Reply to Ulrich Hanke

Dear Ulrich Hanke,

We thank you very much for taking the time to review our manuscript, for your valuable comments/suggestions and the points of discussion you raised. We will wisely revise our manuscript according to your suggestions. Please find our detailed responses below:

The authors employ compound-class 14C measurements of long-chain leaf waxes (C_ 25) after removing the shorter chain lengths (C < 25) during the laboratory analyses to reduce the impact of petrogenic C (and reduce uncertainties from microbial reworking). However, even long chain leaf waxes contain a fraction of petrogenic carbon for which the authors introduce a factor and correct their 14C values to then discuss the pre-aging. Further, they translate their extracted 14C values to obtain calendar years yet hardly discuss the additional sensitivities introduced during "calibrating" with the 14C reference Intcal13. Or do the authors speak about 14C years? The former can be tricky because the paleo-fluvial sedimentary sequence seems to have features of recent biological activity and contemporary carbon that can complicate any attempt of absolute age dating.

➔ Indeed, our heated and corrected 14C ages are reported as absolute/calibrated calendar age ranges because we wanted to test the chronostratigraphic integrity of the leaf wax n-alkanes in our fluvial sequence to assess their value for paleoenvironmental interpretations. To do so, we compared the n-alkane ^{14}C ages with ^{14}C-dated charcoal pieces from the sequence, the latter given as calibrated calendar ages and indicating the timing of sediment deposition. As a result, it appeared that n-alkane ^{14}C ages from the intensively developed paleosols fall into the timing of soil formation and are therefore chronostratigraphically consistent. In contrast, n-alkanes from fluvial sediment layers are much older than the timing of sediment deposition and are therefore chronostratigraphically not consistent. Since the latter n-alkanes are affected by pre-aging effects and furthermore represent a mixed signal of leaf waxes from the catchment and to a much lesser degree also from microbial activity, the calibrated and uncalibrated ages/age ranges give a very heterogenic integrated age information. However, we will give a more detailed description about our ^{14}C dating and calibration approach in the methods section.

The excellent combination of molecular-level geochemical tools to trace the fate of carbon in past fluvial deposits is of great interest to earth scientists from various disciplines and, to my understanding, well suited for publication in HESS. The manuscript is scientific sound, entails adequate illustrations and details. However, the current version could benefit from (i) improve clarity in several sections (sentence length and perhaps language);

➔ We will carefully revise the manuscript and check it for clarity and language.

(ii) some clear statement on catchment-wide molecular-level 14C data that consists of an age distribution of 14C rather than a single value;

➔ Will be done

(iii) a statement on the informative value on ACL vs isotopes (13C and 14C);

➔ Will be done in the Introduction

(iv) discussion of data in the light of contemporary and pre-aged carbon;

➔ We do not understand this comment, since we already carefully discussed the difference between pre-aged and contemporary n-alkanes.

(v) some more informative details on potentials and limits on the geochemical constraints of molecular environmental 14C data compared to conventional 14C dating (in archeology).

➔ Will be included into the introduction chapter.

Probably some of my comments may already be included in the manuscript and might become clear after some careful checking/shortening of sentences and the addition of some clear statements. Overall a great study.

➔ Thank you very much for this valuable and positive feedback!

Some specific comments:
1,17: is 'direct' the correct term since you clean your fractions prior to 14C analyses?

- ➔ "direct" means that we can directly ^{14}C-date the n-alkanes, and therefore derive an n-alkane-derived ^{14}C-age. Cleaning the n-alkane fraction aims to obtain a more homogeneous fraction. However, we can remove the term "direct".

1,19-20: 'in-situ signal from local biomass': do you mean contemporary or on-site from litter fall?

- ➔ We mean local biomass that derives on-site (in-situ) at the studied site, and that gets incorporated into the soil with the litterfall. However, as suggested by both reviewers, we will change the term in-situ to on-site.

1, 30: 'were estimated': how do you determine the petrogenic C contributions? If only estimated, you may need to add some more details on the rationale and the precision of your approach

- ➔ Petrogenic contributions are based on the quantified n-alkane proportion of Jurassic black shales from the catchment. We will specify this.

