SOIL Discuss., author comment AC3
https://doi.org/10.5194/soil-2020-107-AC3, 2021

Reply on RC3

Carrie L. Thomas et al.

Author comment on "Transformation of n-alkanes from plant to soil: a review" by Carrie L. Thomas et al., SOIL Discuss., https://doi.org/10.5194/soil-2020-107-AC3, 2021

First of all, we thank Anonymous Referee #3 for the preparation of his/her critical review and appreciate receiving some comments that will certainly help to improve the manuscript. However, we do not fully agree with all of the reviewer's statements and opinions, which also frequently contradict the assessments provided by the other two anonymous referees. Overall, we try to follow all advice given by the Referee as much as possible. However, we can neither change the data nor the general observations. We are grateful that we received two additional reviews, which were, to our opinion, well-founded and more constructive than the review performed by Anonymous Referee #3, who seemed to have overlooked some of our key messages and the general difficulties that arise from extracting data from multiple, quite diverse data sources. We hope that with the responses given to Anonymous Referee #3 and the anticipated changes we can provide an improved version of our manuscript.

Anonymous Referee #3*: "With 'transformation of n-alkanes from plant to soil' Thomas and co-authors have chosen a topic for their review that is an extremely narrow field of research. This is acknowledged by the authors already in their abstract stating 'only a limited number (of studies) have focused on the transformation of these compounds… in soil archives'. Moreover, there is according to my knowledge no discussion or controversy in the scientific community concerning* transformation *of alkanes from plants to soils. This likely explains why no questions are raised by the authors* in *or at the end of the introduction chapter. I* therefore *doubt that the chosen topic merits a review paper that shall attract attention and address a broader readership."*

Reply: We do not agree with the statement that the transformation of n-alkanes from plant to soil is a narrow field of research and that this review manuscript cannot attract attention of a broader readership. The search strings of the systematic literature search resulted in 9297 results dealing with a related topic, i.e., lipid biomarkers and mostly alkanes in soils. As alkanes are often better preserved in soils than other compounds, alkanes have been frequently used for source apportionment of plant-derived organic matter in soils. As several publications showed, even alkane composition changes with degradation in plant-soil systems. However, a systematic assessment of the transformation of alkane composition and underlying degradation processes to our knowledge has not been published before.

Although there is no general controversy in the literature on this topic, the generalization of the observations and focus on potential differences, e.g., between different ecosystems, biomes or soil types, is necessary to better understand the fate of alkanes in plant-soil systems. The other reviewers appreciated seeing the data being summarized in the review manuscript (Anonymous Referee #1: "The review is pertinent and appropriately compiles the main findings described in the most relevant publications dealing with alkane biomarker distribution in soils. To the best of my knowledge, the review is novel and not previously published."; Anonymous Referee #2: "This review is interesting despite the small dataset selected due to the limited number of suitable papers. … The manuscript depicts most of the outcome explaining the evolution of n-alkane pattern with time or in soil either due to degradation pathway or source shift.").

The large number of article views since online publication of the preprint of this manuscript indicates that there is a large interest in the topic with a broad readership of SOIL being interested. In fact, the numbers in the article metrics on SOILD show that there are more article views for our preprint of the manuscript than for any of the other individual preprint manuscripts published over the last weeks.

Anonymous Referee #3*: Moreover, the readers of 'SOIL' do not learn anything new and the manuscript contains flaws. The 'major findings' summed up by the authors (decreasing n-alkane concentrations and decreasing CPI) are trivial, known for a long time* and *described by more than 90% of the cited respective studies.*

Reply: Although it seems "trivial" or well-known that n-alkane concentrations and CPI decrease with degradation, there was no general information available on the order of magnitude so far and if this is identical in all ecosystems and biomes. However, such quantitative information is essential to be able to interpret alkane composition shifts in soils in a systematic way, for instance for the purpose of the reconstruction of past vegetation patterns. Therefore, we summarized the available information rather than relying on fragmented information in different studies.

