

## **Consideration of soil types for the calibration of molecular proxies for soil pH and temperature using global soil datasets and Vietnamese soil profiles**

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### **To cite this version:**

Nina Davtian, Guillemette Ménot, Edouard Bard, Jérôme Poulenard, Pascal Podwojewski. Consideration of soil types for the calibration of molecular proxies for soil pH and temperature using global soil datasets and Vietnamese soil profiles. Organic Geochemistry, 2016, 101, pp.140 - 153.  $10.1016/j.org geochem.2016.09.002$ . hal-01683011

## **HAL Id: hal-01683011 <https://hal.science/hal-01683011>**

Submitted on 2 Feb 2024

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#### **ABSTRACT**

 Distribution of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in soils depends on environmental parameters such as mean annual air 25 temperature (MAAT) and soil pH. MBT'/MBT'<sub>5ME</sub> (methylation index of branched tetraethers) and CBT/CBT′ (cyclization ratio of branched tetraethers) are ratios based on the relative abundances of brGDGTs. Using these ratios, global and regional/local calibrations have been established using surface soils, but generally without any preliminary study of soil types. In this study, we reconsider global MAAT–pH/brGDGT calibrations by assigning soil types to the 358 components of a composite soil dataset. Additionally, we investigate brGDGT-derived proxies in five well-described soil profiles along an altitudinal transect in the Mount Fan Si Pan National Park, northwestern Vietnam. Our results show that at the global scale, traditional MAAT–pH/brGDGT relationships per soil type are significantly different and that MAAT(pH) residuals per soil type may differ as well, for example between Alisols and Podzols. This effect persists when 5- and 6- methyl brGDGTs are quantified separately. In addition, MAAT(pH) residuals per soil type are generally not clearly reduced, including in Leptosols, in which 6-methyl brGDGTs are present. In the Fan Si Pan transect, MBT′/CBT–MAAT estimates showed no significant deviation from expected MAATs. We find, however, that soil type effect – related to vegetation changes and contrasting soil organic carbon properties – may bias MAAT–pH estimates in the Vietnamese soil transect. Additionally, soil

- depth plays a role which differs between the different Fan Si Pan soil
- profiles, likely determined by soil type and history.
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- *Keywords*: calibration, soil, brGDGTs, temperature, pH
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#### **1. Introduction**

 Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are membrane lipids of high molecular weight (Fig. 1) that are of bacterial origin (Weijers et al., 2006a, 2009; Sinninghe Damsté et al., 2011, 2014). They are ubiquitous in aquatic and continental environments (Schouten et al., 2013 and references therein). At the global scale, brGDGT distributions in soils mainly depend on mean annual air temperature (MAAT) and soil pH (e.g., Weijers et al., 2007; Peterse et al., 2012). Several indices have been developed to summarize brGDGT distributions, for instance the methylation index of branched tetraethers (MBT), the cyclization ratio of branched tetraethers (CBT) and the MBT′ index, which is a simplified form of MBT. These indices are linked to continental temperatures and soil pH through 62 two global soil calibrations. However, calibration errors are about  $5.0 \degree C$  and about 0.8 pH unit (Weijers et al., 2007; Peterse et al., 2012). High calibration errors are due to multiple possible biases such as soil texture, humidity and oxygenation (e.g. Peterse et al., 2009a; Huguet et al., 2010; Dirghangi et al., 2013; Menges et al., 2014; Dang et al., 2016), seasonality and/or use of atmospheric rather than soil temperature (e.g., Peterse et al., 2012; Deng et al., 2016; Wang et al., 2016). Indeed, MAAT is an approximation of mean annual soil temperature that is also influenced by other climate-dependent parameters, such as snow cover, vegetation type and soil properties (Smerdon et al., 2004). Recently, new indices such as 72 MBT'<sub>5ME</sub>,  $CBT_{5ME}$  and CBT' have been defined, following analytical

 improvements that have allowed the separate quantification of 5- and 6- methyl brGDGTs (Fig. 1; De Jonge et al., 2014). Poor brGDGT separations also explain part of the scatter in the global calibrations (De Jonge et al., 2014).