2, 3: how you know about the 'local dominance of grasses/herbs throughout the Holocene'. Alkane distribution patterns or isotopes?

- ➔ The vegetation distribution is derived from the n-alkane distribution pattern previously published in Bliedtner et al. 2018 (Quaternary Science Reviews 196, 62-79). We will specify this.

2, 10: 'valuable biomarkers' - for whom? A clear statement on the power of immortal molecules and the informative value could certainly improve the readability. Please check your manuscript throughout.

- ➔ Valuable biomarkers in paleoenvironmental research. Will be specified.

2, 12: 'increasingly used' – there a several groundbreaking studies that have already changed our understanding of the environment. Also, are there other biomarkers that can be used to trace primary productivity?

- ➔ Yes, you are right and we might rephrase this section. Of course there are other interesting biomarkers (e.g. fatty acids, sterols, bile acids etc.) that can be used to reconstruct climate, vegetation, soil erosion and/or human activity, but so far, leaf wax n-alkanes are the most prominent and most often used biomarker proxies.

3, 1: what about ultra-small graphitization lines. Same but different, other labs use conventional sample treatment at similar precision (« 10 _g C)

- ➔ Indeed, same labs use graphitization lines to date ultra-small samples, but it seems that sample preparation and measurement is less time and cost intensive when directly measured as CO_2 with a gas ion source.

3, 2: how does MICADAS enable direct 14C dating of specific OC compounds? Do you mean online EA-AMS?

- ➔ It is because the MICADAS enables ^{14}C dating of very small amounts of carbon (~20 µg C), although small amounts of carbon can also be analyzed by graphitization lines. The possibility to date those small amounts of carbon makes it possible to date specific OC compounds, such as leaf wax n-alkanes, that often occur only in smaller concentrations in sediment archives. It doesn't really matter if you use online EA-AMS or sealed tube combustion, although the analytical procedure with online EA-AMS is easier and less cost/time consuming. We will specify this section.

3, 20: 'this petrogenic contribution should lead to increased: : :'. In 14C, petrogenic is 14C depleted and thus it must be a matter of fraction size. Can you write this more clearly?

- ➔ You are right, and we will rewrite this section.

3, 22: what about microbial processing and impact, is it solely petrogenic?

- ➔ Indeed, we missed to state that n-alkanes can also originate from microbial sources or from microbial utilization. We will include such a statement into the introduction and a more detailed discussion into the discussion part. However, although we cannot completely rule out the influence of microbial utilization, we suggest that non-leaf wax-derived n-alkane contributions in our fluvial sequence are mostly of petrogenic origin. This is based on the fact that short- and mid-chain n-alkanes do not show an odd-over-even predominance, but in case of a dominance of microbial processes we would expect an odd-over-even predominance in these chain lengths.

9, 1-16: In my opinion, you miss the opportunity to inform the general audience about the principle of your measurement: you always measure a mean/median age of your individual or compound-class 14C n-alkanes because of the variable spatial origin and trajectories. This is central to understand that you integrate on spatial and temporal scale. Along these lines, is it correct to use these values for calibration absolute dating with IntCal14 (atmospheric 14C concentration) or better use 14C years only? Given you can, is your 14C age distribution a bell curve and how do you propagate the analytical uncertainties with the correction for petrogenic and the age dating?

➔ We will include a more detailed description of our dating approach into the methods and discussion sections. You are right that we measured a mean ^{14}C-age that can integrate over different spatial and temporal scales, what holds especially true for the n-alkanes derived from fluvial sediment layers. However, our main aim was to test the chronostratigraphic integrity of our n-alkanes in the fluvial sequence by comparing them with an independent charcoal chronology that gives the timing of sedimentation. By dating the n-alkanes from the fluvial sediment layers, we found that these are older than the sedimentation ages and therefore stratigraphically not consistent. Thus, they must be affected by pre-aging effects and contain a mixed leaf wax signal. For a better comparison between our different types of ^{14}C-ages (from n-alkanes and charcoals), calibrated ^{14}C ages seem to be best suited. Unfortunately, we have to note that error propagation after petrogenic correction is difficult and holds a certain uncertainty. Therefore, we simply used the measured ^{14}C errors of the petrogenic-corrected ^{14}C-ages. When corrected, the errors of the ^{14}C-ages should basically become smaller and fall within the measured ^{14}C-error. Thus, when using the errors mentioned above we will slightly overestimate the "true" ^{14}C-error.

