Dear Editor,

Thank you for allowing us to submit a revised version of our manuscript. We greatly appreciate the detailed and constructive comments of two reviewers and two short comments which helped us to improve the manuscript. We addressed all comments as attached below (highlighted in blue) and hope that we adequately solved the requests.

With kind regards,
Xiaojuan Feng

(We attached a version of the manuscript and the supplement with changes highlighted at the end of this pdf.)

Interactive comment on “Multi-molecular tracers of terrestrial carbon transfer across the pan-Arctic – Part 1: Comparison of hydrolysable components with plant wax lipids and lignin phenols” by X. Feng et al.

RC C1463: 'Reviewer comments', Gesine Mollenhauer (Referee #1), 20 Apr 2015

In the study presented by Feng and co-authors, results from an analysis of hydrolysable organic matter in Arctic river-influenced sediments are discussed. The authors focus on the information contained within the molecular marker concentrations of terrigenous organic matter and interpret their results in context of transfer of terrestrial carbon to the Ocean in the Arctic.

The manuscript is well written, and the results are reported in great detail. The study is mainly interesting because hydrolysable OM is rarely investigated, and the information contained within remains largely unexplored. The discussion consequently focuses on how the individual biomarker abundances and biomarker indices could relate to catchment characteristics and how they can inform about sources and pathways of transport. The study is based on only a few sediments, in most cases only one sample per river (except the Colville river, where 2 samples are analysed). Thus the data are likely no accurate characterization of the entire systems. The authors are careful not to deduce any far-reaching conclusions from this limited data set but focus rather on discussing the relative abundances of the individual biomarker groups between the samples, taking into account only some general water shed characteristics (wetland and forest coverage). Generally I thus think that this paper is an interesting contribution to Biogeosciences presenting some novel aspects of organic geochemical research in the Arctic.

However, there are some aspects that I think deserve more consideration and might require some revisions in the manuscript. The major issue I have is that sediments recovered off the mouths of Arctic rivers (Ob’, Yenisey, Lena, Kolyma, Indigirka, Mackenzie, Kalix) likely in various water depths (please add this information to table 1) and at variable distances from the river mouths are compared with material collected from a river bank (Yukon) and directly from the ice covering the river during the spring flood (Colville). While the latter clearly cannot accurately be called sediments, and it is debatable for the Yukon material as well, the authors do not discuss how the differences in the materials might explain much of the variability. The samples from the ice and the river bank will most likely differ in grain-size, age, mineral content, not to mention marine organic matter and inorganic matter contributions, which will affect at least the biomarker concentrations (bulk and OM normalized). I think that it has to be made clear in several locations of the text that different types of material are discussed here. It is for example evident from Figure 2 and most clearly from the PCA (displayed in Figure 8) that the Colville and Yukon materials are different from the marine sediments. Part of the explanation for this discrepancy might be the lack of a marine influence (e.g., by leading to aggregation and flocculation of dissolved and colloidal terrigenous OM when salt water is encountered), which is not mentioned here at all. Overall, I think that the authors need to consider the individual sample settings more carefully before discussing differences between the samples. Besides, it might also be useful to point out that the few samples analysed here, albeit their general agreement with more extensive published data sets from the individual river mouth influences regions (Fig. 5), might not be ideal representatives of the catchment characteristics.

Water depth is added in Table 1. Please also note that there was a typo regarding the latitude and longitude of Lena and Indigirka sampling location in the original Table 1--these are corrected now together with an updated Figure 1. The distribution of permafrost is adjusted to combine discontinuous, sporadic and isolated permafrost.

While “sediment” is used as a general term to describe any deposits derived from aquatic systems (such as riverbank sediment, floodplain sediment, riverbed sediment, etc.), we agree with the reviewer that the Yukon and Colville samples are very different from surface sediments collected from the other river systems and we use more specific terms for their first description in the Method section:

> "A sample of freshly deposited fine-grained fluvial sediment was collected from the Yukon near Pilot Station, Alaska during ice breakup in June 2007. The Pilot Station is considered to be the lowest reach of the river where streamflow is not affected by the Bering Sea and the outflow point for the entire Yukon River basin."
>
> "Two samples were collected from fresh mud that was deposited on the surface of river ice prior to ice break-up close to (within 40 km of) the river mouth in June 2007."

Also, to differentiate from marine surface sediments, we used the term "sedimentary particles" to replace "sediments" where appropriate in the paper.

However, the Colville sample is most likely an accurate reflection of the fluvial suspended load during the freshet, as it was spilling out on top of the ice. We also know that the majority of estuarine sediment is delivered from the rivers during the freshet. Finally, in a paper (Hussain et al., 2015) currently in review there is a comparison of the bulk and molecular composition of suspended, riverbank and floodplain lake sediments in the Mackenzie delta (including lignin phenol data), and the general conclusion is that the deposited material very much looks like the suspended load at freshet. Hence the Colville samples are most likely an accurate reflection of the fluvial suspended load of sedimentary particles during the freshet and represent terrestrial organic matter transported to the river mouth. This explanation is added in the Methods section.

We acknowledge that it is not perfect to employ different sampling strategies for cross-river comparison of sedimentary OC compositions and samples from estuary, shelf edge and within river may be subject to different degree of hydrodynamic sorting. We have added a paragraph in the sampling methods to highlight the method differences and to discuss the potential effects:

> "The contrasting sampling strategies and sample types recovered from the various river systems (estuarine sediments for GRARs and Kalix versus shelf edge sediments for Mackenzie and fluvial deposits near river mouth for Yukon and Colville) may lead to varied contribution and concentrations of terrestrial, marine and relict carbon in the bulk OC. However, for locations where we have compared characteristics of the fluvial suspended load, or where appropriate data is available (i.e., Mackenzie; Vonk et al., submitted; Hussain et al., unpublished data), strong compositional similarities exist between suspended sediments and sediment deposits (on riverbank or riverbed). Therefore, observations described herein should be valid for the basin-scale comparison of the fate of various terrestrial OC biomarkers and their environmental controls, and we focus on the transformation and relative ratio of terrestrial components in the sedimentary OC only. Potential compositional variations induced by sampling methods are discussed in detail in the results."

We also add a section explaining possible variations in sediment texture induced by the sampling method and its effect on OC composition on Page 18:

> "As the Yukon and Colville samples were collected near the river mouth as riverbank and ice deposits, respectively, they had undergone a shorter transport journey and were subject to less hydrodynamic sorting relative to the estuarine sediments of GRARs/Kalix and the shelf edge sediment of Mackenzie. Although we did not conduct grain size analysis on these pan-arctic sediments, the Yukon and Colville samples were possibly enriched with fine-grained materials derived from mineral soils in comparison with the coarser materials accumulated near river mouths and along the shelf (Hedges and Mann, 1979; Keil et al., 1998). Such processes may

> contribute to the enrichment of belowground OC associated with fine-grained materials in the North American samples."

In the Results and Discussion, we add additional sentences elaborating compositional variations potentially caused by different sampling methods (Pages 9, 11-12 and 18-19).

The PCA model is however built on terrestrial biomarker-derived parameters and is hence not influenced by the varied inputs of marine and relict OC in different sedimentary samples. This consideration is added on Page 17. Furthermore, we have modified our PCA model by using an Arcsine transformation to return the proportional data (i.e., biomarker-derived parameters) set to a normal distribution. The method details are added in the Data Analysis section:

> "All ratios were expressed as proportions (with the numerator parameters repeated in the denominator), an Arcsine transformation (calculation of the square root followed by the arcsine) was used to return this proportional data set to a normal distribution, and then data were autoscaled before PCA (Mos et al., 2006). "

Results of the modified PCA model are shown in Figure 8 (with more details in the figure caption). The results are remarkably similar to those of the old model. Explanations on Page 18 are modified accordingly.

Added references:

Keil, R. G., Tsamakis, E., Giddings, J. C., and Hedges, J. I.: Biochemical distributions (amino acids, neutral sugars, and lignin phenols) among size-classes of modern marine sediments from the Washington coast, Geochim. Cosmochim. Ac., 62, 1347-1364, 1998.

Mos, L., Morsey, B., Jeffries, S. J., Yunker, M. B., Raverty, S., De Guise, S., and Ross, P. S.: Chemical and biological pollution contribute to the immunological profiles of free-ranging harbor seals. Environ. Toxicol. Chem., 25, 3110-3117, 2006.

Vonk, J. E., Giosan, L., Blusztajn, J., Montluçon, D., Graf-Pannatier, G., McIntyre, C., Wacker, L., Macdonald, R. W., Yunker, M. B., and Eglinton, T. I.: Spatial variations in geochemical characteristics of the modern Mackenzie Delta sedimentary system, Geochim. Cosmochim. Ac., submitted.

Detailed comments:

P 4723, line 6-8: This sentence is not precisely describing the type of material analysed here: The samples analysed here are either marine surface sediment samples take off the mouths of the rivers, or a river bank sample, or material transported with the spring flood and deposited on the ice shortly before break-up. "surface sediments derived from rivers" is not clear.

"Surface sediments" is replaced with "sedimentary particles". Same in Line 16 of the same page.

P. 4724, line 7: Please consider Hugelius et al., 2014 for an updated estimate of the carbon stocks.

The old reference is replaced by Hugelius et al. (2014).

Line 19: Here and throughout the text: The paper by Winterfeld et al. is now published in Biogeosciences (12, 2261-2283; 2015).

Updated.

Page 4725, line 12/13: "Arctic" with a capital A.

We used “arctic” and “sub-arctic” as adjectives in front of nouns and “Arctic” as a noun.

Pager 4726/4727: Paragraph 2.1: Here, the different samples are described. It has to made clear how the materials from the Yukon and Colville differ from the others (see general comments).

Agree. We have added a paragraph in the sampling methods to highlight the method differences and to discuss the potential effects (see reply to general comments).

Page 4730-4731: Paragraph discussing solvent-extractable lipids: Here, it will be necessary to mention that the Colville material and Yukon river bank sediment (purely terrestrial material) vs. the Mackenzie (with marine influence) are expected to differ between each other in terms of the LMW FA concentration. Same later in the discussion, e.g., page 4733, lines 2-3.

Modified:

> “As the Mackenzie sample was collected from mid-shelf area, it is expected to receive higher contribution of algal or bacterial OC and hence LMW FAs (Yunker et al., 1995; Drenzek et al., 2007) as compared with sediments derived from estuaries (GRARS and Kalix) or within the river systems (Colville and Yukon).”

And added in the following section:

> “As the Yukon and Colville sediments were collected within the river (as riverbank sediment and ice deposits, respectively), they are expected to be mainly terrestrially sourced and contain less bacterial or algal OC as compared with the estuarine sediments of GRARs and Kalix.”

Page 4733, line 10 and line 17: Use consistent expressions for C16-C28 FA.

Changed to “C_{16}–C_{28}”.

Page 4735-4736: discussion on the sources of suberin and cutin: Could the correlation observed between suberin and HMW FA and between cutin and lignin, respectively, perhaps also be caused by similar preservation potentials/similar chemical behaviour of the individual components?

Lignin, enriched in aromatic moieties, has distinct chemical structure, sorptive potentials and decomposition dynamics as compared with aliphatic structures such as suberin, cutin and FAs (Feng et al., 2005; Feng and Simpson, 2008). Hence, the observed correlations are not caused by similar preservation potentials or chemical behavior of individual components. This consideration is added on Page 14.

References:

Feng, X., Simpson, A. J., and Simpson, M. J.: Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces, Org. Geochem., 36, 1553-1566, 2005.

Feng, X., and Simpson, M. J.: Temperature responses of individual soil organic matter components, J. Geophys. Res., 113, G03036, doi: 10.1029/2008JG000743, 2008.

Page 4739, line 18: Delete “alternatively”.

Deleted and replaced with “furthermore”.

Figure 2: Please extend the figure caption significantly describing what is displayed on the individual panels. Plaese also indicate which of the data are cited from prior publications and include the sources.

Extended accordingly.

Interactive comment on Biogeosciences Discuss., 12, 4721, 2015.

RC C3111: 'Reviewer comment', Anonymous Referee #2, 24 Jun 2015

General comments: Understanding the fate of carbon in high latitude watersheds, which contain a significant fraction of the global soil organic carbon and above ground biomass, is critical in an environment that is experiencing a rapidly warming climate. This study adds new insights by characterizing the biomarker composition of sediment organic matter in major and minor river deltas in the Arctic region. As such, this manuscript is a valuable contribution to our understanding of fundamental carbon exchange processes. I have a few suggestions to make this manuscript more appealing to the general readership of "Biogeosciences".

Specific comments: Introduction – I would suggest to be more specific, quantitatively, in the introduction. How much carbon is stored in the general watershed areas, how much carbon is exported from the different rivers, including the dissolved and particulate pool, and how does that compare to net primary production in these watersheds.

Good suggestion. We have added estimates of soil OC stocks (1100-1500 PgC), DOC fluxes (25-36 Tg) in comparison with arctic tundra NPP (0.5 Pg C yr^{-1}) in the Introduction:

> "Fluvial transport currently delivers 25-36 Tg OC in the dissolved form into the Arctic Ocean annually (Raymond et al., 2007; Holmes et al., 2012), representing 5-7% of the net primary production in arctic tundra (0.5 Pg C yr^{-1}; Chapin III et al., 2012). Fluxes of particulate OC (POC) are comparable in some rivers (such as Mackenzie and Colville) but overall much smaller in the arctic fluvial systems (Stein and Macdonald, 2004)."

Added references:

Chapin III, F. S., Matson, P. A., and Vitousek, P. M.: Principles of Terrestrial Ecosystem Ecology, Springer, New York, 2012.

Holmes, R. M., McClelland, J. W., Peterson, B. J., Tank, S. E., Bulygina, E., Eglinton, T. I., Gordeev, V. V., Gurtovaya, T. Y., Raymond, P. A., Repeta, D. J., Staples, R., Striegl, R. G., Zhulidov, A. V., and Zimov, S. A.: Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas, Estuar. Coast., 35, 369-382, 2012.

Hugelius, G., Strauss, J., Zubrzycki, S., Harden, J. W., Schuur, E. A. G., Ping, C.-L., Schirrmeister, L., Grosse, G., Michaelson, G. J., Koven, C. D., O'Donnell, J. A., Elberling, B., Mishra, U., Camill, P., Yu, Z., Palmtag, J., and Kuhry, P.: Estimated stocks of circumpolar permafrost carbon with quantified uncertainty ranges and identified data gaps, Biogeosciences, 11, 6573-6593, 2014.

Raymond, P. A., McClelland, J. W., Holmes, R. M., Zhulidov, A. V., Mull, K., Peterson, B. J., Striegl, R. G., Aiken, G. R., and Gurtovaya, T. Y.: Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers, Global Biogeochem. Cy., 21, GB4011, doi:10.1029/2007GB002934, 2007.

Also, how much sediment (TSS) is exported from the different rivers, this might be interesting in terms of the relative contribution of root material? Some of this information can be summarized in table 1, but should be part of the introduction as well.

We add data of sediment yield normalized to basin areas (in the units of t km^{-2} yr^{-1}) in Table 1 and Methods ("Indigirka and Kolyma have higher sediment yields (36 and 19 t km^{-2} yr^{-1}, respectively) than the other Eurasian rivers (Stein and Macdonald, 2004)…The Yukon River drains northwestern

Canada and central Alaska in the United States into the Bering Sea with the second highest sediment yield (72 t km^{-2} yr^{-1}) in the arctic rivers (Guo et al., 2012)"). Yet sediment yield shows no correlation with either biomarker concentrations or biomarker-based proxies, probably because these sediments may have varied grain size and specific surface areas, which regulate the preservation and delivery of terrestrial OC (including root materials).

Methods – The samples compared in this study have been collected from estuarine sediments, mid-shelf sediments and from river ice. There needs to be a section in methods discussing the potential consequences for the biomarker composition. The authors need to present an explanation, why they think these samples are directly comparable to each other and potential biases resulting from such a heterogeneous sample set.

Agree. Please see reply to the general comment of Reviewer #1. In brief, we have added a paragraph in Methods highlighting the differences in sampling method and discussing the rationales. Potential consequences on biomarker composition are also discussed in the Results and Discussion as highlighted.

The authors also used 2 different extraction methods for different samples, what is the potential error introduced by the different sample preparation methods. Has there been a direct comparison between the 2 methods?

Hydrolysable lipids and lignin phenols were released from all sediments using the same protocols. Solvent-extractable lipids were previously determined in the sediments of GRARs, Kalix and Mackenzie using soxhlet extraction (van Dongen et al., 2008a; Vonk et al., 2008; Drenzek et al., 2007) whereas those of Yukon and Colville sediments were extracted by microwave-assisted reaction system. We did not directly compare these two methods for the investigated sediments. Based on published analysis of FAs in plant tissues, although microwave-assisted extraction has higher lipid yields than soxhlet extraction, lipid composition (especially for saturated FAs) is very similar in both extracts (Szentmihalyi et al., 2002; Qu et al., 2011). Hence, lipid composition is unlikely to be affected by the extraction methods used here. The extract efficiency of solvent-extractable lipids, however, may be higher for Yukon and Colville samples, which may contribute to the higher abundances of solvent-extractable FAs in these two rivers. These considerations are added in the Methods and Results.

Added references:

Qu, W.-X., Mou, Z.-L., Cui, H.-Y., and Zhang, Z.-Q.: Analysis of fatty acids in *A. szechenyianum* Gay. by microwave-assisted extraction and gas chromatography-mass spectrometry, Phytochemical Analysis, 22, 199-204, 2011.

Szentmihályi, K., Vinkler, P., Lakatos, B., Illés, V., and Then, M.: Rose hip (*Rosa canina* L.) oil obtained from waste hip seeds by different extraction methods, Bioresource Technology, 82, 195-201, 2002.

Results - The results and discussion section would benefit from more discussion of the data. One of the main points in this manuscript is the difference between the GRAR and North American rivers with the NA rivers having more root derived and less litter derived OC. What is the mechanism for such difference? Is it the fact that NA rivers carry more sediment (erosion), if so the relative abundance of root derived OC should be related to the TSS loads in the rivers. Did the authors look at such relationship? This would be a potential mechanism explaining the difference and an interesting addition.

We have added sediment yield in Table 1 and in the correlation tests (statistical analysis). However, sediment yield shows no correlation with either biomarker concentrations or biomarker-based proxies, probably because these sediments may have varied grain size and specific surface areas, which regulate the preservation and delivery of terrestrial OC (including root materials).