 As also seen at the global scale, substantial scatter has been observed at the regional/local scale, including for calibrations based on altitudinal transects (Sinninghe Damsté et al., 2008; Peterse et al., 2009b; Yang et al., 2010, 2015b; Ernst et al., 2013; Liu et al., 2013; Anderson et al., 2014; Coffinet et al., 2014; Zhuang et al., 2015; Deng et al., 2016; Nieto-Moreno et al., 2016). Factors other than MAAT and pH, such as vegetation and soil type, length of growing season and topography, have been suggested as causes for part of the scatter (Sinninghe Damsté et al., 2008; Peterse et al., 2009b; Liu et al., 2013; Anderson et al., 2014; Deng et al., 2016; Nieto-86 Moreno et al., 2016). Contrary to the classical MBT' index, MBT'<sub>5ME</sub> is well correlated with MAAT/altitude at Mt. Shennongjia, China (Yang et al., 2015a, 2015b). It is noteworthy that only a few previous brGDGT-based studies have used well-described soils and/or profiles (Huguet et al., 2010; Zech et al., 2012; Menges et al., 2014; Yamamoto et al., 2016). A better consideration of soil pedogenesis may help researchers to properly evaluate the dependency of the observed scatters on soil physico-chemical properties. In the present study, we reassess a composite global soil dataset (Huguet et al., 2010; Peterse et al., 2012; Dirghangi et al., 2013; Anderson et al., 2014; De Jonge et al., 2014) by assigning a soil type to each of its 358





135 With MBT', CBT, MBT' $_{5\text{ME}}$  and CBT' defined as follows:

$$
MBT' = \frac{Ia + Ib + Ic}{Ia + Ib + Ic + IIa + IIb + IIc + IIIa + IIb' + IIb' + IIc' + IIIa'}
$$
(5)

$$
CBT = -\log\left(\frac{Ib + IIb + IIb'}{Ia + IIa + IIa'}\right)
$$
\n(6)

$$
MBT'_{5ME} = \frac{Ia + Ib + Ic}{Ia + Ib + Ic + IIa + IIIb + IIc + IIIa}
$$
 (7)

$$
CBT' = \log \left( \frac{Ic + IIa' + IIb' + IIlc' + IIIa' + IIIb' + IIIc'}{Ia + IIIa + IIIa} \right)
$$
(8)

136 Roman numerals refer to the structures in Fig. 1.

 Prior to any residual per soil type inspection, Z-scores and Tukey box plots were used to eliminate all outliers. Once again, only soil types with at least 10 samples after elimination of outliers and samples with missing data were considered.

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# 142 *2.2. Environmental setting in the Mount Fan Si Pan National Park and*  143 *MAAT modeling*

144 The environmental setting is described in detail by Podwojewski et al.

145 (2011). In short, the Mount Fan Si Pan National Park  $(22^{\circ}18'13''3N,$ 

 $146$   $103^{\circ}46'32''5E$ ) is located in northwestern Vietnam, close to the Chinese

147 border (Fig. 2A). The Fan Si Pan Mountain range is oriented northwest–

148 southeast and culminates at 3143 m above modern sea level, the highest

149 altitude in Vietnam (Podwojewski et al., 2011). The soil bedrock is

150 homogenous throughout the entire mountain range and the anthropic

151 influences are restricted to the foothills, the rest of the mountain range

- 152 being covered with primary  $C_3$  vegetation that follows a pronounced
- 153 altitudinal zonation (Fig. 2B; Podwojewski et al., 2011). The Mount Fan Si
- 154 Pan National Park is subject to a typical monsoonal climate, albeit altered

 by altitude and orientation to the winds as air moisture is high all year round with frequent drizzle and fog (Podwojewski et al., 2011).

 A linear ordinary least square regression of MAAT vs altitude was established using MAAT data as y values from 17 weather stations in Vietnam and China (Supplementary Table S2) in addition to the Hoang Lien Son Mountain MAAT value as reported in Podwojewski et al. (2011). 161 The obtained slope and intercept were  $-4.5 \pm 0.2$  °C/km and  $23.2 \pm 0.2$  °C, 162 the 1-σ root mean square error (RMSE) was 0.6 °C and the *p*-value was much lower than 0.001. The established linear regression was then applied to the Mount Fan Si Pan National Park to derive MAAT at any altitude. 

