

## 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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1	Consideration of soil types for the calibration of molecular
2	proxies for soil pH and temperature using global soil datasets
3	and Vietnamese soil profiles
4	
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#### 22 ABSTRACT

Distribution of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in 23 24 soils depends on environmental parameters such as mean annual air 25 temperature (MAAT) and soil pH. MBT'/MBT'<sub>5ME</sub> (methylation index of 26 branched tetraethers) and CBT/CBT' (cyclization ratio of branched tetraethers) are ratios based on the relative abundances of brGDGTs. Using 27 28 these ratios, global and regional/local calibrations have been established using surface soils, but generally without any preliminary study of soil 29 types. In this study, we reconsider global MAAT-pH/brGDGT calibrations 30 by assigning soil types to the 358 components of a composite soil dataset. 31 Additionally, we investigate brGDGT-derived proxies in five well-described 32 33 soil profiles along an altitudinal transect in the Mount Fan Si Pan National Park, northwestern Vietnam. Our results show that at the global scale, 34 traditional MAAT-pH/brGDGT relationships per soil type are significantly 35 36 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 6-37 methyl brGDGTs are quantified separately. In addition, MAAT(pH) 38 39 residuals per soil type are generally not clearly reduced, including in 40 Leptosols, in which 6-methyl brGDGTs are present. In the Fan Si Pan 41 transect, MBT'/CBT-MAAT estimates showed no significant deviation from expected MAATs. We find, however, that soil type effect – related to 42 43 vegetation changes and contrasting soil organic carbon properties – may 44 bias MAAT-pH estimates in the Vietnamese soil transect. Additionally, soil

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

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### 1. Introduction

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are 51 52 membrane lipids of high molecular weight (Fig. 1) that are of bacterial 53 origin (Weijers et al., 2006a, 2009; Sinninghe Damsté et al., 2011, 2014). They are ubiquitous in aquatic and continental environments (Schouten et 54 al., 2013 and references therein). At the global scale, brGDGT distributions 55 in soils mainly depend on mean annual air temperature (MAAT) and soil pH 56 (e.g., Weijers et al., 2007; Peterse et al., 2012). Several indices have been 57 developed to summarize brGDGT distributions, for instance the methylation 58 59 index of branched tetraethers (MBT), the cyclization ratio of branched tetraethers (CBT) and the MBT' index, which is a simplified form of MBT. 60 These indices are linked to continental temperatures and soil pH through 61 two global soil calibrations. However, calibration errors are about 5.0 °C and 62 about 0.8 pH unit (Weijers et al., 2007; Peterse et al., 2012). High 63 64 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; 65 Dirghangi et al., 2013; Menges et al., 2014; Dang et al., 2016), seasonality 66 67 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 68 69 approximation of mean annual soil temperature that is also influenced by other climate-dependent parameters, such as snow cover, vegetation type 70 and soil properties (Smerdon et al., 2004). Recently, new indices such as 71 72 MBT'<sub>5ME</sub>, CBT<sub>5ME</sub> and CBT' have been defined, following analytical

improvements that have allowed the separate quantification of 5- and 6methyl 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).

77 As also seen at the global scale, substantial scatter has been observed at the regional/local scale, including for calibrations based on altitudinal 78 transects (Sinninghe Damsté et al., 2008; Peterse et al., 2009b; Yang et al., 79 2010, 2015b; Ernst et al., 2013; Liu et al., 2013; Anderson et al., 2014; 80 Coffinet et al., 2014; Zhuang et al., 2015; Deng et al., 2016; Nieto-Moreno et 81 82 al., 2016). Factors other than MAAT and pH, such as vegetation and soil type, length of growing season and topography, have been suggested as 83 causes for part of the scatter (Sinninghe Damsté et al., 2008; Peterse et al., 84 2009b; Liu et al., 2013; Anderson et al., 2014; Deng et al., 2016; Nieto-85 Moreno et al., 2016). Contrary to the classical MBT' index, MBT'<sub>5ME</sub> is well 86 87 correlated with MAAT/altitude at Mt. Shennongjia, China (Yang et al., 2015a, 2015b). It is noteworthy that only a few previous brGDGT-based 88 studies have used well-described soils and/or profiles (Huguet et al., 2010; 89 90 Zech et al., 2012; Menges et al., 2014; Yamamoto et al., 2016). A better consideration of soil pedogenesis may help researchers to properly evaluate 91 92 the dependency of the observed scatters on soil physico-chemical properties. 93 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 94 95 al., 2014; De Jonge et al., 2014) by assigning a soil type to each of its 358

96	components to investigate traditional and newest MAAT–pH/brGDGT
97	relationships as well as MAAT(pH) residuals, per soil type. We also take
98	advantage of a well-characterized altitudinal soil transect with an elevation
99	range of 1400 m in the Mount Fan Si Pan National Park, Vietnam
100	(Podwojewski et al., 2011) to investigate brGDGT distributions. We focus, in
101	particular, on the possible vegetation/soil type and depth effect and assess
102	how well brGDGT-derived proxies reflect MAAT and soil pH in Vietnam.
103	
104	2. Materials and methods
105	2.1. Soil type assignment for the global soil dataset and statistical analysis
106	A composite global soil dataset of 358 previously analyzed samples
107	(Supplementary Table S1; Huguet et al., 2010; Peterse et al., 2012;
108	Dirghangi et al., 2013; Anderson et al., 2014; De Jonge et al., 2014) was
109	used for soil type assignment. For most samples taken from the
110	International Soil Reference and Information Centre (ISRIC), soil types
111	were obtained using the ISRIC Soil Information System (ISIS) database
112	(http://isis.isric.nl, last accessed on Thursday, August 25, 2016). For the
113	other samples, with the exception of those analyzed by Huguet et al. (2010)
114	which were the subject of preliminary pedological studies, the most likely
115	soil type was selected using the SoilInfo App based on SoilGrids1km (Hengl
116	et al., 2014; https://soilinfo-app.org, version 0.5.0, 15 November, 2015,
117	accessed before the update to SoilGrids250m in June 2016).

118	Statistical analysis – correlation tests, lin	near regressions and
119	homogeneity of slopes test/analysis of covariance	ce (ANCOVA) – was
120	conducted using the statistical software R 3.1.2	(R Development Core Team,
121	2016). Prior to the investigation of each MAAT-	-brGDGT and each pH–
122	brGDGT relationship, the outliers were elimina	nted using the car package
123	(Fox and Weisberg, 2011). After conducting rep	eated outlier tests until no
124	more samples with a Bonferroni $p$ -value < $0.05$	remained, all the identified
125	outliers were excluded from further statistical a	analysis. The slope
126	homogeneity test was then conducted to verify	whether regression slopes
127	per soil type for a given MAAT–brGDGT or pH-	-brGDGT relationship were
128	statistically identical – the ANCOVA being con	ducted only when the
129	homogeneity of slopes test was not significant,	i.e. $p$ -value $\geq 0.05$ . Only soil
130	types with at least 10 samples after exclusion o	f outliers and samples with
131	missing data were selected for statistical analy	sis.
132	All MAAT–pH residuals in this study we	re determined using the
133	global soil calibrations of Peterse et al. (2012) fo	ollowing equations (1) and
134	(2), and of De Jonge et al. (2014) following equa	tions (3) and (4):
	$MAAT = 0.81 - 5.67 \times CBT + 31.00 \times MBT'$	(1)
	$pH = 7.90 - 1.97 \times CBT$	(2)
	$MAAT = -8.57 + 31.45 \times MBT'_{5ME}$	(3)
	$pH = 7.15 + 1.59 \times CBT'$	(4)

$$pH = 7.15 + 1.59 \times CBT'$$
 (4)

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

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

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

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

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

141

# 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°18'13"3N,

146 103°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

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 yearround with frequent drizzle and fog (Podwojewski et al., 2011).

