Biogeosciences Discuss., 12, 16709–16754, 2015
www.biogeosciences-discuss.net/12/16709/2015/
doi:10.5194/bgd-12-16709-2015

Biogeosciences
Discussions
Open Access

Distribution of tetraether lipids in agricultural soils – differentiation between paddy and upland management

C. Mueller-Niggemann[1], **S. R. Utami**[2], **A. Marxen**[3], **K. Mangelsdorf**[4],
T. Bauersachs[1], **and L. Schwark**[1,5]

[1]Institute of Geosciences, Christian-Albrechts-University, Kiel, Germany
[2]Soil Science, Faculty of Agriculture, University of Brawijaya, Malang, Indonesia
[3]Department of Soil Physics, Helmholtz Centre for Environmental Research UFZ, Halle (Saale), Germany
[4]Helmholtz Centre Potsdam GFZ German Research Centre for Geosciences, Section 4.3 Organic Geochemistry, Potsdam, Germany
[5]WA-OIGC, Curtin University, Perth, Australia

Received: 7 September 2015 – Accepted: 2 October 2015 – Published: 19 October 2015

Correspondence to: C. Mueller-Niggemann (cmn@gpi.uni-kiel.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Insufficient knowledge of the composition and variation of isoprenoid and branched glycerol dialkyl glycerol tetraethers (GDGTs) in agricultural soils exists, despite of the potential effect of different management types (e.g. soil/water and redox conditions, cultivated plants) on GDGT distribution. Here, we determined the influence of different soil management types on the GDGT composition in paddy (flooded) and adjacent upland (non-flooded) soils, and if available also forest, bushland and marsh soils. To compare the local effects on GDGT distribution patterns, we collected comparable soil samples in various locations from tropical (Indonesia, Vietnam and Philippines) and subtropical (China and Italy) sites. We found that differences in the distribution of isoprenoid GDGTs (iGDGTs) as well as of branched GDGTs (brGDGTs) are predominantly controlled by management type and only secondarily by climatic exposition. In general upland soil had higher crenarchaeol contents than paddy soil, which on the contrary was more enriched in GDGT-0. The GDGT-0/crenarchaeol ratio was 3–27 times higher in paddy soil and indicates the enhanced presence of methanogenic archaea, which were additionally linked to the number of rice cultivation cycles per year (higher number of cycles was coupled with an increase in the ratio). The TEX_{86} values were 1.3 times higher in upland, bushland and forest soils than in paddy soils. In all soils brGDGT predominated over iGDGTs, with the relative abundance of brGDGTs increasing from subtropical to tropical soils. Higher BIT values in paddy soils compared to upland soils together with higher BIT values in soil from subtropical climates indicate effects on the amounts of brGDGT through differences in management as well as climatic zones. In acidic soil CBT values correlated well with soil pH. In neutral to alkaline soils, however, no apparent correlation but an offset between paddy and upland managed soils was detected, which may suggest that soil moisture may exert an additional control on the CBT in these soils. Lower MBT$'$ values and calculated temperatures (T_{MC}) in paddy soils compared to upland soils may indicate a management (e.g. enhanced soil

moisture through flooding practises) induced effect on mean annual soil temperature (MST).

1 Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs) are characteristic cell membrane lipids of archaea (Pearson and Ingalls, 2013; Schouten et al., 2013 and references therein) and bacteria (Weijers et al., 2006a; Sinninghe Damsté et al., 2011). The GDGT core structures differ in both domains, with isoprenoid alkyl chains being specific for archaea and branched alkyl chains for bacteria (for structures see Appendix). Both types of tetraether lipids have a high potential to preserve in the sediment record (Schouten et al., 2013) and have been reported in abundance from terrestrial and marine environments, e.g. in the water column and sediments of oceans and lakes (Hopmans et al., 2000, 2004; Schouten et al., 2012; Tierney and Russel, 2009; Zink et al., 2010; Naeher et al., 2014), in ponds (Tierney et al., 2012; Loomis et al., 2014; Huguet et al., 2015), in hot springs (Pearson et al., 2004; Peterse et al., 2009a; Pitcher et al., 2009), in peat bogs (Sinninghe Damsté et al., 2000; Weijers et al., 2006a, 2010), in grassland soils (Weijers et al., 2007, 2010; Naeher et al., 2014), in forest soils (Hopmans et al., 2004; Weijers et al., 2007, 2010), in permafrost soils (Peterse et al., 2009b; Bischoff et al., 2014), in loess soils (Huguet et al., 2012), in Podzols (Huguet et al., 2010), in garden and agricultural soils (Leininger et al., 2006; Weijers et al., 2010; Sinninghe Damsté et al., 2012) as well as in paddy soils (Bannert et al., 2011; Ayari et al., 2013).

It is well known that archaea are involved in biogeochemically important processes, including methanogenesis, anaerobic methane oxidation (AMO) and aerobic ammonia oxidation (Kuypers et al., 2001; Pancost et al., 2001; Leininger et al., 2006; Pearson and Ingalls, 2013). Distributions of isoprenoid GDGTs (iGDGTs) were initially used to characterize archaeal communities in marine environments with two major groups of archaea being distinguished: *Crenarchaeota* (Group I) and *Euryarchaeota* (Group II) (see Pearson and Ingalls, 2013 and reference therein). An additional archaeal phylum comprising the ammonia-oxidizing *Thaumarchaeota* has been identified more recently (Brochier-Armanet et al., 2008; Spang et al., 2010). Members of this phylum are currently the only known biological sources of crenarchaeol and in addition they contain varying amounts of tetraether lipids with 0 to 4 cyclopentane rings (Sinninghe Damsté et al., 2012; Schouten et al., 2013; Pearson and Ingalls, 2013). Tetraether lipids of methanogenic archaea generally contain GDGT-0 (Koga et al., 1998; Koga and Morii, 2005; Pearson and Ingalls, 2013; Schouten et al., 2013), although in some instances iGDGTs with cyclopentyl moieties have been reported (De Rosa, 1986; Bauersachs et al., 2015). iGDGTs with cyclopentane rings were also reported from methanotrophic archaea of the ANME-1 cluster, *Thaumarchaeota* as well as extremophilic *Euryarchaeota* and *Crenarchaeota* (Blumenberg et al., 2004; Pearson and Ingalls, 2013; Schouten et al., 2013 and references therein). The cell membrane of mesophilic archaea consists, among others, of iGDGT structures usually containing 1 to 4 cyclopentyl moieties (GDGT-1 to GDGT-4) with members of the *Thaumarchaeota* also possessing crenarchaeol, a GDGT structure that contains four cyclopentane ring systems and an additional cyclohexane ring moiety (Sinninghe Damsté et al., 2002).

High abundances of branched GDGT (brGDGTs) have previously been reported from soils worldwide (Weijers et al., 2007, 2010; Peterse et al., 2009a; Huguet et al., 2010, 2012). Information on the biological sources of these components, however, is still very limited (Hopmans et al., 2004; Weijers et al., 2007, 2010; Peterse et al., 2009b, c; Tierney and Russell, 2009; Huguet et al., 2010, 2012; Tierney et al., 2012). Molecular investigations in peat bogs demonstrated that brGDGTs occurred in highest concentrations in the catotelm, the bottom layer of peats (Weijers et al., 2006a, 2010), which suppose an anaerobic and acid tolerant bacterial species as origin, e.g. belonging to *Acidobacteria* the most abundant bacteria in this environment (Weijers et al., 2006a, 2009, 2010). This is supported by the presence of the tetra-methylated brGDGT that was recently identified in two cultured acidobacterial strains (Sinninghe Damsté et al., 2011). In addition, the ether-bound 5-methyl *iso*-diabolic acid was detected in four mesophilic species of the subdivision 4 of the *Acidobacteria* as a potential breakdown product of penta-methylated brGDGT (Sinninghe Damsté et al., 2014). It has consequently been suggested that bacteria producing these lipids are obligate anaerobes and follow a heterotrophic mode of life (Oppermann et al., 2010; Weijers et al., 2006a, 2010). The presence of brGDGTs in oxic soils does not exclude that aerobically living bacteria produce these lipids, but anaerobic bacteria residing in anoxic microhabitats are also possible sources (Schouten et al., 2013). The distribution of brGDGTs in soils is related to growth temperature (mean annual air and soil temperature) and soil pH (Schouten et al., 2002; Weijers et al., 2007, 2009; Peterse et al., 2009a, 2012). Indices which denote the degree of methylation and cyclization of brGDGTs, the MBT and the CBT indices, have previously been employed to reconstruct mean annual air temperatures (MAT) using a global soil calibration (Weijers et al., 2009). More recently, Peterse et al. (2012) defined the MBT$'$, which represents the ratio of tetra-methylated brGDGT (GDGT-Ia, Ib and Ic) vs. the seven most abundant brGDGTs (GDGT-Ia, Ib, Ic, IIa, IIb, IIc and IIIa).

However, factors other than temperature and pH also seem to affect the distribution of brGDGTs in natural ecosystems. For example, the relative broad scatter of calculated MAT in arid soils (Peterse et al., 2012) as well as values deviating from the trend in the highest elevations of a transect sampled on Mt. Kilimanjaro (Sinninghe Damsté et al., 2008) are interpreted to indicate an influence of water content and vegetation type on the brGDGT pool. In addition, several authors noted that changes in the distribution of brGDGT are strongly correlated with MAT on local scales as, for example, in altitudinal transects of Mt. Rungwe and Mt. Gongga (Peterse et al., 2009c; Coffinet et al., 2014). In agricultural soils from the same area, the type of soil management and the vegetation cover can differ, leading to variable soil water contents and soil temperatures (Liu et al., 2014; Awe et al., 2015), which affect the local microbial community. In addition, soil microbes respond to environmental stresses induced by e.g. starvation, oxygen limitation or acidification. The latter results in the predominance of brGDGTs without cyclopentyl moieties in the bacterial cell membrane and explain the dependency of soil pH and CBT (Weijers et al., 2007).

In addition to the pH, the redox potential (Eh) is an important factor that affects the diversity and abundance of soil microorganism. The Eh expresses the activity of electrons (measured in volts), which influence microbial metabolism reactions in soils. As individual microorganisms are adapted to specific Eh conditions, an increase in e.g. soil moisture is accompanied by a decrease in Eh because of the consumption of oxygen by microbes (Husson, 2013). Agricultural management may control redoximorphic conditions. In contrast to upland soil, i.e. without water flooding and associated crop plants, including corn/maize, wheat, barley, rape, cassava, sugar cane, cotton, banana and other vegetables, rice paddy soil management with repetitive puddling of the surface soil as well as frequent flooding and alternating draining practices leads to a reduced Eh in the surface layer (Kögel-Knabner et al., 2010; Kölbl et al., 2014). Prevailing anoxic conditions are assumed to restrict the decomposition rate of organic matter (Lal, 2002; Sahrawat, 2005), leading to high activities of methanogenic archaea (Liesack et al., 2000) and in combination with the application of mineral fertilizer to high denitrification rates producing nitrous oxide (Xiong et al., 2007). In contrast, oxic conditions are associated with high Eh, as in upland soil and in paddy soil after draining ammonia oxidation occurs. The latter is either performed by ammonia-oxidizing archaea (AOA) or bacteria (AOB) (Leininger et al., 2006) depending on the soil pH, with AOA being more active in acidic soils and AOB in alkaline soils (Jiang et al., 2015).

Here, we investigated the environmental controls that affected the tetraether lipid composition in soils of different management systems, which developed in subtropical (Italy, SW-China) as well as in tropical (Indonesia, Philippines, Vietnam) climates. Additionally to the management type, including differences in cropping style (upland crop plants vs. wetland rice), the intensity of the management and the duration of utilization were distinctive criteria in the investigation of effects on microbial lipids in upland, paddy and forest soils. Only limited information on the distribution of tetraether lipids in paddy soils is currently available (Bannert et al., 2011; Ayari et al., 2013), although an area of 157 million ha, contributing 18 % area to the ten major crops worldwide, is covered by rice paddy management (FAO, 2003). To the best of our knowledge, this is the first study, which compares non-flooded and flooded agroecosystems with respect to their GDGT composition. The variation in GDGT distribution patterns between soils with different agricultural usage will provide additional information on the sources and properties of GDGTs in terrestrial ecosystems on local and global scale.