*2.3. Fan Si Pan soil profiles and samples*

 The pedological study of Podwojewski et al. (2011) represented an opportunity to couple brGDGT distributions to soil types, as the latter had already been reliably determined. Ten soil pits had previously been excavated along the Fan Si Pan Mountain by Podwojewski et al. (2011). The soils were initially sampled for soil type characterization – soil organic matter properties and geochemical environment – with respect to environmental changes. Five of the initially investigated soil profiles were selected for this study (FAN 1, FAN 2 and FAN 4 to FAN 6; Fig. 2) as they occur along a well-defined transect (Fig. 2A) and cover the entire pedogenetic sequence (Fig. 2B; Podwojewski et al., 2011). The selected soil profiles and horizons are described in detail by Podwojewski et al. (2011). In



 grasslands (Podwojewski et al., 2011 and references therein; IUSS Working Group WRB, 2015) – represented by FAN 6. *2.4. Sample preparation and brGDGT analysis* The samples were air dried and sieved through a 2 mm sieve before being ground and homogenized using a mortar and pestle. Between 0.8 and 207 2.2 g of each sample, depending on  $C_{org}$  concentration, was then extracted 208 with DCM:MeOH (9:1, v:v) using an accelerated solvent extractor ASE 350 Dionex at 120 °C and 10<sup>7</sup> Pa. Total lipid extracts were separated following the automated procedure established by Sanchi et al. (2013). BrGDGT analyses were performed at CEREGE by high-performance liquid chromatography–atmospheric pressure chemical ionization mass spectrometry (HPLC–APCI-MS) using positive ions on a HPLC–MS 1100 Series spectrometer, following Sanchi et al. (2014). The MBT′ and CBT indices were calculated using equations (5) and (6). Since no local/regional calibration has yet been established for Vietnam, MAAT and pH were estimated using the extended global soil calibration developed by Peterse et al. (2012), equations (1) and (2). The BIT index was calculated following Hopmans et al. (2004):  $BIT =$  $Ia + IIa + IIIa + IIa' + IIIa'$  $Cren + Ia + IIa + IIIa + IIa' + IIIa'$  $(9)$  Roman numerals refer to the structures in Fig. 1. Based on duplicate injections of the entire sample set, the mean

222 analytical 1-σ standard deviations (SD, mean of -σ SD to individual mean

223 values) were  $0.003$  for MBT',  $0.006$  for CBT and  $0.001$  for BIT. These 224 correspond to 0.1 °C and 0.01 pH unit mean analytical uncertainties. 

**3. Results**

 *3.1. Global MAAT–pH/brGDGT relationships and MAAT–pH residuals per soil type*

 Twenty-seven different soil types were represented in the 358- component composite global soil dataset (Fig. 3). Visually, the scatters per soil type were not all similar and some soil types such as Luvisols and Regosols were mainly clustered into relatively small MAAT–pH/brGDGT domains and/or comprised a few outliers (Fig. 3 and Supplementary Fig. S1). The composite dataset allowed us to extend the number of soil types suitable for statistical analysis from eight to twelve – from 174 to 298 soil samples. MAAT–pH/brGDGT relationships (Tables 1 and 2) and MAAT(pH) residual distributions (Fig. 4) were thus determined for the most represented soil types only. A few examples of soil types were also selected for more detailed MAAT residual distributions (Fig. 5). The soil samples reconsidered by De Jonge et al. (2014) were used to compare the newest with traditional MAAT–pH/brGDGT relationships per soil type, as well as MAAT(pH) residual distributions per soil type using traditional and newest global soil calibrations (Figs. 4 and 5, Table 2). Using the composite global soil dataset, five soil types had non-

