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Interactive comment on "Millennial-age GDGTs in forested mineral soils: ^{14}C-based evidence for stabilization of microbial necromass" *by* Hannah Gies et al.

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We thank Referee #2 for their thorough and helpful comments and have edited our manuscript accordingly. The Referee raises the issue that GDGTs in general, their turnover and especially the metabolism of their putative precursors are not sufficiently introduced, especially considering that our method setup and conclusions are based on these assumptions. We agree with this assessment and have hence expanded the introduction to improve the manuscript. Additionally, Referee #2 points out that the implications for the use of GDGTs as proxies and tracers have not been sufficiently discussed. We have expanded discussion in the corresponding paragraph to also ad-

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dress the production of GDGTs in aquatic environments. However, as the stability of microbial remnants in soils is the primary focus of this study, we address possible implications as motivation for further research.

Referee: I miss some basic background information in the introduction. Details on the sources/producers of GDGTs in soils, as well as their metabolism is crucial for this paper, but these aspects are only marginally addressed in the current version. [. . .] In addition, there are a couple of studies that provide estimates of the turnover of branched GDGTs in soils. Although they have not used ^{14}C dating, these studies are currently not mentioned in the introduction.

P3 L56: soils are considered a major source of brGDGTs to aquatic systems: I am not convinced that this is still widely believed. Over the past few years, several studies have provided evidence for a primarily in situ, hence aquatic source of brGDGTs in lakes.

P4 L96: Adding to my earlier comment: the authors should better introduce the (supposed) sources of the GDGTs in soils in their introduction, and indicate here on what level their putative biological precursors and formation pathways are considered common. For brGDGTs, this may be true on the level of 'bacteria', but there are indications that the 5-methyl and 6-methyl isomers are produced by different subdivisions of the phylum Acidobacteria (Sinninghe Damsté et al., 2018). Given that the authors have pooled the 5-methyl and 6-methyl brGDGTs in this study, this is important information to add.

P8 section 4.1: I think that the motivation to pool all GDGTs for radiocarbon measurements comes a bit late, as the pooling is a passed station. What if the literature had pointed out that each GDGT was likely to have another isotopic composition? How would you then interpret the pooled results? I feel like this section on the presumed shared metabolism should be moved to the introduction.

Authors' response: We reworked the introduction to include more of the information suggested by the referee. Some of this information was previously embedded in the Discussion, but we recognize that it would be beneficial to include more background in the introductory section:

[...]

"Here we examine the ^{14}C characteristics of Glycerol Dialkyl Glycerol Tetraethers (GDGTs) – characteristic membrane lipids of microorganisms that are ubiquitous in terrestrial and aqueous environments (Schouten et al., 2013). GDGTs are subdivided into two groups of compounds: isoprenoid GDGTs (isoGDGTs) produced by Archaea (De Rosa and Gambacorta, 1988) and branched GDGTs (brGDGTs) which are of putative bacterial origin (Weijers et al., 2006a) and are especially abundant in soils and peats (Weijers et al., 2006b) (for molecular structures see Figure A1). GDGTs have garnered much attention due to their potential as molecular proxies for environmental conditions: the relative abundance of brGDGTs versus isoGDGTs has been used to qualitatively estimate soil-derived carbon input into marine sediments (Hopmans et al., 2004), while the internal distribution of iso- and brGDGT isomers carries information of aquatic and soil conditions (Schouten et al., 2002; Powers et al., 2004, 2010; Liu et al., 2013; Coffinet et al., 2014; Yang et al., 2016). For example, the distribution of different brGDGTs, parameterized as the methylation of branched tetraethers (MBT) and cyclisation of branched tetraethers (CBT) indices (Peterse et al., 2012; De Jonge et al., 2014; Naafs et al., 2017), have been found to correlate with mean annual continental air temperature (MAT) and soil pH (Weijers et al., 2007), respectively. Despite their rapid adoption by biogeochemists and paleoclimatologists as molecular tracers and proxies of environmental conditions, there are numerous aspects regarding their production, turnover and fate that remain enigmatic. While isoGDGTs in soils are most likely produced by ammonia-oxidizing Crenarchaeota and heterotrophic methanogens (Weijers et al. 2010), the biological precursors, metabolic processes and physiological drivers giving rise to brGDGT signatures observed in terrestrial and aquatic systems remain

