and delta D approach for assessing source and delivery processes of terrestrial organic matter within a forested watershed in northern Japan. Geochimica et Cosmochimica Acta, 74(2), 599-613. Shi, W., Sun, M.-Y., Molina, M., Hodson, R.E., (2001) Variability in the distribution of lipid biomarkers and their molecular isotopic composition in Altamaha estuarine sediments: implications for the relative contribution of organic matter from various sources. Organic Geochemistry, 32(4), 453-467. van Dongen, B.E., Rijpstra, W.I.C., Philippart, C.J.M., de Leeuw, J.W., Damste, J.S.S., (2000) Biomarkers in upper Holocene eastern North Sea and Wadden Sea sediments. Organic Geochemistry, 31(12), 1533-1543. Wiesenberg, G.L.B., Schwarzbauer, J., Schmidt, M.W.I., Schwark, L., (2004) Source and turnover of organic matter in agricultural soils derived from n-alkane/n-carboxylic acid compositions and C-isotope signatures. Organic Geochemistry, 35(11-12), 1371-1393.

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