significant MAAT–MBT′/CBT relationships and seven soil types had non-



 Using the global soil dataset of De Jonge et al. (2014), two or three soil types had non-significant traditional and new MAAT–pH/brGDGT relationships (Table 2). For MAAT–MBT′/CBT vs MAAT–MBT′5ME, the *R*<sup>2</sup> range was 0.1–0.9 vs 0.0–0.9 and the RMSE range was 1.6–6.8 °C vs 2.4–5.6 <sup>265</sup> °C. For pH–CBT vs pH–CBT′, the  $R^2$  range was 0.1–0.7 vs 0.0–0.9 and the RMSE range was 0.5–1.1 pH units vs 0.2–0.6 pH units (Table 2). Ranges of MAAT–MBT′/CBT coefficients were 60.6 for MBT′ slope, 10.9 for CBT slope 268 and 22.2 for intercept whereas ranges of MAAT–MBT $\gamma_{5ME}$  coefficients were



292 pH–CBT' global soil calibration of De Jonge et al.  $(2014)$  varied between –0.2 and 0.3 pH units (data not shown).

 *3.2. BrGDGT distributions and proxies in the Fan Si Pan National Park* BrGDGTs were present in all Fan Si Pan soil samples. Compounds Ia 297 and  $IIa/IIa'$  were the most abundant in each sample, representing together at least 86% of total brGDGTs (Supplementary Table S3). Conversely, 299 compounds IIIb/IIIb' and IIIc/IIIc' were all reliably detected in only one- third of the samples, precluding the use of MBT and associated soil calibrations.

302 BIT, MBT' and CBT were calculated for all Fan Si Pan soil samples 303 (Fig. 6, Table 3). The BIT range was  $0.94-1.00$ , the MBT' range was  $0.57-$  0.93 and the CBT range was 1.02–2.01 (Table 3). The MBT′/CBT-based MAAT estimate range was 10.0–20.5 °C using the global soil calibration of Peterse et al. (2012), corresponding to differences with modeled MAAT 307 between –2.8 and 6.2 °C – on average  $2.3 \pm 1.7$  °C (Table 3). The CBT-based pH estimate range was 3.9–5.9 pH units using the global soil calibration of Peterse et al. (2012), corresponding to differences with measured pH 310 between –0.1 and 2.1 pH units – on average  $0.9 \pm 0.6$  pH units (Table 3). BIT varied with depth by maximum 0.04 in all soil profiles (Fig. 6). MBT′ decreased with depth by 0.14–0.21 in Podzols (even if FAN 5 had only three points), looked globally stable in FAN 1 (also with only three points), and was stable in the other soil profiles. CBT was stable in FAN 5,





*4.1. Global soil dataset*

*4.1.1. Soil type diversity and implications for MAAT–pH reconstructions*

 The 27 soil types represented in the 358-component composite global soil dataset denote its high diversity (Fig. 3 and Supplementary Fig. S1, Supplementary Table S1). Most of the soil samples were taken from surficial and/or A horizons (Supplementary Table S1). Thus, we may assume that soil depth has no significant effect on the global brGDGT distributions considered in this study.

 Pedogenetic processes depend on multiple factors such as climate, vegetation type, topography and parent material (e.g., IUSS Working Group WRB, 2015). These differential processes in soil formation and erosion may



 could be distinguished from another group comprising Cambisols, Fluvisols and Leptosols based on their pH–CBT slopes and associated standard errors (Table 1). In addition, some soil types such as Alisols, Fluvisols, Phaeozems and Regosols had peculiar MAAT–MBT′/CBT relationships when compared with most other soil types (Table 1). This suggests that high soil heterogeneity has an impact on (acido)bacterial communities involved in brGDGT production (Jones et al., 2009) and that different communities may respond in different ways to environmental changes. The soil type effect on brGDGTs and their producers is also supported by the different distributions of MAAT residuals per soil type (Fig. 4A), as well as pH residuals per soil type to a lesser extent (data not shown). Six soil types had mainly negative residuals, two soil types had mainly positive residuals and four soil types had roughly equal numbers of positive as negative residuals (Fig. 4A). These three groups of soil types in terms of MAAT residuals were not distinguished by their typical moisture regimes (Fig. 4A, Supplementary Table S1). In addition, some soil types such as Alisols and Podzols had very high MAAT residuals (Figs. 4A, 5A and 5B). Thus, (almost) systematic biases on MAAT–pH reconstructions may occur for a given soil type when using global soil calibrations. This also implies that not all soil types contribute equally to global scatters (Figs. 4A, 5A, 5B and Supplementary Fig. S1).