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poorly constrained, despite their ubiquity in soils and other environmental matrices. The bacteria producing brGDGTs are supposedly heterotrophs (Pancost & Sinninghe Damsté, 2003; Weijers et al., 2010; Colcord et al., 2017). Acidobacteria have been suggested as potential precursor organisms (Weijers et al., 2009; Sinninghe Damsté et al., 2011), though other phyla cannot be excluded (Sinninghe Damsté et al., 2018).

Previous estimations of the turnover time of GDGTs have been based on stable isotopes and incubation experiments (Weijers et al., 2010; Huguet et al., 2017). Corresponding turnover times are on the order of a few decades, and similar to that of other plant and microbial biomarkers (Schmidt et al., 2011), but these approaches tend to reflect turnover of the new carbon inputs from plants and yield faster SOM turnover rates than ^{14}C-based estimates that measure overall organic matter turnover (Trumbore, 2000). Moreover, the focus of these studies has been on the SOM-rich upper soil horizons and may obscure slow-cycling carbon pools that predominate at depth (Rumpel & Kögel-Knabner, 2010). In this context, natural abundance-level radiocarbon measurements of these compounds may provide a valuable approach to better understand their source(s) and turnover rates, while also shedding light on processes that influence their abundance and distribution (Mendes-Millan et al., 2013; van der Voort et al., 2017).

Prior ^{14}C-based studies of GDGTs have primarily focused on the isoprenoid compounds in marine waters and sediments (Pearson et al., 2001; Smittenberg et al., 2004; Ingalls et al., 2006; Mollenhauer et al., 2007, 2008; Shah et al., 2008). The only reported investigation of branched GDGT ^{14}C characteristics in lake sediments (Birkholz et al., 2013) yielded $\Delta^{14}C$ values that were lower than those of the depositional age of the sediment, although the causes of this pre-aged signal were not established.

In soils, however, the ^{14}C signature of GDGTs has not yet been reported. Thus, we presently lack crucial information concerning the production and cycling of this distinctive group of microbial lipids in the context of soil C cycling, as well as the implications for their use as molecular tracers and proxies.

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In the present study, we used molecular-level natural-abundance ^{14}C measurements [. . .]

Referee: Finally, the implications of the results for both soil organic carbon cycling as well as for paleoclimate reconstruction have not been given sufficient attention. The authors mention that there are implications for the use of GDGTs as 'tracers and proxies', but it is not clear what those will be exactly. MBT'5me and CBT' ratio values are reported in the results, but these indices are nowhere explained, and the values are not discussed. The aspect of in situ production and thus a contribution of aquatic sourced GDGTs (both branched and isoprenoid) has not been mentioned in the manuscript, and should be addressed in the implication section (and introduction, where appropriate).

P10 L323: as mentioned earlier, I am not convinced that brGDGTs systematically trace soil OC given the evidence for in situ production in aquatic systems (rivers and lakes), or the loss of the soil signal upon entering a river

Authors' response: We agree with the Referee (and Referee #1 who raised the same issue) that we did not discuss or provide context for the MBT'$_{5ME}$ and CBT' indices sufficiently. Thus, we have added paragraphs in section 3.2 and 4.3 describing the variations of these indices within the cores and discussing the implications of these results, respectively (for the exact wording of these paragraphs see the Authors' response for Referee #1).