2 Material and methods

2.1 Sampling

From 2008 to 2014, a total of 170 Indonesian, Vietnamese, Philippine, Chinese and Italian soils with different land-use systems were collected, including 119 paddy, 37 upland, 9 forest, 2 bushland and 3 marsh samples from the topsoil horizon (0–30 cm depth). The study sites are located in tropical as well as in subtropical climate zones (Fig. 1, Table 1) and agricultural soils were subject to different management techniques. Detailed soil characteristics and geographical positions of the sampling sites are given in Table S1 (Supplement). Topsoils were sampled with a soil auger as described by Klotzbücher et al. (2014).

In addition, successive land reclamation in the Chinese location Cixi via dyke construction on marine tidal flats over the last > 1000 yr (Feng and Bao, 2005) led to differently aged soils, which allow studying a 2000 yr chronosequence. Based on the time of dyke construction and information from the Edit Committee of Chorography of Cixi County (1992), differently aged marsh soils (10–35 yr) and agricultural soils under continuous non-irrigated upland use (50–700 yr) as well as wetland rice cultivation (50–2000 yr) were selected and sampled. The local cropping system on paddy fields is paddy-upland rotation, with one wetland rice season and one inter-crop (vegetables, wheat or cereals) season per year (Cheng et al., 2009). Paddy and upland topsoils were sampled with a soil auger. Three composite samples, composed of 7 sub-samples, being representative for the complete field were investigated at each location.

2.2 Bulk geochemistry

All soils were lyophilized, sieved to a size < 2 mm and ground to a fine powder using agate pestle and mortar prior to analyses. Soil pH was measured in a suspension of the soil in 0.01 M $CaCl_2$, using a 1 : 2.5 (w/v) soil/liquid ratio. The pH was determined with a pH meter Model FG2-438 (Mettler-Toledo AG, Switzerland) at ambient temperature and atmospheric pressure. The total carbon (TC) and total nitrogen (TN) contents were measured on a CNS elemental analyser Vario EL III (Elementar Analysensysteme GmbH, Germany). The total inorganic carbon (TIC) content was determined using the Vario EL III elemental analyser coupled to SoliTIC module. The soil organic carbon (SOC) was calculated as the difference between TC and TIC.

2.3 GDGT preparation and HPLC-MS analysis

Core lipids of iGDGTs and brGDGTs were obtained by automated solvent extraction using an ASE 200 (Dionex, USA) at a temperature of 75 °C and a pressure 5.0×10^6 Pa. Each sample was extracted for 20 min using a solvent mixture of dichloromethane (DCM)/MeOH (93 : 7, v/v). The total lipid extracts were separated over an aluminium oxide column into apolar and polar fractions using *n*-hexane/DCM (9 : 1, v/v) and DCM/MeOH (1 : 1, v/v) as respective eluents. The polar fractions were dried under a gentle stream of N_2, re-dissolved in *n*-hexane/2-propanol (99 : 1, v/v) and filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter prior to analysis.

All samples were analysed by high performance liquid chromatography coupled to atmospheric pressure positive ionisation mass spectrometry (HPLC/APCI-MS) using an Alliance 2690 (Waters, UK) and a Quattro LC triple quadrupole mass spectrometer (Micromass, UK) and following the analytical protocol described by Hopmans et al. (2000) and Schouten et al. (2007). Briefly, 10 µL of the filtered polar fractions were injected on an analytical Prevail Cyano column (2.1 × 150 mm, 3 µm particle size, Grace, USA), maintained at a temperature of 30 °C with a constant flow rate of 0.2 mL min^{-1}. Tetraether lipids were eluted isocratically with 99 % *n*-hexane and 1 % 2-propanol for

5 min, followed by a linear gradient to 1.8 % 2-propanol in 36 min and subsequently to 10 % 2-propanol in 5 min, after which the system was held isocratic for 5 min. The column was re-equilibrated with 99 % *n*-hexane and 1 % 2-propanol for 12 min before the next injection. The MS was operated as outlined in Heyng et al. (2015) with isoprenoid and branched GDGTs being detected in selective ion recording (SIR) mode of their protonated molecules $[M+H]^+$.

2.4 Calculation of GDGT indices

Acronyms in the below equations refer to the relative abundance of GDGTs displayed in the Appendix. The relationship between the commonly less occurring cyclopentane ring containing iGDGTs (GDGT-1 to GDGT-3 vs. the crenarchaeol regioisomer) was considered with using the TEX_{86} (tetraether index of tetraethers consisting of 86 carbons). The TEX_{86} was calculated according to Schouten et al. (2002):

$$\begin{aligned}\mathrm{TEX}_{86} = &(\text{GDGT-2} + \text{GDGT-3} + \text{Cren regioisomer})/\\ &(\text{GDGT-1} + \text{GDGT-2} + \text{GDGT-3} + \text{Cren regioisomer})\end{aligned} \tag{1}$$

The Cyclization ratio of Branched Tetraethers (CBT) was calculated using the relative abundance of tetra- and penta-methylated brGDGT according to Weijers et al. (2007):

$$\mathrm{CBT} = -\log((\mathrm{Ib} + \mathrm{IIb})/(\mathrm{Ia} + \mathrm{IIa})) \tag{2}$$

The Methylation index of Branched Tetraethers (MBT′) index was calculated as described by Peterse et al. (2012):

$$\mathrm{MBT}' = (\mathrm{Ia} + \mathrm{Ib} + \mathrm{Ic})/(\mathrm{Ia} + \mathrm{Ib} + \mathrm{Ic} + \mathrm{IIa} + \mathrm{IIb} + \mathrm{IIc} + \mathrm{IIIa}) \tag{3}$$

The MBT′ and CBT derived MAT (T_{MC}) was calculated after Peterse et al. (2012):

$$T_{\mathrm{MC}} = 0.81 - 5.67 \times \mathrm{CBT} + 31.0 \times \mathrm{MBT}' \tag{4}$$

The Branched and Isoprenoid Tetraether (BIT) index was determined as given in Hopmans et al. (2004):

$$\mathrm{BIT} = (\mathrm{Ia} + \mathrm{IIa} + \mathrm{IIIa})/(\mathrm{Ia} + \mathrm{IIa} + \mathrm{IIIa} + \mathrm{Cren}) \quad (5)$$

2.5 Statistical analysis

Statistical analysis was conducted using the PASW Statistics 18 software. Principal component analysis (PCA) was performed on relative abundances of iGDGTs, brGDGTs and the different GDGT-based indices, to explore and characterize the variability within the GDGT distribution in differently managed soils. To identify relationships between variables, a correlation analysis was performed. Results were given as r for Pearson's correlation regression coefficient together with the p value (two-tailed test), which denotes a significance if p is < 0.001.

3 Results

SOC (Table 1) varied from 0.4 to 5.0 % with highest contents present in paddy soils from the Philippine Ifugao (5.0 %) and Laguna (4.0 %), the Indonesian Sukabumi (4.4 %) and the Vietnamese Tien Giang (4.4 %) sites. The forest and bushland soils had a mean SOC of 2.7 ± 0.9 % ($n = 11$), which was higher than in most upland soils (1.6 ± 0.9 %, $n = 37$). The pH ranged from 3.7 in Tien Giang (Vietnam) to 8.2 in Cixi (China; Table 1). In general, no differences in pH values were noticed for soils with paddy (5.3 ± 1.0 %, $n = 119$) or upland (5.3 ± 1.1 %, $n = 37$) management. Forest and bushland soils had the lowest mean pH of 4.5 ± 0.5 % ($n = 11$).

Both iGDGT and brGDGT were detected in variable abundances in all soils. The brGDGT/iGDGT ratio was > 80 in Indonesian paddy soils (Jasinga), > 20–80 in forest and bushland soils, and as low as 1.9 in the remaining soils (Supplement, Fig. S1). The lowest proportion of brGDGT was noted in Italian upland soils, in very young Chinese marsh soils (< 30 yr) and upland soils. A specific feature of soil from the Chinese Cixi area is its development from tidal wetland sediment. The GDGT signature of these soils was distinct from the one in other soils investigated in this study and represents a mixed signature of the parent substrate (tidal wetland sediments) and the recent SOM (soil organic matter).

4 Discussion

4.1 Distribution of isoprenoid GDGTs in soils

iGDGTs constitute between 0.9 and 25.7 % (and in soils of Cixi 35 %) of all GDGTs (Table 1), indicating substantial contributions of archaeal lipids to most investigated soils. Forest and bushland soils had lowest relative mean abundances of iGDGTs (5.8 ± 2.6 %), followed by tropical paddy (9.3 ± 4.0 %) and upland soils (9.8 ± 6.0 %). The proportion of iGDGTs was highest in Chinese and Italian upland soils (21.1 ± 8.0 %) compared to their adjacent paddy soils and all other remaining soils (13.3 ± 5.0 %). The fact that the iGDGT content was lower in tropical compared to subtropical soils suggests that the composition of the microbial consortia varies on regional to global scales. In addition, the differentiation between upland and paddy soils with higher amounts of iGDGTs in the former may indicate management (regulating the water regime, nutrient availability, oxygen availability and/or redox conditions) induced variations of GDGT containing microorganism. In general, at locations with the same climate and substrate, different management types best explain different GDGT distribution. Regardless of whether paddy, upland or forest management, all differ in their microbial lipid pattern that may be influenced by differing inputs of plant organic matter, differing fertilization practises and redox conditions. The latter is controlled by flooding and draining practises on paddy soils, which seem to favour growth and input of brGDGT containing bacteria compared to the adjacently located upland soils.

The distribution of iGDGTs in soils may provide detailed insights into the archaeal community structure and the biological processes that they mediate (Koga et al., 1998;

Pancost et al., 2001; Blumenberg et al., 2004; Koga and Morii, 2005). The most abundant iGDGTs in our sample set are GDGT-0 and crenarchaeol. The latter is considered a highly specific biological maker for ammonia-oxidizing *Thaumarchaeota* (Leininger et al., 2006; Pitcher et al., 2010; Sinninghe Damsté et al., 2012; Pearson and Ingalls, 2013). Molecular investigations on cultivated *Thaumarchaeota* revealed separation between group I.1a *Thaumarchaeota* (aquatic) and group I.1b *Thaumarchaeota* (terrestrial/soil) based on the relative abundance of the crenarchaeol regioisomer. Abundances of the crenarchaeol regioisomer $< 5\,\%$ are indicative for group I.1a and > 10–$20\,\%$ for group I.1b *Thaumarchaeota* (Sinninghe Damsté et al., 2012). The same authors demonstrated that in soils group I.1a *Thaumarchaeota* and group I.1b *Thaumarchaeota* produce higher abundances of the crenarchaeol regioisomer than in marine or lacustrine environments (Sinninghe Damsté et al., 2012). Crenarchaeol and its regioisomer are present in all analysed soil samples, which is in agreement with a previous study (Weijers et al., 2006b). The amount of crenarchaeol is generally higher in upland soils ($46.4 \pm 12.9\,\%$, $n = 37$) compared to adjacent paddy soils ($22.5 \pm 14.5\,\%$, $n = 119$; Fig. 2a), possibly suggesting management induced differences in the archaeal community structure. The abundance of the crenarchaeol regioisomer varies from 3 to 21 % to that of crenarchaeol (mean value of $9 \pm 4\,\%$, $n = 170$), and shows no differences between soils and/or management types (Fig. S2).