A linear ordinary least square regression of MAAT vs altitude was 157 158 established using MAAT data as y values from 17 weather stations in Vietnam and China (Supplementary Table S2) in addition to the Hoang 159 Lien Son Mountain MAAT value as reported in Podwojewski et al. (2011). 160 161 The obtained slope and intercept were  $-4.5 \pm 0.2$  °C/km and  $23.2 \pm 0.2$  °C, the 1-o root mean square error (RMSE) was 0.6 °C and the *p*-value was 162 much lower than 0.001. The established linear regression was then applied 163 to the Mount Fan Si Pan National Park to derive MAAT at any altitude. 164 165

166 2.3. Fan Si Pan soil profiles and samples

The pedological study of Podwojewski et al. (2011) represented an 167 opportunity to couple brGDGT distributions to soil types, as the latter had 168 169 already been reliably determined. Ten soil pits had previously been excavated along the Fan Si Pan Mountain by Podwojewski et al. (2011). The 170 soils were initially sampled for soil type characterization – soil organic 171 172 matter properties and geochemical environment – with respect to environmental changes. Five of the initially investigated soil profiles were 173 174 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 175 pedogenetic sequence (Fig. 2B; Podwojewski et al., 2011). The selected soil 176 177 profiles and horizons are described in detail by Podwojewski et al. (2011). In

178	short, P	odwojewski et al. (2011) described shallow (< 1 m deep) and very	
179	acidic so	oils (3.5–4.7 pH units, measured with a 1:2.5 soil:water ratio) with	
180	variable	bulk organic carbon ( $\mathrm{C}_{\mathrm{org}}$ ) concentrations (0.4–44.1%) and high	
181	water co	ontent values (40–215%). $\delta^{13}$ C analyses enabled Podwojewski et al.	
182	(2011) to confirm $C_{org}$ inputs from dominant $C_3$ vegetation at every altitude.		
183	Podwoje	wski et al. (2011) also made a floristic inventory at each soil	
184	sampling site (Fig. 2B) and distinguished three main climate/vegetation-		
185	depende	ent soil types:	
186	(i)	Low altitude Acrisols/Alisols – strongly weathered acidic soils with	
187		low base saturation at some depth, typical under warm and wet	
188		conditions (Podwojewski et al., 2011 and references therein; IUSS	
189		Working Group WRB, 2015) – represented by FAN 1 and FAN 2.	
190	(ii)	Mid-altitude Podzols – acidic soils with an organic layer and an	
191		ash-looking eluvial horizon directly underlain by the illuvial <i>spodic</i>	
192		or Bs horizon due to the accumulation of organo-metallic (Fe, Al)	
193		complexes leached by rainwater, typical in cold/temperate forests	
194		and in tropical mountain forests (Podwojewski et al., 2011 and	
195		references therein; IUSS Working Group WRB, 2015) –	
196		represented by FAN 4 and FAN 5.	
197	(iii)	High altitude Umbrisols – soils with dark topsoil, thick, well-	
198		humified and desaturated in the Mount Fan Si Pan National Park,	
199		typical under humid conditions with little or no moisture deficit in	
200		cool/temperate areas and in (sub)tropical mountain shrub and	

grasslands (Podwojewski et al., 2011 and references therein; IUSS 201 Working Group WRB, 2015) – represented by FAN 6. 202 203 Sample preparation and brGDGT analysis 204 2.4.205 The samples were air dried and sieved through a 2 mm sieve before 206 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 with DCM:MeOH (9:1, v:v) using an accelerated solvent extractor ASE 350 208 Dionex at 120 °C and 107 Pa. Total lipid extracts were separated following 209 210 the automated procedure established by Sanchi et al. (2013). 211 BrGDGT analyses were performed at CEREGE by high-performance 212 liquid chromatography-atmospheric pressure chemical ionization mass spectrometry (HPLC-APCI-MS) using positive ions on a HPLC-MS 1100 213 214 Series spectrometer, following Sanchi et al. (2014). 215 The MBT' and CBT indices were calculated using equations (5) and (6). Since no local/regional calibration has yet been established for Vietnam, 216 MAAT and pH were estimated using the extended global soil calibration 217 218 developed by Peterse et al. (2012), equations (1) and (2). 219 The BIT index was calculated following Hopmans et al. (2004):  $BIT = \frac{Ia + IIa + IIIa + IIa' + IIIa'}{Cren + Ia + IIa + IIIa + IIIa' + IIIa'}$ (9)220 Roman numerals refer to the structures in Fig. 1. 221 Based on duplicate injections of the entire sample set, the mean

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

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

226 **3. Results** 

227 3.1. Global MAAT-pH/brGDGT relationships and MAAT-pH residuals
228 per soil type

229 Twenty-seven different soil types were represented in the 358component composite global soil dataset (Fig. 3). Visually, the scatters per 230 soil type were not all similar and some soil types such as Luvisols and 231 232 Regosols were mainly clustered into relatively small MAAT-pH/brGDGT domains and/or comprised a few outliers (Fig. 3 and Supplementary Fig. 233 234 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 235 samples. MAAT-pH/brGDGT relationships (Tables 1 and 2) and MAAT(pH) 236 237 residual distributions (Fig. 4) were thus determined for the most represented soil types only. A few examples of soil types were also selected 238 for more detailed MAAT residual distributions (Fig. 5). The soil samples 239 240 reconsidered by De Jonge et al. (2014) were used to compare the newest 241 with traditional MAAT-pH/brGDGT relationships per soil type, as well as 242 MAAT(pH) residual distributions per soil type using traditional and newest global soil calibrations (Figs. 4 and 5, Table 2). 243 Using the composite global soil dataset, five soil types had non-244

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

246	significant pH–CBT relationships (Table 1). For MAAT–MBT'/CBT, the $R^2$
247	range was 0.0–0.8 and the RMSE range was 2.2–7.0 °C. For pH–CBT, the $R^2$
248	range was 0.0–0.8 and the RMSE range was 0.4–1.0 pH units (Table 1).
249	Ranges of MAAT–MBT'/CBT coefficients were 46.9 for MBT' slope, 11.7 for
250	CBT slope and 24.7 for intercept (Table 1). Some pairs of soil types, – for
251	example Andosols and Cambisols – had similar coefficients whereas other
252	pairs of soil types such as Cambisols and Luvisols had at least one
253	coefficient that was significantly different (Table 1). Ranges of pH–CBT
254	coefficients were 2.4 for slope and 3.4 for intercept (Table 1). After the
255	homogeneity of slopes test (F = 4.83, $p$ < 0.001), pH–CBT slopes per soil type
256	were not all similar. For instance, they were similar between Cambisols and
257	Leptosols, but not between Cambisols and Luvisols (Table 1). When
258	compared to the global MAAT–pH/brGDGT relationships, three soil types
259	had similar MAAT–MBT'/CBT coefficients and three soil types had similar
260	pH–CBT coefficients (Table 1).