We have also added information regarding the aquatic production of GDGTs to the introduction and also reworked section 4.3. Nevertheless, we kept this section rather short, as the main focus of this manuscript is on GDGTs dynamics in soils and we are in the process of applying the GDGT separation method to river sediments in order to investigate the GDGT-specific radiocarbon signals in aquatic environments and how they compare to soils:

"In addition to the insights into soil carbon turnover, the observed ^{14}C signatures of

GDGTs in the two soil profiles carry implications for their application as proxies of environmental conditions and as tracers of soil carbon input to aquatic environments. The putative application of brGDGTs as soil tracers has been undermined by the growing evidence pointing towards in-situ production as a major source of brGDGTs in aquatic environments (e.g., de Jonge et al., 2014; Sinninghe Damsté, 2016; Miller et al., 2018; Guo et al., 2020). Nevertheless, prior radiocarbon analyses of branched GDGTs in aquatic sediment sequences have revealed older GDGT ages than depositional ages (Smittenberg et al., 2005; Birkholz et al., 2013), consistent with a contribution of aged brGDGTs that were subjected to protracted storage in and mobilization from deeper mineral soils."

Further detailed and textual comments:

P3, section 2.1: also add the amount of samples included in this study. It later appears that one sample from every soil horizon has been analyzed. Provide this information here.

We added this information as suggested:

"At each site, soil cores were taken on 16 locations on a regular grid on a 1600 m^2 plot following protocols implemented as part of the LWF sampling program (van der Voort, 2016) and bulked to yield representative samples for three depth layers at each site: a sample from the A-Horizon comprising the top 5 cm of the soil , a second ranging from 10 to 20 cm depth, and a third from the B-Horizon between 20 to 40 cm and 60 to 80 cm depth at the Beatenberg and Lausanne site, respectively."

P4 L124: Was the purity check done on full scan, or using selected ion monitoring as mentioned in Hopmans et al., 2016? In the latter case, how can you assure that there were no potentially co-eluting compounds present?

The aliquot of the polar fraction with the internal standard that was used to determine the concentration of GDGTs was measured using selected ion monitoring, while the

purity check on the isolated fractions for ^{14}C analysis was performed in full scan mode. We added this information to line 124:

"The isolated compound classes and the subset of the initial polar fraction set aside previously were analyzed for purity and quantification using the same HPLC system coupled to a quadrupole mass spectrometer (Agilent 6130) according to Hopmans et al. (2016) with the exception that the purity of the isolated fractions was tested in full scan instead of selected ion monitoring mode."

P5 section 2.4: can you give a slightly more elaborate description of the different pools? What kind of compounds do you expect, or are assumed to be part of the fast cycling and passive pools, respectively?

The concept behind the two-pool model is that soil organic matter cycles on a continuum of time scales, even at the compound scale, as despite their same structure the compounds may vary in their degree of interaction with minerals or aggregates, impacting their stabilization and decomposition rate. Thus, the fast and the slow pool are a simplified representation of GDGTs with different decomposition rates.

P6L164-168: Given the uncertainties associated with the sample size, and the minimal sample sizes mentioned here (at least 20 ugC for samples with a radiocarbon age <1800) and at least 50 ugC for samples older than 6000) compared to the relatively small sample size used in this study (at least 15 ugC), I think it is important to include the sample sizes of each sample in a (supplementary) data table.

We agree, and have hence added the amount of C in the supplementary data table. The sample sizes mentioned here are not required minimum sample sizes, but the recommended sample size needed to keep the amount of the extraneously added carbon below 5% of the total measured carbon. Smaller samples are possible, but the resulting uncertainties will correspondingly be higher.

P8L212: what do you mean with 'light fraction'?

The 'light' fraction is the low-density fraction mentioned in the previous sentence. We will add the information that this fraction is *"the so-called particulate organic matter consisting of little decomposed residues"* and restructure the sentence to make this clearer. The preparation of this fraction is described in the referenced publication by Van der Voort et al. (2017): dried soil was immersed in sodiumpolytungstate at a density of 1.6 g/cm^3 in a 5:1 (v:v) ratio and first left to settle for 1 hour, then centrifuged at 500 rpm for 20 minutes. After centrifugation, the floating material was separated on a pre-combusted 0.7 mm glass fiber filter (GFF) and rinsed with deionized (DI) water.