Angel et al. (2012) observed that methanogenic archaea are ubiquitous in soils and being active only in anoxic, highly reducing environments, e.g. under flooded conditions. One distinct feature of paddy soil management vs. management of all other soils is the periodic flooding and draining of soils, which leads to highly variable redox conditions throughout the time course of a year (Kögel-Knabner et al., 2010; Kölbl et al., 2014). Paddy soils are known for high methanogenic activity and as significant sources of atmospheric CH_4 (Conrad, 2007; Thauer et al., 2008; Serano-Silva et al., 2014) without any changes in the methanogenic community structure between floodings (Krüger et al., 2005; Watanabe et al., 2006, 2009). In turn, this suggests that the overall lipid pool in paddies does not change significantly after draining the fields for harvesting.

The ratio of GDGT-0/crenarchaeol, initially proposed for lake environments, may be used to indicate the dominance of methanogenic archaea (Blaga et al., 2009) or of *Thaumarchaeota* in a given sedimentary environment. The latter are members performing the first and rate-limiting step in nitrification: the aerobically oxidation of ammonia (Stahl and de la Torre, 2012; Stieglmeier et al., 2014). In various studies, it was shown that a GDGT-0/crenarchaeol ratio > 2 is diagnostic for methanogens (Blaga et al., 2009; Naeher et al., 2014). In the analysed soils, the GDGT-0/crenarchaeol ratio ranged from 0.1 to 121.6, with highest ratios observed in Philippine and Vietnamese paddy soils (Fig. 2c, Table 1). In oxic upland and forest soils the mean GDGT-0/crenarchaeol ratio was ≤ 1, which indicates that methanogenic archaea are only a minor component of the microbial community at these sites. In addition, a few paddy soils (e.g. sites in Chinese Cixi and in Italy) had GDGT-0/crenarchaeol ratios comparable to those observed in upland soils, which can be explained by the management form including higher intensities of crop-rotation with upland crops under non-flooded conditions on these fields. However, if soils from the same region are compared, the ratio was generally 3–27 times higher in soils which are under paddy management compared to adjacent upland soils, indicating increased abundances and activity of methanogens in flooded soils.

The TEX_{86} values determined ranged from 0.3 to 0.9 (Fig. 2d, Table 1) without an apparent geographical trend. However, within a region TEX_{86} values were on average 1.3 times higher in upland, bushland and forest soils compared to the adjacent paddy soils. Highest values (upland/paddy-TEX_{86} = 1.5) were observed in the subtropical locations of Cixi and Italy (Table 1). None or only minor differences in TEX_{86} values were noted in the Jasinga and Ngawi soils of Indonesia. Because of the relation between the TEX_{86} and temperature, one explanation for the difference could be that the periodic water layer on paddy soils may protect the soil surface from excessive heating and therefore results in lower mean annual soil temperatures (MST) in both soil types. Previous studies of altitudinal mountain transects support this suggestion, as the soil TEX_{86} was negatively correlated with elevation and therefore with decreasing temperatures e.g.

in the Qinghai-Tibetan Plateau ($r = -0.81$, $r^2 = 0.65$, $p < 0.01$; Liu et al., 2013) and Tanzania ($r = -0.71$, $r^2 = 0.50$, $p < 0.0001$; Coffinet et al., 2014).

In the soils investigated here, the relative proportion of GDGT-3 and the crenarchaeol regioisomer together with GDGT-1 mainly affected the tetraether index. Low TEX_{86} values, as observed in paddy soils, are the result of high relative abundances of GDGT-1 and low proportions of GDGT-3. This suggests that paddy soil characteristics such as alternating redox conditions and higher water content control the presence of GDGT-1. High contents of cyclopentyl moieties in archaeal membrane lipids were associated with anaerobic methanotrophic (ANME) archaea, which synthesize significant quantities of GDGT-1, GDGT-2 and GDGT-3 (Pancost et al., 2001; Blumenberg et al., 2004). Interestingly, two divergent trends in direction of increased TEX_{86} values were observed for GDGT-2 (Fig. 3a), with an increase of the GDGT-2 content to a TEX_{86} value of 0.70 and a subsequent decrease if values exceed this threshold (Fig. 3a). This change may again indicate that the archaeal community differs in dry upland/forest soils and flooded soils.

Figure 3b shows that there is only a weak relationship between the relative abundance of GDGT-0 and TEX_{86} (logarithmic $r = -0.67$, $r^2 = 0.45$, $p < 0.0001$). However, both the TEX_{86} and the GDGT-0/crenarchaeol ratio show clear differences in soils under paddy (grey background in Fig. 3b) and upland management for adjacent sites suggesting that they may be used to determine anoxic or oxic conditions in soils. In general, paddy soils plotted within a field characterized by GDGT-0/crenarchaeol ratios > 2 and TEX_{86} values < 0.6 (Fig. 3b), possibly denoting a diagnostic area for the loading of methanogenic archaea. The GDGT-0/crenarchaeol ratio also differs between the various paddy soils, with exceptional high ratios in the Philippine Ifugao and Vietnamese Lào Cai soil (Table S1). At these sites, longer flooding periods (> 5 month per year) compared to Chinese and Indonesian soils are the likely explanation for the high ratios.

4.2 Distribution of branched GDGTs in soils

In the soils investigated here, the relative proportion of brGDGTs within the total GDGT pool was high and varied from 65.0 to 99.1 % (Table 1). Forest soils generally contained the highest abundances of brGDGTs (> 92 %), while they were significantly lower in upland and paddy soils (Fig. 4a). Pearson's correlation analysis indicated that the SOC content was not related to the relative abundance of brGDGT ($r = 0.22$, $r^2 = 0.05$, $p <$ 0.01).

In general, the tetra-methylated GDGT-Ia was the most abundant brGDGT in acidic soil and was the only brGDGT to increase in relative abundance with decreasing pH ($r = -0.75$, $r^2 = 0.56$, $p < 0.001$; Fig. 5). All other brGDGTs increased in relative abundance with pH ($p < 0.001$; Table S2), with the highest correlations observed for GDGT Ib ($r = 0.83$, $r^2 = 0.69$), GDGT IIb ($r = 0.79$, $r^2 = 0.62$) and GDGT IIIb ($r = 0.71$, $r^2 = 0.50$). Our results thus suggest that especially the monocyclization of brGDGT is strongly controlled by pH ($r = 0.86$, $r^2 = 0.74$, $p < 0.001$) with alkaline conditions favouring the synthesis of brGDGT with one cyclopentane moiety (Fig. 5). Similar observations have previously been made in a set of globally distributed upland soils (Weijers et al., 2007; Peterse et al., 2012).

Weijers et al. (2007) explained the lower number of cyclopentyl moieties in brGDGT as a protection mechanism of bacterial cell membranes within acidic soils. The decrease in the amount of cyclopentyl moieties in brGDGT is associated with a decrease in membrane permeability, which regulates the internal pH of bacteria under acidic conditions (Weijers et al., 2007). In soils investigated here, the CBT ratio varied between −0.04 to 2.13 (Table 1) and showed a negative correlation with increasing soil pH ($r = -0.81$, $r^2 = 0.65$, $p < 0.001$; Fig. 6a). In neutral to alkaline soils (with pH values > 6.5) CBT values stayed rather constant with an offset observed between paddy soils (mean 0.34) and upland soils (mean −0.01; Fig. 6a). Wang et al. (2014) also found no apparent correlation between pH and CBT in alkaline soils in a study of arid and subhumid Chinese soils. However, a predominant dependency of CBT with soil water content and the mean annual precipitation (MAP) was observed (Wang et al., 2014). In our study, soil moisture could be one potential factor for the varying CBT values in paddy and upland soil, especially under alkaline conditions (Fig. 6a).

The degree of methylation of brGDGTs (MBT$'$) has previously been shown to correlate with MAT and pH (Weijers et al., 2007; Peterse et al., 2012). Our results demonstrate that the MBT$'$ generally shows low values in paddy soils compared to the adjacently located upland soils, except for the Chinese soils of Cixi (Table 1). The difference in MBT$'$ between soils from the same sampling area denotes a lower influence of MAT on the MBT$'$ than on the pH, which was weakly related to the MBT$'$ ($r = -0.55$, $r^2 = 0.31$, $p < 0.001$; Fig. 6b). The MBT$'$ was mainly controlled by the relative abundance of GDGT-Ia and GDGT-IIa, both of which were strongly related to MAP (Peterse et al., 2012). As the latter is largely similar at adjacent sites, we consider the paddy soil specific management techniques, including periodically flooding of soils, as responsible for the low GDGT-Ia and high GDGT-IIa content in paddy soils compared to upland soils (Table S1). This indicates that moisture is an important environmental variable affecting the distribution of brGDGT in soil. Moisture is also known to affect soil temperature, in particular in surface soils. Indeed, calculated T_{MC} values were generally lower in paddy soils compared to the adjacent upland soils (Table 1), indicating that temperature denotes more the mean annual soil temperature.

A recently developed method separates the structural isomers of brGDGTs with their methyl groups located in positions 5 and 6 (De Jonge et al., 2013). De Jonge et al. (2014) showed that the new CBT$_{5\mathrm{ME}}$, calculated without 6-methyl brGDGTs, to correlate stronger with soil pH than the regular CBT, which includes both isomers, the 5- and 6-methyl brGDGTs. In addition, they found no correlation between pH and the newly developed MBT$'_{5\mathrm{ME}}$, which is calculated without the 6-methyl isomer but a stronger correlation of MBT$'_{5\mathrm{ME}}$ with MAT. De Jonge et al. (2014) thus demonstrated that co-elution of GDGTs can affect estimation of pH values. Conventional methods as applied in this study, use a Prevail cyano column upon HPLC-MS analysis, which does not separate these isomers. Therefore, it is possible that our CBT-based pH reconstruction revealed some scatter (Fig. 6a) due to the presence of unresolved 5- and 6-methyl brGDGTs. The overall covariation of CBT and pH, however, was unaffected by this co-elution.

4.3 Influence of management systems on GDGT distribution

The BIT index quantifies the relationship between acyclic brGDGTs and crenarchaeol and has been used previously to determine the input of terrestrially derived organic matter to marine and lake environments (Hopmans et al., 2004; Weijers et al., 2007). The interpretation of BIT values in soil is not that straight forward as crenarchaeol originates from terrestrial *Thaumarchaeota* with less well constrained crenarchaeol abundances. Wang et al. (2013) observed a positive correlation between increasing soil water content and BIT values in Chinese marsh soils. In our sample set, the BIT index was slightly higher in paddy soils than in the adjacent upland soils (Fig. 4b). Furthermore, higher values were observed generally in paddy soil from tropic (1.02–1.04 fold) compared to subtropic (1.07–1.11 fold) locations. In contrast to the general trend, we found highest BIT values (1.27 fold) in the subtropical paddy soil of the Chinese Cixi location. In this area the BIT values in marsh and upland soil (0.61–0.89) were comparatively low, indicating that the latter have a mixed lipid composition with crenarchaeol originating predominantly from the residual parent substrate (tidal wetland sediment) and in smaller quantities also from the current microbial soil community. Comparable results were observed in a study of the plant wax lipids, which confirm the mixed lipid composition in these soils (Mueller-Niggemann and Schwark, 2015). Despite the higher contribution of crenarchaeol to the marsh soils, our results show that brGDGT producing bacteria clearly dominate over *Thaumarchaeota* in all of the investigated soil types. Interestingly, crenarchaeol producing *Thaumarchaeota* seem to be more abundant in upland soils compared to forest and periodical flooded paddy soils (Fig. 4b). This is the opposite to results of an 152 day experimental study, with a higher production rate of crenarchaeol in soils that were incubated with different types of water (river, ocean or distilled water) to simulate the development of an aquatic environment under aerobic conditions (Peterse et al., 2015). Low redox conditions as assumed for paddy soils may thus lead to an enrichment of brGDGTs either by higher production or increased preservation of brGDGTs compared to crenarchaeol in wetland soils.