261 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 262 relationships (Table 2). For MAAT–MBT'/CBT vs MAAT–MBT' $_{5ME}$ , the  $R^2$ 263 range was 0.1-0.9 vs 0.0-0.9 and the RMSE range was 1.6-6.8 °C vs 2.4-5.6264 °C. For pH–CBT vs pH–CBT', the  $R^2$  range was 0.1–0.7 vs 0.0–0.9 and the 265 RMSE range was 0.5–1.1 pH units vs 0.2–0.6 pH units (Table 2). Ranges of 266 MAAT-MBT'/CBT coefficients were 60.6 for MBT' slope, 10.9 for CBT slope 267 and 22.2 for intercept whereas ranges of MAAT–MBT'<sub>5ME</sub> coefficients were 268

46.2 for slope and 34.2 for intercept (Table 2). Ranges of pH–CBT vs pH-
CBT' coefficients were 1.9 vs 1.8 for slope and 3.0 vs 2.8 for intercept (Table
2). For all bivariate traditional and newest MAAT–pH/brGDGT
relationships, slopes/intercepts per soil type were not all similar after the
homogeneity of slopes tests/ANCOVA (Table 2). When compared to the
global MAAT–brGDGT relationships, four soil types had similar MAAT–
MBT'/CBT coefficients and six soil types had similar MAAT–MBT' $_{\rm 5ME}$
coefficients (Table 2). When compared to the global pH–brGDGT
relationships, three soil types had similar pH–CBT coefficients and two soil
types had similar pH–CBT' coefficients (Table 2).
Using the composite global soil dataset, mean MAAT residuals per
soil type based on the MAAT–MBT'/CBT global soil calibration of Peterse et
al. (2012) varied between $-7.0$ and 3.5 °C (Figs. 4A, 5A and 5B). Mean pH
residuals per soil type based on the pH–CBT global soil calibration of
Peterse et al. (2012) varied between $-1.3$ and $0.4$ pH units (data not shown).
Using the global soil dataset of De Jonge et al. (2014), mean MAAT
residuals per soil type based on the MAAT–MBT'/CBT global soil calibration
of Peterse et al. (2012) varied between $-7.5$ and $3.5$ °C (Figs. 4B, 5C and 5E).
Mean MAAT residuals per soil type based on the MAAT–MBT' $_{\rm 5ME}$ global soil
calibration of De Jonge et al. (2014) varied between $-3.5$ and $2.5$ °C (Figs.
4C, 5D and 5F). Mean pH residuals per soil type based on the pH–CBT $$
global soil calibration of Peterse et al. (2012) varied between $-1.4$ and $0.2$
pH units (data not shown). Mean pH residuals per soil type based on the

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

294

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
and IIa/IIa' were the most abundant in each sample, representing together
at least 86% of total brGDGTs (Supplementary Table S3). Conversely,
compounds IIIb/IIIb' and IIIc/IIIc' were all reliably detected in only onethird of the samples, precluding the use of MBT and associated soil
calibrations.

BIT, MBT' and CBT were calculated for all Fan Si Pan soil samples 302 303 (Fig. 6, Table 3). The BIT range was 0.94–1.00, the MBT' range was 0.57– 304 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 305 306 Peterse et al. (2012), corresponding to differences with modeled MAAT between -2.8 and 6.2 °C – on average  $2.3 \pm 1.7$  °C (Table 3). The CBT-based 307 pH estimate range was 3.9–5.9 pH units using the global soil calibration of 308 309 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). 311 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 312 three points), looked globally stable in FAN 1 (also with only three points), 313 314 and was stable in the other soil profiles. CBT was stable in FAN 5,

fluctuated by 0.25–0.50 in FAN 6, and decreased with depth by 0.24–0.66 in 315 316 the other soil profiles. CBT-based pH variations with depth were opposite 317 and roughly twice as high as CBT variations with depth in all soil profiles. 318 Measured pH increased with depth by 0.5–1.3 pH units in all soil profiles, 319 except FAN 5 with only two points (Fig. 6). However, in FAN 4 and FAN 6, 320 changes in measured pH with depth shifted from decreases in A horizons to 321 increases in B horizons, with variations of 0.2–0.6 pH units in FAN 6 and of 0.4–1.0 pH units in FAN 4. MBT'/CBT-based MAAT decreased with depth 322 by about 4-6 °C in Podzols, increased by about 2.5 °C in Acrisols/Alisols, and 323 324 was stable in Umbrisols (Fig. 6).

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		<b>D</b> '	•
326	4.	Discu	Ission

327 4.1. Global soil dataset

328 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

338	have an impact on the production, transformation and preservation of labile
339	substrates for brGDGT producers, including in surficial horizons. Indeed,
340	brGDGT producers are partially attributable to Acidobacteria (Weijers et
341	al., 2009; Sinninghe Damsté et al., 2011, 2014) and their metabolism is
342	thought to be the heterotrophic assimilation of labile substrates or the
343	chemoautotrophic consumption of respired $\mathrm{CO}_2$ (Weijers et al., 2010).
344	Given the specificity of soil types to climatic ranges such as moisture
345	regime/mean annual precipitation (MAP, Fig. 4, Supplementary Table S1),
346	some soil types have small MAAT and/or pH domains that may be
347	associated with small MBT' and/or CBT domains, which may result in non-
348	significant MAAT–pH/brGDGT relationships (Fig. 3, Table 1 and
349	Supplementary Table S1). For instance, Acrisols, Alisols, Ferralsols, Podzols
350	and Umbrisols did not show a significant pH–CBT anti-correlation, likely
351	due to their typically low pH values and high CBT values (Table 1 and
352	Supplementary S1). Alisols and Ferralsols also had typically high MAAT
353	and MBT' values, resulting in non-significant MAAT–MBT'/CBT
354	relationships (Table 1 and Supplementary Table S1).
355	Regression coefficients and performances of MAAT–MBT'/CBT and
356	pH–CBT differed at times between different soil types, whose MAAT–
357	pH/brGDGT relationships were not always similar to global ones (Table 1).
358	After the homogeneity of slopes test, at least one soil type had a
359	significantly different pH–CBT relationship from the others: the wettest and
360	driest soils – Acrisols, Alisols, Ferralsols, Podzols, Regosols and Umbrisols –

could be distinguished from another group comprising Cambisols, Fluvisols 361 and Leptosols based on their pH–CBT slopes and associated standard errors 362 363 (Table 1). In addition, some soil types such as Alisols, Fluvisols, Phaeozems and Regosols had peculiar MAAT-MBT'/CBT relationships when compared 364 365 with most other soil types (Table 1). This suggests that high soil 366 heterogeneity has an impact on (acido)bacterial communities involved in 367 brGDGT production (Jones et al., 2009) and that different communities may respond in different ways to environmental changes. 368 The soil type effect on brGDGTs and their producers is also supported 369 370 by the different distributions of MAAT residuals per soil type (Fig. 4A), as 371 well as pH residuals per soil type to a lesser extent (data not shown). Six 372 soil types had mainly negative residuals, two soil types had mainly positive 373 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 374 375 MAAT residuals were not distinguished by their typical moisture regimes (Fig. 4A, Supplementary Table S1). In addition, some soil types such as 376 Alisols and Podzols had very high MAAT residuals (Figs. 4A, 5A and 5B). 377 378 Thus, (almost) systematic biases on MAAT-pH reconstructions may occur 379 for a given soil type when using global soil calibrations. This also implies 380 that not all soil types contribute equally to global scatters (Figs. 4A, 5A, 5B and Supplementary Fig. S1). 381

382

# 383 4.1.2. Traditional vs improved chromatographic method: is there an impact 384 on the soil type effect?

385 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 386 387 soil heterogeneity, following the hypothesis that 5- and 6-methyl brGDGTs are not produced by the same microorganisms (De Jonge et al., 2014). 388 389 Regression coefficients and performances differed at times between different soil types for traditional and newest MAAT-pH/brGDGT relationships 390 (Table 2). In addition, not all soil types had similar traditional and new 391 392 MAAT-pH/brGDGT relationships to the global ones. After the homogeneity of slopes tests/ANCOVA, at least one soil type had a significantly different 393 394 pH–CBT, MAAT–MBT'<sub>5ME</sub> and pH–CBT' relationship from the others (Table 2). Acrisols, Ferralsols, Podzols and Regosols could be distinguished from 395 Cambisols, Fluvisols and Leptosols by their pH–CBT slopes (Table 2). Some 396 397 soil types such as Fluvisols and Regosols had peculiar MAAT-MBT'/CBT relationships when compared with most other soil types (Table 2). The main 398 soil types generally had similar MAAT-MBT'<sub>5ME</sub> slopes, but Fluvisols had a 399 400 significantly higher intercept than the other soil types (Table 2). Cambisols, 401 Leptosols and Regosols could be distinguished from Fluvisols and Podzols by 402 their pH–CBT' slopes (Table 2). Thus, the effect of soil type on MAAT– pH/brGDGT relationships remains significant when 5- and 6-methyl 403 brGDGTs are quantified separately. 404