Our data suggest that the higher coverage of tundra in the watershed and possible variations in sample texture induced by the sampling method and location may explain the elevated contribution of root derived OC in NA rivers. The explanation is added on Page 18:

> "As the Yukon and Colville samples were collected near the river mouth as riverbank and ice deposits, respectively, they had undergone a shorter transport journey and were subject to less hydrodynamic sorting relative to the estuarine sediments of GRARs/Kalix and the shelf edge sediment of Mackenzie. Although we did not conduct grain size analysis on these pan-arctic sediments, the Yukon and Colville samples were possibly enriched with fine-grained materials derived from mineral soils in comparison with the coarser materials accumulated near river mouths and along the shelf (Hedges and Mann, 1979; Keil et al., 1998). Such processes may contribute to the enrichment of belowground OC associated with fine-grained materials in the North American samples. Alternatively, the watersheds of Yukon and Colville have a higher coverage of tundra (Brabets et al., 2000; Walker et al., 2002). As tundra has the highest root-to-shoot ratio of all terrestrial biomes (Jackson et al., 1996), its wide distribution in the watershed is likely to increase the input of belowground OC to riverine export."

Added references:

Keil, R. G., Tsamakis, E., Giddings, J. C., and Hedges, J. I.: Biochemical distributions (amino acids, neutral sugars, and lignin phenols) among size-classes of modern marine sediments from the Washington coast, Geochim. Cosmochim. Ac., 62, 1347-1364, 1998.

Could the information in figure 2 be summarized in table form, including standard deviations? This would reduce the number of Figures in the manuscript.

All detailed concentration data are provided in Appendix Table A1. Analytical error associated with biomarker extraction and GC/MS analysis is typically <10% (this is now added in the figure caption and methods). We feel that figures do a better job at highlighting the trends and summarizing such a big dataset and hence keep Figure 2 in the paper.

The discussion of acid to aldehyde ratios being either an indicator for source or degree of oxidation could use some refinement. If used as an indicator for degradation than the western Eurasian rivers should be less degraded because of the higher abundance of wetlands, however, the data show that the eastern river sediments have a higher OC content and the authors argue for the colder temperature and dryer climate as he main reasons. Acid/aldehyde ratios are also affected by preferential leaching as indicated by the authors, why would the acid/aldehyde ratio of vanillyl phenols be affected differently than the syringyl phenols? This does not seem to be reflected in the leached dissolved fractions presented by Hernes et al. (2007).

Indeed, the acid to aldehyde ratios are also subject to variations induced by OC source alterations and dissolution processes other than oxidation (Benner et al., 1990; Hernes et al., 2007). This is now added on Page 16.

OC content and acid to aldehyde ratios are however not correlated based on published sediment or soil data. While lignin oxidation is strongly dependent on oxic conditions, microbial degradation of other non-phenolic OC components is more strongly (if not mostly) controlled by temperature (Davidson and Janssens, 2006; Gudasz et al., 2010). Hence, discussion of the oxidation and dissolution controls on the $(Ad/Al)_v$ and $(Ad/Al)_p$ ratios is likely valid.

As we explained in the discussion, the different behavior of $(Ad/Al)_s$ and $(Ad/Al)_v$ ratios is not caused by dissolution or oxidation processes but mainly attributed to source variations (relative contribution of root/bark versus leaf). This source effect is not obvious for the $(Ad/Al)_v$ ratio likely because, unlike syringyl phenols that are specific to angiosperms, vanillyl phenols are universal in vascular plants and the Ad/Al variations as recorded by syringyl phenols in the root/bark versus leaf of angiosperm may be obscured by inputs from gymnosperm tissues. This is added on Page 17.

References:

Davidson, E. A., and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440, 165-173, 2006.

Gudasz, C., Bastviken, D., Steger, K., Premke, K., Sobek, S., and Tranvik, L. J.: Temperature-controlled organic carbon mineralization in lake sediments, Nature, 466, 478-481, 2010.

Interactive comment on Biogeosciences Discuss., 12, 4721, 2015.

SC C2454: 'Comment on "Multi-molecular tracers of terrestrial carbon transfer across the pan-Arctic: I. Comparison of hydrolysable components with plant wax lipids and lignin phenols"', Hongyan Bao, 27 May 2015

Feng et al. presented a study of organic biomarkers of the pan-Arctic sediments. The authors focused on using those biomarkers to trace the organic matter sources, and compared the distribution of hydrolysable components with plant wax lipids and lignin phenols among those sediments. The manuscript is well written, and the results and discussions are presented in detail. The information derived from this manuscript is interest. I have some miner comments regarding the methods and background data.

1. Page 4727, 2.2 Bulk analysis. Please show details about how the sediment samples were processed, e.g., were they ground? Besides, are all the OC% and N% data from the published papers? If some of them were measured in present study, please show how the N% were determined and the data quality control?

This section is now revised:

> "Bulk sediments were kept frozen at −20°C after collection and freeze-dried prior to analysis. A small aliquot of the Yukon and Colville samples were ground and used for TOC, total nitrogen and bulk $\delta^{13}C$ analyses at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution. The TOC, total nitrogen and $\delta^{13}C$ values of other sediments were derived from Drenzek et al. (2007) for Mackenzie, van Dongen et al. (2008a) for GRARs and Vonk et al. (2008) for Kalix."

2. The authors compared different parameter (e.g., (Ad/Al)v in Fig. 5) with the wetland coverage in the drainage basin. However, there is a gap between the sampling year and the wetland coverage data presented, e.g., the Kalix sample was collected in 2005, however, the wetland coverage data is approximately 30 years ago (Hjort, 1971). I am not sure whether this would affect the results, however, it would be better to have data that close to the sampling period.

We used the most updated vegetation coverage in the literature, including that of the Kalix (Ingri et al., 2005), which is similar to that reported in Hjort (1971). Both references are listed in the Method now.

Interactive comment on Biogeosciences Discuss., 12, 4721, 2015.

SC C2613: 'Commets for X Feng's "Multi-molecular tracers of terrestrial carbon transfer across the pan-Arctic: I. Comparison of hydrolysable components with plant wax lipids and lignin phenols"', Ying Wu, 06 Jun 2015

Feng et al., manuscript presented the compositions and distribution of terrestrial organic matter in the Pan-Arctic. The multi-molecular tracers were applied to investigate the molecular composition and source, degradation of hydrolysable compounds from the Arctic region, especially addressed the distribution and fate of suberin- and cutin derived organic carbon and did the comparison of them with plant wax lipids and lignin phenols. There is very limited information available about the behavior of terrestrial organic matter in Pan-Arctic scale, especially with such detailed studies. The paper is well written and organized based on their data sets and successfully provided the comprehensive, multi-molecular informants related to the terrestrial organic matter. I have some comments and suggestion about some points:

1) The sediments samples were collected from different years as presented in method part, and more detailed information (e.g., which month which year) may be helpful to improve the reliability of PCA analysis results in discussion part.

All samples were collected in during or post summer freshet: the GRAR sediments in August-September of 2004-2005, Kalix in June 2005, Mackenzie in July and August 1987, and Yukon and Colville in June 2007. Based on the sedimentation rate, the estuarine and shelf surface sediments (GRARs, Kalix, and Mackenzie) all represent more than one season/year of sedimentation so it should not be sensitive to the exact month of collection. This consideration as well as the exact month of sampling is added in the Methods (Page 5). Please also note that the PCA model is modified by using an Arcsine transformation to return the proportional data (i.e., biomarker-derived parameters) set to a normal distribution. The method details are added in the Data Analysis section:

> "All ratios were expressed as proportions (with the numerator parameters repeated in the denominator), an Arcsine transformation (calculation of the square root followed by the arcsine) was used to return this proportional data set to a normal distribution, and then data were autoscaled before PCA (Mos et al., 2006). "

Results of the modified PCA model are shown in Figure 8 (with more details in the figure caption). The results are remarkably similar to those of the old model. Explanations on Page 18 are modified accordingly.

2) The information of suberin-signal indicated the root-derived organic matter is more dominant in North American Arctic rivers, how about the hydrodynamic process from the North American Arctic rivers to GRARs? If there is some grain size information available, it will be really helpful.

Unfortunately, we did not conduct grain size analysis on these sediments. We do however acknowledge possible effects on biomarker composition from hydrodynamic process. This discussion is added on Page 18:

> "As the Yukon and Colville samples were collected near the river mouth as riverbank and ice deposits, respectively, they had undergone a shorter transport journey and were subject to less hydrodynamic sorting relative to the estuarine sediments of GRARs/Kalix and the shelf edge sediment of Mackenzie. Although we did not conduct grain size analysis on these pan-arctic sediments, the Yukon and Colville samples were possibly enriched with fine-grained materials derived from mineral soils in comparison with the coarser materials accumulated near river mouths and along the shelf (Hedges and Mann, 1979; Keil et al., 1998). Such processes may

> contribute to the enrichment of belowground OC associated with fine-grained materials in the North American samples. Alternatively, the watersheds of Yukon and Colville have a higher coverage of tundra (Brabets et al., 2000; Walker et al., 2002). As tundra has the highest root-to-shoot ratio of all terrestrial biomes (Jackson et al., 1996), its wide distribution in the watershed is likely to increase the input of belowground OC to riverine export."

3) The data of Kalix is quite different from other system, including PCA results, better to well addressed for the reason.

The Kalix sediment is quite different from the others in biomarker composition mainly due to a much higher moss input (as reflected by the moss- and peat-input indicators, including $C_{25}/(C_{25}+C_{29})$ *n*-alkanes, P/V, 3,5Bd/V, *p*Cd/Fd and Pn/P). This observation is in accordance with the high coverage of wetland and, to a lesser degree, non-permafrost soils in the Kalix basin in comparison to other arctic watersheds. This explanation is added on Page 18.

4) Based on the Figure 7, authors summarized (Ad/Al)s can be regarded as source indicators instead of diagenetic parameters, I think the point is not so convincible, since the parameters listed in this figures, all related to the diagenetic status, even root input indicator also has the relation with short chain FA ratios, as discussed in this paper.

As shown in Figure 5, the $(Ad/Al)_s$ ratio is positively correlated with the $(Ad/Al)_v$ ratio in the published lignin data of pan-arctic sediments and hence it can be used as a diagenetic parameter in general. However, in our sample set, the $(Ad/Al)_s$ ratio shows opposite diagenetic trend to that indicated by the $(Ad/Al)_v$ and HMW FAs/*n*-alkanes ratios (Figure 7b-c). It therefore suggests that the $(Ad/Al)_s$ ratio must be affected by processes other than diagenesis. It appears that the $(Ad/Al)_s$ ratio increases with increasing ratio of ∑Suberin/∑Cutin. The latter ratio, although subject to diagenetic alterations, is primarily used as a root input indicator. We hence postulate that the acid-to-aldehyde ratio of syringyl phenols may be strongly influenced by the relative inputs of root/bark versus leaf tissues. Most importantly, in our second paper stemming from this study (submitted to Global Biogeochemical Cycles), we found that suberin-specific biomarkers have younger ^{14}C ages in sediments with a higher $(Ad/Al)_s$ value. This cannot be explained if the $(Ad/Al)_s$ ratio indicates diagenetic status in our samples because we would expect older ages in more oxidized OC. Hence, we are quite confident that the $(Ad/Al)_s$ ratio increases with increasing inputs of fresh roots in our sample set. This effect is not obvious for the $(Ad/Al)_v$ ratio likely because, unlike syringyl phenols that are specific to angiosperms, vanillyl phenols are universal in vascular plants and the Ad/Al variations in the root/bark versus leaf of angiosperm may be obscured by inputs from gymnosperm tissues. These explanations are rephrased a bit in the text to clarify.

5) The implication of Figure 5 is not well organized, I could not see what the main points for those plots are and how to prove it.

The purpose of Figure 5 is to compare our data with the published biomarker data on pan-Arctic river sediments and to test if observations/correlations found in our sample set apply to the wider range of sedimentary samples. As shown in Figures 5 a and f, two peat/moss indicators (P/V and 3,5Bd/V) show positive correlations in all pan-arctic sediments similar to our data whereas the $(Ad/Al)_v$ and $(Ad/Al)_s$ ratios show opposite correlations to the pattern observed in our dataset. The other ratios do not show any correlation with vegetation coverage as observed in our sample set, likely because the published data include a much wider range of samples from different sedimentary settings (including delta, shelf, and river suspended sediments). Hydrodynamic sorting and diagenesis associated with land-ocean transfer processes may alter lignin phenol composition and obscure the relationships. We feel that Figure 5 is a good way of summarizing the published data in comparison with ours and are inclined to keep it in the paper.

Multi-molecular tracers of terrestrial carbon transfer across the pan-Arctic: I. Comparison of hydrolysable components with plant wax lipids and lignin phenols

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Abstract

Hydrolysable organic carbon (OC) comprises a significant component of sedimentary particulate matter transferred from land into oceans via rivers. Its abundance and nature are however not well studied in the arctic river systems, and yet may represent an important pool of carbon whose fate remains unclear in the context of mobilization and related processes associated with changing climate. Here, we examine the molecular composition and source of hydrolysable compounds isolated from ~~surface sediments~~ sedimentary particles derived from nine rivers across the pan-Arctic. Bound fatty acids (b-FAs), hydroxy FAs, *n*-alkane-α,ω-dioic acids (DAs) and phenols were the major components released upon hydrolysis of these sediments. Among them, b-FAs received considerable inputs from bacterial and/or algal sources, whereas ω-hydroxy FAs, mid-chain substituted acids, DAs, and hydrolysable phenols were mainly derived from cutin and suberin of higher plants. We further compared the distribution and fate of suberin- and cutin-derived compounds with those of other terrestrial biomarkers (plant wax lipids and lignin phenols) from the same arctic river sedimentary particles and conducted a benchmark assessment of several biomarker-based indicators of OC source and extent of degradation. While suberin-specific biomarkers were positively correlated with plant-derived high-molecular-weight (HMW) FAs, lignin phenols were correlated with cutin-derived compounds. These correlations suggest that, similar to leaf-derived cutin, lignin was mainly derived from litter and surface soil horizons, whereas suberin and HMW FAs incorporated significant inputs from belowground sources (roots and deeper soil). This conclusion is supported by the negative correlation between lignin phenols and the ratio of suberin-to-cutin biomarkers. Furthermore, the molecular composition of investigated biomarkers differed between Eurasian and North American arctic rivers: while lignin dominated in the terrestrial OC of Eurasian river sediments, hydrolysable OC represented a much larger fraction in the sedimentary particles from Colville River. Hence, studies exclusively focusing on either plant wax lipids or lignin phenols will not be able to fully unravel the mobilization and fate of bound OC in the arctic rivers. More comprehensive, multi-molecular investigations are needed to better constrain the land-ocean transfer of carbon in the changing Arctic, including further research on the degradation and transfer of both free and bound components in the arctic river sediments.

1 Introduction

The drainage basins of the arctic rivers are estimated to contain 1,100-1,500 Pg of carbon, representing more than half of the global soil organic carbon (OC) reservoir ~~(Tarnocai et al., 2009)~~ (Hugelius et al., 2014), and are warming two to three times faster than the other regions on Earth (IPCC, 2013). Fluvial transport currently delivers 25-36 Tg OC in the dissolved form ~~large amounts of terrestrial OC~~ into the Arctic Ocean annually (Raymond et al., 2007; Holmes et al., 2012~~Dittmar and Kattner, 2003; Semiletov et al., 2011~~), representing 5-7% of the net primary production in arctic tundra (0.5 Pg C yr^{-1}; Chapin III et al., 2012). Fluxes of particulate OC (POC) are comparable in some rivers (such as Mackenzie and Colville) but overall much smaller in the arctic fluvial systems (Stein and Macdonald, 2004). ~~and t~~The flux and nature of exported OC is projected to change in the coming decades (Holmes et al., 2013; Feng et al., 2013; O'Donnell et al., 2014). It is thus important to understand the transformation and preservation of terrestrial OC during land-ocean transfer in order to assess its fate and impact on regional and global carbon cycles.

The transport and fate of terrestrial OC in arctic riverine and estuarine sediments have been widely investigated, and two groups of molecular tracer compounds have typically been employed, i.e., plant wax lipids and lignin phenols (Yunker et al., 1993, 1995; Lobbes et al., 2000; van Dongen et al., 2008a, b; Vonk et al., 2010; Gustafsson et al., 2011; Karlsson et al., 2011; Schreiner et al., 2013; Winterfeld et al., 2015). By comparison, cutin- and suberin-derived ester-bound compounds have been much less extensively investigated and used to trace terrestrial carbon transfer in the Arctic (Zegouagh et al., 1996; Goñi et al., 2000; Tesi et al., 2014). Cutin and suberin are protective coatings on vascular plant leaves/fruits/seeds and roots/barks, respectively (Kögel-Knabner, 2002). While they are relatively minor contributors to plant biomass (much less than 10%) as compared with lignin (~30%), structures of cutin and suberin accumulate in plant litter and mineral soil during decomposition (Kögel-Knabner, 1993) and they are hence key hydrolysable components of terrestrial organic matter. Cutin and suberin are considered to be more resistant to microbial decomposition as compared with plant wax lipids (Feng et al., 2008; Feng and Simpson, 2008) and may thus survive longer-range fluvial transport. These different groups of compounds originate from various terrestrial biological sources (roots versus leaves; woody versus non-woody parts), potentially display varying degrees of association with mineral surfaces (Feng et al., 2005), and are hence expected to show different provenance and fate during the land-ocean transfer (Gordon and Goñi, 2003; Huguet et al., 2008; Mead and Goñi, 2008; Feng et al., 2013). Investigating their composition and distribution will allow a broader assessment of the fate of mobilized terrestrial OC in the Arctic, including a significant pool (hydrolysable carbon) that has received minimal scrutiny previously.

Here we utilize sedimentary particles ~~the surface sediments~~ derived from nine major arctic and sub-arctic river drainage basins to conduct a multi-tracer comparison of terrestrial OC composition and fate across the pan-Arctic. The investigated systems, including three North American arctic rivers (Mackenzie, Yukon, and Colville), five Great Russian Arctic Rivers (GRARs, namely Ob', Yenisey, Lena, Indigirka and Kolyma), and a sub-arctic Scandinavian river (Kalix), exhibit varied hydrogeographic characteristics, vegetation and permafrost coverage in their resepective drainage basins (Table 1). This comparison across different rivers facilitates an evaluation of controls on terrestrial OC transfer in various watersheds. This paper is the first of two stemming from the same study (the second paper focusing on the ^{14}C age of individual biomarkers), and builds on prior investigations of lignin and plant wax characteristics in a subset of these rivers (Drenzek et al., 2007; van Dongen et al., 2008a; Feng et al., 2013). The objectives are three-fold: (1) to investigate the molecular composition and source of hydrolysable compounds from arctic and sub-arctic riverine sediments; (2) to compare the distribution and fate of suberin- and cutin-derived OC versus plant wax lipids and lignin phenols; and (3) to provide a benchmark assessment of the biomarker-based OC source and degradation indicators across the pan-Arctic.