PCA was performed to obtain information on the major factors that control the variability of the distribution of iGDGTs and brGDGTs. Results of this analysis indicate that crenarchaeol exerts a major iGDGT in upland soils (Fig. 7a). The component loading score of GDGT-0 is opposite to crenarchaeol and has the highest negative score in PC1. In general, soils can be sorted into two groups on the basis of their scores on the first component. Paddy soils load negatively and all other soils load positively on PC1. Paddy soils that plot in the quadrant of upland soils are characterized by a higher intensity of crop-rotation with upland crops on the fields. The iGDGT composition of periodically flooded paddy soils is mainly controlled by GDGT-0 and that of non-paddy upland soils by crenarchaeol derived from *Thaumarchaeota*. In flooded rice paddy soils, oxygen availability determines the development of microbial consortia adapted to more anoxic conditions such as GDGT-0 synthesizing methanogenic archaea (Koga et al., 1998; Koga and Morii, 2005). The variance on PC2 is mainly associated with the relative abundance of GDGT-2 and separating forest and bushland soils from all other soils. The larger scatter of paddy soils on PC2 is explained by the number of rice cultivation cycles per year, which apparently influence the GDGT-2 contents significantly (Fig. 7b). Methanogenic archaea were found to be phylogenetically related to ANME living archaea (Krüger et al., 2003; Shima et al., 2012). ANME archaea are a well known source of iGDGTs (including GDGT-2) in natural environments (Pancost et al., 2001; Blumenberg et al., 2004). Both, the interaction of methanogenic and methanotrophic archaea as well as the fact that ANME are an abundant source of GDGT-2, could explain the relationship between higher numbers of rice cultivation cycles, which induce increased methanogenesis through abundant redox cycling, and the presence of GDGT-2. MAT and MAP had no obvious influence on discrimination of agricultural soil via iGDGT distribution (Fig. S3).

PCA analysis on the relative abundances of brGDGT shows an opposite relation of GDGT-Ia to all other brGDGTs, with the highest component loading score on PC1 for GDGT-Ia (Fig. 8). The cyclopentane containing GDGT-IIb and -IIIb plot negatively on PC1. Higher contents of GDGT-Ia in upland soils compared to adjacent paddy soils (Table S1) confirm that tetra-methylated brGDGTs may be useful in separating different agricultural soils. GDGT-IIa has the lowest loading score on PC1 but the highest on PC2. Upland soils load separately from paddy soils along the PC2 with variation of relative abundance of the cyclic GDGT-Ib and GDGT-Ic playing the most important role. In contrast, paddy soils are mainly influenced by the abundance of GDGT-IIa and GDGT-IIIa, which both show only a low correlation with pH (Table S2). We rather, assume their dependency on soil moisture. The first PC, explaining 69.11 % of the variance, indicates a separation between locations, with a strong negative score in subtropical Italian and Chinese soils and more positive scores in soils originating from the tropics (Fig. 8a). The MAP (Fig. 8b) and MAT (Fig. S4) gradients of sampling locations on PC1, confirms a relation of climatic parameters to the variation of acyclic brGDGTs.

PCA analysis on environmental parameters as well as on indices of bacterial and archaeal GDGTs indicated that separation of paddy and upland soil is mainly controlled by the intensity of methanogenesis (Fig. 9a). The GDGT-0/crenarchaeol ratio and the BIT index had the highest positive loading score on PC2. The SOC and TN loaded in the same quadrant as the BIT index, suggesting that a positive correlation between the amount of organic matter and acyclic brGDGT, especially in paddy soils, prevailed. Alternating anoxic conditions in paddy soils are known to favour the preservation and therefore the accumulation of organic matter (Lal et al., 2002), which could lead to an increase of heterotrophic and brGDGT producing bacteria. In general, the CBT loaded opposite of the soil pH on PC1, indicating their negative relation to each other. The internal separation of paddy soils via the number of rice cultivation cycles is evident by high loading scores of the CBT and MBT′ (Fig. 9b). Apparently, the increase of the MBT′ is linked with the number of rice cycles, and therefore with lowering of penta- and hexa-methylated brGDGT during increasing redox cycles. Similar loading scores as well as similar directions of climatic parameters, such as MAP and MAT, and of CBT and MBT′ also indicated a linkage to each other. In addition to methanogenesis, differences in MAT and soil water content seemed to be secondary factors controlling the distribution of brGDGT in soils, which also allowed a separation between upland and paddy management. It should be considered though that MAT is not identical to MST as the latter was also affected by e.g. the albedo and soil management, which can be different in the adjacent soils (Liu et al., 2014; Awe et al., 2015 and references therein). The reflection coefficient of the surface differs in agricultural soils as a consequence of management practises, which influence the soil bulk density (via tillage), the plant cover (function of the crop leaf area index) and the soil water content. For example, Awe et al. (2015) found differences in soil temperature as consequence of management practises with lower temperatures in soils under chiselling and conventional tillage compared to no-tillage.

4.4 Effects of long-term management on GDGT distributions

Changes in GDGT distribution within two Cixi chronosequences with different cropping systems, one under continuous non-flooded upland and the other under paddy management, indicated specific adaption processes during the long-term usage at each site. Marsh soils were the first soils to develop after the construction of dykes on tidal wetland sediments and therefore represent the starting point of the subsequent soil development. We observed high BIT values (∼ 0.77) already in the surface horizon of the marsh soils, indicating the rapid adaption of the microbial community to more terrestrial conditions. A plot of the brGDGT/iGDGT ratio over time provides evidence for a dominance of brGDGT over iGDGT in all soils, with values of this ratio varying between 2 and 6 in upland soils (Fig. 10a). In contrast to paddy soils, which had a fourfold increase of the ratio after 2000 yr rice cultivation, this suggests an influence of long-term processes on the proportion of archaeal and bacterial soil microorganism. These processes may include desalinization, decalcification through leaching as shown in changes of soil pH values (Fig. S5a), fertilization activities, organic matter input and accumulation (Fig. S5b). Paddy soil management is known to strongly affect the accumulation of organic matter (Wu, 2011; Mueller-Niggemann et al., 2012; Kölbl et al., 2014) as the periodically anaerobic conditions result in a slower degradation of organic matter (Lal et al., 2002). Kölbl et al. (2014) investigated the response of redox dynamics to changing water conditions over a one year time period in 100, 700 and 2000 yr old paddy soils. They noted a change of the redox potential towards anoxic conditions, already after 5 days of flooding. After stabilization, the redox potential was in the same range in all soils (−170 to −200 mV), independent of the duration of paddy management. In upland soils, permanent oxic conditions were persistent throughout the time period investigated. Results of Kölbl et al. (2014) demonstrate that the rapid establishment of anoxic conditions and the long-term usage of paddy soils may lead to an increase of organic carbon concentrations over time.

Within the upland soil chronosequence, the TEX_{86} does not change significantly over the 700 yr cultivation time and averages 0.7 (Fig. 10b). In paddy soils, on the contrary, the TEX_{86} decreased from the initial marsh soil value of 0.7 to values of 0.3 within only 50 yr of paddy management. Rotation between paddy- and upland-type of cultivation resulted in a high TEX_{86} value of 0.5 in the 2000 yr-old paddy soils (Fig. 10b). Our results thus suggest that management systems significantly affect the microbial soil community. Long-time paddy management also led to the successive increase of ammonia-oxidizing *Thaumarchaeota* based on high relative abundances of crenarchaeol, indicating either a recovering process of water-stressed soil *Thaumarchaeota* or the enrichment of fossil crenarchaeol. The latter is potentially explainable by the management type used in the Cixi area, with one wetland rice season and one dry inter-crop season per year that influence the presence of aerobic and anaerobic microbes in these paddy soils. In particular, the periodically anaerobic conditions may result in a slower degradation of organic matter (Lal et al., 2002). GDGTs may originate from a mixed source of microbial membrane lipids that were recently deposited (during the oxic as well as in the anoxic period) additionally to the previously preserved ones. Thus, higher proportions of crenarchaeol e.g. as marker for terrestrial ammonia oxidizers, being active during the oxic inter-crop period, were detected but in lower amounts as commonly observed in upland soils (Table S1). At the same time, the proportion of methanogenic archaea, which was estimated by using GDGT-0/crenarchaeol ratio, decreased during the long-term paddy management from 5.0 in the 50 yr to 2.8 in the 2000 yr old paddy soil.

The pH values ranged between 8.0 in marsh soil and 5.5 in the 2000 yr paddy soil. The paddy management (including flooding practises) thus leads to enhanced decalcification of soils compared to the non-flooded upland management. However, most soils have an alkaline or neutral pH with exceptions of the 700 yr upland soil and the 2000 yr paddy soils, which all had pH values < 6.5 (Fig. S5a). It has previously been demonstrated that the CBT is negatively correlated with increasing pH values (Weijers et al., 2007; Peterse et al., 2012). In the alkaline soils of the Cixi chronosequences a negative correlation was also observed, which was higher for paddy soils ($r = -0.94$, $r^2 = 0.88$, $n = 4$, $p < 0.001$) than for upland soils ($r = -0.69$, $r^2 = 0.47$, $n = 5$, $p < 0.001$). Interestingly, an offset of CBT values between paddy and upland soils with no apparent changes during cultivation time was noted (Fig. 10c). In addition, the CBT was higher in the younger of both marsh soils, probably because of the greater soil water content in the ~ 10 yr old compared to the ~ 35 yr old marsh soil as result of the progressive dewatering during marsh soil pedogenesis. The observation for the CBT values supports the idea that soil moisture in addition to pH controls the degree of cyclization of brGDGTs under alkaline conditions; possibly as a reaction to water stress or oxygen deprivation on microorganism. The increase of CBT values in acidic soils (Fig. 10c) also suggests that low soil pH results in the increased synthesis of brGDGTs with no cyclopentyl moieties.

Except for the youngest paddy soils (50 yr), the MBT′ was slightly lower in Cixi upland soils compared to their corresponding paddy soils with identical cultivation time (Fig. 10d). This is in contrast to the observations that paddy soils in general showed a lower MBT′ compared to the adjacent upland soils (Fig. 6b). This may indicate that soil bacteria living under contrasting pH regimes adapt the composition of their membrane lipids in a different fashion, even if the agricultural management is comparable.

The CBT and MBT′ are both considered to be strongly related to MAT (Weijers et al., 2007; Peterse et al., 2012), which is largely similar for paddy and upland soils from the same sampling region. However, the calculated T_{MC} was different in adjacent paddy and upland soils (Table S1) and gradually increased during long-term management in both chronosequences (Fig. 11) from 14.4 to 17.8 °C in paddy soils and from 17.1 to 19.3 °C in upland soils, respectively. In general, temperatures were approximately 1.4 °C higher in upland soils compared to soils under paddy management with the same cultivation time. This implies that the management type affects the MST, which in turn controls the membrane lipid composition of brGDGT producing bacteria.

5 Conclusions

Our results show that archaeal and bacterial GDGTs were ubiquitously distributed in paddy, upland, forest, bushland and marsh soils of tropical and subtropical climate regimes. Independent of the soil usage, the brGDGTs predominated over iGDGTs in all soils, but had lower relative proportions in soils located in the subtropics compared to soils in tropical latitudes. This implies that warm and humid environments favour the growth of bacteria that produce brGDGT.

Agricultural management was a major factor that controlled the distribution of the archaeal community in soils. Biomarker for methanogens were enhanced in subaquatic paddy soils compared to predominantly thaumarchaeal ammonia oxidation in dry upland soils. In addition, the number of – or a long-term duration of – rice cultivation cycles per year significantly affected the composition of iGDGT with an increase of the GDGT-0/crenarchaeol ratio in soils with a higher number of cultivation cycles.

CBT values were correlated with soil pH and were controlled by a predominance of acyclic brGDGT in acidic soils. In alkaline soils, CBT values were rather invariant but the offset between soils under periodical flooding (paddy soils) and soils under non-flooded upland management suggests that parameters other than pH affected the distribution of brGDGTs as well (e.g. soil moisture that in addition to soil pH and MAT exerts a control on the degree of cyclization of brGDGTs). MBT′ values differed in adjacent paddy and upland soils, confirming that other factors than MAT and MAP affect the degree of methylation of brGDGT on a regional scale. brGDGT-based temperatures (T_{MC}) were higher in soils under upland management than under paddy management and these differences in T_{MC} suggest that the specific management influenced the soil moisture, which in turn affects MST. The results of the Cixi chronosequence covering 2000 yr soil development confirm that the SOC, the pH value and the soil moisture controlled the distribution of brGDGT during long-term paddy soils usage.