405	When considering MAAT–MBT' $_{\rm 5ME}$ instead of MAAT–MBT'/CBT per
406	soil type, $R^2$ changes varied between –0.4 and 0.2, and RMSEs changes
407	varied between $-1.2$ and $1.1$ °C (Table 2). When considering pH–CBT'
408	instead of pH–CBT per soil type, $R^2$ changes varied between –0.5 and 0.8,
409	and RMSEs changes varied between $-0.7$ and $0.0$ pH units (Table 2).
410	Therefore, MAAT–pH/brGDGT relationships per soil type – and in
411	particular,MAAT-brGDGTrelationships-arenotsystematicallyimproved
412	when 5- and 6-methyl brGDGTs are quantified separately. In addition, the
413	improvements or deteriorations of MAAT-pH/brGDGT relationships clearly
414	depend on soil type (Table 2).
415	Decreases in MAAT(pH) residuals per soil type were not very clear

when 5- and 6-methyl brGDGTs were quantified separately, except in 416 417 Regosols (Figs. 4B and 4C). A more detailed inspection of MAAT residual distributions in Leptosols and in Regosols (Fig. 5C and E) revealed that 418 419 these two soil types had high and opposite MAAT residuals using the 420 MAAT-MBT'/CBT calibration of Peterse et al. (2012). When using the 421 MAAT-MBT'<sub>5ME</sub> calibration of De Jonge et al. (2014), MAAT residuals of four Regosols decreased much more than the other Regosols and Luvisols 422 423 (Fig. 5D and F). These four Regosols highlighted by De Jonge et al. (2014) not only had MAP values  $\leq 550$  mm, but they also had very high 6-methyl 424 brGDGT relative abundances (> 60% of total brGDGTs; Supplementary 425 Table S1). Despite the more substantial MAAT residual reduction in 426 427 Regosols, MAAT residual distributions per soil type were still not all

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

430 Averaged MAP values per soil type varied between 472 and 1870 mm, 431 which suggests that moisture regime clearly depends on soil type. Likewise, 432 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 433 434 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 435 and 6-methyl brGDGT relative abundances (Supplementary Table S1), 436 437 which is consistent with the greatest improvement of their pH-brGDGT relationship and the greatest decreases in MAAT(pH) residuals (Fig. 4B and 438 439 C, Table 2). Conversely, soil types with averaged MAP values > 1000 mm had the lowest averaged pH values and 6-methyl brGDGT relative 440 abundances (Supplementary Table S1), so no improvement of MAAT-441 442 pH/brGDGT relationships nor clear decrease in MAAT(pH) residuals was expected. However, pH-brGDGT relationships were improved in the wettest 443 soils (Fig. 4B and C, Table 2). In addition, soil types with averaged MAP 444 values between 500 and 1000 mm showed no intermediate behaviors 445 446 between the wettest and the driest soils (Fig. 4B and C, Table 2). This likely 447 explains why the separate quantification of 5- and 6-methyl brGDGTs barely reduces the soil type effect on brGDGTs. 448

449

450 4.2. Fan Si Pan soil transect

#### 451 4.2.1. BrGDGT-derived proxies

BIT values in Fan Si Pan soils (Table 3) are close to the reported 452 453 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; 454 455 Loomis et al., 2011; Dirghangi et al., 2013). For MAAT, only one Fan Si Pan soil fell outside the global MAAT-MBT'/CBT RMSE of Peterse et al. (2012) 456 457 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 458 means that globally 66% of the soils will fall within this error range, Fan Si 459 460 Pan soils adhere quite well to the variabilities of the global soil calibration dataset of Peterse et al. (2012), especially for MAAT-MBT'/CBT. 461 462 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 463 due to their very small pH domain (3.5–4.7 pH units, Table 3) and/or to the 464 465 differential relationships per soil type (Fig. 6, Table 3). Indeed, CBT and measured pH were anti-correlated in Acrisols/Alisols, positively correlated 466

467 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
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

474	transects studied so far in China, India and Tanzania (Peterse et al., 2009b;
475	Yang et al., 2010; Ernst et al., 2013; Coffinet et al., 2014; Deng et al., 2016),
476	which may be due to 6-methyl brGDGTs as well. Conversely, soil depth
477	effect is not a plausible explanation as the soil samples considered for
478	altitudinal lapse rate studies were taken from surficial horizons.
479	
480	4.2.2. Soil type effect on brGDGTs: a focus on contrasting soil organic matter
481	properties
482	For the Fan Si Pan surficial soils – sampled from horizons with a
483	mean soil depth < 10 cm – MBT' and MBT'/CBT-based MAAT mainly
484	decreased between the lowest and highest altitude soils, in particular
485	between the Podzols FAN4.1/FAN5.1 and the Umbrisols FAN6.1/FAN6.2
486	(Fig. 6, Table 3). Conversely, MAAT estimates did not decrease with altitude
487	between the Acrisol FAN1.1, the Alisols FAN2.A0/FAN2.1 and the Podzol
488	FAN4.1. Despite our difficulties in separating the effects of vegetation/soil
489	type and adiabatic cooling on brGDGT distributions along the Fan Si Pan
490	transect, the absence of a decrease in MAAT estimates between the four
491	lowest altitude soils suggests the importance of the diversity of soils
492	encountered along this transect.
493	The different main soil types present along the Fan Si Pan transect
494	have contrasting $C_{\rm org}$ sources, stocks and mineralization rates (Podwojewski
495	et al., 2011). In the Fan Si Pan Acrisols, $C_{\rm org}$ has a rapid turnover due to
496	relatively high temperatures and constant inputs from leaves, resulting in a

497 thin litter layer and rapid C<sub>org</sub> mineralization. In the Fan Si Pan Podzols, Corg decomposition rate is lower, partially due to cooler temperatures and 498 499 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<sub>org</sub> 501 stocks. In addition, the second major change in vegetation type along the 502 Fan Si Pan transect has induced the transition from Podzols to Umbrisols with a thinning of the litter layer, resulting in lower topsoil Corg stocks and a 503 different C<sub>org</sub> source (Fig. 2B; Podwojewski et al., 2011). Indeed, C<sub>org</sub> inputs 504 for Podzols are exogenic – mainly from the thick litter layer – whereas C<sub>org</sub> 505 506 inputs for Umbrisols are endogenic, mainly from bamboo roots and thus 507 more homogenous.

508 Substantial changes in C<sub>org</sub> sources, stocks and/or mineralization rates in soils may induce changes in substrate nature and/or nutrient 509 availability for brGDGT producers, which may modify brGDGT distributions 510 511 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 512 should be jointly investigated, preferentially along lateral and local soil 513 514 transects with as many constant environmental parameters as possible, 515 such as MAAT, soil temperature, vegetation type and parent material.