2 Materials and methods

2.1 Study area and sampling

The three eastern GRARs (Lena, Indigirka and Kolyma) drain into the Laptev Sea (Lena) and the East Siberian Sea (Indigirka and Kolyma; Figure 1), with a cold and semiarid climate in the drainage basins and a vast coverage (79-100%) of continuous permafrost. This contrasts with the two western GRARs (Ob' and Yenisey) draining the west Siberian lowland into the Kara Sea and the Kalix River flowing through sub-arctic Scandinavia into the Baltic Sea, which are all characterized by wetter climates, milder winters, and a much lower coverage of permafrost (Table 1). The GRAR drainage basins are characterized by various tundra and wetlands in the north and by forests in the south (FAO, 2001; van Dongen et al., 2008a). The Kalix watershed mainly consists of forests (60%) and wetland (20%; Hjort, 1971; Ingri et al., 2005). All rivers have comparable drainage-area-normalized fluxes of total organic carbon (TOC) and ~~particulate organic carbon (~~POC~~;~~ (Table 1; Stein and Macdonald, 2004; Ingri et al., 2005). Indigirka and Kolyma have higher sediment yields (36 and 19 t km^{-2} yr^{-1}, respectively) than the other Eurasian rivers (Stein and Macdonald, 2004). A more detailed description of the drainage basins is provided elsewhere (van Dongen et al., 2008a; Vonk et al., 2008). Surface sediments (0-2 cm) were collected using a grab sampler from the GRAR estuaries during the second and third Russia-United States cruises (on H/V Ivan Kireev) in August-September of 2004 and 2005, and from the Kalix in June 2005 on the research vessel "KBV005" from the Umeå Marine Research Center (UMF, Norrbyn, Sweden). These sediments were mainly delivered by the annual spring freshet of the rivers and by coastal erosion during the past ~20 years based on the sedimentation rate of 0.11-0.16 cm/year (van Dongen et al., 2008a, b; Vonk et al., 2012), so their composition should not be so sensitive to the exact month of collection.

The Mackenzie River in North America is the largest fluvial source of both sediment and POC to the Arctic Ocean (Table 1). Its drainage basin spans the western alpine region of the Cordillera Mountains to the Canadian Shield and includes forests, swamps, grasslands, and permafrost soils. Previous studies have established that petrogenic OC, mainly supplied by immature bitumen, shales, or coals from the Devonian Canol formation, is actively cycling through the Mackenzie system (Yunker et al., 2002; Goñi et al., 2005; Drenzek et al., 2007). Surface sediments (0-2 cm) were collected from the Mackenzie shelf edge in July and August 1987 by a Smith-McIntyre grab sampler (Yunker et al., 1990). Previous radiocarbon analysis of marine biomarkers from the site implies deposition of recent years (Drenzek et al., 2007).

The Yukon River drains northwestern Canada and central Alaska in the United States into the Bering Sea with the second highest sediment yield (72 t km^{-2} yr^{-1}) in the arctic rivers (Guo et al., 2012). Its drainage basin is characterized by diverse ecosystems including forests, shrublands, tundra, and extensive areas of permafrost (Brabets et al., 2000). ~~A river bank sediment sample was collected near Pilot Station, Alaska during ice breakup in June 2007.~~ A sample of freshly deposited fine-grained fluvial sediment was collected from the Yukon near Pilot Station, Alaska during ice breakup in June 2007. The Pilot Station is considered to be the lowest reach of the river where streamflow is not affected by the Bering Sea and the outflow point for the entire Yukon River basin. By comparison, the Colville River, originating in the Brooks Range in northern Alaska, is much smaller in terms of watershed area (Table 1), but is the largest North American river (both in terms of freshwater and sediment load) that exclusively drains continuous permafrost (Walker, 1998). It flows across the foothills of the Brooks Range and the adjacent arctic coastal plain to the Beaufort Sea and the watershed is characterized by dwarf and low shrub tundra, with mossy carpets and moist peaty soils (Walker et al., 2002). ~~Two sediment samples were collected from the surface of the river ice when flood water was running over the ice in June 2007.~~ Two samples were collected from fresh mud that was deposited on the surface of river ice prior to ice break-up close to (within 40 km of) the river mouth in June 2007. As the majority of sediment is delivered from arctic rivers during the freshet, the Colville samples are most likely an accurate reflection of the fluvial suspended load of sedimentary particles during the freshet and represent terrestrial organic matter transported to the river mouth.

The contrasting sampling strategies and sample types recovered from the various river systems (estuarine sediments for GRARs and Kalix versus shelf edge sediments for Mackenzie and fluvial deposits near river mouth for Yukon and Colville) may lead to varied contribution and concentrations of terrestrial, marine and relict carbon in the bulk OC. However, for locations where we have compared characteristics of the fluvial suspended load, or where appropriate data is available (i.e., Mackenzie; Vonk et al., submitted; Hussain et al., unpublished data), strong compositional similarities exist between suspended sediments and sediment deposits (on riverbank or riverbed). Therefore, observations described herein should be valid for the basin-scale comparison of the fate of various terrestrial OC biomarkers and their environmental controls, and we focus on the transformation and relative ratio of terrestrial components in the sedimentary OC only. Potential compositional variations induced by sampling methods are discussed in detail in the results.

2.2 Bulk analyses

Bulk sediments were kept frozen at −20°C after collection and freeze-dried prior to analysis. A small aliquot of the Yukon and Colville samples ~~was~~ were ground and used for TOC~~ and~~, total nitrogen and bulk δ^{13}C analyses at ~~the UC Davis Stable Isotope Facility (for GRARs and Kalix) and~~ the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution~~ (for North American rivers)~~. The TOC, total nitrogen and δ^{13}C values of other sediments were derived from Drenzek et al. (2007) for Mackenzie, van Dongen et al. (2008a) for GRARs and Vonk et al. (2008) for Kalix.

2.3 Biomarker extractions

Total lipid extracts (TLEs) were obtained from freeze-dried sediments (~70-160 g) using dichloromethane/methanol (2/1) by soxhlet extraction (24 h; GRARs, Kalix and Mackenzie) or microwave-assisted reaction system (MARS, CEM Corporation; Yukon and Colville). The composition of solvent-extractable *n*-alkanes and *n*-alkanoic acids (fatty acids; FAs) was determined previously for the GRAR (van Dongen et al., 2008a), Kalix (Vonk et al., 2008) and Mackenzie sediments (Drenzek et al., 2007). Similarly, *n*-alkanes and FAs were purified and isolated from the TLEs of Yukon and Colville sediments using protocols as described previously (Galy et al., 2011). Briefly, TLEs were saponified with 0.5 M KOH in methanol/water (99/1; 70 °C, 2 h). “Neutral” and “acid” fractions were extracted with hexane and hexane/dichloromethane (4/1) at pH 7 and 2 (adjusted with HCl), consecutively. The latter fraction, containing FAs, was methylated with methanol/HCl (95/5; 70 °C, 12 h). Fractions containing alkanes and fatty acid methyl esters (FAMEs) were separated from the “neutral” and methylated “acid” fractions by liquid chromatography on a Pasteur pipette column filled with 1% deactivated silica gel and eluted with hexane and hexane/toluene (1/1), respectively. While microwave-assisted extraction is reported to show higher lipid yields than soxhlet extraction, lipid composition (especially for saturated FAs) is very similar in both TLEs (Szentmihalyi et al., 2002; Qu et al., 2011). Hence, lipid composition is unlikely to be affected by the extraction methods used here.

Hydrolysable lipids were released from the solvent-extracted residues (excluding the Mackenzie sample) by treatment with 1 M KOH in methanol/water (4/1; 100 °C, 3 h) using a microwave-assisted reaction system. The resulting solution was separated from the solid residue by centrifugation and the residue was washed with methanol/water (1/1) twice. A spike of C_{19} FA and C_{18} *n*-alkane was added as internal standards. Similar to the TLE analysis, “neutral” and “acid” fractions were then recovered from the hydrolysed solution with hexane and hexane/dichloromethane (4/1) at high (not acidified) and low pHs (pH 2, acidified with HCl), consecutively. The latter fraction, containing bound FAs (b-FAs) and specific biomarkers for cutin and suberin such as *n*-alkane-α,ω-dioic acids (DAs), and hydroxy FAs, was methylated with methanol/HCl (95/5; 70 °C, 12 h), extracted with hexane/dichloromethane (4/1), and concentrated under N_2 for further analysis.

Lignin and hydroxy phenols were further released from the dried hydrolysed residues using alkaline CuO oxidation on the microwave-assisted reaction system (Feng et al., 2013). For each sample, approximately 5 g of CuO, 0.6 g of ferrous ammonium sulfate, and 25 mL of N_2-bubbled NaOH solution (2 M) were loaded into vessels containing sediments (3-10 g) with ~50 mg of TOC. All vessels were vacuum-purged with N_2 four times and oxidized at 150°C for 1.5 h. The oxidation products was spiked with an internal standard (ethyl vanillin), extracted with ethyl acetate after acidification to pH 2 and concentrated under N_2 for further analysis.

2.4 Quantification and composition analysis

Small aliquots of the methylated "acid" fraction of hydrolysis products and lignin oxidation products were derivatized with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine (70 °C, 1 h) to yield trimethylsilyl (TMS) derivatives. The molecular composition of biomarkers (including *n*-alkanes, FAs, b-FAs, DAs, hydroxy FAs, lignin and hydroxy phenols) was examined on an Agilent 6890 Series gas chromatograph (GC) coupled to a mass spectrometry detector (Agilent Technologies, Santa Clara, CA, USA) using an Agilent DB-5MS column (50 m × 0.2 mm i.d., film thickness, 0.33 μm) for separation. Temperature increased from 100 °C (initial hold time, 2 min) to 300 °C at a rate of 3 °C min^{-1} and helium was used as carrier gas (1 mL min^{-1}). Spectra were obtained by scanning over the range 50-600 amu, with a cycle time of 1 s. Electron impact ionization (EI) at 70 eV was used for all analyses. Quantification was achieved by comparison with internal standards (C_{18} *n*-alkane for *n*-alkanes, C_{19} FA for other lipid compounds, and ethyl vanillin for phenols). Errors associated with the biomarker concentration data are typically <10% based on replicate analysis of the same sediment sample.

2.5 ~~Statistical~~ Data analysis

Relationships between the abundances of various biomarkers, biomarker-based parameters, sediment yield, and vegetation coverage in the drainage basin were assessed using simple linear regression analysis. Correlation was considered to be significant at a level of $p < 0.05$. A principal component analysis (PCA) model was ~~further performed~~built to investigate how the distribution of different biomarkers and source/degradation parameters related to each other and explained the compositional variance among different arctic river sediments. All ratios were expressed as proportions (with the numerator parameters repeated in the denominator), an Arcsine transformation (calculation of the square root followed by the arcsine) was used to return this proportional data set to a normal distribution, and then data were autoscaled before PCA (Mos et al., 2006).

3 Results and discussion

3.1 Sediment bulk properties

Bulk chemical properties of the ~~surface~~ sedimentary particles in the nine arctic and sub-arctic rivers are listed in Table 1. The Kalix and Lena sediments had the highest (4.5%) and lowest (0.5%) OC content, respectively. The Mackenzie sediment, collected from the Mackenzie mid-shelf, had the lowest mass ratio of OC to nitrogen (OC/N; 4.7), consistent with significant inputs of petrogenic OC as well as contributions from marine OC (Goñi et al., 2005). All the other samples showed significantly higher OC/N ratios (from 10.0 to 15.9) and similar $\delta^{13}C$ values (–25.0 to –27.4 ‰), indicating terrestrially dominated OC sources (see discussion in van Dongen et al., 2008a).

3.2 Molecular composition and sources of biomarkers

3.2.1 Solvent-extractable *n*-alkanes and FAs

Solvent-extractable *n*-alkanes in the Yukon and Colville sediments were dominated by odd-numbered homologues in the range of C_{20}–C_{34} with C_{27} *n*-alkane being the most abundant in all samples (Figure 2a and Table A1). Their composition was similar to those in the GRAR (van Dongen et al., 2008a) and Kalix sediments (Vonk et al., 2008), revealing a predominance of terrestrial OC with very minor contributions from aquatic biomass or petrogenic (rock-derived) carbon. The concentration of higher-plant-derived high-molecular-weight (HMW) *n*-alkanes (C_{20}–C_{34}) ranged 0.49–0.87 mg/g OC, lower than those of Indigirka and Ob' but similar to the others (Table A1). Among the investigated sediments, the Kolyma and Yukon samples had the highest values of carbon preference index for *n*-alkanes ($CPI_{25\text{-}33}$ as defined in Figure 2; 7.3 and 6.9, respectively) whereas Mackenzie exhibited a C_{27} and C_{29} *n*-alkane predominance with the lowest $CPI_{25\text{-}33}$ value of 2.3, corroborating the influence of petrogenic OC (Drenzek et al., 2007).

Solvent-extractable FAs in the Yukon and Colville sediments were dominated by even-numbered FAs in the range of C_{16}–C_{30} with C_{24} FA being the most abundant (Figure 2b and Table A1). The concentration of higher-plant-derived HMW FAs (C_{20}–C_{30}) ranged 0.67–0.68 mg/g OC in Colville and was much higher in Yukon (1.19 mg/g OC) than in other sediments (Table A1). The $CPI_{20\text{-}30}$ values showed a very narrow range in both Colville and Yukon sediments (5.1–5.2), similar to that in Kalix and higher than the rest (Figure 2b), indicating a predominance of higher plant input in these two rivers. It is notable that FAs in the Mackenzie sediment had a much higher concentration of low-molecular-weight (LMW; $<C_{20}$, especially C_{16}) FAs as compared with the others~~,~~. As the Mackenzie sample was collected from mid-shelf area, it is expected to receive higher contribution of ~~suggesting more~~ algal or bacterial ~~contributions to the sedimentary~~ OC and hence LMW FAs ~~in the Mackenzie mid-shelf area~~ (Yunker et al., 1995; Drenzek et al., 2007) as compared with sediments derived from estuaries (GRARS and Kalix) or within the river systems (Colville and Yukon).

3.2.2 Hydrolysable compounds

The acid fraction of the alkaline hydrolysis products yielded four major classes of compounds: b-FAs, hydroxy FAs (including α-, β-, ω-hydroxy FAs, and mid-chain substituted acids), DAs, and hydrolysable phenols (Table A1). Small amounts of steroids and terpenoids were also found, but not included in this study.

b-FAs: As compared with solvent-extractable FAs, b-FAs were dominated by LMW (C_{14}–C_{19}) homologues (with maxima at C_{16}) with significant contributions from *iso*-/*anteiso*-branched and mono-unsaturated counterparts (Figure 2c). The concentration of HMW b-FAs (C_{20}–C_{30}) ranged from 0.08 mg/g OC in Lena to 1.17 mg/g OC in Colville 2, showing similar (in Kalix, Ob' and Colville) or lower (eastern GRARs and Yukon) values than HMW FAs from the same sediments. b-FAs exhibited similar $CPI_{20\text{-}30}$ values to FAs for Kalix, Indigirka and Kolyma and lower values for the rest of the rivers. In contrast to the FAs, the most abundant HMW b-FA varied, being C_{20} b-FA in Ob', Yenisey, Kolyma and Colville 1, C_{24} b-FA in Lena and Colville 2, C_{22} b-FA in Kalix and C_{26} in Indigirka. The marked difference in the molecular composition of these two types of lipids suggests varied sources in the ~~surface~~ sediments. While solvent-extractable FAs were mainly derived from higher plant waxes, b-FAs received much more inputs from bacterial and/or algal sources as indicated by the dominance of LMW homologues, the presence of branched and mono-unsaturated FAs, and slightly lower $CPI_{20\text{-}30}$ values. Such source variations have also been found for the solvent-extractable and hydrolysable lipids in other marine sediments (Zegouagh et al., 1996; Garcette-Lepecq et al., 2004).

Hydroxy FAs: Hydroxy FAs were the most abundant hydrolysable compounds in the arctic sediment samples examined. Among them, exclusively even-numbered **ω-hydroxy FAs** in the range of C_{16}–C_{26} were the dominant component (Figure 2d), ranging from 1.16 mg/g OC in Lena to 8.78 mg/g OC in Kolyma, representing 14% (in Kalix) to 50% (in Yukon) of the total hydrolysable lipids. The composition of ω-hydroxy FAs is very similar to those in soils and plant litter (Riederer et al., 1993; Rumpel et al., 2004; Otto and Simpson, 2006a; Feng et al., 2010), suggesting that they are mainly derived from higher plant cutin, suberin and epicuticular waxes. The HMW (>C_{20}) homologues, in particular, are considered to be specific to suberin. As another main component of higher plant cutin and suberin, seven **mid-chain hydroxy and epoxy acids** in the range of C_{15}–C_{18} were also found in the sediments at slightly lower concentrations than ω-hydroxy FAs in Kalix and GRARs and in much lower abundances in Yukon and Colville (Figure 2e). Among them, C_{15}, C_{16} mid-chain hydroxy DAs and C_{15}, C_{16} x,ω-dihydroxy FAs are considered to derive solely from cutin, whereas 9,10-epoxy C_{18} DA originates from suberin (Otto and Simpson, 2006a). By comparison, **α-hydroxy acids** in the range of C_{15}–C_{26} occurred in much lower abundances (0.22–1.61 mg/g OC; Figure 2f). α-Hydroxy acids have been found in the hydrolysis products of leaf waxes, wood as well as microalgae and seagrasses (de Leeuw et al., 1995; Volkman et al., 1998; van Dongen et al., 2000; Freire et al., 2002; Otto and Simpson, 2006a). They are hence not considered to be source-specific biomarkers.

Additionally, **β-hydroxy FAs** were observed in the range of C_{10}–C_{20}, with branched homologues at C_{14}–C_{17} and maxima at C_{14}, C_{16} or *i*-C_{17} (Figure 2g). These compounds showed similar concentrations to LMW b-FAs in Kalix and GRARs (0.82–2.75 mg/g OC) and lower abundances in Yukon and Colville sediments (0.77–0.89 mg/g OC). Similar compounds have been reported in the hydrolysis products of sediments from a freshwater lake (Goossens et al., 1989) and the Danube delta (Garcette-Lepecq et al., 2004) and are considered to derive mainly from bound moieties in bacterial cell walls (Goossens et al., 1986). As the Yukon and Colville sediments were collected within the river (as riverbank sediment and ice deposits, respectively), they are expected to be mainly terrestrially sourced and contain less bacterial or algal OC as compared with the estuarine sediments of GRARs and Kalix.

DAs: DAs in the range of C_{16}–C_{28} represented 12–15% of total hydrolysable lipids in the arctic sediments, showing an even-over-odd predominance and maxima at C_{22} in all samples (Figure 2h). DAs in sediments have several potential sources. First, medium- and long-chain (C_{16}–C_{28}~~C_{16-28}~~) DAs predominating at C_{26} and C_{28} are found in seagrasses (Nichols et al., 1982). This molecular distribution is different from the DAs in our samples. Furthermore, it is well documented that phytobenthic species are either absent or only occur in low abundance in arctic zones (Romankevich, 1984), and hence inputs from seagrasses are unlikely. DAs have also been suggested as oxidation products of FAs and/or ω-hydroxy FAs (Johns and Onder, 1975; van Bergen et al., 1998), where their distribution should parallel that of their precursors. This possibility can be ruled out as well because the molecular composition of DAs (C_{16}–C_{28} with maxima at C_{22}) does not match that of solvent-extractable FAs (with maxima at C_{24}), b-FAs (C_{14}–C_{30} with maxima at C_{20}, C_{22}, C_{24} or C_{26}), or ω-hydroxy FAs (only even-numbered in the range of C_{16}–C_{26}) from the same sediment. Hence, DAs in these arctic sediments most likely originate from cutin and/or suberin of higher plants (Goñi and Hedges, 1990; Otto and Simpson, 2006a; Feng et al., 2010). Similar to ω-hydroxy FAs, the HMW ($>C_{20}$) DAs are considered to be specific to suberin in particular.