Appendix

Chemical structures of branched GDGTs (brGDGTs) and isoprenoid GDGTs (iGDGTs) investigated in this study (Fig. A1).

The Supplement related to this article is available online at doi:10.5194/bgd-12-16709-2015-supplement.

Acknowledgements. We thank the German Research Foundation (DFG) for financial support (Schw554/20). Asian and European partners of Research Initiative FOR 995 as well as of the LEGATO project are thanked for field work collaboration.

References

Angel, R., Claus, P., and Conrad, R.: Methanogenic archaea are globally ubiquitous in aerated soils and become active under wet anoxic conditions, ISME J., 6, 847–862, 2012.
Awe, G. O., Reichert, J. M., and Wendroth, O. O.: Temporal variability and covariance structures of soil temperature in a sugarcane field under different management practices in southern Brazil, Soil Till. Res., 150, 93–106, 2015.

Ayari, A., Yang, H., and Xie, S.: Flooding impact on the distribution of microbial tetraether lipids in paddy rice soil in China, Front. Earth Sci., 7, 384–394, 2013.

Bannert, A., Mueller-Niggemann, C., Kleineidam, K., Wissing, L., Cao, Z. H., Schwark, L., and Schloter, M.: Comparison of lipid biomarker and gene abundance characterizing the archaeal ammonia-oxidizing community in flooded soils, Biol. Fert. Soils, 47, 839–843, 2011.

Bauersachs, T., Weidenbach, K., Schmitz, R. A., and Schwark, L.: Distribution of glycerol ether lipids in halophilic, methanogenic and hyperthermophilic archaea, Org. Geochem., 83–84, 101–108, 2015.

Bischoff, J., Mangelsdorf, K., Schwamborn, G., and Wagner, D.: Impact of lake-level and climate changes on microbial communities in a terrestrial permafrost sequence of the El'gygytgyn crater, Far East Russian Arctic, Permafrost Periglac. Process., 25, 107–116, 2014.

Blaga, C. I., Reichart, G. J., Heiri, O., and Sinninghe Damsté, J. S.: Tetraether membrane lipid distributions in water-column particulate matter and sediments: a study of 47 European lakes along a north–south transect, J. Paleolimnol., 41, 523–540, 2009.

Blumenberg, M., Seifert, R., Reitner, J., Pape, T., and Michaelis, W.: Membrane lipid patterns typify distinct anaerobic methanotrophic consortia, P. Natl. Acad. Sci. USA, 101, 11111–11116, 2004.

Brochier-Armanet, C., Boussau, B., Gribaldo, S., and Forterre, P.: Mesophilic *Crenarchaeota*: proposal for a third archaeal phylum, the *Thaumarchaeota*, Nat. Rev. Microbiol., 6, 245–252, 2008.

Cheng, Y. Q., Yang, L. Z., Cao, Z. H., Ci, E., and Yin, S.: Chronosequential changes of selected pedogenic properties in paddy soils as compared with non-paddy soils, Geoderma, 151, 31–41, 2009.

Coffinet, S., Huguet, A., Williamson, D., Fosse, C., and Derenne, S.: Potential of GDGTs as a temperature proxy along an altitudinal transect at Mount Rungwe (Tanzania), Org. Geochem., 68, 82–89, 2014.

Conrad, R.: Microbial ecology of methanogens and methanotrophs, Adv. Agron., 96, 1–63, 2007.

De Jonge, C., Hopmans, E. C., Stadnitskaia, A., Rijpstra, W. I. C., Hofland, R., Tegelaar, E., and Sinninghe Damsté, J. S.: Identification of novel penta- and hexamethylated branched glycerol dialkyl glycerol tetraethers in peat using HPLC-MS^2, GC-MS and GC-SMB-MS, Org. Geochem., 54, 78–82, 2013.

De Jonge, C., Hopmans, E. C., Zell, C. I., Kim, J. H., Schouten, S., and Sinninghe Damsté, J. S.: Occurrence and abundance of 6-methyl branched glycerol dialkyl glycerol tetraethers in soils: implications for palaeoclimate reconstruction, Geochim. Cosmochim. Ac., 141, 97–112, 2014.

De Rosa, M., Gambacorta, A., Lanzotti, V., Trincone, A., Harris, J. E., and Grant, W. D.: A range of ether core lipids from the methanogenic archaebacterium Methanosarcina barkeri, Biochim. Biophys. Acta, 875, 487–492, 1986.

Edit Committee of Chorography of Cixi County: Chorography of Cixi County, Zhejiang, Peoples Express House, Hangzhou, 1992.

FAO: World Agriculture: Towards 2015/2030, an FAO Perspective, edited by: Bruinsma, J., Earthscan Publications Ltd., London, 2003.

Feng, L. H. and Bao, Y. X.: Impact of human activity on the estuary of the Qiantang River and the reclamation of tidal flats and river regulation, Environ. Geol., 49, 76–81, 2005.

Heyng, A. M., Mayr, C., Lücke, A., Moschen, R., Wissel, H., Striewski, B., and Bauersachs, T.: Middle and Late Holocene paleotemperatures reconstructed from oxygen isotopes and GDGTs of sediments from Lake Pupuke, New Zealand, Quatern. Int., 374, 3–14, 2015.

Hopmans, E. C., Schouten, S., Pancost, R. D., van der Meer, M. T. J., and Sinninghe Damsté, J. S.: Analysis of intact tetraether lipids in archaeal cell material and sediments by high performance liquid chromatography/atmospheric pressure chemical ionization mass spectrometry, Rapid Commun. Mass Spectrom., 14, 585–589, 2000.

Hopmans, E. C., Weijers, J. W. H., Schefuß E., Herfort, L., Sinninghe Damsté, J. S., and Schouten, S.: A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids, Earth Planet. Sc. Lett., 224, 107–116, 2004.

Huguet, A., Fosse, C., Metzger, P., Fritsch, E., and Derenne, S.: Occurrence and distribution of extractable glycerol dialkyl glycerol tetraethers in podzols, Org. Geochem., 41, 291–301, 2010.

Huguet, A., Wiesenberg, G. L. B., Gocke, M., Fosse, C., and Derenne, S.: Branched tetraether membrane lipids associated with rhizoliths in loess: rhizomicrobial overprinting of initial biomarker record, Org. Geochem., 43, 12–19, 2012.

Huguet, A., Grossi, V., Belmahdi, I., Fosse, C., and Derenne, S.: Archaeal and bacterial tetraether lipids in tropical ponds with contrasted salinity (Guadeloupe, French West Indies): implications for tetraether-based environmental proxies, Org. Geochem., 83–84, 158–169, 2015.

Husson, O.: Redox potential (Eh) and pH as drivers of soil/plant/microorganism systems: a transdisciplinary overview pointing to integrative opportunities for agronomy, Plant Soil, 362, 389–417, 2013.

Jiang, X., Hou, X., Zhou, X., Xin, X., Wright, A., and Jia, Z.: pH regulates key players of nitrification in paddy soils, Soil Biol. Biochem., 81, 9–16, 2015.

Koga, Y. and Morii, H.: Recent advances in structural research on ether lipids from archaea including comparative and physiological aspects, Biosci. Biotechnol. Biochem., 69, 2019–2034, 2005.

Koga, Y., Morii, H., Akagawa-Matsushita, M., and Ohga, M.: Correlation of polar lipid composition with 16S rRNA phylogeny in methanogens. Further analysis of lipid component parts, Biosci. Biotechnol. Biochem., 62, 230–236, 1998.

Kögel-Knabner, I., Amelung, W., Cao, Z. H., Fiedler, S., Frenzel, P., Jahn, R., Kalbitz, K., Kölbl, A., and Schloter, M.: Biogeochemistry of paddy soils, Geoderma, 157, 1–14, 2010.

Kölbl A., Schad, P., Jahn, R., Amelung, W., Bannert, A., Cao, Z. H., Fiedler, S., Kalbitz, K., Lehndorff, E., Müller-Niggemann, C., Schloter, M., Schwark, L., Vogelsang, V., Wissing, L., and Kögel-Knabner, I.: Accelerated soil formation due to paddy management on marshlands (Zhejiang Province, China), Geoderma, 228–229, 67–89, 2014.

Klotzbücher T., Marxen, A., Vetterlein, D., Schneiker, J., Türke, M., van Sinh, N., Manh, N. H., van Chien, H., Marquez, L., Villareal, S., Bustamante, J. V., and Jahn, R.: Plant-available silicon in paddy soils as a key factor for sustainable rice production in Southeast Asia, Basic Appl. Ecol., doi:10.1016/j.baae.2014.08.002, 2014.

Krüger M., Meyerdierks, A., Glöckner F. O., Amann, R., Widdel, F., Kube, M., Reinhardt, R., Kahnt, J., Böcher, R., Thauer, R. K., and Shima, S.: A conspicuous nickel protein in microbial mats that oxidize methane anaerobically, Nature, 426, 878–881, 2003.

Krüger M., Frenzel, P., Kemnitz, D., and Conrad, R., Activity, structure and dynamics of the methanogenic archaeal community in a flooded Italian rice field, FEMS Microbiol. Ecol., 51, 323–331, 2005.

Kuypers, M. M. M., Blokker, P., Erbacher, J., Kinkel, H., Pancost, R. D., Schouten, S., Sinninghe Damsté, J. S.: Massive expansion of marine archaea during a mid-cretaceous oceanic anoxic event, Science, 293, 92–94, 2001.

Lal, R.: Soil carbon sequestration in China through agricultural intensification, and restoration of degraded and desertified ecosystems, Land Degrad. Dev., 13, 469–478, 2002.

Leininger, S., Urich, T., Schloter, M., Schwark, L., Qi, J., Nicol, G. W., Prosser, J. I., Schuster, S. C., and Schleper, C.: Archaea predominate among ammonia-oxidizing prokaryotes in soils, Nature, 442, 806–809, 2006.

Liesack, W., Schnell, S., and Revsbech, N. P.: Microbiology of flooded rice paddies, FEMS Microbiol. Rev., 24, 625–645, 2000.

Liu, W., Wang, H., Zhang, C. L., Liu, Z., and He, Y.: Distribution of glycerol dialkyl glycerol tetraether lipids along an altitudinal transect on Mt. Xiangpi, NE Qinghai-Tibetan Plateau, China, Org. Geochem., 57, 76–83, 2013.

Liu, Y., Wang, J., Liu, D., Li, Z., Zhang, G., Tao, Y., Xie, J., Pan, J., and Chen, F.: Straw mulching reduces the harmful effects of extreme hydrological and temperature conditions in citrus orchards, PLoS One, 9, e87094, doi:10.1371/journal.pone.0087094, 2014.

Loomis, S. E., Russell, J. M., Heureux, A. M., D'Andrea, W. J., and Sinninghe Damsté, J. S.: Seasonal variability of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in a temperate lake system, Geochim. Cosmochim. Ac., 144, 173–187, 2014.

Mueller-Niggemann, C. and Schwark, L.: Chemotaxonomy and diagenesis of aliphatic hydrocarbons in rice plants and soils from land reclamation areas in the Zhejiang Province, China, Org. Geochem., 83–84, 215–226, 2015.

Mueller-Niggemann, C., Bannert, A., Schloter, M., Lehndorff, E., and Schwark, L.: Intra- versus inter-site macroscale variation in biogeochemical properties along a paddy soil chronosequence, Biogeosciences, 9, 1237–1251, doi:10.5194/bg-9-1237-2012, 2012.