516

### 517 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

520	deep soils as opposed to topsoils were reported in two Podzol profiles under
521	different climates (Huguet et al., 2010), a trend that also occurred in the
522	Fan Si Pan Podzol profiles, but not in the other Fan Si Pan soil profiles (Fig.
523	6). Likewise, changes in CBT-based pH with depth were not similar between
524	the different Fan Si Pan soil profiles (Fig. 6). We do not know to what extent
525	(acido)bacterial communities change with depth in the different Fan Si Pan
526	soil profiles nor to what extent such changes impact brGDGT distributions
527	in soils. For this reason, we put forward various explanations for the
528	observed changes in brGDGT distributions with soil depth.
529	Every Fan Si Pan sample was 2-mm sieved (Podwojewski et al.,
530	2011), meaning that root-associated brGDGTs in subsoils (Huguet et al.,
531	2013b) cannot explain the decreased MAAT estimates in the deep Fan Si
532	Pan Podzols. Nevertheless, given that bamboo roots (abundant in the
533	Umbrisol profile FAN 6) are more mineralizable than tree roots (abundant
534	in the Podzol profiles FAN 4 and FAN 5), brGDGT producing communities
535	may change differently with depth between the main Fan Si Pan soil types,
536	resulting in differential associated biases on MAAT-pH estimates, following
537	the hypothesis that different (acido)bacterial species do not all produce the
538	same brGDGTs (Sinninghe Damsté et al., 2011, 2014; De Jonge et al., 2014).
539	Alternatively, Podzols have the peculiarity of having a subsoil enriched in
540	Fe, Al and organic matter – including lipids – due to rainwater percolation
541	(e.g., Huguet et al., 2010; Podwojewski et al., 2011). Therefore, substantial
542	changes with depth in biotic and abiotic processes not related to brGDGT

producers – for instance, lipid transfer to a non-extractable pool via organometallic 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 548 549 soils. Former agricultural activities – mainly maize crops (Fig. 2B; Podwojewski et al., 2011) – may have impacted brGDGT distributions in the 550 FAN 1 soil profile. Additionally, the transition from primary broad-leaved 551 552 forests to alpine vegetation (Fig. 2B; Podwojewski et al., 2011) has shifted upwards in altitude under the effect of the present global warming (IPCC, 553 554 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 555 brGDGT turnover times reported so far – from a few months to less than 45 556 557 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 558 mineral phase and/or be incorporated within the macromolecular matrix in 559 deeper soil horizons (e.g., Huguet et al., 2010), whereas microbial activity 560 561 may decrease with depth, resulting in substantially longer brGDGT 562 turnover times in deep soils. The latter is suggested by decreases in C<sub>org</sub>normalized brGDGT absolute abundances with depth in FAN 1, FAN 2 and 563 FAN 4 (data not shown). Additionally, imprints of former communities may 564 565 be muted by the post-depositional effect (e.g., Zech et al., 2012; Yamamoto et

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).

- 569
- 570

### 5. Conclusions and perspectives

571 Soil types were assigned to a composite global dataset of 358 soils to 572 investigate MAAT-pH/brGDGT relationships and MAAT(pH) residuals per soil type. Distributions of brGDGTs were also investigated in five soil 573 profiles excavated along an altitudinal transect in the Mount Fan Si Pan 574 575 National Park. Surrounding vegetation, geological setting, as well as soil sequence had previously been intensively characterized, providing an 576 577 opportunity to investigate their impact on proxies intensively used in paleo-578 studies.

The soil type diversity of the global dataset was high, traditional 579 580 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 581 global MAAT(pH)/brGDGT scatters. Additionally, the soil type effect on 582 583 MAAT–pH relationships remained significant when 5- and 6-methyl 584 brGDGTs were quantified separately and no obvious reduction in 585 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 586 Park, MBT'/CBT-based MAATs were not significantly different to modeled 587 588 MAATs when the global calibration error of 5 °C was taken into account.

However, the decrease in MAAT estimates along the altitudinal transect 589 lacked clarity when the focus was on surficial soils, and the pH–CBT 590 591 relationship was absent when all Fan Si Pan soils were considered. On the 592 one hand, substantial changes in soil/vegetation type along the Fan Si Pan 593 transect may induce biases on MAAT–pH reconstructions in surficial soils. On the other hand, MBT'/CBT indices varied slightly or substantially with 594 595 depth in the Fan Si Pan soil profiles, possibly as a function of soil type and history. 596

To better understand the biases on brGDGT-based estimates, more 597 soil profiles should be investigated along topo-sequences, as attempted in 598 our work. Indeed, this study reveals the importance of direct collaborations 599 600 between organic geochemists and pedologists, ensuring that specific organic 601 compounds and physico-chemical soil properties are jointly investigated. To consider the evolution of soil properties through time, as well as the transfer 602 603 time of soil C<sub>org</sub>, radiocarbon analyses on bulk soil C<sub>org</sub> and on specific organic compounds should be conducted. Additionally, future 604 global/regional/local soil MAAT-pH/brGDGT calibrations should consider 605 606 sample sizes of a few dozen to a few hundred per soil type to ensure 607 adequate specificity for all given soil types. 608 Acknowledgements 609 G.M. thanks Anneke de Rouw and the HYDRARIDE consortium for 610

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617	
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619	
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803	64.
804	

805 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
different α5 and/or ω5 positions and the different α6 and/or ω6 positions of
the methyl groups.

811

Fig. 2. (A) Maps showing the locations of the study site (left-hand map) and 812 the studied soil profiles (right-hand map). Contour interval is 200 m and 813 814 contour lines indicate altitudes between 1000 and 3000 m on the right-hand 815 map, with darker tones for higher altitudes. Modified from maps generated 816 from GeoMapApp (http://www.geomapapp.org). (B) Profile showing the 817 studied soil pits. Altitudinal zonation of vegetation types is indicated in green. The profile does not pass exactly through the soil pits, which explains 818 819 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 820 Podwojewski et al. (2011): orange-yellow tones for A horizons, blue tones for 821 822 Bw horizons and green tones for Bs horizons. Like tones correspond to like 823 horizons. The horizons considered for soil brGDGT distributions are 824 indicated in red. Adapted from Podwojewski et al. (2011). 825

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

827 (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.
(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.

834

Fig. 4. Box-whisker plots of mean annual air temperature (MAAT) residuals 835 per soil type showing minima and maxima with whiskers, medians with 836 horizontal bars, 1<sup>st</sup> and 3<sup>rd</sup> quartiles with boxes, and means with pluses. 837 838 Plot (A) is based on the composite global soil dataset (Huguet et al., 2010; 839 Peterse et al., 2012; Dirghangi et al., 2013; Anderson et al., 2014; De Jonge 840 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-841 842 MBT'/CBT global soil calibration of Peterse et al. (2012). In plot (C), residuals are based on the MAAT-MBT'<sub>5ME</sub> global soil calibration of De 843 Jonge et al. (2014). Only soil types comprising at least 10 soils from the 844 global datasets are considered. When outliers are identified for a given soil 845 846 type, their number is indicated as (initial number of samples – number of outliers) below the number of samples actually considered. Moisture 847 regimes based on averaged mean annual precipitation (MAP) values per soil 848 type are specified with the following color-coding of the numbers of samples 849

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

852

853	Fig. 5. Mean annual air temperature (MAAT) residual distributions for (A)
854	Podzols, (B) Alisols, (C) and (D) Leptosols, and (E) and (F) Regosols. Plots
855	(A) and (B) are based on the composite global soil dataset (Huguet et al.,
856	2010; Peterse et al., 2012; Dirghangi et al., 2013; Anderson et al., 2014; De
857	Jonge et al., 2014). Plots (C), (D), (E) and (F) are based on the soils
858	reconsidered by De Jonge et al. (2014). In plots (A), (B), (C) and (E),
859	residuals are based on the MAAT–MBT'/CBT global soil calibration of
860	Peterse et al. (2012). In plots (D) and (F), residuals are based on the MAAT-
861	$\rm MBT'_{\rm 5ME}$ global soil calibration of De Jonge et al. (2014). Gaussians indicate
862	the mean values with their standard deviations. Filled circles represent the
863	medians and filled diamonds represent the extreme values and the $1^{\mathrm{st}}$ and
864	$3^{rd}$ quartiles. When outliers are identified for a given soil type, their number
865	is indicated as (initial number of samples – number of outliers) below the
866	number of samples actually considered.
867	