 *4.1.2. Traditional vs improved chromatographic method: is there an impact on the soil type effect?*

 Using the soil samples reconsidered by De Jonge et al. (2014), we assess if 5- and 6-methyl brGDGT producers are influenced by the very high soil heterogeneity, following the hypothesis that 5- and 6-methyl brGDGTs are not produced by the same microorganisms (De Jonge et al., 2014). Regression coefficients and performances differed at times between different soil types for traditional and newest MAAT–pH/brGDGT relationships (Table 2). In addition, not all soil types had similar traditional and new MAAT–pH/brGDGT relationships to the global ones. After the homogeneity of slopes tests/ANCOVA, at least one soil type had a significantly different pH–CBT, MAAT–MBT′5ME and pH–CBT′ relationship from the others (Table 2). Acrisols, Ferralsols, Podzols and Regosols could be distinguished from Cambisols, Fluvisols and Leptosols by their pH–CBT slopes (Table 2). Some soil types such as Fluvisols and Regosols had peculiar MAAT–MBT′/CBT relationships when compared with most other soil types (Table 2). The main 399 soil types generally had similar MAAT–MBT'<sub>5ME</sub> slopes, but Fluvisols had a significantly higher intercept than the other soil types (Table 2). Cambisols, Leptosols and Regosols could be distinguished from Fluvisols and Podzols by their pH–CBT′ slopes (Table 2). Thus, the effect of soil type on MAAT– pH/brGDGT relationships remains significant when 5- and 6-methyl brGDGTs are quantified separately.



four Regosols decreased much more than the other Regosols and Luvisols

(Fig. 5D and F). These four Regosols highlighted by De Jonge et al. (2014)

424 not only had MAP values  $\leq$  550 mm, but they also had very high 6-methyl

brGDGT relative abundances (> 60% of total brGDGTs; Supplementary

Table S1). Despite the more substantial MAAT residual reduction in

Regosols, MAAT residual distributions per soil type were still not all

 similar, as there remained some soil types with high and/or mainly positive or negative residuals (Fig. 4C).

 Averaged MAP values per soil type varied between 472 and 1870 mm, which suggests that moisture regime clearly depends on soil type. Likewise, averaged soil pH values per soil type varied between 4.4 and 7.3 pH units, whereas averaged 6-methyl brGDGT relative abundances per soil type varied between 1.4 and 51.7% of total brGDGTs (Supplementary Table S1). Regosols had on average the lowest MAP values, and the highest pH values and 6-methyl brGDGT relative abundances (Supplementary Table S1), which is consistent with the greatest improvement of their pH–brGDGT relationship and the greatest decreases in MAAT(pH) residuals (Fig. 4B and C, Table 2). Conversely, soil types with averaged MAP values > 1000 mm had the lowest averaged pH values and 6-methyl brGDGT relative abundances (Supplementary Table S1), so no improvement of MAAT– pH/brGDGT relationships nor clear decrease in MAAT(pH) residuals was expected. However, pH–brGDGT relationships were improved in the wettest soils (Fig. 4B and C, Table 2). In addition, soil types with averaged MAP values between 500 and 1000 mm showed no intermediate behaviors between the wettest and the driest soils (Fig. 4B and C, Table 2). This likely explains why the separate quantification of 5- and 6-methyl brGDGTs barely reduces the soil type effect on brGDGTs.