Hydrolysable phenols: Other than lipids, alkaline hydrolysis released minor amounts of phenol moieties (Table A1). These phenols, ranging 0.18–1.45 mg/g OC in total, amounted to < 6% of lignin phenols released by CuO oxidation (see the section below) from the Kalix, GRAR and Yukon sediments and 9–13% of lignin phenols from Colville. As hydrolysable phenols are ester-bound in the sediments, they are considered to derive from the suberin macromolecule instead of ‘true’ lignin, which is dominated by ether linkages (cf. Otto and Simpson, 2006a; 2007). Moreover, the concentration of hydrolysable phenols was most significantly correlated with suberin biomarkers (∑Suberin as defined in Section 3.3; $p < 0.01$), and less so with lignin phenols ($p = 0.04$), supporting the notion that they are mainly derived from suberin.

3.2.3 Lignin and hydroxy phenols

Eight phenols characteristic of lignin (vanillyl, syringyl, cinnamyl phenols (VSC); Hedges and Mann, 1979) were detected in much higher concentrations in the Eurasian rivers (11.15–22.78 mg/g OC) than in the North American ones (2.08–7.51 mg/g OC), including the universal and most abundant vanillyl phenols (vanillin, acetovanillone, vanillic acid), angiosperm-specific syringyl phenols (syringaldehyde, acetosyringone, syringic acid), and cinnamyl phenols found in non-woody tissues (*p*-coumaric acid, ferulic acid; Table 2). These concentrations fall within the range reported for lignin VSC in the surface sediments of East Siberian shelf (receiving riverine inputs from Lena, Indigirka, and Kolyma; 0.3–38.2 mg/g OC; Tesi et al., 2014), in the sediment cores of Hudson Bay (0.4–14.6 mg/g OC; Kuzyk et al., 2008) and in the surface and suspended sediments from Buor Khaya Bay and Lena river (9.4–51.6 mg/g OC; Winterfeld et al., 2015) as well as from Beaufort shelf and Mackenzie river (3.01–12.22 mg/g OC; Goñi et al., 2000; 2005). The Colville river sediments in this study had slightly less VSC (2.08–2.11 mg/g OC) as compared with Colville delta surface sediments (4.1–14.6 mg/g OC; Schreiner et al., 2013). This difference may be attributed to OC source variations between the river and delta regions. Although mostly terrestrially sourced, the ice deposits near Colville river mouth may contain a higher proportion of easily degradable plant OC (such as carbohydrates) which dilutes lignin in the bulk OC.~~.~~

Additionally, CuO oxidation released considerable amounts of *p*-hydroxy (P) phenols and 3,5-dihydroxybenzoic acid (3,5Bd) from all sediments, which also exhibited higher abundances in the Eurasian river sediments (ranging at 2.90–6.72 and 0.96–2.70 mg/g OC, respectively) than in the North American rivers (1.13–1.87 and 0.26–0.70 mg/g OC, respectively). Again, the abundances of these phenols fall within the range reported for the sediments of Beaufort shelf, Buor Khaya Bay, Lena and Mackenzie rivers (Goñi et al., 2000; 2005; Winterfeld et al., 2015). Unlike VSC units, these phenols may derive from protein and “tannin-like” compounds (Prahl et al., 1994; Goñi and Hedges, 1995; Goñi et al., 2000). In particular, it is found that the non-methoxylated hydroxy phenols (in particular, *p*-hydroxyacetophenone (Pn)) are enriched in *Sphagnum* (Erickson and Miksche, 1974; Lehto et al., 1985; Williams and Yavitt, 2003; Zaccone et al., 2008), and 3,5Bd, while absent in plant tissues, is most enriched in peat (Prahl et al., 1994; Goñi et al., 2000; Amon et al., 2012) and may indicate macrophytes (such as kelp) in certain environment (Kuzyk et al., 2008).

3.3 OC source and degradation parameters

Building on the above discussion, indicators of OM source and degradation stage are calculated using the aforementioned biomarkers (Table 3) and compared with the existing data (mainly on lignin phenols) on arctic sediments from the literature (Goñi et al., 2000, 2005; Kuzyk et al., 2008; Schreiner et al., 2013; Tesi et al., 2014; Winterfeld et al., 2015).

3.3.1 Suberin and cutin inputs

Suberin- and cutin-specific biomarkers in the hydrolysable products were summarized and calculated based on parameters developed by Otto and Simpson (2006a). Suberin biomarkers ($\sum$Suberin = C_{20}–C_{26} ω-hydroxy FAs + C_{20}–C_{28} DAs + 9, 10-epoxy C_{18} DA) ranged from 1.39 to 8.93 mg/g OC while cutin biomarkers ($\sum$Cutin = C_{15}, C_{16} mid-chain hydroxy DAs + C_{15}, C_{16} x, ω-dihydroxy FAs) ranged from 0.81 to 5.16 mg/g OC in the pan-arctic sediments (Table 3). $\sum$Cutin showed much higher concentrations in the Kolyma and Indigirka sediments while $\sum$Suberin had the highest and lowest abundance in the Kolyma and Lena sediments, respectively. Comparison with other terrestrial biomarkers revealed that $\sum$Suberin was positively correlated with HMW FAs across the pan-arctic transect ($p = 0.04$) whereas $\sum$Cutin was not (Figure 3a). Conversely, lignin VSC was correlated with $\sum$Cutin (Figure 3b; $p = 0.02$), but not with $\sum$Suberin or HMW FAs. Lignin, enriched in aromatic moieties, has distinct chemical structure, sorptive potentials and decomposition dynamics as compared with aliphatic structures such as suberin, cutin and FAs (Feng et al., 2005; Feng and Simpson, 2008). Hence, the observed correlations are not caused by similar preservation potentials or chemical behavior of individual components. Instead, these ~~This~~ suggest~~s~~ that, similar to cutin acids, lignin is mainly derived from surface litter and shallow soil, whereas suberin and HMW FAs incorporate significant inputs from belowground sources (i.e., roots and deeper mineral soils). This conclusion is in line with the relatively younger age of lignin phenols as compared to plant wax lipids in the Eurasian arctic river sediments (Gustafsson et al., 2011; Feng et al., 2013) and is further supported by the negative correlation between VSC and the $\sum$Suberin/$\sum$Cutin ratio (Figure 3c; $p = 0.03$), an indicator of the relative input of root/bark- versus leaf-derived OC (Goñi and Hedges, 1990; Otto and Simpson, 2006a; Feng et al., 2010).

The $\sum$Suberin/$\sum$Cutin ratio increased from ~1.6–1.7 in eastern GRARs to ~6.5 in Yukon (Table 3) and was positively correlated with both ratios of ω-C_{16}/$\sum C_{16}$ and ω-C_{18}/$\sum C_{18}$ (ratio of C_{16} or C_{18} ω-hydroxy FA to the summation of ~~all~~ C_{16} or C_{18} ω-hydroxy FAs, DAs, and mid-chain hydroxy and epoxy acids~~hydroxy FAs and DAs~~; Figures 4a-b; $p < 0.001$ and 0.01, respectively). Ratios of ω-C_{16}/$\sum C_{16}$ and ω-C_{18}/$\sum C_{18}$ have been reported to increase with progressive cutin degradation in marine sediments, presumably due to the preferential degradation of cutin acids containing double bonds or more than one hydroxyl group (Goñi and Hedges, 1990). However, they also exhibit high values in fresh root tissues (Otto and Simpson, 2006a; Feng et al., 2010). The observed patterns may hence collectively suggest a higher input of root-derived OC in the sediments of North American arctic rivers relative to the GRARs and Kalix.

3.3.2 Indicators of moss and peat input

The ratio of $C_{25}/(C_{25}+C_{29})$ *n*-alkanes is used to indicate the relative input of *Sphagnum* mosses, which are particularly enriched in C_{25} *n*-alkane (Baas et al., 2000; Nott et al., 2000; Pancost et al., 2002; Nichols et al., 2006; Vonk and Gustafsson, 2009). This ratio was highest in Kalix (0.62) and lowest in Indigirka (0.38; Table 3). Similarly, ratios of P/V and 3,5Bd/V may indicate *Sphagnum* and peat inputs, respectively. These three parameters were positively correlated with each other in the pan-arctic sediments analyzed in this study (Figures 4c-d; $p = 0.001$ and 0.02, respectively), and the 3,5Bd/V ratio generally increases with increasing P/V ratio in a broader range of sedimentary samples stemming from these arctic rivers (Figure 5a). In particular, both ratios of $C_{25}/(C_{25}+C_{29})$ *n*-alkanes and P/V increased with increasing wetland coverage in the drainage basin (Figures 6a-b; $p < 0.05$ and 0.03, respectively). As *Sphagnum* mosses are most abundant in wetlands, such correlations corroborate the role of both ratios as moss indicators.

High ratios of *p*-coumaric acid to ferulic acid (*p*Cd/Fd) and *p*-hydroxyacetophenone to hydroxy phenols (Pn/P) have also been reported for mosses and peat (Williams et al., 1998; Amon et al., 2012). However, neither ratio (Table 3) was correlated with the aforementioned moss/peat indicators or with the wetland coverage, undermining their utility as source proxies for mosses and peat in the study area. Instead, both *p*Cd/Fd and Pn/P ratios decreased with increasing ratios of $\omega\text{-}C_{18}/\sum C_{18}$ (Figures 4e-f; $p = 0.002$ and 0.01, respectively). As discussed previously, the $\omega\text{-}C_{18}/\sum C_{18}$ ratio may indicate the relative input of root OC, whereas elevated *p*Cd/Fd ratios have also been reported in leaves and needles (Hedges and Parker, 1976; Hedges and Mann, 1979). Their negative correlation may hence point to an increasing proportion of root-derived OC over leaf/needle-derived OC in the watersheds of Kalix < GRARs < Yukon and Colville. The Pn/P ratio may be affected by such variations as well.

3.3.3 Lignin source and degradation stage

Lignin source indicator S/V and C/V ratios ranged from 0.24–0.70 and from 0.05–0.38, respectively (Table 3), generally within the range reported for the surface sediments of arctic rivers and deltas (0.23–2.09 and 0.02–0.32, respectively; Goñi et al., 2000; 2005; Kuzyk et al., 2008; Tesi et al., 2014; Winterfeld et al., 2015) and implying a predominance of gymnosperm wood-derived OC with minor inputs from angiosperms and non-woody tissues (Hedges and Mann, 1979; Goñi and Hedges, 1995). The Colville river sediments had particularly high C/V ratios (0.28–0.38), even as compared with the Colville delta sediments (0.12–0.24; Schreiner et al., 2013), likely due to OC inputs from tundra vegetation into riverine sediments, which is reported to show elevated C/V ratios (Ugolini et al., 1981). Both S/V and C/V were negatively correlated with the forest coverage in the drainage basins (Figures 6c-d; p = 0.02 and 0.01, respectively), consistent with the dominance of gymnosperm woods in the forests of these arctic watersheds. Such correlations are however obscured by the scatter of the published S/V and C/V ratios for a wider range of sedimentary samples consisting of suspended river sediments to shelf deposits (Figures 5b-c), because lignin phenol composition is subject to alteration during hydrodynamic sorting and diagenesis associated with land-ocean transfer processes (Opsahl, and Benner , 1995; Gordon and Goñi, 2003).

Lignin degradation through side chain oxidation (e.g., by white-rot decay) is typically assessed by the acid-to-aldehyde (Ad/Al) ratios of V and S phenols ($(\mathrm{Ad/Al})_v$ and $(\mathrm{Ad/Al})_s$, respectively; Ertel et al., 1986; Hedges et al., 1988; Goñi and Hedges, 1992; Opsahl and Benner, 1995; Otto and Simpson, 2006b), while degradation of hydroxy phenols is also evaluated by the ratio of *p*-hydroxybenzoic acid to *p*-hydroxybenzaldehyde ($(\mathrm{Ad/Al})_p$; Dittmar and Lara, 2001). These ratios are however also subject to variations induced by OC source alterations and dissolution processes (Benner et al., 1990; Hernes et al., 2007). Similar to the other lignin parameters, the Ad/Al ratios of V and S phenols in this study fall within the range reported for the surface sediments of arctic rivers and deltas elsewhere (Table 3; Goñi et al., 2000; 2005; Kuzyk et al., 2008; Tesi et al., 2014; Winterfeld et al., 2015) with the exception of the Colville sediments. The latter showed much higher Ad/Al values (0.59–0.70 and 0.83–0.99 for V and S phenols, respectively) as compared with the surface sediments of Colville delta (0.25–0.32 and 0.22–0.31 for V and S phenols, respectively; Schreiner et al., 2013), implying a more oxidized source of lignin (such as soil) for the sediments deposited over ice within the river. Alternatively, as delta sediment incorporates OC inputs throughout the year, its composition may be overwhelmed by the high input of relatively “fresh” lignin supplied from surface layers during freshet, whereas sediment deposits collected at the start of the ice breakup period incorporate more degraded OC from deeper soils that is accumulated within the river before ice breaking.

The (Ad/Al)$_v$ and (Ad/Al)$_p$ ratios were positively correlated (Figure 7a; $p = 0.01$) and showed higher values in the GRARs and Yukon relative to Kalix, Colville and Mackenzie (Table 3). Interestingly, both ratios were negatively correlated with the wetland coverage (Figures 6e-f; $p = 0.01$), implying that vanillyl and hydroxy phenols were less oxidized in wetland-dominated watersheds. As anoxic conditions in peat and wetlands are known to limit the activity of phenol-oxidizing enzymes (Freeman et al., 2001; 2004), our observations provide basin-scale evidence for suppression of phenolic compound oxidation in wetlands. Alternatively, the acidic phenols (i.e., vanillic acid and *p*-hydroxybenzoic acid) may have “leached” out in wetlands due to their higher solubility (Benner et al., 1990; Hernes et al., 2007), leading to lower Ad/Al values in the remaining sediments. Again, the correlation of Ad/Al values with wetland coverage is missing when extended to a wider range of sedimentary samples (Figures 5d-e) where other environmental factors (such as hydrodynamic sorting patterns) likely overrule lignin oxidation.

In general, the (Ad/Al)$_s$ ratio increases with increasing (Ad/Al)$_v$ ratio for arctic sedimentary samples (Figure 5f) as diagenetic parameters in general. Within our dataset, however, the (Ad/Al)$_s$ ratio was negatively correlated with the (Ad/Al)$_v$ ratio (Figure 7b; $p = 0.02$) and exhibited lower values in the GRAR sediments (Table 3). These contrasting patterns may be related to the scale of the values examined as our ratios also fit in the general pattern of the bigger dataset (Figure 5f).~~ Alternatively~~Furthermore, the (Ad/Al)$_s$ ratio in our samples increased with an increasing ratio of HMW FAs (C$_{20}$–C$_{30}$) to HMW *n*-alkanes (C$_{20}$–C$_{34}$) (HMW FAs/*n*-alkanes; Table 3; Figure 7c; $p = 0.001$), with the latter indicating enhanced FA preservation (van Dongen et al., 2008a). This relationship is counterintuitive and suggests that the (Ad/Al)$_s$ ratio may be complicated by factors other than side chain oxidation alone in arctic drainage basins. As the (Ad/Al)$_s$ ratio also increased with an increasing ∑Suberin/∑Cutin ratio (Figure 7d; $p = 0.004$), we ~~conclude ~~postulate that the acid-to-aldehyde ratio of syringyl phenols may be strongly influenced by the relative inputs of root/bark versus leaf tissues. The (Ad/Al)$_s$ ratio hence may more strongly reflect lignin source than its oxidation state in our sample set. This effect is not obvious for the (Ad/Al)$_v$ ratio likely because, unlike syringyl phenols that are specific to angiosperms, vanillyl phenols are universal in vascular plants and the Ad/Al variations as recorded by syringyl phenols in the root/bark versus leaf of angiosperm may be obscured by inputs from gymnosperm tissues.

3.4 Variations in terrestrial OC composition and preservation across pan-arctic river basins

To compare the distribution and degradation of terrestrial OC in the pan-arctic sediments, a PCA model was ~~performed~~ built based on the abundance of various groups of biomarkers (Table A1) and the biomarker-derived parameters (Table 3, with all ratios expressed as proportions), respectively. The ~~latter~~PCA model is built on the relative ratio of (mainly) terrestrially derived biomarkers, and is not influenced by the varied inputs of marine and relict OC in different sedimentary samples. It also provides a better explanation of the variance (74.1% for the first and second ~~principle~~ principal component (PC) combined; Figure 8) among the nine rivers investigated (with Mackenzie excluded due to the absence of data on the hydrolysable compounds)~~ and is hence presented here (Figure 8)~~. In agreement with the previous discussion, the (Ad/Al)$_s$ ratio clustered with all the root-input indicators ($\sum$Suberin/$\sum$Cutin, ω-C_{16}/$\sum C_{16}$ and ω-C_{18}/$\sum C_{18}$) in the ~~fourth~~ lower right quadrant on the opposite side of the PC–1 axis ~~to~~ from the other phenol-oxidation parameters ((Ad/Al)$_v$ and (Ad/Al)$_p$). Similarly, while all the moss- and peat-input indicators (including $C_{25}/(C_{25}+C_{29})$ *n*-alkanes, P/V, 3,5Bd/V, *p*Cd/Fd and Pn/P) plotted on the positive side of the PC–2 axis, the *p*Cd/Fd and Pn/P ratios were on the opposite side of the PC-1 axis from the others. Root-input indicators were the largest contributors to PC–1 while moss-indicators contributed most to PC2~~–2~~. Based on these parameters, the nine arctic rivers were grouped into three distinct clusters. Two North American rivers (Yukon and Colville) were separated from GRARs mainly by PC-1 due to higher root inputs to their sediments while Kalix River was separated from all the others by PC–2 due to a much higher moss input. The latter observation is in accordance with the high coverage of wetland and, to a lesser degree, non-permafrost soils in the Kalix basin in comparison to other arctic watersheds.