868 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

870 (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

872 (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.</li>

877

## 878 Table captions

879 **Table 1** 

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

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

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

890

## 891 **Table 2**

Number of samples (n), coefficients (a, b, c, S, I and R<sup>2</sup>), 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;

896	Dirghangi et al., 2013; Anderson et al., 2014; De Jonge et al., 2014)
897	reconsidered by De Jonge et al. (2014). Only soil types comprising at least 10
898	soils from the global dataset are considered for the linear regressions. When
899	outliers are identified for a given MAAT–pH/brGDGT relationship per soil
900	type, their number is indicated as (initial number of samples – number of
901	outliers) next to the number of samples actually considered. Statistical
902	significance is reached for $p$ -values < 0.05.
903	
904	Table 3
905	BrGDGT-derived proxies and MBT'/CBT-derived mean annual air
906	temperature (MAAT) and pH based on the extended soil calibration (Peterse
907	et al., 2012) along the Fan Si Pan Mountain transect. Altitude, coordinates,
908	horizon, mean depth, organic carbon ( $C_{\rm org}$ ) concentration, water content
	$(\mathbf{H}_{0})$ 1 1 $\mathbf{H}_{0}$ $(\mathbf{D}_{1})$ 1 $(2011)$ 1 - 4

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

## Figure 1

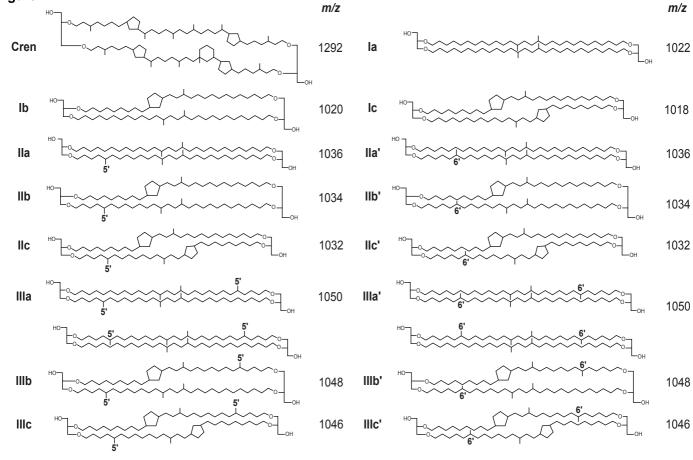
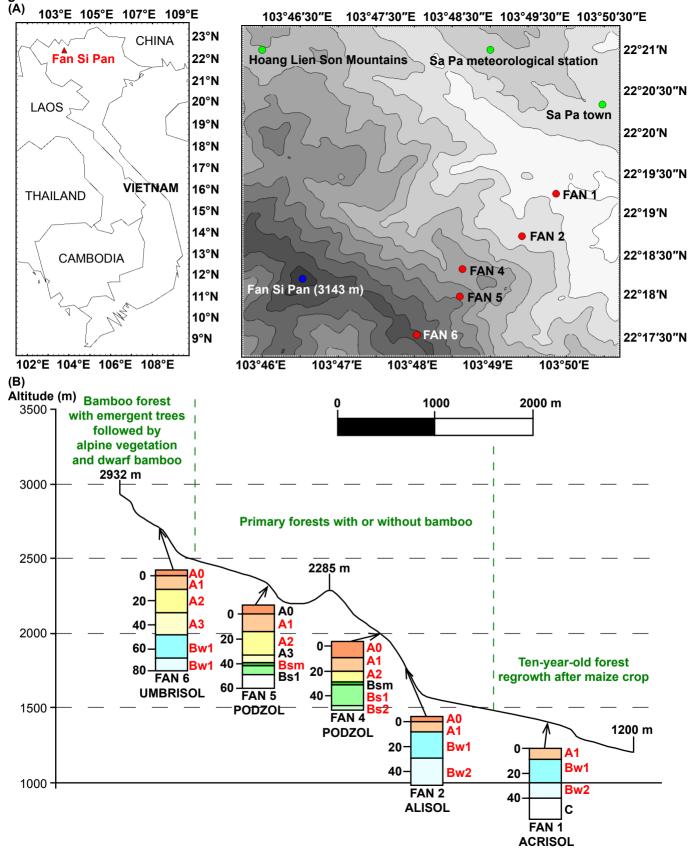
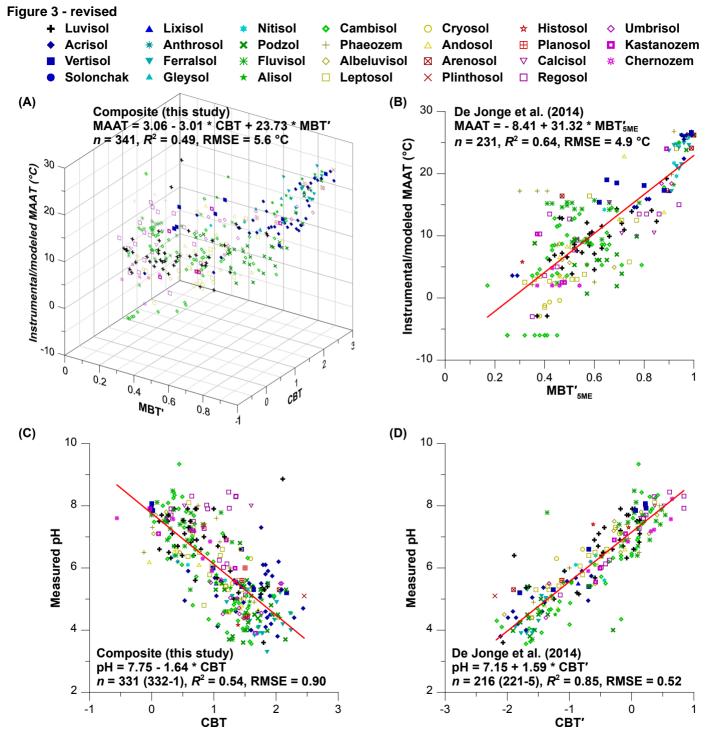
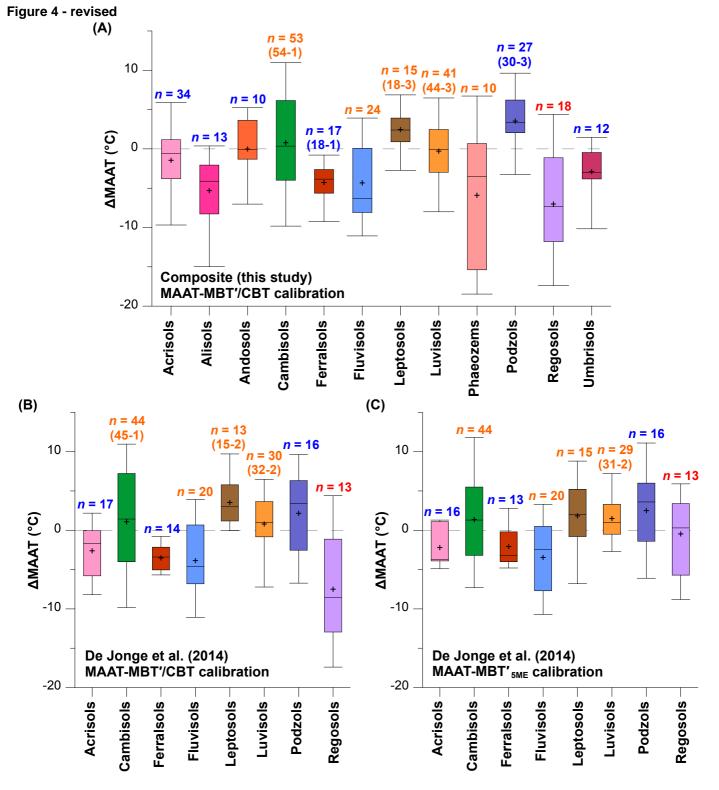
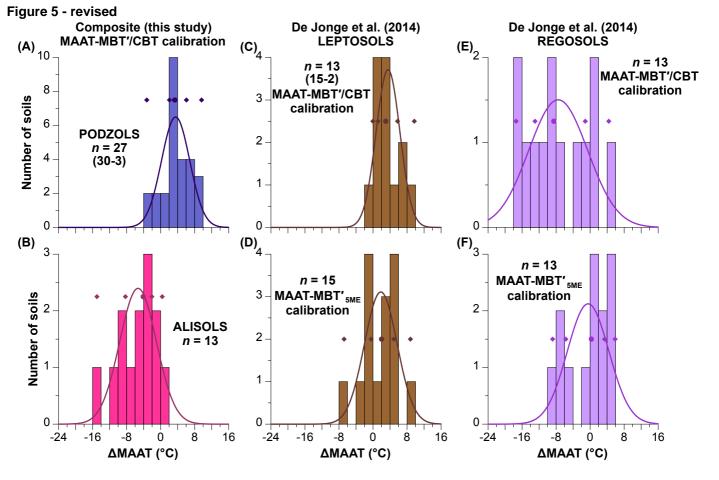