Anonymous Referee #3*: The first part of the third 'major finding' (preferential degradation of odd chain length) is equal to* major *finding (2) just in other words and the second part of the third 'major finding' (preferential degradation of* shorten *chain length n-alkanes) is simply wrong and not supported by the majority of the studies cited by the authors (see ll. 164ff and l. 262).*

Reply: We thank the reviewer for this comment. We will combine the major findings 2 and 3 as they are rather similar and do not deserve separate numbering. However, we think that the Referee misunderstood our statement in lines 164ff "Other studies noted decreases in the relative concentration of long-chain n-alkanes (Chikaraishi and Naraoka, 2006; Otto and Simpson, 2005; Hirave et al., 2020), while Nguyen Tu et al. (2001) noted a preferential decrease in shorter chain lengths from fresh leaves to litter of *Gingko biloba*." Most of the authors found either a decrease in shorter chain lengths or an increasing relative concentration of long-chain n-alkanes, which is identical to a relative depletion of short-chain alkanes when compared to long-chain alkanes. In Fig. 2 and 4 this leads to increasing ACL values in most of the studies from plant material towards mineral soil. We will modify the text to "…increase in concentration…".

Anonymous Referee #3*: Actually interesting or striking features such as the accumulation of soil microbial-derived medium-chain n-alkanes or the increase of n-alkane concentrations at coniferous forest sites (Fig. 3b) are unfortunately not or insufficiently emphasized or wrongly explained (the increase can be simply explained with needles producing no n-alkanes but understory in coniferous forests contributing to the soil n-alkane pool).*

Reply: Unfortunately, there is scarce literature available on microbial sources of alkanes in soils and the available literature is quite old and was not confirmed by newer studies to the best of our knowledge. All of our ACL calculations for studies from which primary data were available were based on data ranging from 27 to 33 carbons (line 100). Thus, mid-chain alkanes (typically with chain length of 20 to 25) are not entirely included and short-chain alkanes (<20 carbons) were entirely excluded, preventing us from drawing conclusions on these components. Thus, the connection of the data to microbial-derived mid-chain alkanes is not possible. We agree that making such a connection is valuable and will emphasize in our conclusions the direction of future study needed for this, now that our review has shown that it is not possible based on the presently available data.

Anonymous Referee #3*: A review focussing on* plant *to soil transformation should not include subsoils or peat archives. Statements or citations like in l. 200 or alkane depth functions of peat archives like in Fig. 5 are not helpful and in the* worst case *misleading, because in steppe biomes there is high bioturbation in typically loose eolian sediments* and *in peat archives the vegetation may have changed.*

Reply: We disagree with the referee as: (1) incorporation of plant-derived alkanes is not limited to the top of the soils and litterfall of aboveground biomass, but can include contributions of soil alkanes from roots, which is much stronger in deeper part of the soils than in the top layer. (2) Transformation of organic matter is continuing in deeper soil layers, if litter-derived alkanes are translocated, e.g., by particulate transport. Therefore, only the whole continuum from fresh plant leaves, which is often taken as the sole source of soil alkanes, towards deeper soil horizons can reflect all transformation processes. Strong bioturbation, indeed occurs in steppe biomes, but is not limited to these biomes. Bioturbation will of course influence the vertical stratigraphy of n-alkanes. However, that does not mean one cannot interpret n-alkane patterns with depth. Where mixing via bioturbation may complicate the interpretation of n-alkane patterns for certain purposes such as paleo-ecological reconstructions, it may in fact enhance their applicability for other purposes, e.g. reconstructing SOC transformations as influenced by bioturbation. Of course, peat archives are special types of hydromorphic soils, where degradation of organic matter is limited. Nevertheless, they are part of the whole soil domain and thus reflecting a considerable part of the (hydromorphic) soils worldwide. Similar to oxic soils, it is important to understand the transformation processes of alkane in hydromorphic soils. This is particularly so, because the biomass accumulation in peat deposits leads to a favorable time/depth axis that makes them valuable archives of n-alkanes for paleo-ecological reconstructions (e.g. Jansen et al.,2010: https://doi.org/10.1016/j.palaeo.2009.10.029) Therefore, and as both of the other referees did not raise such concerns, we prefer to keep the whole sample set inside the manuscript.