Naeher, S., Peterse, F., Smittenberg, R. H., Niemann, H., Zigah, P. K., and Schubert, C. J.: Sources of glycerol dialkyl glycerol tetraethers (GDGTs) in catchment soils, water column and sediments of Lake Rotsee (Switzerland) – implications for the application of GDGT-based proxies for lakes, Org. Geochem., 66, 164–173, 2014.

Oppermann, B. I., Michaelis, W., Blumenberg, M., Frerichs, J., Schulz, H. M., Schippers, A., Beaubien, S. E., and Krüger, M.: Soil microbial community changes as a result of long-term exposure to a natural CO_2 vent, Geochim. Cosmochim. Ac., 74, 2697–2716, 2010.

Pancost, R. D., Hopmans, E. C., and Sinninghe Damsté, J. S.: Archaeal lipids in mediterranean cold seeps: molecular proxies for anaerobic methane oxidation, Geochim. Cosmochim. Ac., 65, 1611–1627, 2001.

Pearson, A. and Ingalls, A. E.: Assessing the Use of archaeal lipids as marine environmental proxies, Annu. Rev. Earth Planet. Sci., 41, 359–384, 2013.

Pearson, A., Huang, Z., Ingalls, A. E., Romanek, C. S., Wiegel, J., Freeman, K. H., Smittenberg, R. H., and Zhang, C. L.: Nonmarine crenarchaeol in Nevada hot springs, Appl. Environ. Microbiol., 70, 5229–5237, 2004.

Peterse, F., Schouten, S., van der Meer, J., van der Meer, M. T. J., and Sinninghe Damsté, J. S.: Distribution of branched tetraether lipids in geothermally heated soils: implications for the MBT/CBT temperature proxy, Org. Geochem., 40, 201–205, 2009a.

Peterse, F., Kim, J. H., Schouten, S., Kristensen, D. K., Koç, N., and Sinninghe Damsté, J. S.: Constraints on the application of the MBT/CBT palaeothermometer at high latitude environments (Svalbard, Norway), Org. Geochem., 40, 692–699, 2009b.

Peterse, F., van der Meer, M. T. J., Schouten, S., Jia, G., Ossebaar, J., Blokker, J., and Sinninghe Damsté, J. S.: Assessment of soil *n*-alkane δD and branched tetraether membrane lipid distributions as tools for paleoelevation reconstruction, Biogeosciences, 6, 2799–2807, doi:10.5194/bg-6-2799-2009, 2009c.

Peterse, F., van der Meer, J., Schouten, S., Weijers, J. W. H., Fierer, N., Jackson, R. B., Kim, J. H., and Sinninghe Damsté, J. S.: Revised calibration of the MBT-CBT paleotemperature proxy based on branched tetraether membrane lipids in surface soils, Geochim. Cosmochim. Ac., 96, 215–229, 2012.

Peterse, F., Moy, C. M., and Eglinton, T. I.: A laboratory experiment on the behaviour of soil-derived core and intact polar GDGTs in aquatic environments, Biogeosciences, 12, 933–943, doi:10.5194/bg-12-933-2015, 2015.

Pitcher, A., Schouten, S., and Sinninghe Damsté, J. S.: In situ production of crenarchaeol in two California hot springs, Appl. Environ. Microbiol., 75, 4443–4451, 2009.

Pitcher, A., Rychlik, N., Hopmans, E. C., Spieck, E., Rijpstra, W. I. C., Ossebaar, J., Schouten, S., Wagner, M., and Sinninghe Damsté, J. S.: Crenarchaeol dominates the membrane lipids of Candidatus Nitrososphaera gargensis, a thermophilic group I.1b Archaeon, ISME J., 4, 542–552, 2010.

Sahrawat, K. L.: Fertility and organic matter in submerged rice soils, Curr. Sci., 88, 735–739, 2005.

Schouten, S., Hopmans, E. C., Schefuß, E., and Sinninghe Damsté, J. S.: Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures?, Earth Planet. Sci. Lett., 204, 265–274, 2002.

Schouten, S., Huguet, C., Hopmans, E. C., Kienhuis, M. V. M., and Sinninghe Damsté, J. S.: Analytical methodology for TEX_{86} paleothermometry by high-performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry, Anal. Chem., 79, 2940–2944, 2007.

Schouten, S., Rijpstra, W. I. C., Durisch-Kaiser, E., Schubert, C. J., and Sinninghe Damsté, J. S.: Distribution of glycerol dialkyl glycerol tetraether lipids in the water column of Lake Tanganyika, Org. Geochem., 53, 34–37, 2012.

Schouten, S., Hopmans, E. C., and Sinninghe Damsté, J. S.: The organic chemistry of glycerol dialkyl glycerol tetraether lipids: a review, Org. Geochem., 54, 19–61, 2013.

Serrano-Silva, N., Sarria-Guzmán Y., Dendooven, L., and Luna-Guido, M.: Methanogenesis and methanotrophy in soil: a review, Pedosphere, 24, 291–307, 2014.

Shima, S., Krueger, M., Weinert, T., Demmer, U., Kahnt, J., Thauer, R. K., and Ermler, U.: Structure of a methyl-coenzyme M reductase from Black Sea mats that oxidize methane anaerobically, Nature, 481, 98–101, 2012.

Sinninghe Damsté, J. S., Hopmans, E. C., Pancost, R. D., Schouten, S., and Geenevasen, J. A. J.: Newly discovered non-isoprenoid glycerol dialkyl glycerol tetraether lipids in sediments, Chem. Commun., 17, 1683–1684, 2000.

Sinninghe Damsté, J. S., Schouten, S., Hopmans, E. C., van Duien, A. C. T., and Geenevasen, J. A. J.: Crenarchaeol: the characteristic core glycerol dibiphytanyl glycerol tetraether membrane lipid of cosmopolitan pelagic crenarchaeota, J. Lipid Res., 43, 1641–1651, 2002.

Sinninghe Damsté, J. S., Ossebaar, J., Schouten, S., and Verschuren, D.: Altitudinal shifts in the branched tetraether lipid distribution in soil from Mt. Kilimanjaro (Tanzania): implications for the MBT/CBT continental palaeothermometer, Org. Geochem., 39, 1072–1076, 2008.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Hopmans, E. C., Weijers, J. W. H., Foesel, B. U., Overmann, J., and Dedysh, S. N.: 13,16-Dimethyl octacosanedioic acid (iso-Diabolic Acid), a common membrane-spanning lipid of *Acidobacteria* subdivisions 1 and 3, Appl. Environ. Microbiol., 77, 4147–4154, 2011.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Hopmans, E. C., Jung, M. Y., Kim, J. G., Rhee, S. K., Stieglmeier, M., and Schleper, C.: Intact polar and core glycerol dibiphytanyl glycerol tetraether lipids of group I.1a and I.1b *Thaumarchaeota* in soil, Appl. Environ. Microbiol., 78, 6866–6874, 2012.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Hopmans, E. C., Foesel, B. U., Wüst P. K., Overmann, J., Tank, M., Bryant, D. A., Dunfield, P. F., Houghton, K., and Stott, M. B.: Ether- and ester-bound iso-diabolic acid and other lipids in members of *Acidobacteria* subdivision 4, Appl. Environ. Microb., 80, 5207–5218, 2014.

Spang, A., Hatzenpichler, R., Brochier-Armanet, C., Rattei, T., Tischler, P., Spieck, E., Streit, W., Stahl, D. A., Wagner, M., and Schleper, C.: Distinct gene set in two different lineages of ammonia-oxidizing archaea supports the phylum *Thaumarchaeota*, Trends Microbiol., 18, 331–340, 2010.

Stahl, D. A. and de la Torre, J. R.: Physiology and diversity of ammonia-oxidizing archaea, Annu. Rev. Microbiol., 66, 83–101, 2012.

Stieglmeier, M., Klingl, A., Alves, R. J. E., Rittmann, S. K. M. R., Melcher, M., Leisch, N., and Schleper, C.: Nitrososphaera viennensis gen. nov., sp. nov., an aerobic and mesophilic, ammonia-oxidizing archaeon from soil and a member of the archaeal phylum *Thaumarchaeota*, Int. J. Syst. Evol. Microbiol., 64, 2738–2752, 2014.

Thauer, R. K., Kaster, A.-K., Seedorf, H., Buckel, W., and Hedderich, R.: Methanogenic archaea: ecologically relevant differences in energy conservation, Nat. Rev. Microbiol., 6, 579–591, 2008.

Tierney, J. E. and Russell, J. M.: Distributions of branched GDGTs in a tropical lake system: implications for lacustrine application of the MBT/CBT paleoproxy, Org. Geochem., 40, 1032–1036, 2009.

Tierney, J. E., Schouten, S., Pitcher, A., Hopmans, E. C., and Sinninghe Damsté, J. S.: Core and intact polar glycerol dialkyl glycerol tetraethers (GDGTs) in Sand Pond, Warwick, Rhode Island (USA): insights into the origin of lacustrine GDGTs, Geochim. Cosmochim. Ac., 77, 561–581, 2012.

Wang, H., Liu, W., Zhang, C. L., Liu, Z., and He, Y.: Branched and isoprenoid tetraether (BIT) index traces water content along two marsh-soil transects surrounding Lake Qinghai: implications for paleo-humidity variation, Org. Geochem., 59, 75–81, 2013.

Wang, H., Liu, W., and Zhang, C. L.: Dependence of the cyclization of branched tetraethers on soil moisture in alkaline soils from arid–subhumid China: implications for palaeorainfall reconstructions on the Chinese Loess Plateau, Biogeosciences, 11, 6755–6768, doi:10.5194/bg-11-6755-2014, 2014.

Watanabe, T., Kimura, M., and Asakawa, S.: Community structure of methanogenic archaea in paddy field soil under double cropping (rice-wheat), Soil Biol. Biochem., 38, 1264–1274, 2006.

Watanabe, T., Kimura, M., and Asakawa, S.: Distinct members of a stable methanogenic archaeal community transcribe mcrA genes under flooded and drained conditions in Japanese paddy field soil, Soil Biol. Biochem., 41, 276–285, 2009.

Weijers, J. W. H., Schouten, S., Hopmans, E. C., Geenevasen, J. A. J., David, O. R. P., Coleman, J. M., Pancost, R. D., and Sinninghe Damsté, J. S.: Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits, Environ. Microbiol., 8, 648–657, 2006a.

Weijers, J. W. H., Schouten, S., Spaargaren, O. C., and Sinninghe Damsté, J. S.: Occurrence and distribution of tetraether membrane lipids in soils: implications for the use of the TEX_{86} proxy and the BIT index, Org. Geochem., 37, 1680–1693, 2006b.

Weijers, J. W. H., Schouten, S., van den Donker, J. C., Hopmans, E. C., and Sinninghe Damsté, J. S.: Environmental controls on bacterial tetraether membrane lipid distribution in soils, Geochim. Cosmochim. Ac., 71, 703–713, 2007.

Weijers, J. W. H., Panoto, E., van Bleijswijk, J., Schouten, S., Rijpstra, W. I. C., Balk, M., Stams, A. J. M., and Sinninghe Damsté, J. S.: Constraints on the biological source(s) of the orphan branched tetraether membrane lipids, Geomicrobiol. J., 26, 402–414, 2009.

Weijers, J. W. H., Wiesenberg, G. L. B., Bol, R., Hopmans, E. C., and Pancost, R. D.: Carbon isotopic composition of branched tetraether membrane lipids in soils suggest a rapid turnover and a heterotrophic life style of their source organism(s), Biogeosciences, 7, 2959–2973, doi:10.5194/bg-7-2959-2010, 2010.

Wu, J.: Carbon accumulation in paddy ecosystems in subtropical China: evidence from landscape studies, Eur. J. Soil Sci., 62, 29–34, 2011.

Xiong, Z. Q., Xing, G. X., and Zhu, Z. L.: Nitrous oxide and methane emissions as affected by water, soil and nitrogen, Pedosphere, 17, 146–155, 2007.