*4.2. Fan Si Pan soil transect*

#### *4.2.1. BrGDGT-derived proxies*

 BIT values in Fan Si Pan soils (Table 3) are close to the reported 453 mean soil BIT value of  $0.90 \pm 0.14$  (Schouten et al., 2013) and are consistent with those observed in wet and acidic soils (e.g., Weijers et al., 2006b; Loomis et al., 2011; Dirghangi et al., 2013). For MAAT, only one Fan Si Pan 456 soil fell outside the global MAAT–MBT'/CBT RMSE of Peterse et al. (2012) of 5 °C (Table 3). For pH, half of the Fan Si Pan soils fell outside the global pH–CBT RMSE of Peterse et al. (2012) of 0.8 pH units (Table 3). As RSME means that globally 66% of the soils will fall within this error range, Fan Si Pan soils adhere quite well to the variabilities of the global soil calibration dataset of Peterse et al. (2012), especially for MAAT–MBT′/CBT. The absence of correlation between measured pH and CBT (*r* = –0.11,  $p = 0.67$ , Fig. 6) when all Fan Si Pan soils are considered together is likely due to their very small pH domain (3.5–4.7 pH units, Table 3) and/or to the differential relationships per soil type (Fig. 6, Table 3). Indeed, CBT and

 measured pH were anti-correlated in Acrisols/Alisols, positively correlated in Umbrisols, and had no clear relationship in Podzols.

 MAAT–pH reconstructions along the Fan Si Pan transect may be substantially biased by the co-elution of 5- and 6-methyl brGDGTs due to our chromatographic method. Indeed, Yang et al. (2015a) have shown that 471 6-methyl brGDGTs significantly deteriorate the performance of MBT' as a MAAT/altitude proxy along Mt. Shennongjia, China. Additionally, MBT′ is not (well) correlated with MAAT/altitude along most other altitudinal



497 thin litter layer and rapid  $C_{org}$  mineralization. In the Fan Si Pan Podzols, 498  $C_{org}$  decomposition rate is lower, partially due to cooler temperatures and seasonal inputs from leaves (Podwojewski et al., 2011). The Fan Si Pan 500 Podzols thus have a thicker litter layer, resulting in very high topsoil  $C_{org}$  stocks. In addition, the second major change in vegetation type along the Fan Si Pan transect has induced the transition from Podzols to Umbrisols 503 with a thinning of the litter layer, resulting in lower topsoil  $C_{org}$  stocks and a 504 different  $C_{org}$  source (Fig. 2B; Podwojewski et al., 2011). Indeed,  $C_{org}$  inputs 505 for Podzols are exogenic – mainly from the thick litter layer – whereas  $C_{\text{org}}$  inputs for Umbrisols are endogenic, mainly from bamboo roots and thus more homogenous.

508 Substantial changes in  $C_{org}$  sources, stocks and/or mineralization rates in soils may induce changes in substrate nature and/or nutrient availability for brGDGT producers, which may modify brGDGT distributions and so bias MAAT–pH reconstructions, as suggested by previous workers such as Anderson et al. (2014). Thus, biases due to vegetation and soil types should be jointly investigated, preferentially along lateral and local soil transects with as many constant environmental parameters as possible, such as MAAT, soil temperature, vegetation type and parent material.

#### *4.2.3. Effects of soil depth on brGDGT-derived proxies*

 The soil collection of the Fan Si Pan transect allows to investigate five well-studied soil profiles. Substantially lower brGDGT-based MAATs in



 producers – for instance, lipid transfer to a non-extractable pool via organo- metallic complexation – may occur in podzol soils (e.g., Huguet et al., 2010). Nevertheless, such processes – which also include soil bioturbation by soil fauna and soil reworking by rooted trees – are unlikely to be restricted to Podzols.

 BrGDGT distributions may also be influenced by the history of the soils. Former agricultural activities – mainly maize crops (Fig. 2B; Podwojewski et al., 2011) – may have impacted brGDGT distributions in the FAN 1 soil profile. Additionally, the transition from primary broad-leaved forests to alpine vegetation (Fig. 2B; Podwojewski et al., 2011) has shifted upwards in altitude under the effect of the present global warming (IPCC, 2013). This transition is now close to the FAN 6 site, which may thus have experienced a major temporal change in vegetation type. However, the brGDGT turnover times reported so far – from a few months to less than 45 years (Peterse et al., 2010; Weijers et al., 2010; Huguet et al., 2013a) – may be true for surficial soils only. Indeed, brGDGTs may be associated with the mineral phase and/or be incorporated within the macromolecular matrix in deeper soil horizons (e.g., Huguet et al., 2010), whereas microbial activity may decrease with depth, resulting in substantially longer brGDGT 562 turnover times in deep soils. The latter is suggested by decreases in  $C_{org}$ - normalized brGDGT absolute abundances with depth in FAN 1, FAN 2 and FAN 4 (data not shown). Additionally, imprints of former communities may be muted by the post-depositional effect (e.g., Zech et al., 2012; Yamamoto et