Anonymous Referee #3*: Apart from Fig. 5, also Figs. 3, 4* and *6 are hardly readable. Concerning Fig. 3b, I can hardly imagine (actually it cannot be) that fresh deciduous forest material and* fresh *mixed forest material* contains *no alkanes. Please check and correct your data and figures.*

Reply: Many thanks for mentioning the readability. We shall try to improve this by increasing the font size of the figures. In Figure 3b, the figure does not show that there are no alkanes in the fresh deciduous forest material and fresh mixed forest material, though the values are quite low. As is noted in the caption, Figure 3b shows the total concentration of n-alkanes relative to the amount of organic carbon. Therefore, due to high amounts of organic carbon in fresh material, the relative concentration of n-alkanes is quite low. In the revised version, we will try to further improve the readability of these figures by adjusting the sizes of the axis so that it is more clear that these values are not at zero.

Anonymous Referee #3*: Last but not least, it does not become clear what the knowledge gaps are. The authors encourage expanding the dataset to less researched geographic areas… I consider it to be rather unlikely that this approach will help* increasing *our understanding of plant to soil transformation of n-alkanes.*

Reply: There are multiple knowledge gaps that are not limited to geographic areas. The major issue that was highlighted in the review was the limited comparability of the data which coincides with the diverse reporting of data and even the lack of additional information that is published together with molecular data, which is why we came to our recommendations. With increasing need to collectively analyze all available data like Big Data analytics, it became obvious that even molecular data needs to be reported according to the FAIR principles to better use the data also in future research.

Anonymous Referee #3*: To sum up, the issues raised above demonstrate that the overall aim formulated by the authors at the end of the introduction (l. 68ff: 'consolidation of the available information on the fate of n-alkanes in soils… better process understanding of degradation…') is only inadequately achieved. Most importantly, soil microbial build-up of n-alkanes is insufficiently addressed.*

Reply: We disagree with the referee in these points, which also contradict the conclusions of the other two referees. For instance Anonymous Referee #1 wrote "The review is pertinent and appropriately compiles the main findings described in the most relevant publications dealing with alkane biomarker distribution in soils.", which contradicts the statement that we "inadequately achieved" the "overall aim". We were overwhelmed to find almost 9300 articles after our systematic literature search, but the disappointment was that after half a year of screening these articles only 37 articles contained enough relevant and extractable information that allowed us to properly summarize the data. The reasons were quite diverse but clearly show that although there have been many studies performed, it is extremely hard to extract this data and to make sense out of this. We hope our manuscript can help to improve these issues in the future. As mentioned before, microbial alkanes were not the focus of the review and most of the studies that we found did not include data on mid- or short-chain lengths as we would have included also these in the data evaluation otherwise.

Specific Comments

Anonymous Referee #3*: l. 48 and 50: I exemplarily checked both Marzi et al., 1993 and Hoefs et al., 2002 and found them to be inappropriately cited. Marzi and Hoefs use CPI and OEP, but not in the sense that their studies or results support what the authors cite them for, namely well preserved or highly degraded plant organic matter. Please be more specific with your citations.*

Reply: Many thanks for this comment. We will replace these with Cranwell,1981, Organic Geochemistry and Zech et al., 2009, E&G Quaternary Science Journal.

Anonymous Referee #3*: Result chapter: numbering of subchapter makes no sense*

Reply: Many thanks for pointing to this. We will modify the subchapters to 3.1, 3.2, and 3.3 rather than 3.1.1, 3.1.2, and 3.1.3. and we will remove the current headline 3.1. This was a leftover of a previous version of the manuscript.

Anonymous Referee #3*: l. 238: cannot be correct, oxidation of alcohols does certainly not produce n-alkanes. The succession of oxidation is aliphatic – aldehyde – alcohol – acid.*

Reply: Thanks a lot for this comment. We will modify this in the revised version.

Anonymous Referee #3: *l. 283ff: I do not agree with the statement that 'retaining the range of chain length and the most abundant chain length' 'evidences that there is limited change… no preferential degradation...'. Fig. 2a shows that all ACL lines increase.*

Reply: We kindly point the reviewer to the supplement as indicated in line 284, where it becomes more obvious that there is no preferential degradation or preservation that can be drawn. The range of alkanes as well as the most abundant compound always stays the same. The changes in the ACL in Fig. 2a are rather small. However, we will rephrase that part.