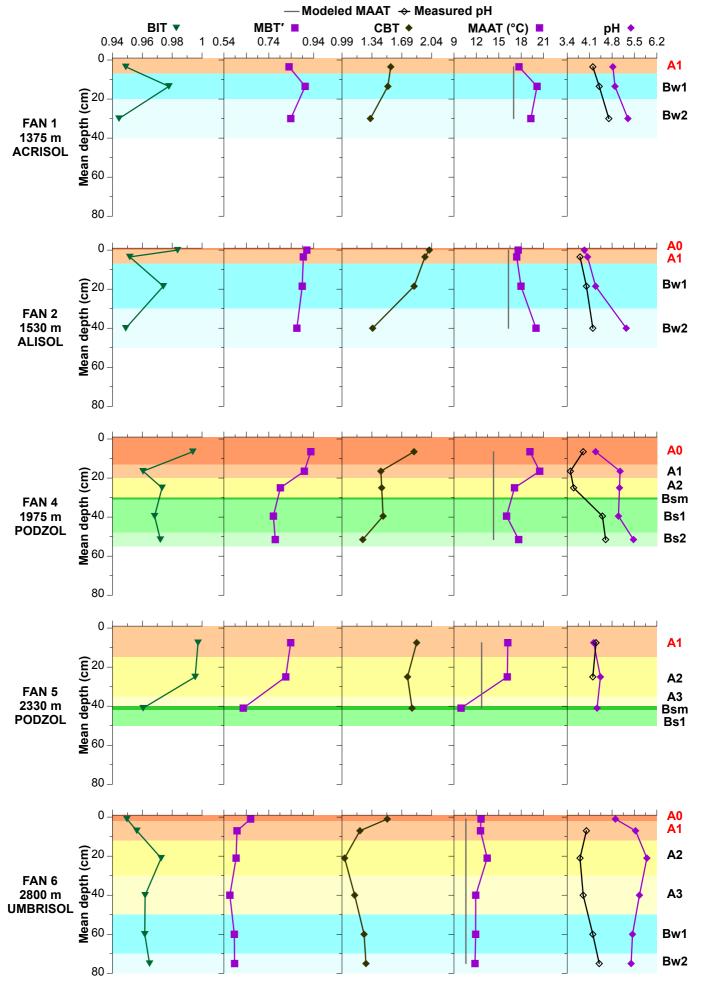
Figure 2 - revised











	MAAT = a	* MBT' + b * CBT	+ c	pH = S * CBT + I									
	n	a	b	с	$R^2$	р	Е	n	S	Ι	$R^2$	р	Е
All soils	341	$23.73 \pm 1.43$	$-3.01\pm0.65$	$3.06\pm0.72$	0.5	< 0.001	5.6	331 (332–1)	$-1.64\pm0.08$	$7.75\pm0.11$	0.5	< 0.001	0.9
Acrisols	33 (34–1)	$38.23 \pm 3.71$	$-4.20\pm1.48$	$-6.32\pm2.72$	0.8	< 0.001	3.1	33	$-0.16\pm0.32$	$5.45 \pm 0.53$	0.0	0.61	0.8
Alisols	13	$0.46 \pm 5.49$	$4.49 \pm 2.17$	$15.37 \pm 4.17$	0.4	0.10	2.3	13	$-0.66\pm0.30$	$5.79 \pm 0.49$	0.3	0.052	0.4
Andosols	10	$24.61 \pm 9.77$	$-4.22\pm2.61$	$2.89 \pm 6.10$	0.6	0.049	4.4	10	$-1.28\pm0.23$	$6.74\pm0.25$	0.8	< 0.001	0.4
Cambisols	54	$23.64 \pm 5.27$	$-7.20\pm1.91$	$4.72\pm2.18$	0.3	< 0.001	6.3	53	$-2.32\pm0.25$	$8.25\pm0.27$	0.6	< 0.001	0.9
Ferralsols	18	$24.07\pm15.22$	$-1.90\pm2.12$	$5.05 \pm 14.80$	0.2	0.21	2.5	18	$-0.42\pm0.50$	$5.19\pm0.91$	0.0	0.41	0.6
Fluvisols	24	$5.16 \pm 7.84$	$-0.66\pm2.72$	$11.45\pm2.23$	0.0	0.78	3.8	24	$-1.91\pm0.49$	$8.06\pm0.33$	0.4	0.001	0.9
Leptosols	18	$30.55\pm6.70$	$-2.19\pm3.34$	$-4.63\pm3.95$	0.6	0.001	4.6	18	$-1.89\pm0.44$	$7.92\pm0.53$	0.5	0.001	0.7
Luvisols	42 (44–2)	$15.02\pm2.78$	$-4.09 \pm 1.02$	$5.83 \pm 1.21$	0.5	< 0.001	3.1	40 (41-1)	$-1.46\pm0.22$	$7.81 \pm 0.20$	0.5	< 0.001	0.7
Phaeozems	10	$4.79 \pm 8.88$	$-7.19\pm4.19$	$18.33 \pm 6.17$	0.4	0.21	7.0	10	$-0.95\pm0.55$	$7.52\pm0.59$	0.3	0.12	1.0
Podzols	30	$23.24\pm5.53$	$-2.48\pm2.98$	$-1.74\pm4.75$	0.4	0.001	4.3	29	$-0.32\pm0.48$	$5.27\pm0.77$	0.0	0.51	0.8
Regosols	17 (18–1)	$-8.65\pm8.55$	$4.27\pm2.12$	$7.69 \pm 2.35$	0.2	0.15	3.4	17	$-0.73\pm0.60$	$8.07\pm0.60$	0.1	0.25	1.0
Umbrisols	12	$15.34\pm3.92$	$-0.89\pm2.15$	$6.71 \pm 3.05$	0.7	0.01	2.2	12	$0.09\pm0.43$	$4.81\pm0.65$	0.0	0.84	0.5