The relative proportion of various groups of higher-plant-derived biomarkers (including HMW *n*-alkanes, HMW FAs, HMW b-FAs, $\sum$Suberin, $\sum$Cutin, lignin VSC, and hydroxy phenols) within the pan-arctic sediments confirmed the PCA results (Figure 9a). Lignin VSC was the dominating component in Eurasian river sediments, making up 52–62% of all the higher-plant-derived biomarkers analyzed, followed by hydroxy phenols (11–26%), $\sum$Suberin (8–20%), and $\sum$Cutin (3–12%). By comparison, the Colville and Yukon sediments were characterized by a much higher proportion of $\sum$Suberin (30–43%) and HMW FAs (6–7%) and a lower proportion of lignin VSC (18–43%) and hydroxy phenols (10–11%). This lends further weight to our previous conclusions based on the biomarker-derived ratios, and suggests that there is a greater proportional supply of belowground OC to the sediments of the North American arctic rivers relative to the GRARs and the Kalix river. As the Yukon and Colville samples were collected near the river mouth as riverbank and ice deposits, respectively, they had undergone a shorter transport journey and were subject to less hydrodynamic sorting relative to the estuarine sediments of GRARs/Kalix and the shelf edge sediment of Mackenzie. Although we did not conduct grain size analysis on these pan-arctic sediments, the Yukon and Colville samples were possibly enriched with fine-grained materials derived from mineral soils in comparison with the coarser materials accumulated near river mouths and along the shelf (Hedges and Mann, 1979; Keil et al., 1998). Such processes may contribute to the enrichment of belowground OC associated with fine-grained materials in the North American samples. Alternatively, the watersheds of Yukon and Colville have a higher coverage of tundra (Brabets et al., 2000; Walker et al., 2002). As tundra has the highest root-to-shoot ratio of all terrestrial biomes (Jackson et al., 1996), its wide distribution in the watershed is likely to increase the input of belowground OC to riverine export.

In terms of absolute abundances, Kalix had the highest concentration of higher-plant-derived biomarkers per gram of sediment (1.15 $mg/g_{sediment}$) among the eight arctic and sub-arctic rivers (with Mackenzie excluded), followed by Kolyma and Indigirka (0.75 and 0.54 $mg/g_{sediment}$ respectively). This pattern largely tracks the TOC content of these sediments (Table 1), which exerts a strong control over the abundance of biomarkers in sediments. When normalized to the TOC content, Kolyma and Indigirka had the highest overall sedimentary concentrations of higher-plant-derived biomarkers, approximately 1.5–3 times the amount found in the other rivers (Figure 9b). This is consistent with the previous findings that plant-derived sterols (campesterol and β-sitosterol) were in much higher concentrations in these two rivers relative to the other GRARs (van Dongen et al., 2008a). These observations suggest that land-derived carbon is better preserved in eastern Siberia, probably due to the cold and dry climate in the drainage basins and/or a greater input of less degraded OC supplied by the widespread ice complexes (“Yedoma”) in the basins (Vonk et al., 2012; Sánchez-García et al., 2014). Alternatively, terrestrial OC may be less diluted by other carbon sources (such as marine or rock-derived OC) in eastern Siberian sediments (Semiletov et al., 2005; Dudarev et al., 2006). It is also notable that surface-derived OC, as represented by $\sum$Cutin and lignin VSC, was most abundant in the sediments of Kolyma and Indigirka, probably because surface runoff predominates as the mobilization pathways of terrestrial OC in these two continuous-permafrost-dominated watersheds (Feng et al., 2013). Such was however not true for the sediments from Colville River, whose watershed is fully covered by continuous permafrost as well. Again, collected as ice deposits near the river mouth, the Colville sample may have integrated more belowground OC from local mineral soils. Alternatively, ~~T~~the difference may be explained by the ~~varied vegetation coverage between these basins (as discussed below)~~high coverage of tundra in the Colville watershed.

Regardless of the geographic variations, hydrolysable components, including ∑Suberin, ∑Cutin, and HMW b-FAs, made up a significant fraction of the terrestrial OC buried in these arctic river sediments, amounting to 13% to 60% of all the higher-plant-derived biomarkers analyzed. This was particularly true for the Colville sediments that were characterized by the lowest content of lignin, in line with the low forest coverage (2%; Table 1) in the watershed. Accordingly, the Colville sediments had the highest content of ∑Suberin. As discussed previously, ~~This~~ this is probably related to the high tundra coverage in its watershed (Walker et al., 2002)~~, as tundra has the highest root-to-shoot ratio of all terrestrial biomes (Jackson et al., 1996)~~ among other influences. Tundra is widely dispersed in the Arctic, and is expected to experience rapid change in response to regional climate variations (Schuur et al., 2009; Elmendorf et al., 2012). Our results suggest that the “bound” OC warrants greater attention both as an important (and even predominant) component of the carbon transferred from these landscapes into rivers and as molecular informants on biomass source and transport pathways.

4 Conclusions and Implications

Hydrolysable compounds, consisting of b-FAs, hydroxy FAs, DAs, and phenols, were a major component of the sedimentary OC exported from nine arctic and sub-arctic river basins, and revealed distinct carbon sources versus solvent-extractable lipids and lignin phenols. As compared with solvent-extractable FAs, b-FAs were influenced by bacterial and/or algal sources as indicated by the dominance of LMW homologues and the presence of branched and mono-unsaturated ~~Fas~~FAs. In contrast, ω-hydroxy FAs, mid-chain substituted acids, DAs, and hydrolysable phenols were mainly derived from cutin and suberin of higher plants. Several parameters based on these biomarkers were used to investigate relative input of root- and moss-derived OC as well as OC degradation stages. Ratios of ω-C_{16}/∑C_{16} and ω-C_{18}/∑C_{18} were found to increase with increasing suberin/cutin (∑Suberin/∑Cutin) ratio, potentially providing a proxy for assessing fresh root input in these river sediments. Ratios of $C_{25}/(C_{25}+C_{29})$ *n*-alkanes and P/V increased with increasing wetland coverage in the drainage basin, corroborating their role as moss indicators. The Ad/Al ratios of both vanillyl and hydroxy phenols were negatively correlated with wetland coverage, probably reflecting the inhibited oxidation of phenolic compounds in these environments. The $(Ad/Al)_s$ ratio instead was sensitive to relative inputs of root/bark versus leaf tissues and hence informed on lignin source rather than its oxidation state in the transect. These comparisons provide a benchmark assessment of the OC source and degradation indicators across the pan-Arctic.

Suberin-specific biomarkers were found to positively correlate with HMW FAs across the pan-arctic sediments whereas lignin phenols were correlated with cutin-derived compounds. These correlations suggest that, similar to leaf-derived cutin, lignin is mainly derived from surface litter and soil, whereas suberin and HMW FAs incorporate significant inputs from belowground sources (roots and deeper soils). In addition, hydrolysable components displayed varied distribution patterns as compared with lignin or plant wax lipids in the pan-arctic sediments, depending on the vegetation input and preservation in the drainage basins. While lignin dominates in the terrestrial OC transferred into the sediments of Eurasian rivers, hydrolysable OC mainly originating from suberin and cutin appears much more important in sediments derived from Colville watershed. Studies exclusively focusing on plant wax lipids or lignin phenols will fail to capture the diverse sources and sources involved in the mobilization and fate of OC in the arctic rivers. To better constrain land-ocean transfer of carbon in the changing Arctic, bound OC warrants greater attention both as an important component of sedimentary carbon mobilized by rivers and as molecular informants on biomass source and transport pathways.

Author contribution

Ö.G., R.M.H., J.E.V., B.E.v.D., I.P.S., O.V.D., M.B.Y. and R.W.M. collected samples. B.E.v.D. and J.E.V. prepared samples for bulk organic carbon and stable isotope analyses. X.F. conducted biomarker analysis with assistance of D.B.M. and T.I.E. X.F. prepared the manuscript with contributions from all co-authors.

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Table 1. Sample location, drainage basin characteristics and bulk sediment properties of the pan-arctic rivers.

	Kalix	**Ob'**	**Yenisey**	**Lena**	**Indigirka**	**Kolyma**	**Colville1**	**Colville2**	**Yukon**	**Mackenzie**
Latitude; Longitude	65.44°N; 23.20°E	72.65°N; 73.44°E	72.61°N; 79.86°E	71.96°N; 129.54°E	72.06°N; 150.46°E-71.02°N; 152.60°E[*]	70.00°N; 163.70°E	70.22°N; 150.98°W	70.22°N; 150.99°W	61.93°N; 162.88°W	70.17°N; 133.43°W
Water depth (m)	13	< 2	< 2	< 2	8-11	< 2	na	na	na	25
Forest coverage (%)[§]	60	30	49	84	21	31	2	2	51	63
Wetland coverage (%)[§]	20	11	3	1	3	1	na	na	14	18
Permafrost coverage[¶]	5/15	2/24	33/55	79/20	100/0	100/0	100/0	100/0	23/76	16/66
Basin area (10^6 km^2)[‖]	0.024	2.54-2.99	2.44-2.59	2.40-2.49	0.34-0.36	0.65-0.66	0.06	0.06	0.83	1.75
Discharge (km^3/yr)[**]	10	427	673	588	54	136	19	19	208	316
Runoff (mm/yr)[**]	417	145	263	245	159	209	317	317	251	181
Sediment yield (t km^{-2} yr^{-1})[††]	na	6	2	8	36	19	6	6	72	74
TOC/POC flux (t km^{-2} yr^{-1})[††]	1.4/0.099	1.1/0.14	1.8/0.066	1.9/0.49	1.2/0.47	1.5/0.48	4.6/2.6	4.6/2.6	3.0/1.07	2.1/1.1
OC (%)	4.5	0.9	1.9	0.5	1.5	1.7	1.78	0.85	1.16	1.56
OC/N[‡‡]	10.9 ± 0.3	10.0 ± 0.1	10.5 ± 0.1	12.3 ± 0.8	14.7 ± 0.2	15.9 ± 1.2	12.8	13.7	15.5	4.7
δ^{13}C-TOC (‰)[‡‡]	–27.1	–27.4	–26.5	–25.0	–26.6	–26.7	–26.4	–26.7	–26	–26

na: not available.

[*] Combined surface sediments along a transect;

[§] Data from Revenga et al. (1998) and Ingri et al. (2005);

[¶] Given as % continuous/ % (discontinuous+sporadic+isolated) (Gustafsson et al., 2011; Holmes et al., 2013);

[‖] Data from Gordeev et al. (1996); Holmes et al. (2002); Rachold et al. (2004) and Ingri et al. (2005);

[**] Data from Milliman et al. (1995); Stein and Macdonald (2004); Ingri et al. (2005) and Holmes et al. (2013);

[††] Kalix data from Ingri et al. (2005), Colville data from McClelland et al. (2014), Yukon data from Guo et al. (2012), and the rest from Stein and Macdonald (2004);

[‡‡] Mass ratio of OC to total nitrogen (OC/N) and δ^{13}C values from Drenzek et al. (2007) for Mackenzie, van Dongen et al. (2008a) for GRARs and Vonk et al. (2008) for Kalix.

Table 2. Abundances of lignin and hydroxy phenols in the pan-arctic sediments (mg/g OC).

	Kalix	Ob’	Yenisey	Lena	Indigirka	Kolyma	Coville1	Coville2	Yukon	Mackenzie
3,5-dihydroxybenzoic acid (3,5Bd)	2.70	1.66	0.96	1.68	1.56	1.52	0.26	0.26	0.70	0.55
p-Hydroxybenzaldehyde	2.92	1.02	0.75	0.99	0.90	0.93	0.30	0.37	0.53	0.95
p-Hydroxyacetophenone	1.32	0.75	0.43	0.50	0.44	0.81	0.11	0.12	0.21	0.22
p-Hydroxybenzoic acid	2.49	2.36	1.72	2.18	3.03	3.06	0.72	0.66	1.12	0.70
***p*-Hydroxy phenols (P)**	**6.72**	**4.13**	**2.90**	**3.67**	**4.36**	**4.80**	**1.13**	**1.15**	**1.85**	**1.87**
Vanillin	4.06	3.11	2.94	3.64	4.58	5.17	0.58	0.63	2.76	1.70
Acetovanillone	2.04	1.80	1.76	2.30	3.68	3.38	0.15	0.15	0.71	0.59
Vanillic acid	2.34	2.35	2.38	2.78	3.62	3.69	0.41	0.37	1.81	0.79
Vanillyl phenols (V)	**8.45**	**7.26**	**7.09**	**8.72**	**11.88**	**12.24**	**1.14**	**1.15**	**5.28**	**3.09**
Syringaldehyde	1.73	2.51	1.75	1.13	3.90	4.20	0.27	0.28	0.58	0.45
Acetosyringone	0.75	1.06	0.58	0.32	1.55	1.75	0.11	0.09	0.28	0.17
Syringic acid	1.42	1.45	0.87	0.67	2.16	2.60	0.26	0.23	0.63	0.45
Syringyl phenols (S)	**3.89**	**5.02**	**3.21**	**2.12**	**7.60**	**8.55**	**0.64**	**0.60**	**1.49**	**1.07**
p-Coumaric acid (*p*Cd)	1.60	0.56	0.52	0.40	0.78	0.93	0.10	0.05	0.13	0.09
Ferulic acid (Fd)	0.41	0.52	0.34	0.18	1.11	1.05	0.33	0.28	0.61	0.07
Cinnamyl phenols (C)	**2.01**	**1.09**	**0.86**	**0.58**	**1.89**	**1.98**	**0.43**	**0.33**	**0.74**	**0.17**
Lignin phenols (VSC)	**14.35**	**13.36**	**11.15**	**11.41**	**21.37**	**22.78**	**2.21**	**2.08**	**7.51**	**4.32**

Table 3. Biomarker-based parameters of organic matter (OM) sources and degradation stages used in this paper.

Indication	Proxy	Kalix	Ob’	Yenisey	Lena	Indigirka	Kolyma	Coville1	Coville2	Yukon	Mackenzie
Inputs of suberin and cutin	∑Suberin	2.29	3.80	2.79	1.39	5.05	8.93	4.88	4.86	5.28	na
	∑Cutin	0.84	1.30	1.37	0.87	3.00	5.16	1.23	0.89	0.81	na
	∑Suberin/∑Cutin	2.72	2.93	2.03	1.60	1.68	1.73	3.98	5.44	6.54	na
	ω-$C_{16}/\Sigma C_{16}$	0.18	0.26	0.27	0.21	0.22	0.23	0.33	0.39	0.51	na
	ω-$C_{18}/\Sigma C_{18}$	0.20	0.35	0.40	0.33	0.47	0.46	0.62	0.66	0.75	na
Moss and peat input	$C_{25}/(C_{25}+C_{29})$ *n*-alkanes	0.62	0.52	0.44	0.39	0.38	0.41	0.47	0.55	0.43	0.44
	P/V	0.80	0.57	0.41	0.42	0.37	0.39	0.99	1.00	0.35	0.60
	3,5Bd/V	0.32	0.23	0.14	0.19	0.13	0.12	0.23	0.22	0.13	0.18
	*p*Cd/Fd	3.91	1.08	1.53	2.19	0.70	0.89	0.29	0.17	0.21	1.23
	Pn/P	0.20	0.18	0.15	0.14	0.10	0.17	0.10	0.11	0.11	0.12
Lignin source	S/V	0.46	0.69	0.45	0.24	0.64	0.70	0.56	0.52	0.28	0.35
	C/V	0.24	0.15	0.12	0.07	0.16	0.16	0.38	0.28	0.14	0.05
Oxidation of phenols	$(Ad/Al)_v$	0.58	0.76	0.81	0.76	0.79	0.71	0.70	0.59	0.66	0.47
	$(Ad/Al)_s$	0.82	0.58	0.50	0.60	0.55	0.62	0.99	0.83	1.10	0.99
	$(Ad/Al)_p$	0.85	2.33	2.31	2.21	3.38	3.28	2.40	1.78	2.12	0.74
FA preservation	HMW FAs/*n*-alkanes	1.49	0.14	0.24	0.56	0.32	0.83	1.38	0.78	1.83	0.96

Abbreviations: ∑Suberin = C_{20}–C_{26} ω-hydroxy fatty acids (FAs) + C_{20}–C_{28} diacids (DAs) + 9,10-epoxy C_{18} DA; ∑Cutin = C_{15}, C_{16} mid-chain hydroxy DAs + C_{15}, C_{16} x,ω-dihydroxy FAs; ω-$C_{16}/\sum C_{16}$ or ω-$C_{18}/\sum C_{18}$ = ratio of C_{16} or C_{18} ω-hydroxy FA to the summation of ~~all~~ C_{16} or C_{18} ω-hydroxy FAs, DAs, and mid-chain hydroxy and epoxy acids~~hydroxy FAs and DAs~~; P: *p*-hydroxy phenols; V: vanillyl phenols; S: syringyl phenols; C: cinnamyl phenols; 3,5Bd: 3,5-dihydroxybenzoic acid; *p*Cd: *p*-coumaric acid; Fd: ferulic acid; Pn: *p*-hydroxyacetophenone; Ad/Al: the acid-to-aldehyde ratio of V, S and P phenols; HMW FAs/*n*-alkanes = high-molecular-weight (HMW) FAs (C_{20}–C_{30}) to HMW *n*-alkanes (C_{20}–C_{34}); na: not available.

Figure captions

Figure 1. Sampling locations (red dots) and watersheds of the nine arctic and sub-arctic rivers.

Figure 2. Abundances of solvent-extractable and hydrolysable lipids in the pan-arctic ~~surface sediments~~sedimentary particles, including *n*-alkanes (a), fatty acids (FAs; b), bound fatty acids (b-FAs; c), ω-hydroxy FAs (d), mid-chain hydroxy and epoxy acids (e), α-hydroxy FAs (f), β-hydroxy FAs (g), and diacids (DAs; h). Carbon preference index (CPI) is defined as $\mathrm{CPI}_{25\text{-}33} = (\sum C_{25,27,29,31,33}/ \sum C_{24,26,28,30,32} + \sum C_{25,27,29,31,33}/\sum C_{26,28,30,,32,34})/2$ for *n*-alkanes, $\mathrm{CPI}_{20\text{-}30} = (\sum C_{20,22,24,26,28,30}/ \sum C_{19,21,23,25,27,29} + \sum C_{20,22,24,26,28,30}/\sum C_{21,23,25,27,29,31})/2$ for ~~fatty acids (~~FAs~~)~~ and ~~bound FAs (~~b-FAs~~)~~, $\mathrm{CPI}_{20\text{-}28} = (\sum C_{20,22,24,26,28}/\sum C_{19,21,23,25,27} + \sum C_{20,22,24,26,28}/\sum C_{21,23,25,27,29})/2$ for ~~diacids (~~DAs~~)~~. Data of solvent-extractable *n*-alkanes and FAs are derived from van Dongen et al. (2008a) for GRARs, Vonk et al. (2008) for Kalix, and Drenzek et al. (2007) for Mackenzie.

Figure 3. Correlations between the abundances of various terrestrial biomarkers in the pan-arctic sediments. Open diamonds and filled squares in (a) represent suberin (∑Suberin) and cutin (∑Cutin) biomarkers, respectively (contents defined in Table 3). HMW FAs: high-molecular-weight fatty acids (C_{20}-C_{30}). VSC: vanilyl, syringyl and cinnamyl lignin phenols.