Zink, K.-G., Vandergoes, M. J., Mangelsdorf, K., Dieffenbacher-Krall, A. C., and Schwark, L.: Application of bacterial glycerol dialkyl glycerol tetraethers (GDGTs) to develop modern and past temperature estimates from New Zealand lakes, Org. Geochem., 41, 1060–1066, 2010.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Table 1. List of sampling areas, environmental characteristics and minimum as well as maximum of GDGT proportions (expressed as a percentage of total GDGTs or as indices).

Country	Sampling area	Soil type	Dataset	N	MAT	MAP	SOC (%)		pH		iGDGTs (%)		brGDGTs (%)	
			code		(°C)	(mm)	Min	Max	Min	Max	Min	Max	Min	Max
Italy	Zeme	Upland	IT-NP	1	12.5	954	0.73		4.1		25.1		74.9	
		Paddy	IT-P	1	12.5	954	1.15		4.9		9.6		90.4	
	Vercelli	Paddy	IT-P	4	12.1	923			6.1	7.0	5.5	11.5	88.5	94.5
China	Cixi	Marsh	C-Marsh	3	16.6	1266	0.43	0.63	8.0	8.0	12.4	29.8	70.2	87.6
		Upland	C-NP	5	16.6	1266	0.72	1.10	6.0	8.2	15.2	35.0	65.0	84.8
		Paddy	C-P	21	16.6	1266	0.92	2.88	5.2	7.5	7.7	22.5	77.5	92.3
	Red Soil Station	Upland	C-NP	3	18.5	1731	0.70	0.85	4.1	5.1	15.5	16.0	84.0	84.5
		Paddy	C-P	5	18.5	1731	2.04	2.75	4.2	4.5	6.6	11.4	88.6	93.4
Indonesia	Jasinga	Upland	JAV-NP	3	26.9	3252	2.08	3.22	3.8	5.6	5.6	9.1	90.9	94.4
		Paddy	JAV-P	4	26.9	3252	1.97	2.30	4.2	4.4	0.9	2.0	98.0	99.1
	Ngawi	Upland	JAV-NP	3	27.0	2034	1.46	1.74	4.7	5.4	6.9	14.2	85.8	93.1
		Paddy	JAV-P	3	27.0	2034	1.40	1.81	6.4	7.2	6.8	9.5	90.5	93.2
	Padas	Paddy	JAV-P	1	26.7	2162	1.73		6.8		15.3		84.7	
	Simo village	Paddy	JAV-P	3	26.9	2100	1.52	1.86	6.9	7.5	15.4	23.2	76.8	84.6
	Sukabumi	Upland	JAV-NP	3	23.5	2806	3.50	4.34	4.4	4.8	13.6	22.9	77.1	86.4
		Paddy	JAV-P	3	23.5	2806	4.02	4.41	5.1	5.3	5.5	6.1	93.9	94.5
	Sumbermujer	Paddy	JAV-P	1	17.8	2693	2.49		5.2		11.5		88.5	
		Bamboo	JAV-Bamb	1	17.8	2693	3.57		5.2		3.1		96.9	
	Sumatra	Paddy	SUM-P	4	21.8	2170	1.39	2.54	4.7	5.4	6.5	10.2	89.8	93.5
Philippines	Ifugao	Forest	PH-For	3	21.4	2376	2.38	3.22	4.8	5.2	1.8	3.5	96.5	98.2
		Upland	PH-NP	5	21.4	2376	1.21	2.09	4.4	5.6	2.7	7.3	92.7	97.3
		Paddy	PH-P	10	21.4	2376	1.16	5.04	4.3	5.5	3.6	17.6	82.4	96.4
	Laguna	Upland	PH-NP	5	27.1	2064	1.77	2.17	5.1	5.7	4.0	10.0	90.0	96.0
		Paddy	PH-P	10	27.1	2064	1.59	4.01	4.7	6.2	7.8	13.9	86.1	92.2
	Nueva Ecija	Upland	PH-NP	4	27.1	1821	0.54	1.30	4.6	6.5	6.7	25.7	74.3	93.3
		Paddy	PH-P	10	27.1	1821	0.83	1.95	4.3	6.2	5.7	14.4	85.6	94.3
Vietnam	Hai Duong	Upland	VN-NP	2	24.1	1608	0.79	1.17	4.9	7.4	7.7	10.4	89.6	92.3
		Paddy	VN-P	8	24.1	1608	1.13	1.68	4.8	5.7	4.6	9.0	91.0	95.4
	Lào Cai	Bamboo	VN-Bamb	1	16.2	2223	2.97		4.2		2.3		97.7	
		Bushland	VN-Bush	2	16.2	2223	2.56	3.32	4.1	4.4	4.1	4.4	95.6	95.9
		Forest	VN-For	2	16.2	2223	2.77	3.88	4.1	4.1	3.0	3.6	96.4	97.0
		Paddy	VN-P	10	16.2	2223	0.83	2.48	4.3	5.2	4.8	10.7	89.3	95.2
	Tien Giang	Paddy	VN-P	13	27.4	1450	2.06	4.43	3.7	4.8	7.6	10.9	89.1	92.4
	Vinh Phúc	Bamboo	VN-Bamb	1	23.6	1687	0.69		4.3		4.4		95.6	
		Forest	VN-For	1	23.6	1687	1.30		3.8		8.1		91.9	
		Upland	VN-NP	3	23.6	1687	0.58	1.64	4.0	6.1	5.0	18.8	81.2	95.0
		Paddy	VN-P	8	23.6	1687	1.12	2.41	4.3	4.8	9.1	16.1	83.9	90.9

Table 1. Continued.

Country	Sampling area	Soil type	Dataset code	N	MAT (°C)	MAP (mm)	GDGT-0/cren		$\text{Tex}_{86'}$		CBT		MBT′		T_{MC} (°C)
							Min	Max	Min	Max	Min	Max	Min	Max	mean
Italy	Zeme	Upland	IT-NP	1	12.5	954	0.42		0.66		1.41		0.52		8.8
		Paddy	IT-P	1	12.5	954	2.67		0.44		0.90		0.51		11.6
	Vercelli	Paddy	IT-P	4	12.1	923	0.37	1.53	0.54	0.71	0.14	0.65	0.33	0.49	11.6
China	Cixi	Marsh	C-Marsh	3	16.6	1266	0.22	0.57	0.64	0.72	−0.03	0.38	0.47	0.50	14.7
		Upland	C-NP	5	16.6	1266	0.14	0.37	0.62	0.72	−0.02	0.19	0.53	0.63	18.2
		Paddy	C-P	21	16.6	1266	0.29	5.77	0.30	0.68	0.26	0.67	0.49	0.70	16.8
	Red Soil Station	Upland	C-NP	3	18.5	1731	0.32	0.48	0.76	0.78	1.56	2.13	0.72	0.77	13.3
		Paddy	C-P	5	18.5	1731	2.07	3.51	0.49	0.68	0.99	1.21	0.69	0.76	17.1
Indonesia	Jasinga	Upland	JAV-NP	3	26.9	3252	0.20	0.89	0.72	0.84	0.64	1.86	0.92	0.96	22.0
		Paddy	JAV-P	4	26.9	3252	2.01	2.26	0.61	0.68	1.60	1.83	0.91	0.92	19.3
	Ngawi	Upland	JAV-NP	3	27.0	2034	0.12	0.16	0.72	0.74	0.84	1.15	0.92	0.94	24.0
		Paddy	JAV-P	3	27.0	2034	0.58	1.20	0.68	0.71	0.34	0.65	0.72	0.80	21.8
	Padas	Paddy	JAV-P	1	26.7	2162	0.40		0.70		0.42		0.83		24.1
	Simo village	Paddy	JAV-P	3	26.9	2100	0.38	1.24	0.71	0.75	0.29	0.38	0.67	0.82	21.8
	Sukabumi	Upland	JAV-NP	3	23.5	2806	0.36	1.28	0.66	0.72	0.90	1.48	0.88	0.90	21.3
		Paddy	JAV-P	3	23.5	2806	0.38	0.45	0.68	0.71	1.16	1.24	0.77	0.80	18.4
	Sumbermujer	Paddy	JAV-P	1	17.8	2693	2.73		0.42		0.82		0.79		20.6
		Bamboo	JAV-Bamb	1	17.8	2693	1.80		0.63		1.10		0.95		23.9
	Sumatra	Paddy	SUM-P	4	21.8	2170	0.49	5.78	0.46	0.71	0.94	1.34	0.75	0.82	19.1
Philippines	Ifugao	Forest	PH-For	3	21.4	2376	0.32	1.05	0.59	0.69	0.74	0.88	0.80	0.87	22.3
		Upland	PH-NP	5	21.4	2376	0.39	2.02	0.59	0.70	0.78	1.27	0.81	0.90	22.1
		Paddy	PH-P	10	21.4	2376	3.67	121.6	0.45	0.58	0.70	1.23	0.63	0.80	18.1
	Laguna	Upland	PH-NP	5	27.1	2064	0.14	2.48	0.68	0.85	0.56	1.39	0.87	0.94	23.8
		Paddy	PH-P	10	27.1	2064	0.19	5.65	0.50	0.86	0.70	1.08	0.77	0.89	21.2
	Nueva Ecija	Upland	PH-NP	4	27.1	1821	0.17	0.92	0.74	0.83	0.51	1.33	0.85	0.91	23.0
		Paddy	PH-P	10	27.1	1821	0.15	9.66	0.48	0.81	0.52	1.65	0.73	0.86	19.2
Vietnam	Hai Duong	Upland	VN-NP	2	24.1	1608	0.40	1.66	0.59	0.76	−0.04	0.91	0.71	0.73	20.6
		Paddy	VN-P	8	24.1	1608	1.42	5.63	0.45	0.59	0.45	0.81	0.65	0.72	18.3
	Lào Cai	Bamboo	VN-Bamb	1	16.2	2223	0.95		0.66		1.26		0.89		21.2
		Bushland	VN-Bush	2	16.2	2223	1.31	3.08	0.65	0.73	1.36	1.61	0.90	0.90	20.3
		Forest	VN-For	2	16.2	2223	0.83	1.10	0.63	0.72	1.23	1.60	0.87	0.89	20.1
		Paddy	VN-P	10	16.2	2223	0.79	20.73	0.35	0.62	0.80	1.44	0.59	0.86	15.7
	Tien Giang	Paddy	VN-P	13	27.4	1450	0.72	17.39	0.54	0.61	0.99	1.14	0.79	0.85	20.4
	Vinh Phúc	Bamboo	VN-Bamb	1	23.6	1687	0.66		0.75		1.83		0.95		19.8
		Forest	VN-For	1	23.6	1687	0.55		0.79		2.00		0.86		16.1
		Upland	VN-NP	3	23.6	1687	0.57	1.30	0.75	0.77	0.88	1.77	0.87	0.93	20.7
		Paddy	VN-P	8	23.6	1687	0.88	8.19	0.50	0.70	0.88	1.60	0.75	0.85	18.4

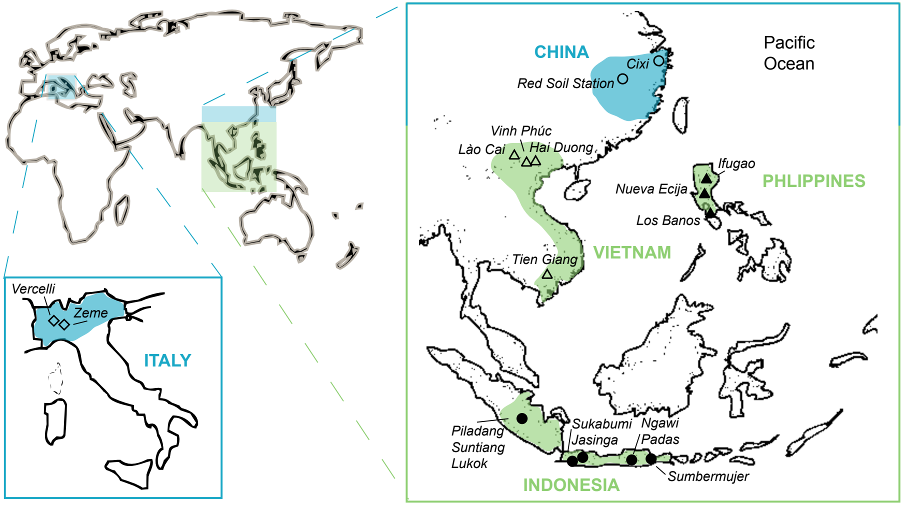

Figure 1. Map of sampling locations. Blue coloured area denotes subtropical sampling locations and green denotes tropical sampling locations.