566 al., 2016), and such an effect is indeed suggested by an increase in  $C_{org}$ . normalized brGDGT absolute abundances with depth in FAN 6 (data not shown).

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### **5. Conclusions and perspectives**

 Soil types were assigned to a composite global dataset of 358 soils to investigate MAAT–pH/brGDGT relationships and MAAT(pH) residuals per soil type. Distributions of brGDGTs were also investigated in five soil profiles excavated along an altitudinal transect in the Mount Fan Si Pan National Park. Surrounding vegetation, geological setting, as well as soil sequence had previously been intensively characterized, providing an opportunity to investigate their impact on proxies intensively used in paleo-studies.

 The soil type diversity of the global dataset was high, traditional MAAT–pH/relationships per soil type were not all similar and different soil types (e.g., Alisols and Podzols) did not all provide the same contribution to global MAAT(pH)/brGDGT scatters. Additionally, the soil type effect on MAAT–pH relationships remained significant when 5- and 6-methyl brGDGTs were quantified separately and no obvious reduction in MAAT(pH) residuals per soil type occurred in general (e.g., in Leptosols, which contained 6-methyl brGDGTs). In the Mount Fan Si Pan National Park, MBT′/CBT-based MAATs were not significantly different to modeled MAATs when the global calibration error of 5 °C was taken into account.

 However, the decrease in MAAT estimates along the altitudinal transect lacked clarity when the focus was on surficial soils, and the pH–CBT relationship was absent when all Fan Si Pan soils were considered. On the one hand, substantial changes in soil/vegetation type along the Fan Si Pan transect may induce biases on MAAT–pH reconstructions in surficial soils. 594 On the other hand, MBT/CBT indices varied slightly or substantially with depth in the Fan Si Pan soil profiles, possibly as a function of soil type and history.

 To better understand the biases on brGDGT-based estimates, more soil profiles should be investigated along topo-sequences, as attempted in our work. Indeed, this study reveals the importance of direct collaborations between organic geochemists and pedologists, ensuring that specific organic compounds and physico-chemical soil properties are jointly investigated. To consider the evolution of soil properties through time, as well as the transfer 603 time of soil  $C_{org}$ , radiocarbon analyses on bulk soil  $C_{org}$  and on specific organic compounds should be conducted. Additionally, future global/regional/local soil MAAT–pH/brGDGT calibrations should consider sample sizes of a few dozen to a few hundred per soil type to ensure adequate specificity for all given soil types. **Acknowledgements** G.M. thanks Anneke de Rouw and the HYDRARIDE consortium for

making this study and the connection with pedologists possible through



















**Figure captions**

 **Fig. 1.** Structures of crenarchaeol (Cren), 5-methyl (Roman numbers with no prime symbol) and 6-methyl (Roman numbers with a prime symbol) branched glycerol dialkyl glycerol tetraethers (brGDGTs, I-II-III) with the 809 different  $a_5$  and/or  $a_5$  positions and the different  $a_6$  and/or  $a_6$  positions of the methyl groups.

 **Fig. 2.** (A) Maps showing the locations of the study site (left-hand map) and the studied soil profiles (right-hand map). Contour interval is 200 m and contour lines indicate altitudes between 1000 and 3000 m on the right-hand map, with darker tones for higher altitudes. Modified from maps generated from GeoMapApp (http://www.geomapapp.org). (B) Profile showing the studied soil pits. Altitudinal zonation of vegetation types is indicated in green. The profile does not pass exactly through the soil pits, which explains why their altitudes in the profile do not correspond to their actual altitudes. Horizons are delimited and color-coded as per the samples taken by Podwojewski et al. (2011): orange-yellow tones for A horizons, blue tones for Bw horizons and green tones for Bs horizons. Like tones correspond to like horizons. The horizons considered for soil brGDGT distributions are indicated in red. Adapted from Podwojewski et al. (2011). 