Figure 4. Correlations between the biomarker-based OC source parameters in the pan-arctic sediments. Blue arrows indicate direction of change in the parameters with increased inputs of roots or mosses. See Table 3 for abbreviations and specific values.

Figure 5. Comparisons of the lignin parameters from this study (black diamond) versus published data in the pan-arctic sediments (colored symbols). Original data are found in Schreiner et al. (2013) for Colville delta sediments, Goñi et al. (2000; 2005) for Mackenzie river suspended sediments and Beaufort shelf sediments, Winterfeld et al. (2015) for Buor Khaya Bay sediments (receiving Lena river), Tesi et al. (2014) for Lena, Indigirka and Kolyma delta sediments and Kuzyk et al. (2008) for surface sediments of Hudson Bay.

Figure 6. Influence of vegetation coverage on the OC source and degradation parameters in the arctic watersheds. Panels a and b indicate more moss inputs at higher values. Panels c and d indicate more angiosperm and non-woody inputs, respectively, at higher values. Panels e and f indicate a more oxidized state of vanillyl and *p*-hydroxy phenols, respectively, at higher values. Refer to Table 3 for abbreviations and detailed values. Note that the Colville data are not included for the absence of information on its wetland coverage.

Figure 7. Relationships between the acid-to-aldehyde (Ad/Al) ratios and other OC parameters. Ratios of $(Ad/Al)_v$, HMW FAs/*n*-alkanes and ∑Suberin/∑Cutin increase with increasing oxidation of vanillyl phenols, FA preservation and root inputs, respectively. Refer to Table 3 for abbreviations and detailed values.

Figure 8. Principal ~~Principle~~ component analysis (PCA) of biomarker-based parameters in the pan-arctic river sediments. The PCA results are expressed as a biplot, where the distance and direction from axis centre has the same meaning for river samples and biomarker variables. The eight arctic river samples (solid black circles) are grouped into three clusters as indicated by the shaded areas. Names and circles for variables (the~~Numbers represent~~ biomarker-based source and degradation parameters) are ~~as~~ colored according to their classic indications. Refer to Table 3 for ~~the~~ abbreviations ~~and detailed values of~~for the ~~used~~ parameters.

Figure 9. The relative proportion (a) and abundances (b) of various terrestrial biomarkers analyzed in the pan-arctic sediments. VSC: vanilyl, syringyl and cinnamyl phenols; HMW: high-molecular-weight; b-FAs: bound fatty acids; ∑Suberin and ∑Cutin: suberin and cutin biomarkers as defined in Table 3.


Pacific Ocean
Yukon
Kolyma
Colville
Mackenzie
Indigirka
Lena
Yenisey
Arctic Ocean
Ob'
75°N
Kalix
60°N
Atlantic Ocean
45°N

Figure 1.

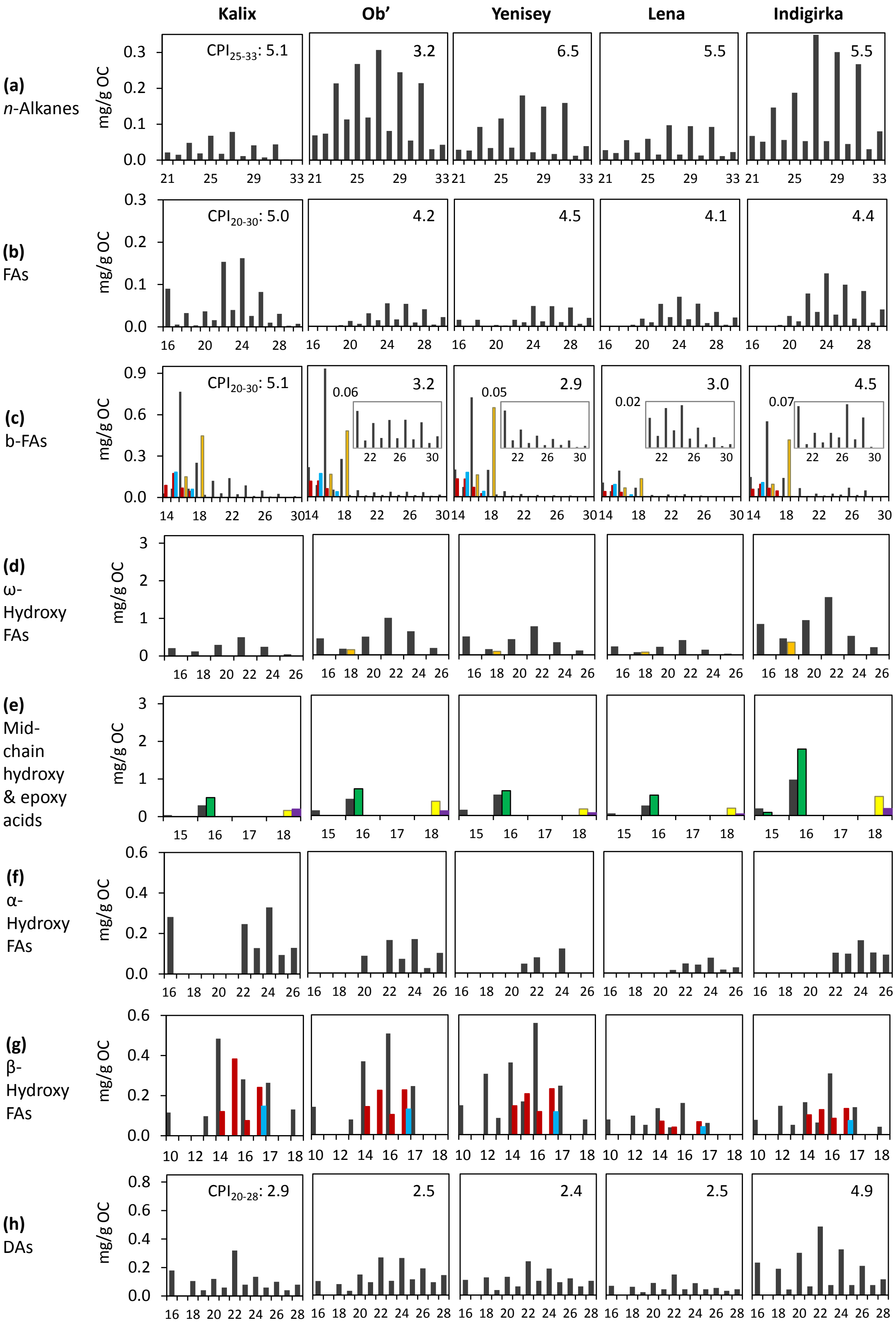
Kalix
Ob’
Yenisey
Lena
Indigirka
(a)
n-Alkanes
mg/g OC
CPI25-33: 5.1
3.2
6.5
5.5
5.5
(b)
FAs
CPI20-30: 5.0
4.2
4.5
4.1
4.4
(c)
b-FAs
CPI20-30: 5.1
3.2
2.9
3.0
4.5
0.06
0.05
0.02
0.07
(d)
ω-Hydroxy FAs
(e)
Mid-chain hydroxy & epoxy acids
(f)
α-Hydroxy FAs
(g)
β-Hydroxy FAs
(h)
DAs
CPI20-28: 2.9
2.5
2.4
2.5
4.9

Figure 2(i)

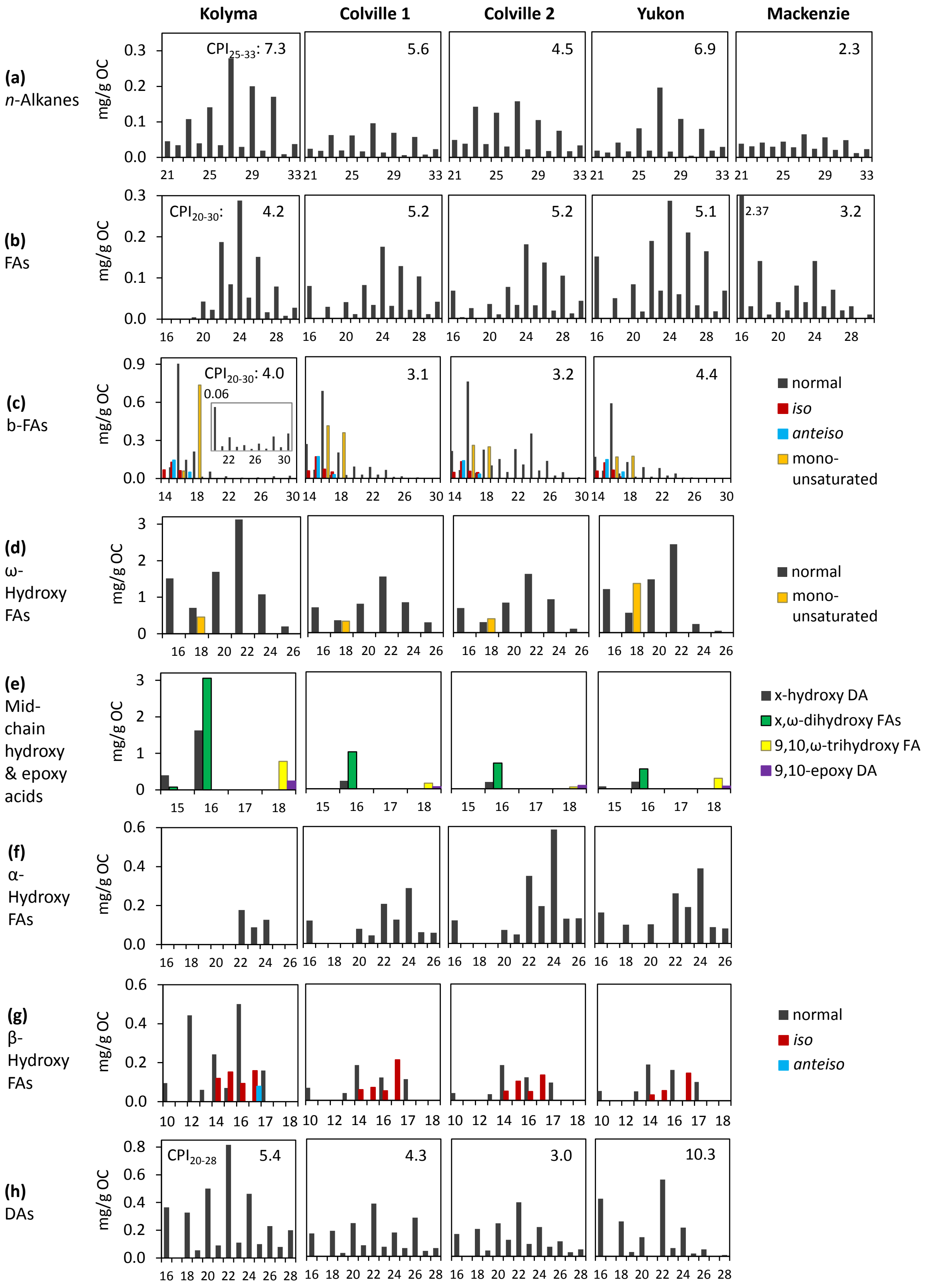
Kolyma
Colville 1
Colville 2
Yukon
Mackenzie
(a) n-Alkanes
mg/g OC
CPI25-33: 7.3
5.6
4.5
6.9
2.3
(b) FAs
CPI20-30: 4.2
5.2
5.2
5.1
2.37
3.2
(c) b-FAs
CPI20-30: 4.0
0.06
3.1
3.2
4.4
normal
iso
anteiso
mono-unsaturated
(d) ω-Hydroxy FAs
normal
mono-unsaturated
(e) Mid-chain hydroxy & epoxy acids
x-hydroxy DA
x,ω-dihydroxy FAs
9,10,ω-trihydroxy FA
9,10-epoxy DA
(f) α-Hydroxy FAs
(g) β-Hydroxy FAs
normal
iso
anteiso
(h) DAs
CPI20-28 5.4
4.3
3.0
10.3

Figure 2(ii)

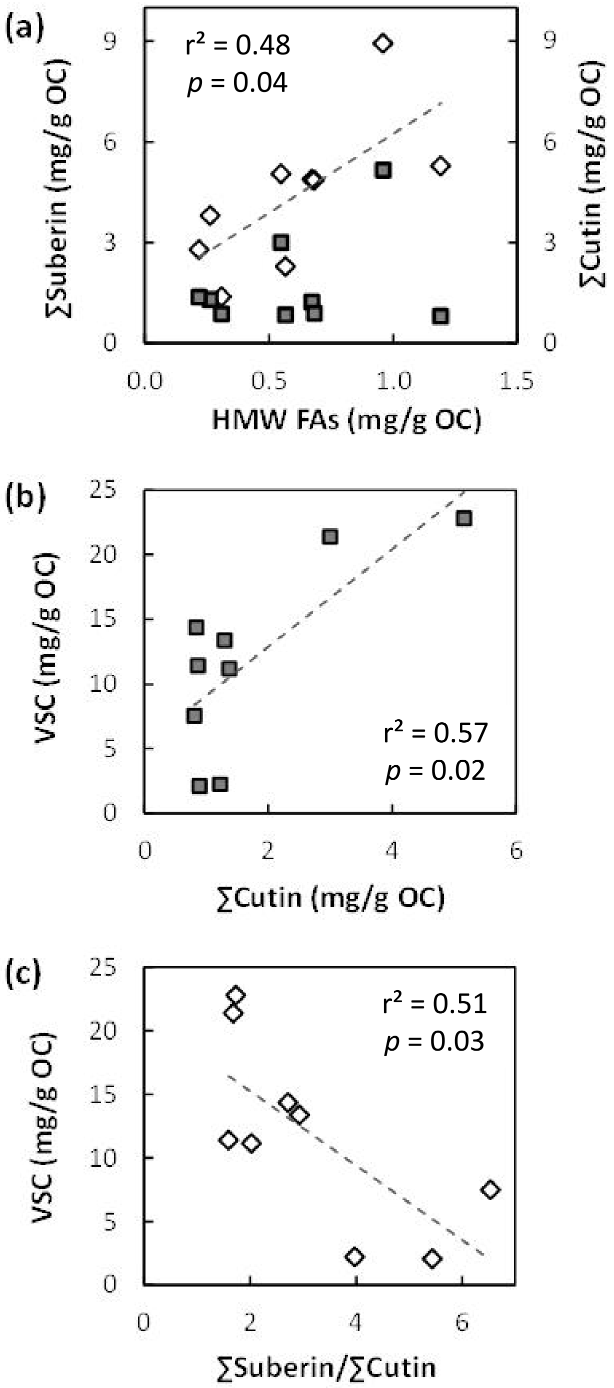
(a)
r² = 0.48
p = 0.04
∑Suberin (mg/g OC)
∑Cutin (mg/g OC)
0
3
6
9
0.0
0.5
1.0
1.5
HMW FAs (mg/g OC)
(b)
r² = 0.57
p = 0.02
VSC (mg/g OC)
0
5
10
15
20
25
0
2
4
6
∑Cutin (mg/g OC)
(c)
r² = 0.51
p = 0.03
VSC (mg/g OC)
0
5
10
15
20
25
0
2
4
6
∑Suberin/∑Cutin

Figure 3.

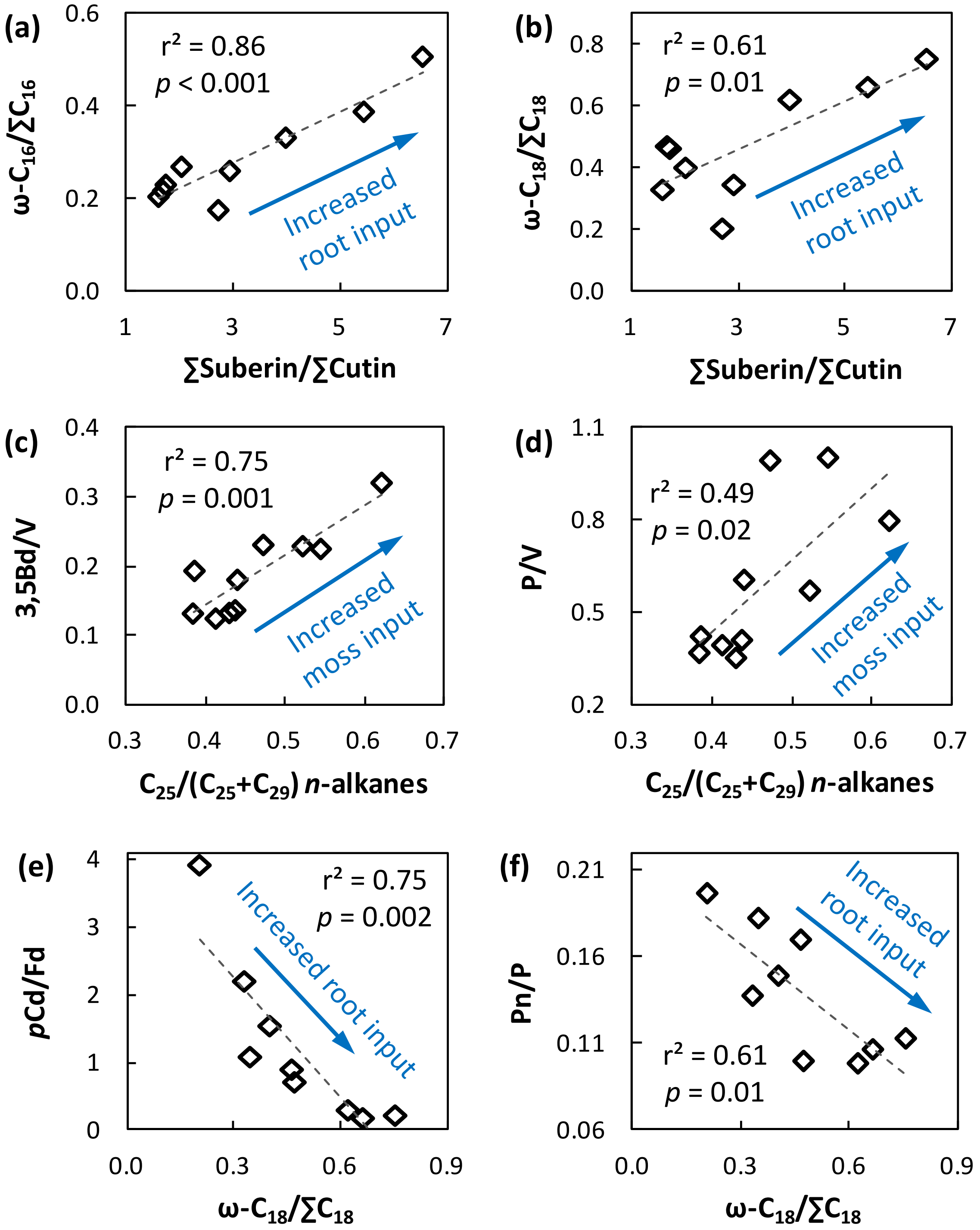
(a)
0.6
0.4
0.2
0.0
ω-C16/∑C16
r² = 0.86
p < 0.001
Increased root input
1
3
5
7
∑Suberin/∑Cutin
(b)
0.8
0.6
0.4
0.2
0.0
ω-C18/∑C18
r² = 0.61
p = 0.01
Increased root input
1
3
5
7
∑Suberin/∑Cutin
(c)
0.4
0.3
0.2
0.1
0.0
3,5Bd/V
r² = 0.75
p = 0.001
Increased moss input
0.3
0.4
0.5
0.6
0.7
C25/(C25+C29) n-alkanes
(d)
1.1
0.8
0.5
0.2
P/V
r² = 0.49
p = 0.02
Increased moss input
0.3
0.4
0.5
0.6
0.7
C25/(C25+C29) n-alkanes
(e)
4
3
2
1
0
pCd/Fd
r² = 0.75
p = 0.002
Increased root input
0.0
0.3
0.6
0.9
ω-C18/∑C18
(f)
0.21
0.16
0.11
0.06
Pn/P
Increased root input
r² = 0.61
p = 0.01
0.0
0.3
0.6
0.9
ω-C18/∑C18

Figure 4.