MBT' + b \* CBT + c

		All soils	Acrisols	Cambisols	Ferralsols	Fluvisols	Leptosols	Luvisols	Podzols	Regosols
$MAAT = a \times MBT' + b \times CBT + c$	n	234 (235–1)	17	45	14	19 (20-1)	15	30 (32–2)	16	12 (13–1)
	a	$27.47 \pm 1.79$	$37.02\pm2.99$	$23.61 \pm 6.27$	$37.78 \pm 14.23$	$-10.47\pm9.61$	$28.52\pm8.02$	$22.14\pm4.70$	$24.32\pm9.20$	$-22.85 \pm 9.57$
	b	$-4.53\pm0.78$	$-2.53 \pm 1.23$	$-7.05\pm2.29$	$-3.92 \pm 1.69$	$1.33 \pm 2.94$	$-1.84\pm3.87$	$-5.28\pm1.16$	$-3.05\pm6.42$	$3.81 \pm 2.24$
	с	$2.35\pm0.88$	$-6.48\pm2.33$	$4.28\pm2.66$	$-4.99 \pm 14.52$	$15.77\pm2.37$	$-4.34\pm4.48$	$3.42\pm2.02$	$-1.43\pm9.82$	$12.02\pm2.96$
	$R^2$	0.5	0.9	0.3	0.6	0.1	0.5	0.6	0.4	0.5
	p	< 0.001	< 0.001	0.001	0.003	0.44	0.01	< 0.001	0.053	0.07
	Е	5.8	2.3	6.8	1.6	2.9	5.0	3.2	5.9	3.0
$MAAT = S \times MBT'_{5ME} + I$	n	231	16	44	13	20	15	31	16	13
Homogeneity of slopes test:	$\mathbf{S}$	$31.32 \pm 1.55$	$32.96 \pm 2.79$	$31.21 \pm 5.31$	$50.07 \pm 28.84$	$3.91 \pm 9.70$	$31.51\pm6.27$	$25.80 \pm 4.40$	$24.41 \pm 7.99$	$15.98 \pm 5.75$
F = 1.59, p = 0.14	Ι	$-8.41 \pm 1.01$	$-7.65\pm2.40$	$-9.74\pm2.80$	$-24.01\pm27.14$	$10.17\pm5.39$	$-10.36\pm3.57$	$-6.18\pm2.62$	$-6.59\pm5.25$	$0.61 \pm 3.43$
ANCOVA:	$R^2$	0.6	0.9	0.5	0.2	0.0	0.7	0.5	0.4	0.4
F = 5.34, p < 0.001	p	< 0.001	< 0.001	< 0.001	0.11	0.69	< 0.001	< 0.001	0.01	0.02
	$\mathbf{E}$	4.9	2.5	5.6	2.4	3.7	4.1	3.2	5.5	4.1
$pH = S \times CBT + I$	n	231 (232–1)	16	44	14	20	15	31 (32–1)	16	13
Homogeneity of slopes test:	$\mathbf{S}$	$-1.75\pm0.10$	$-0.63\pm0.27$	$-2.44\pm0.29$	$-0.56\pm0.63$	$-2.20\pm0.51$	$-2.11\pm0.36$	$-1.55\pm0.23$	$-0.54\pm0.50$	$-0.77\pm0.80$
F = 3.83, p = 0.001	Ι	$7.90\pm0.12$	$5.86 \pm 0.44$	$8.35\pm0.31$	$5.47 \pm 1.12$	$8.18\pm0.32$	$8.31 \pm 0.42$	$7.84 \pm 0.22$	$5.32\pm0.83$	$8.11\pm0.86$
	$R^2$	0.6	0.3	0.6	0.1	0.5	0.7	0.6	0.1	0.1
	p	< 0.001	0.03	< 0.001	0.39	< 0.001	< 0.001	< 0.001	0.30	0.36
	Е	0.9	0.6	0.9	0.7	0.9	0.5	0.7	0.5	1.1
$pH = S \times CBT' + I$	n	216 (221-5)	15	42 (44–2)	10	17 (19–2)	15	31	14	12
Homogeneity of slopes test:	$\mathbf{S}$	$1.59\pm0.05$	$1.14\pm0.20$	$1.78\pm0.10$	$1.97 \pm 1.03$	$0.56\pm0.61$	$1.66\pm0.11$	$1.29\pm0.18$	$0.18\pm0.33$	$1.76\pm0.19$
F = 4.64, p < 0.001	Ι	$7.15\pm0.05$	$6.49 \pm 0.30$	$7.04\pm0.10$	$7.59 \pm 1.65$	$7.32\pm0.16$	$7.43 \pm 0.12$	$7.25\pm0.14$	$4.75\pm0.49$	$7.11\pm0.11$
	$R^2$	0.8	0.7	0.9	0.3	0.1	0.9	0.6	0.0	0.9
	p	< 0.001	< 0.001	< 0.001	0.09	0.37	< 0.001	< 0.001	0.59	< 0.001
	E	0.5	0.4	0.5	0.5	0.5	0.2	0.6	0.5	0.4

Sample	Altitude (m)	Coordinates	Horizon	Mean depth (cm)	Corg (%)	H <sub>2</sub> O (%)	Measured pH	Modeled MAAT (°C)	BIT	MBT'	CBT	Calculated MAAT (°C)	Calculated pH
FAN1.1	1375	22°19′15″N	A1	3.5	8.27	76	4.2	17.0	0.95	0.83	1.56	17.7	4.8
FAN1.2		103°49′52″E	Bw1	13.5	2.72	nd	4.4		0.98	0.90	1.53	20.1	4.9
FAN1.3			Bw2	30	0.62	60	4.7		0.94	0.84	1.32	19.3	5.3
FAN2.A0	1530	22°18′44″N	A0	0	nd	nd	nd	16.3	0.98	0.91	2.01	17.6	3.9
FAN2.1		103°49′25″E	A1	3.5	4.30	80	3.8		0.95	0.89	1.96	17.4	4.0
FAN2.2			Bw1	18.5	2.54	nd	4.0		0.97	0.89	1.83	18.0	4.3
FAN2.3			Bw2	40	0.66	50	4.2		0.95	0.87	1.35	20.0	5.2
FAN4.1	1975	22°18′20″N	A0	6.5	44.13	nd	3.9	14.3	0.99	0.93	1.83	19.2	4.3
FAN4.2		103°48′38″E	A1	16.5	8.11	215	3.5		0.96	0.90	1.45	20.5	5.1
FAN4.3			A2	25	3.59	66	3.6		0.97	0.79	1.46	17.1	5.0
FAN4.5			Bs1	39.5	1.22	40	4.5		0.97	0.76	1.47	16.0	5.0
FAN4.6			Bs2	51.5	1.16	nd	4.6		0.97	0.77	1.23	17.7	5.5
FAN5.1	2330	22°18′00″N	A1	7.5	5.99	114	4.3	12.7	1.00	0.84	1.86	16.2	4.2
FAN5.2		103°48′36″E	A2	25	4.38	nd	4.2		1.00	0.82	1.76	16.1	4.4
FAN5.4			Bsm	41	nd	nd	nd		0.96	0.63	1.81	10.0	4.3
FAN6.1	2800	22°17′32″N	A0	1	6.14	nd	nd	10.6	0.95	0.66	1.52	12.6	4.9
FAN6.2		103°48′02″E	A1	7	3.89	106	4.0		0.96	0.60	1.20	12.6	5.5
FAN6.3			A2	21	2.95	nd	3.8		0.97	0.59	1.02	13.5	5.9
FAN6.4			A3	40	2.07	53	3.9		0.96	0.57	1.14	11.9	5.7
FAN6.5			Bw1	60	0.77	nd	4.2		0.96	0.59	1.25	11.9	5.4
FAN6.6			Bw2	75	0.39	nd	4.4		0.96	0.59	1.27	11.8	5.4