P8L212-213: Can you add the range of the estimated turnover times, for reference? How do the turnover times based on the two different approaches compare?

We have added a reference to Table 1, where the turnover times of the fast pool are listed. The two different approaches lead to GDGT turnover times that differ by less than 5%; we have added this information to the text as follows:

"[. . .] its potential influence is hence already covered by the range of the turnover time estimates of the fast pool (Table 1), the resulting GDGT turnover times based on either short-chain FAs or the light fraction differ by less than 5%."

P10 L301: How do you match the previously reported turnover rates of GDGTs in surface soils of years to decades to centennia to even millennia, as you find here?

In the study by Weijers et al. (2010), the turnover times of brGDGTs are found to be similar to the turnover times of long-chain fatty acids and slightly shorter than long-chain n-alkanes. In the surface soil at the Beatenberg site, the turnover times of brGDGTs are in range with the turnover times of these other compounds, hence our findings of centennial turnover times do not contradict with these previously reported

turnover rates of decades considering that all studied compounds in this soil have turnover times on the order of hundreds of years. In the Lausanne soil, our calculation assumes that the fast cycling pool of GDGTs has a turnover time of a few decades similar to the short-chain fatty acids in this soil. However, the low $\Delta^{14}C$ values of GDGTs require an additional slow cycling fraction of GDGTs that increases the overall turnover time to several hundred years. The methods used by Weijers et al. (2010) (single-pool model using stable carbon isotopes) and Huguet et al. (2017) (dividing lipid concentration in sample by incubation production rate) are not capturing the stabilized fraction of GDGTs with a slow turnover time as they trace the turnover of recent C inputs into the soil, yielding relative fast cycling rates (Trumbore, 2000). Here, we can only guess why GDGTs turn over especially slow in the Lausanne soil, but given that the the Lausanne topsoil had high contents of clay and highly reactive amorphous Fe and Al-oxides and hydroxides, it seems likely that stabilization by the interaction with mineral surfaces is a primary reason. This slow-cycling fraction is likely predominating in deeper soil horizons, manifesting itself through the observed old ^{14}C ages (millennial turnover rates).

We address the reason for the slow GDGT turnover at the end of section 4.2:

"[...] The older GDGT ^{14}C age in the lowest depth interval of the Cambisol at Lausanne compared to the subalpine Podzol at Beatenberg with a bleached eluvial horizon also supports this conclusion. The Lausanne soil has higher contents of clay and highly reactive amorphous Fe and Al-oxides and hydroxides (Table 2) which are known to play a key role in the sorptive stabilization of SOM (Kaiser and Guggenberger 2003; Kleber et al., 2007)."

L335-337: Is there any way we can test the protection of GDGTs through association with mineral surfaces?

A possibility would be to test whether mineral surface area and GDGT concentration correlate in a broad range of soil and sediment samples that differ in their organic matter and mineral content and composition. Also, density fractions of soils could be

analyzed for their concentration of GDGTs and their respective ^{14}C ages. An increase of GDGTs relative to organic carbon in the high-density (mineral-associated) fraction compared to the fractions of lower density would support the assumption that a significant proportion of GDGTs in soils are closely associated with mineral surfaces. An additional approach would be to measure GDGTS directly in mineral-protected OM following oxidization with sodium hypochlorite and subsequent dissolution of minerals by 10% hydrofluoric acid (HF) (Mikutta et al., 2006). We added a sentence in section 5:

"The potential sorptive stabilization of GDGTs could be verified by measuring GDGTS and their 14C contents directly in mineral-protected OM (Mikutta et al., 2006), which, however, could be hindered by their low concentration.

All typing errors, formatting suggestions and grammar issues highlighted by the referee have been addressed. Also, the inverse order of figure panels compared to discussion in the text is curious and could indeed be confusing, but as the figure panels in Figure 3 are arranged according to the position of the samples in the map it was actually more convenient to just swap the respective paragraphs in the text to solve this issue.

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