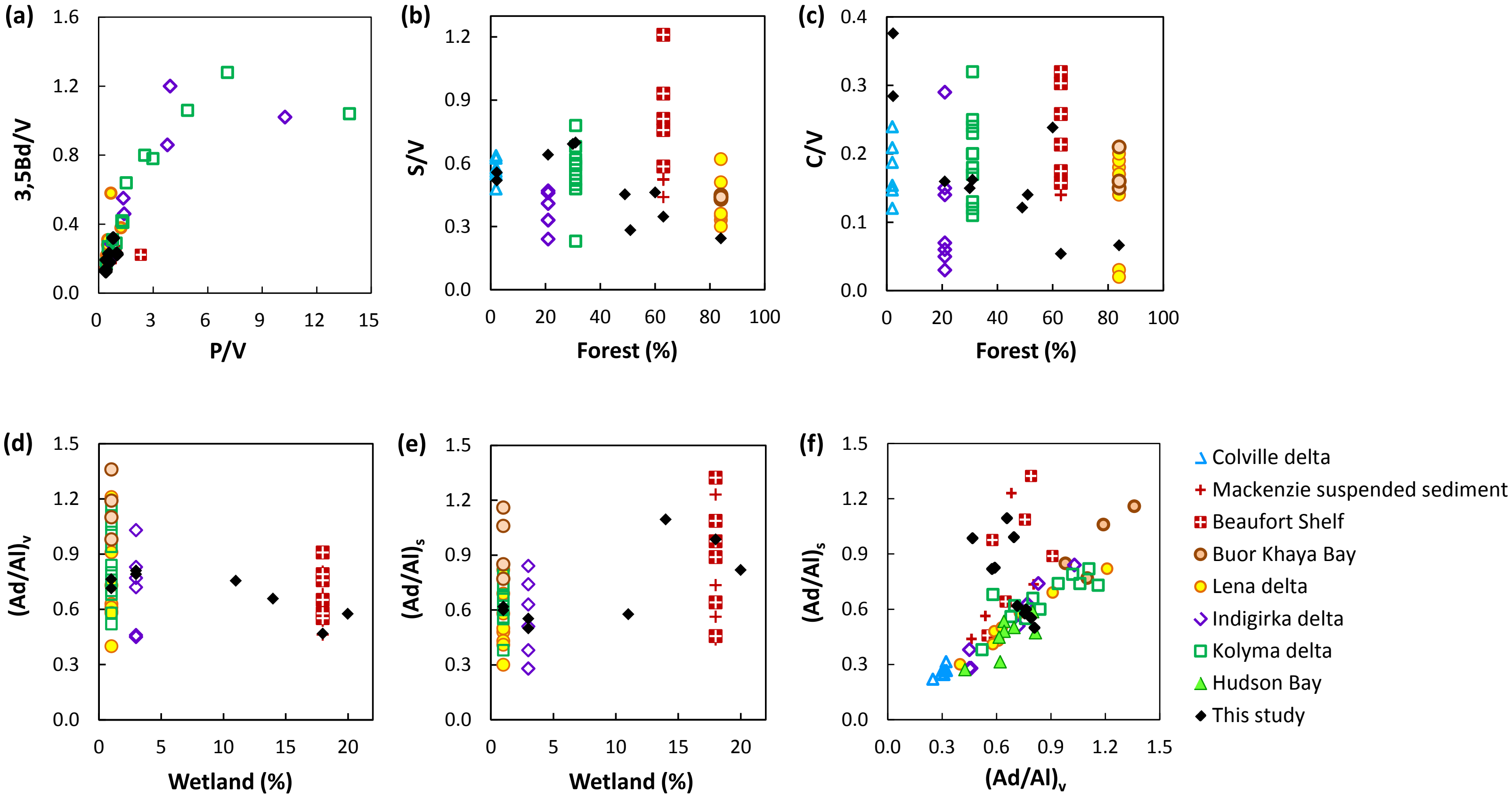
(a)
3,5Bd/V
P/V
1.6
1.2
0.8
0.4
0.0
0
3
6
9
12
15
(b)
S/V
Forest (%)
1.2
0.9
0.6
0.3
0.0
0
20
40
60
80
100
(c)
C/V
Forest (%)
0.4
0.3
0.2
0.1
0.0
0
20
40
60
80
100
(d)
(Ad/Al)v
Wetland (%)
1.5
1.2
0.9
0.6
0.3
0.0
0
5
10
15
20
(e)
(Ad/Al)s
Wetland (%)
1.5
1.2
0.9
0.6
0.3
0.0
0
5
10
15
20
(f)
(Ad/Al)s
(Ad/Al)v
1.5
1.2
0.9
0.6
0.3
0.0
0.0
0.3
0.6
0.9
1.2
1.5
Colville delta
Mackenzie suspended sediment
Beaufort Shelf
Buor Khaya Bay
Lena delta
Indigirka delta
Kolyma delta
Hudson Bay
This study

Figure 5.

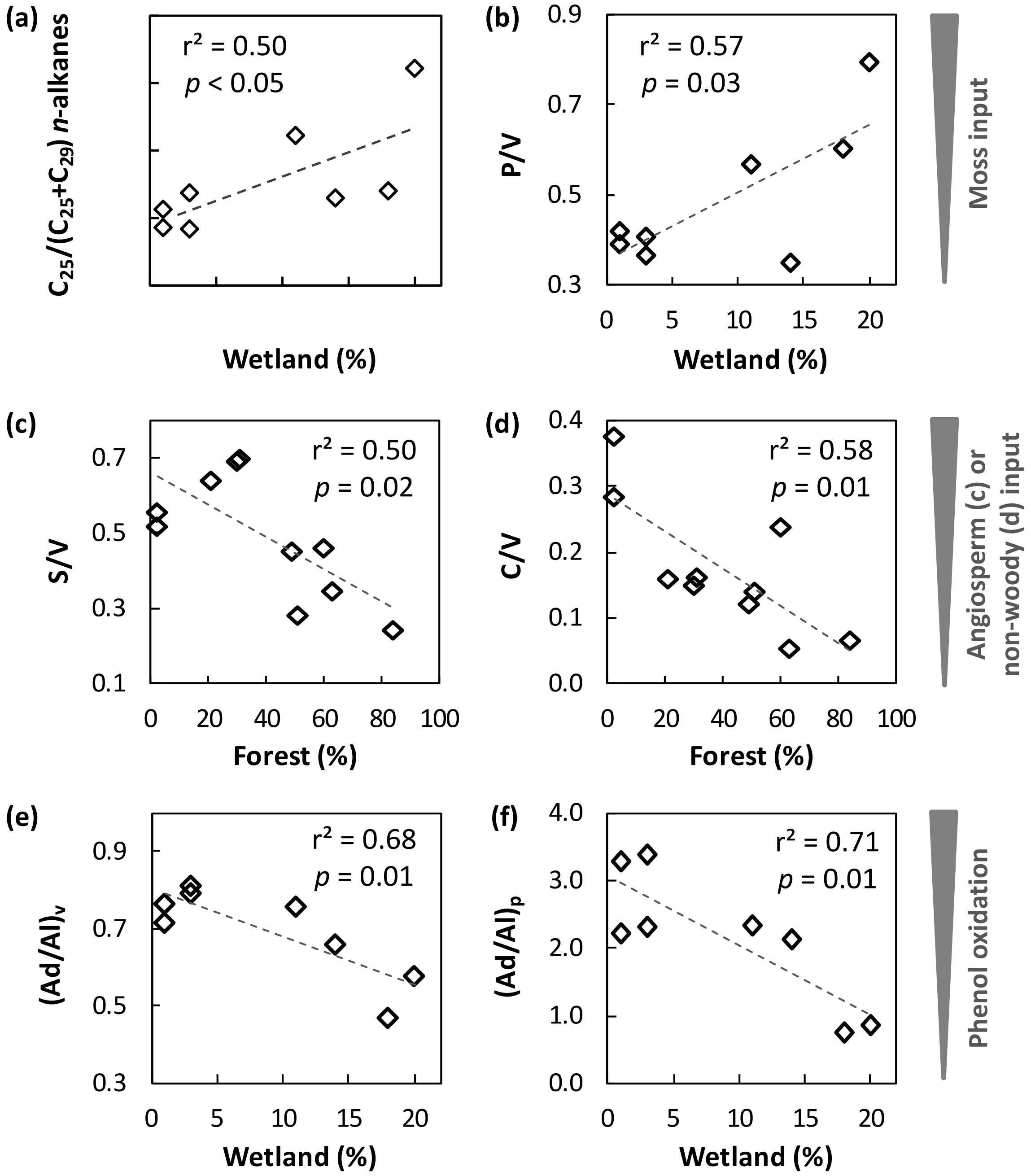
(a)
C25/(C25+C29) n-alkanes
r² = 0.50
p < 0.05
Wetland (%)
(b)
0.9
0.7
0.5
0.3
P/V
r² = 0.57
p = 0.03
0
5
10
15
20
Wetland (%)
Moss input
(c)
0.7
0.5
0.3
0.1
S/V
r² = 0.50
p = 0.02
0
20
40
60
80
100
Forest (%)
(d)
0.4
0.3
0.2
0.1
0.0
C/V
r² = 0.58
p = 0.01
0
20
40
60
80
100
Forest (%)
Angiosperm (c) or
non-woody (d) input
(e)
0.9
0.7
0.5
0.3
(Ad/Al)v
r² = 0.68
p = 0.01
0
5
10
15
20
Wetland (%)
(f)
4.0
3.0
2.0
1.0
0.0
(Ad/Al)p
r² = 0.71
p = 0.01
0
5
10
15
20
Wetland (%)
Phenol oxidation

Figure 6.

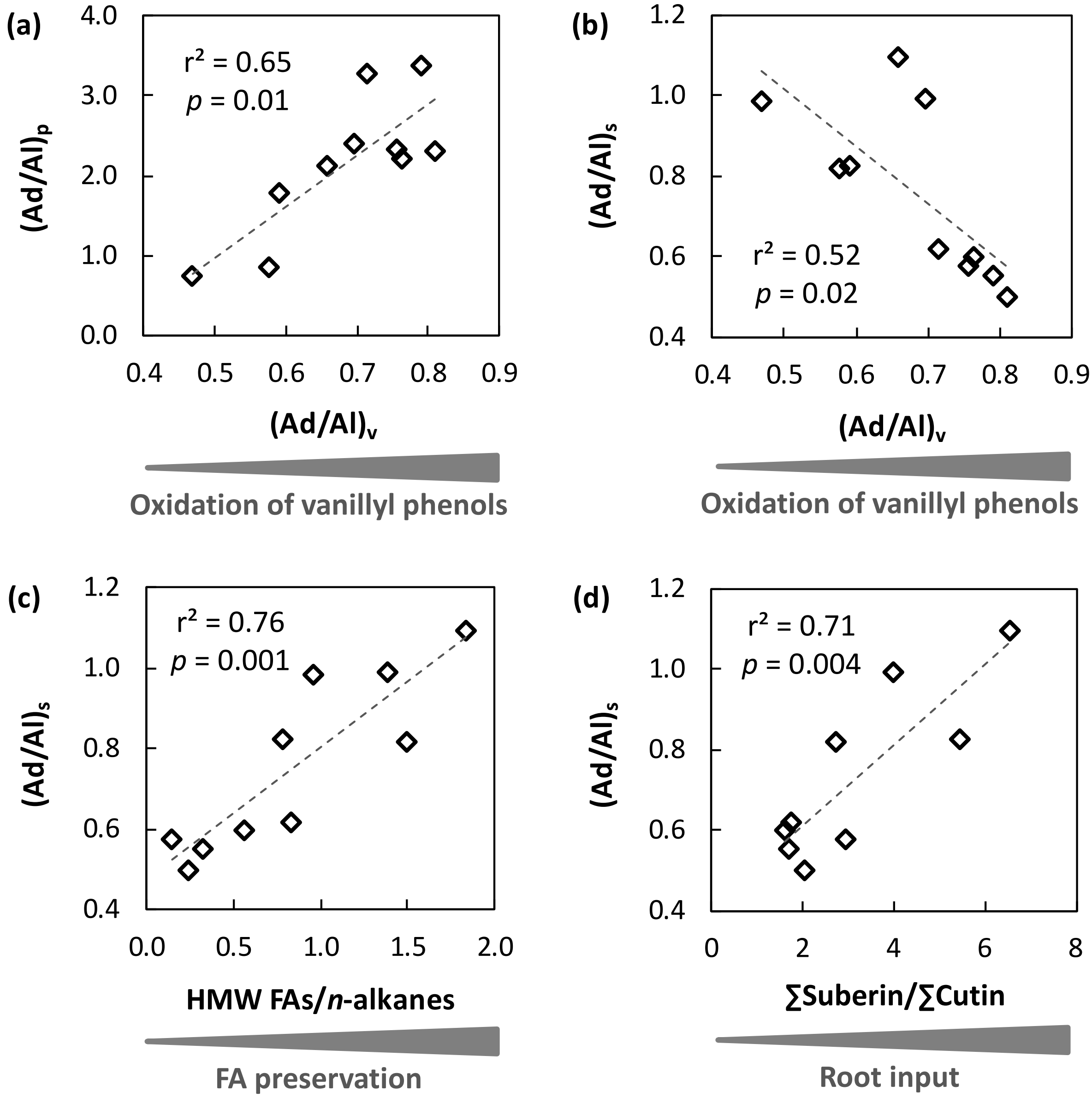
(a)
r² = 0.65
p = 0.01
(Ad/Al)p
(Ad/Al)v
4.0
3.0
2.0
1.0
0.0
0.4
0.5
0.6
0.7
0.8
0.9
Oxidation of vanillyl phenols
(b)
r² = 0.52
p = 0.02
(Ad/Al)s
(Ad/Al)v
1.2
1.0
0.8
0.6
0.4
0.4
0.5
0.6
0.7
0.8
0.9
Oxidation of vanillyl phenols
(c)
r² = 0.76
p = 0.001
(Ad/Al)s
HMW FAs/n-alkanes
1.2
1.0
0.8
0.6
0.4
0.0
0.5
1.0
1.5
2.0
FA preservation
(d)
r² = 0.71
p = 0.004
(Ad/Al)s
∑Suberin/∑Cutin
1.2
1.0
0.8
0.6
0.4
0
2
4
6
8
Root input

Figure 7.

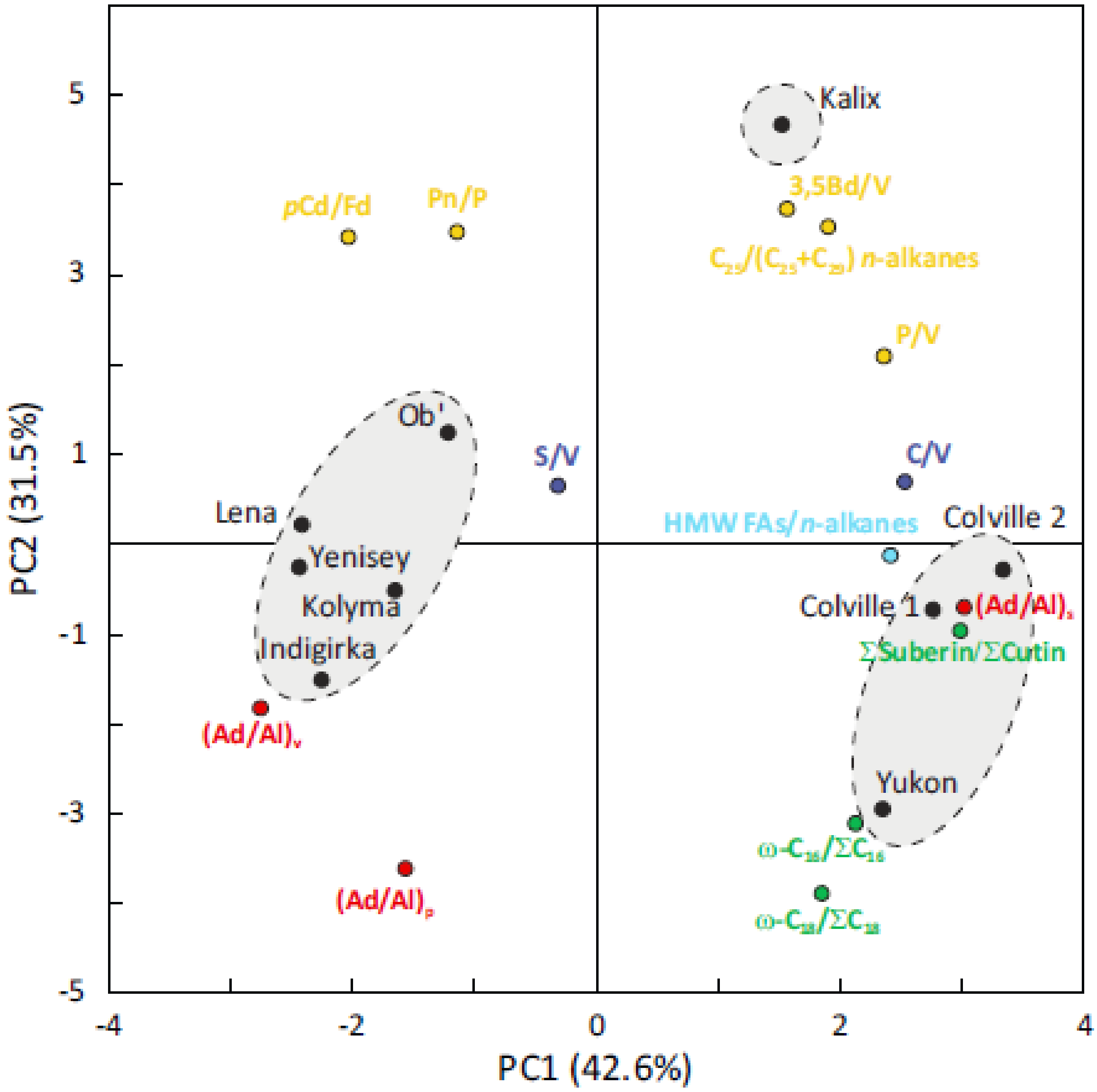
Kalix
3,5Bd/V
$C_{25}/(C_{25}+C_{29})$ *n*-alkanes
P/V
*p*Cd/Fd
Pn/P
Ob'
S/V
C/V
Lena
Yenisey
Kolyma
Indigirka
HMW FAs/*n*-alkanes
Colville 2
Colville 1
$(Ad/Al)_s$
ΣSuberin/ΣCutin
$(Ad/Al)_v$
Yukon
$\omega\text{-}C_{16}/\Sigma C_{16}$
$\omega\text{-}C_{18}/\Sigma C_{18}$
$(Ad/Al)_p$
PC2 (31.5%)
PC1 (42.6%)
5
3
1
-1
-3
-5
-4
-2
0
2
4

Figure 8..