9, 21: here you assume that your factor remains constant over the entire sequence while you source contributions likely are variable. Please add a statement.

➔ Will be added.

10, 5-6: is it only erosion? What about sub-surface flow and export in addition to erosion of soil mineral horizon? Depending on the level of water saturation, would this impact your trajectories?

➔ We think that the degree of pre-ageing of the leaf wax n-alkanes from the catchment is mainly controlled by surficial soil erosion. It is true that organic material from catchment soils might also be relocated by sub-surface flow, but those effects are hard to quantify. Nevertheless, our ^{14}C-results indicate that the catchment-derived leaf waxes carry an old and pre-aged signal from the catchment, most likely due to surficial soil erosion processes in the catchment that were also observed in the field.

10, 27: are you sure your leaf wax n-alkanes are in-situ rather than originate from litter fall from vegetation on-site or transported by wind and water?

➔ "In-situ" means that the leaf wax n-alkanes from the paleosols originate from local biomass/vegetation at the investigated site, i.e. it basically means "on-site". However, we cannot exclude that some of the n-alkanes in the paleosols were also transported by wind or water from neighbouring sites. However, the n-alkane-^{14}C-ages from the paleosols indicate they also that material could not have had a significant age-offset with the timing of sedimentation.

11, 5ff: Any thoughts on the role and extent of overprint by contemporary biological activity? Your results point towards some spatial and time integrated value that is characteristic for a catchment. But how well does the sequence (depth profile) record the catchment changes in the past versus the soil development by contemporary vegetation?

➔ In our previous publication (Bliedtner et al. 2018, Quaternary Science Reviews 196, 62-79) we report that based on micromorphological analyses we found some rhizo-microbial activity in the fluvial sediment layers. This indicates some overprinting by post-sedimentary processes. However, generally high carbonate contents in those layers indicate only short-time pedogenesis on the active floodplain what leads us to the assumption that post-sedimentary processes did not play an important role in our sequence. Moreover, the leaf wax ^{14}C-results indicate that our sequence is at least partly well suited to record former vegetation changes: While the catchment signal is challenging to interpret in terms of paleoenvironmental changes due to a spatially and temporarily integrated signal, the signal in the intensively developed paleosols originating from the investigated site is chronostratigraphically consistent and can therefore well be interpreted.

11, 22: do you mean reworking?

- ➔ Here we discuss the leaf wax signal from the (paleo)soils that is mostly incorporated from the local vegetation during soil development.

11, 24: 'indicate high grass/herb percentages'. Please be specific. If you know the percentages, share it with the reader.

- ➔ The percentages of grasses/herbs are only semi-quantitative estimates that are based on a correction approach that is discussed more in detail in Bliedtner et al. 2018 (QSR 196, 62-79). Given that the percentages can exceed 100% a statement about precise percentages would therefore be misleading. However, we will provide a more detailed description of the grass/herb percentage ratio here.

11, 25: 'not biased by pre-aging and reworking effects' – what do you mean? Please consider rephrasing

- ➔ We mean that leaf waxes from the intensively developed (paleo)soils are chronostratigraphically consistent and not affected by pre-aging and reworking. We will rephrase this section accordingly.

12, 3: 'this is caused' seems a quite strong statement. Please adjust

- ➔ Will be adjusted.

12, 4: 'this is further: : :' Please check that sentence carefully, it reads bulky.

- ➔ Will be changed.

12, 13: by anthropogenic activity: how? By any disturbance events, eg. deforestation?

- ➔ Mainly by deforestation and land-use in the catchment. Will be specified.

12, 15: no older ages were determined? Âˇ nÂˇ nÂˇ nSo, this is the oldest?

- ➔ Yes, this is the oldest age. However, we were not able to date the two lowermost fluvial sediment layers and therefore do not have age information of them.

12, 26: 'deposition than before'? please check

- ➔ Will be changed.

13, 7: only shale or also microbial?

- ➔ Mainly shale, but we will include a more detailed discussion about microbial influences in the discussion part.