**Fig. 3.** BrGDGT-derived proxy data from the composite global soil dataset

(Huguet et al., 2010; Peterse et al., 2012; Dirghangi et al., 2013; Anderson et

 al., 2014; De Jonge et al., 2014), with 27 soil types being distinguished. (A) Instrumental/modeled mean annual air temperature (MAAT) vs MBT′/CBT. 830 (B) Instrumental/modeled MAAT vs MBT'<sub>5ME</sub>. (C) Measured pH vs CBT. (D) Measured pH vs CBT′. The outliers are also shown in each plot. The red lines in plots (B), (C) and (D) correspond to the global linear regressions on the composite global soil dataset after outlier removal.

 **Fig. 4.** Box-whisker plots of mean annual air temperature (MAAT) residuals per soil type showing minima and maxima with whiskers, medians with 837 horizontal bars,  $1^{st}$  and  $3^{rd}$  quartiles with boxes, and means with pluses. Plot (A) is based on the composite global soil dataset (Huguet et al., 2010; Peterse et al., 2012; Dirghangi et al., 2013; Anderson et al., 2014; De Jonge et al., 2014). Plots (B) and (C) are based on the soils reconsidered by De Jonge et al. (2014). In plots (A) and (B), residuals are based on the MAAT– 842 MBT'/CBT global soil calibration of Peterse et al. (2012). In plot (C), 843 residuals are based on the MAAT–MBT'<sub>5ME</sub> global soil calibration of De Jonge et al. (2014). Only soil types comprising at least 10 soils from the global datasets are considered. When outliers are identified for a given soil type, their number is indicated as (initial number of samples – number of outliers) below the number of samples actually considered. Moisture regimes based on averaged mean annual precipitation (MAP) values per soil type are specified with the following color-coding of the numbers of samples

 per soil type: blue if MAP > 1000 mm, orange if MAP 500–1000 mm and red if MAP < 500 mm.



**Fig. 6.** BIT (Hopmans et al., 2004), MBT′ (Peterse et al., 2012), CBT

869 (Weijers et al., 2007), and MBT'/CBT-derived mean annual air temperature

(MAAT) and pH based on the extended soil calibration (Peterse et al., 2012)

in the studied Fan Si Pan soil profiles. Modeled MAAT and measured pH

(Podwojewski et al., 2011 for the latter) are shown for comparison. Horizons

are delimited and color-coded as described in the caption for Fig. 2B.

 Symbols with error bars next to axis titles represent mean 1-σ standard deviations to mean values of duplicates. Surficial horizons, with a mean depth < 10 cm, are indicated in red.

#### **Table captions**

**Table 1**

880 Number of samples  $(n)$ , coefficients  $(a, b, c, S, I, and R^2)$ , and root mean

square errors (E) of traditional mean annual air temperature (MAAT)–

pH/brGDGT linear regressions per soil type using the composite global soil

dataset (Huguet et al., 2010; Peterse et al., 2012; Dirghangi et al., 2013;

Anderson et al., 2014; De Jonge et al., 2014). Only soil types comprising at

least 10 soils from the global dataset are considered for the linear

regressions. When outliers are identified for a given MAAT–pH/brGDGT

relationship per soil type, their number is indicated as (initial number of

samples – number of outliers) next to the number of samples actually

considered. Statistical significance is reached for *p*-values < 0.05.

#### **Table 2**

892 Number of samples  $(n)$ , coefficients  $(a, b, c, S, I \text{ and } R^2)$ , and root mean square errors (E) of traditional and newest mean annual air temperature (MAAT)–pH/brGDGT linear regressions per soil type using the soils of the composite global soil dataset (Huguet et al., 2010; Peterse et al., 2012;



- 909 (H<sub>2</sub>O), and measured pH are from Podwojewski et al. (2011). nd = not
- determined.

#### **Figure 1**



*m/z*

**Figure 2 - revised**