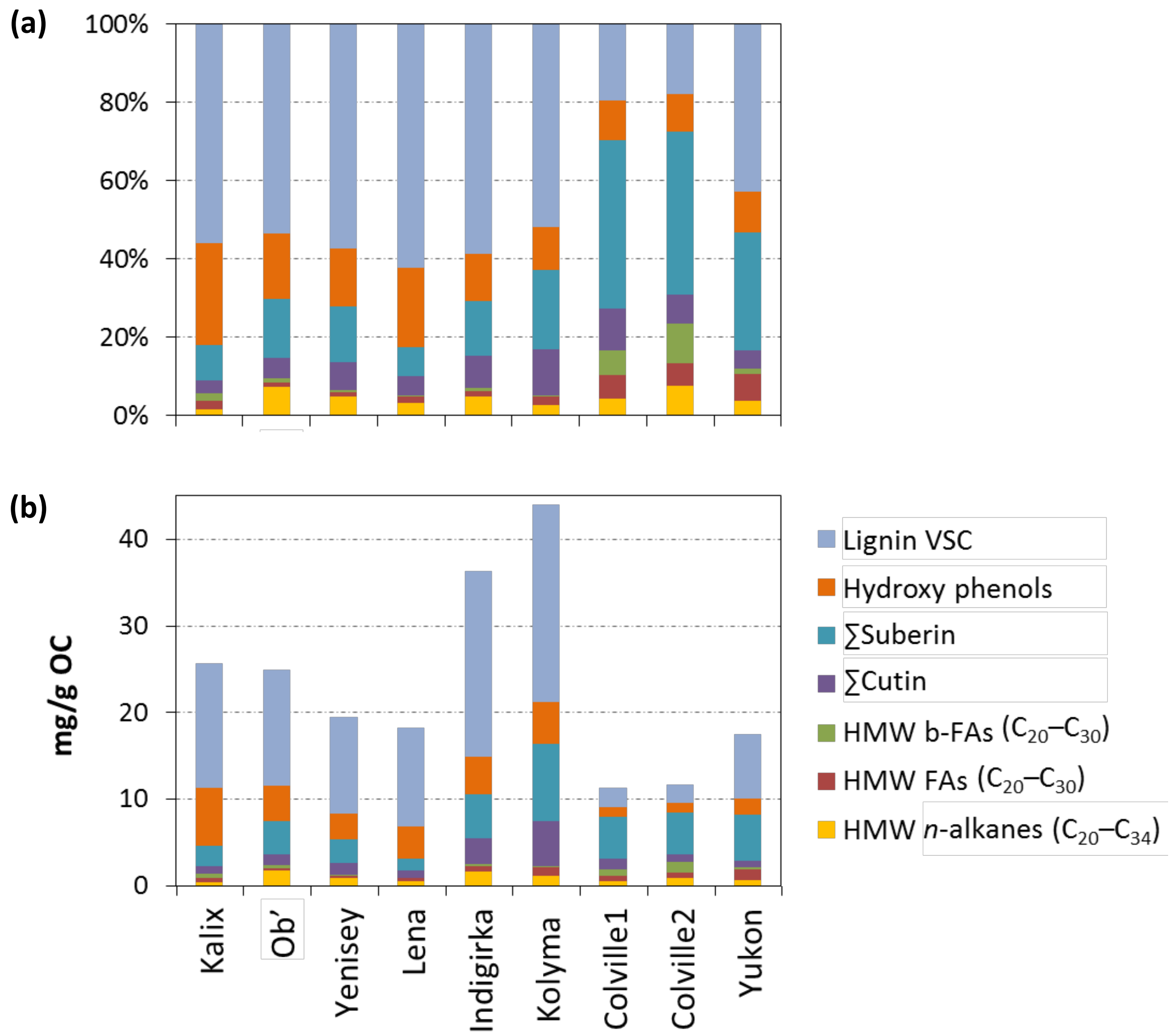
(a)
100%
80%
60%
40%
20%
0%
(b)
mg/g OC
40
30
20
10
0
Lignin VSC
Hydroxy phenols
∑Suberin
∑Cutin
HMW b-FAs (C_{20}–C_{30})
HMW FAs (C_{20}–C_{30})
HMW *n*-alkanes (C_{20}–C_{34})
Kalix
Ob’
Yenisey
Lena
Indigirka
Kolyma
Colville1
Colville2
Yukon

Figure 9.

Appendix Table A1: Abundances of solvent-extractable *n*-alkanes, FAs, and hydrolysable compounds in pan-arctic river sediments (mg/g OC). Analytical error associated with biomarker analysis is typically <10%. The *n*-alkane and FA data are from Vonk et al., 2008 (Kalix), van Dongen et al., 2008a (GRARs), and Drenzek et al., 2007 (Mackenzie).

	Kalix	**Ob'**	**Yenisey**	**Lena**	**Indigirka**	**Kolyma**	**Colville1**	**Colville2**	**Yukon**	**Mackenzie**
SOLVENT-EXTRACTABLE LIPIDS										
***n*-Alkanes**										
C_{20}	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02		0.03
C_{21}	0.02	0.07	0.03	0.03	0.07	0.05	0.02	0.05	0.02	0.04
C_{22}	0.01	0.07	0.03	0.02	0.05	0.03	0.02	0.04	0.01	0.03
C_{23}	0.05	0.21	0.09	0.05	0.14	0.11	0.06	0.14	0.04	0.04
C_{24}	0.02	0.11	0.03	0.02	0.06	0.04	0.02	0.04	0.02	0.03
C_{25}	0.07	0.26	0.11	0.06	0.19	0.14	0.06	0.12	0.08	0.04
C_{26}	0.02	0.12	0.03	0.02	0.05	0.03	0.02	0.03	0.02	0.03
C_{27}	0.08	0.30	0.18	0.10	0.34	0.28	0.10	0.16	0.19	0.06
C_{28}	0.01	0.08	0.02	0.02	0.05	0.03	0.01	0.02	0.02	0.02
C_{29}	0.04	0.24	0.15	0.09	0.30	0.20	0.07	0.10	0.11	0.06
C_{30}	0.01	0.05	0.02	0.01	0.04	0.02	0.01	0.02	0.00	0.02
C_{31}	0.04	0.21	0.16	0.09	0.26	0.17	0.06	0.07	0.08	0.05
C_{32}	0.00	0.03	0.01	0.01	0.03	0.01	0.01	0.02	0.02	0.01
C_{33}	0.00	0.04	0.04	0.02	0.08	0.04	0.02	0.03	0.03	0.02
C_{34}		0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.01	0.01
HMW *n*-alkanes (C_{20}-C_{34})	**0.38**	**1.83**	**0.91**	**0.55**	**1.70**	**1.16**	**0.49**	**0.87**	**0.65**	**0.50**
FAs										

C_{16}	0.09		0.02				0.08	0.07	0.15	2.37
C_{18}	0.03		0.02				0.03	0.03	0.05	0.14
C_{20}	0.04	0.01	0.00	0.02	0.02	0.04	0.04	0.04	0.08	0.04
C_{21}	0.02	0.01	0.00	0.01	0.01	0.02	0.01	0.01	0.02	0.02
C_{22}	0.15	0.03	0.02	0.05	0.08	0.19	0.08	0.08	0.19	0.08
C_{23}	0.04	0.01	0.01	0.02	0.03	0.08	0.03	0.03	0.07	0.04
C_{24}	0.16	0.05	0.05	0.07	0.12	0.29	0.17	0.18	0.29	0.14
C_{25}	0.03	0.02	0.01	0.02	0.03	0.05	0.03	0.03	0.06	0.03
C_{26}	0.08	0.05	0.05	0.05	0.10	0.15	0.13	0.14	0.21	0.07
C_{27}	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.03	0.02
C_{28}	0.03	0.04	0.04	0.03	0.08	0.08	0.10	0.10	0.16	0.03
C_{29}	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.00
C_{30}	0.01	0.02	0.02	0.02	0.04	0.03	0.04	0.04	0.07	0.01
HMW FAs (C_{20}-C_{30})	**0.57**	**0.26**	**0.22**	**0.31**	**0.55**	**0.96**	**0.67**	**0.68**	**1.19**	**0.48**
HYDROLYSABLE COMPOUNDS										
b-FAs										
i-C_{14}	0.09	0.11	0.13	0.04	0.06	0.07	0.06	0.05	0.06	
C_{14}	0.03	0.21	0.20	0.10	0.14	0.00	0.27	0.21	0.17	
i-C_{15}	0.17	0.11	0.13	0.08	0.09	0.13	0.17	0.13	0.12	
a-C_{15}	0.18	0.17	0.18	0.09	0.10	0.14	0.17	0.14	0.15	
C_{15}	0.06	0.09	0.07	0.04	0.06	0.09	0.07	0.06	0.06	
i-C_{16}	0.07	0.06	0.07	0.03	0.06	0.06	0.07	0.06	0.06	
$C_{16:1}$	0.15	0.16	0.16	0.06	0.09	0.06	0.41	0.26	0.17	
C_{16}	0.77	0.93	0.72	0.19	0.55	0.90	0.68	0.76	0.59	
i-C_{17}	0.04	0.00	0.02	0.00	0.04	0.00	0.05	0.05	0.01	

a-C_{17}	0.06	0.04	0.04	0.01	0.00	0.05	0.03	0.03	0.05	
C_{17}	0.06	0.05	0.00	0.00	0.00	0.15	0.03	0.04	0.04	
$C_{18:1}$	0.45	0.48	0.65	0.13	0.41	0.74	0.36	0.25	0.17	
C_{18}	0.25	0.27	0.19	0.07	0.14	0.21	0.20	0.22	0.13	
C_{19}	0.02	0.01	0.02	0.00	0.01	0.01	0.03	0.10	0.01	
C_{20}	0.12	0.05	0.04	0.01	0.06	0.05	0.19	0.15	0.09	
C_{21}	0.03	0.01	0.01	0.01	0.01	0.01	0.06	0.05	0.01	
C_{22}	0.14	0.03	0.02	0.02	0.02	0.02	0.18	0.23	0.08	
C_{23}	0.02	0.01	0.01	0.01	0.01	0.01	0.06	0.11	0.02	
C_{24}	0.09	0.04	0.01	0.02	0.02	0.01	0.13	0.35	0.04	
C_{25}	0.01	0.01	0.00	0.00	0.02	0.00	0.03	0.06	0.01	
C_{26}	0.05	0.04	0.01	0.01	0.07	0.01	0.03	0.14	0.01	
C_{27}	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.02	0.00	
C_{28}	0.03	0.03	0.01	0.00	0.05	0.02	0.01	0.05	0.00	
C_{29}	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
C_{30}	0.01	0.02	0.00	0.00	0.00	0.02	0.01	0.01	0.00	
LMW b-FAs (C_{14}-C_{19})	**2.41**	**2.70**	**2.57**	**0.85**	**1.75**	**2.61**	**2.59**	**2.36**	**1.79**	
HMW b-FAs (C_{20}-C_{30})	**0.51**	**0.26**	**0.12**	**0.08**	**0.27**	**0.15**	**0.71**	**1.17**	**0.26**	
ω-Hydroxy FAs										
C_{16}	0.21	0.44	0.49	0.23	0.82	1.52	0.70	0.67	1.19	
$C_{18:1}$	0.00	0.14	0.09	0.07	0.34	0.46	0.31	0.38	1.34	
C_{18}	0.12	0.16	0.16	0.07	0.44	0.71	0.34	0.29	0.54	
C_{20}	0.30	0.49	0.42	0.22	0.93	1.69	0.79	0.82	1.46	
C_{22}	0.50	0.99	0.76	0.40	1.54	3.13	1.53	1.61	2.42	
C_{24}	0.24	0.63	0.34	0.14	0.51	1.08	0.83	0.92	0.24	
C_{26}	0.05	0.19	0.12	0.03	0.20	0.20	0.28	0.11	0.05	

Total ω-Hydroxy FAs	**1.42**	**3.04**	**2.38**	**1.16**	**4.78**	**8.78**	**4.79**	**4.79**	**7.24**	
Mid-chain hydroxy and epoxy acids										
x-Hydroxy C_{15} DA	0.04	0.14	0.15	0.06	0.19	0.40	0.00	0.00	0.07	
x,ω-Dihydroxy C_{15} FAs	0.00	0.00	0.00	0.00	0.08	0.07	0.00	0.00	0.00	
x-Hydroxy C_{16} DA	0.30	0.45	0.56	0.27	0.96	1.63	0.21	0.19	0.19	
x,ω-Dihydroxy C_{16} FAs	0.50	0.71	0.66	0.54	1.77	3.05	1.01	0.70	0.55	
x,ω-Dihydroxy C_{18} FAs	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
9,10,ω-Trihydroxy C_{18} FA	0.16	0.38	0.18	0.19	0.51	0.78	0.16	0.05	0.29	
9,10-Epoxy C_{18} DA	0.20	0.12	0.07	0.04	0.19	0.24	0.06	0.09	0.07	
Total mid-chain acids	**1.20**	**1.80**	**1.62**	**1.10**	**3.69**	**6.18**	**1.44**	**1.03**	**1.17**	
α-Hydroxy FAs										
C_{15}	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.05	
C_{16}	0.28	0.00	0.00	0.00	0.00	0.00	0.12	0.12	0.16	
C_{18}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	
C_{20}	0.00	0.08	0.00	0.00	0.00	0.00	0.07	0.07	0.10	
C_{21}	0.00	0.00	0.05	0.01	0.00	0.00	0.04	0.05	0.00	
C_{22}	0.25	0.16	0.08	0.05	0.10	0.18	0.20	0.35	0.26	
C_{23}	0.13	0.07	0.00	0.04	0.10	0.09	0.12	0.19	0.19	
C_{24}	0.33	0.17	0.12	0.08	0.16	0.13	0.28	0.58	0.39	
C_{25}	0.09	0.02	0.00	0.02	0.10	0.00	0.06	0.13	0.08	
C_{26}	0.13	0.10	0.00	0.03	0.09	0.00	0.06	0.13	0.08	
Total α-Hydroxy FAs	**1.21**	**0.61**	**0.25**	**0.22**	**0.55**	**0.39**	**1.02**	**1.61**	**1.40**	
β-Hydroxy FAs										
C_{10}	0.12	0.14	0.15	0.08	0.07	0.10	0.06	0.04	0.05	
C_{12}	0.00	0.00	0.30	0.09	0.14	0.44	0.00	0.00	0.00	
C_{13}	0.10	0.08	0.08	0.05	0.05	0.06	0.04	0.03	0.05	

i-C$_{14}$	0.12	0.14	0.14	0.07	0.10	0.12	0.05	0.05	0.03	
C$_{14}$	0.48	0.37	0.36	0.13	0.16	0.24	0.18	0.18	0.19	
i-C$_{15}$	0.38	0.22	0.20	0.04	0.12	0.15	0.07	0.10	0.05	
C$_{15}$	0.00	0.00	0.17	0.04	0.06	0.07	0.00	0.00	0.00	
i-C$_{16}$	0.08	0.10	0.12	0.00	0.08	0.09	0.05	0.05	0.00	
C$_{16}$	0.28	0.51	0.56	0.16	0.31	0.50	0.12	0.12	0.16	
i-C$_{17}$	0.24	0.22	0.23	0.06	0.13	0.16	0.21	0.13	0.14	
a-C$_{17}$	0.15	0.13	0.11	0.04	0.07	0.08	0.00	0.00	0.00	
C$_{18}$	0.26	0.24	0.25	0.06	0.14	0.16	0.11	0.09	0.10	
C$_{20}$	0.13	0.00	0.08	0.00	0.04	0.00	0.00	0.00	0.00	
Total β-Hydroxy FAs	**2.34**	**2.15**	**2.75**	**0.82**	**1.48**	**2.17**	**0.89**	**0.78**	**0.77**	
DAs										
C$_{16}$	0.18	0.10	0.11	0.06	0.23	0.37	0.17	0.16	0.42	
C$_{18}$	0.10	0.08	0.12	0.06	0.18	0.33	0.19	0.20	0.25	
C$_{19}$	0.04	0.03	0.03	0.02	0.04	0.05	0.03	0.04	0.03	
C$_{20}$	0.12	0.14	0.13	0.08	0.30	0.50	0.24	0.24	0.14	
C$_{21}$	0.06	0.09	0.06	0.04	0.06	0.09	0.08	0.12	0.00	
C$_{22}$	0.32	0.26	0.24	0.14	0.48	0.82	0.38	0.39	0.56	
C$_{23}$	0.08	0.10	0.10	0.04	0.07	0.11	0.07	0.09	0.06	
C$_{24}$	0.14	0.26	0.19	0.08	0.32	0.46	0.17	0.21	0.21	
C$_{25}$	0.06	0.11	0.09	0.04	0.07	0.10	0.06	0.07	0.02	
C$_{26}$	0.10	0.19	0.12	0.05	0.20	0.23	0.28	0.11	0.05	
C$_{27}$	0.04	0.09	0.06	0.03	0.07	0.08	0.04	0.03	0.00	
C$_{28}$	0.08	0.14	0.10	0.04	0.11	0.20	0.06	0.05	0.01	
Total DAs	**1.32**	**1.59**	**1.34**	**0.69**	**2.13**	**3.34**	**1.76**	**1.72**	**1.75**	
Hydrolysable phenols										

Vanillin	0.05	0.03	0.02	0.04	0.05	0.50	0.00	0.00	0.03	
Acetovanillone	0.02	0.03	0.02	0.03	0.04	0.07	0.00	0.00	0.04	
Vanillic acid	0.04	0.06	0.06	0.04	0.10	0.21	0.03	0.05	0.09	
Syringaldehyde	0.03	0.02	0.06	0.02	0.04	0.04	0.02	0.00	0.03	
Syringic acid	0.04	0.04	0.04	0.02	0.09	0.14	0.04	0.05	0.06	
Ferulic acid	0.04	0.09	0.05	0.04	0.23	0.48	0.10	0.16	0.11	
Total hydrolysable phenols	**0.23**	**0.28**	**0.26**	**0.18**	**0.55**	**1.45**	**0.20**	**0.26**	**0.35**	