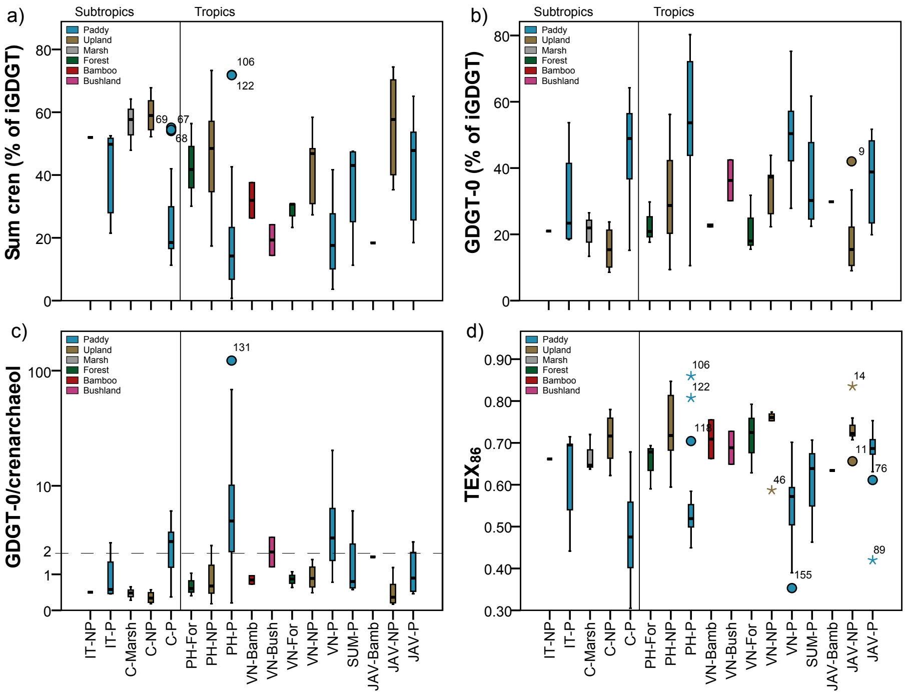

Figure 2. Box-plot diagrams of **(a)** crenarchaeol, **(b)** GDGT-0, **(c)** GDGT-0/crenarchaeol ratio and **(d)** TEX_{86} in upland (NP, brown), paddy (P, blue), marsh (grey), forest (For), bamboo cultivated (Bamb, red) and bushland (Bush, violet) soils. Abbreviations refer to different sampling locations: Italy (IT), China (C), Philippines (PH), Vietnam (VN), Sumatra (SUM) and Java (JAV). The vertical line separates subtropical from tropical locations. Numbers in all plots indicate samples listed in Table S1. The dotted line in **(c)** marks the GDGT-0/crenarchaeol value of 2 that is the boundary to higher proportions of methanogens, which reveal values > 2. Note the logarithmic scale for GDGT-0/crenarchaeol ratios.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◄|
|►
◄
►
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

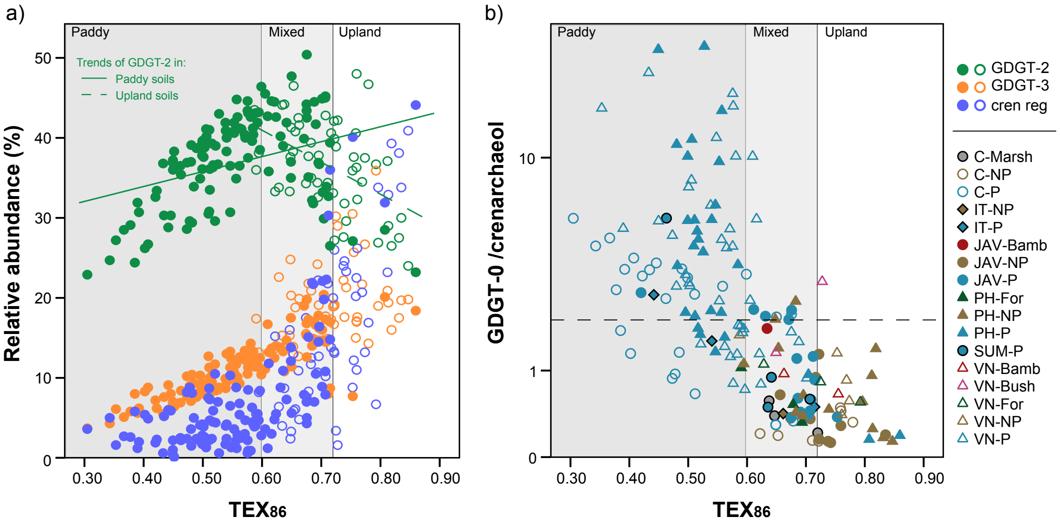

Figure 3. Cross-plots showing **(a)** the relative abundance (% of the sum of GDGT-1, -2, -3 and crenarchaeol regioisomer) vs. TEX_{86} and **(b)** the relationship between the most abundant iGDGTs (GDGT-0 and crenarchaeol) and lower concentrated iGDGTs as TEX_{86} and lower concentrated iGDGTs (GDGT-1, -2, -3, and crenarchaeol regioisomer) as TEX_{86}. GDGT-0/crenarchaeol > 2 and $\text{TEX}_{86} < 0.6$ are diagnostic for methanogens. Two outliers from the Ifugao site (Philippines) with GDGT-0/crenarchaeol ratio > 69 were excluded from the figure. Note the logarithmic scale for GDGT-0/crenarchaeol ratios. The filled circles in **(a)** denote paddy soils and the non-filled circles denote upland, marsh, forest, bamboo and bushland soils.

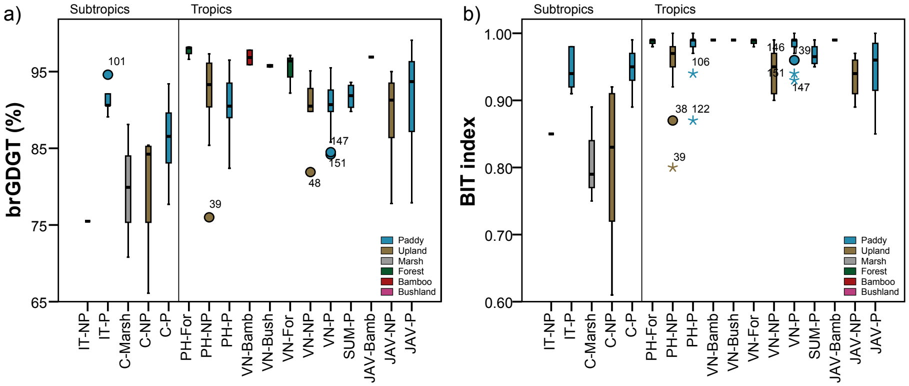

Figure 4. Box-plot diagrams of **(a)** relative proportion of brGDGT in the total GDGT pool and **(b)** the BIT index in soil. Note different symbols (circle or asterisk) for outliers that are more than 1.5 (or 3) box lengths from one hinge of the box. Abbreviations and subdivisions as in Fig. 2.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

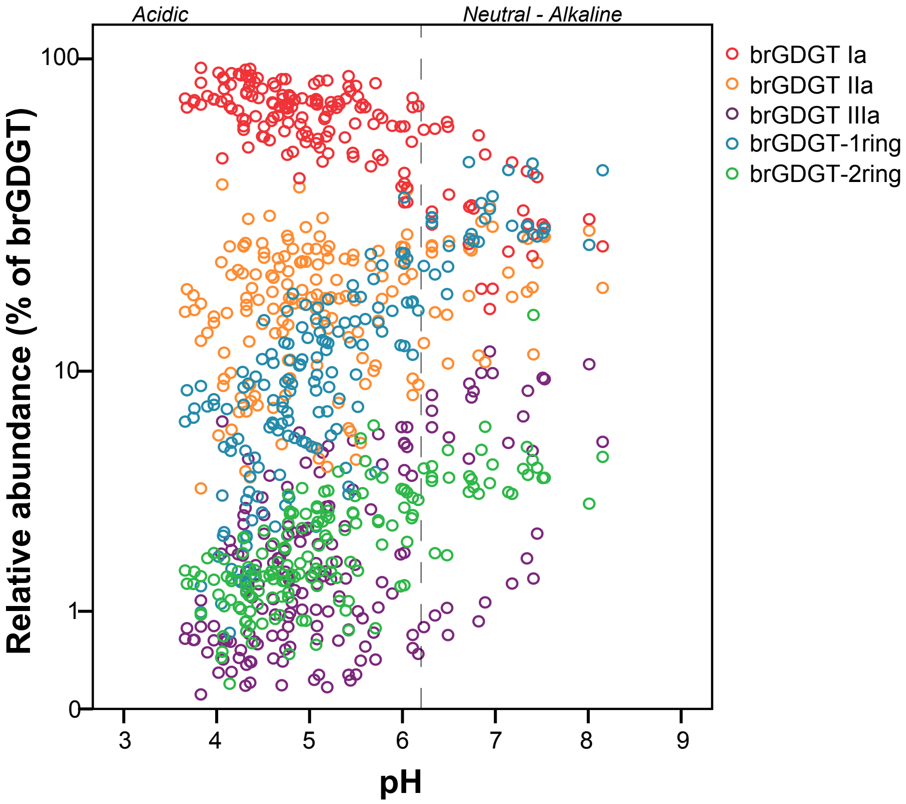

Figure 5. Relative abundance of brGDGT plotted vs. measured soil pH. Note logarithmic scale for relative abundance. Dotted line separates acidic from neutral/alkaline soil.

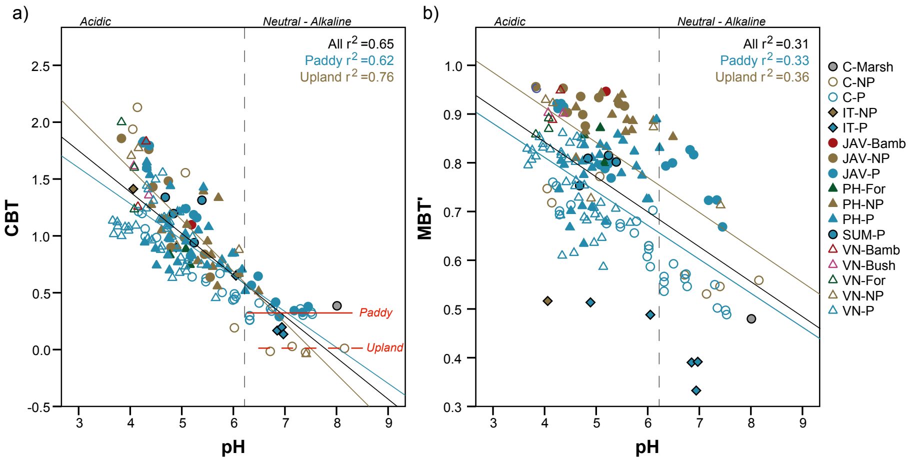

Figure 6. Plot of **(a)** the cyclization ratio of branched tetraethers (CBT) vs. soil pH and of **(b)** the revised methylation index of branched tetraethers (MBT′) vs. soil pH. Dotted line separates acidic from neutral/alkaline soil. Regressions line of all soils is coloured in black, the line of upland, marsh, forest, bamboo and bushland soils is brown and the line for paddy soils is blue. Abbreviations as in Fig. 2. Red lines in **(a)** show the offset between paddy and upland soil, which have > 6.2 pH values.

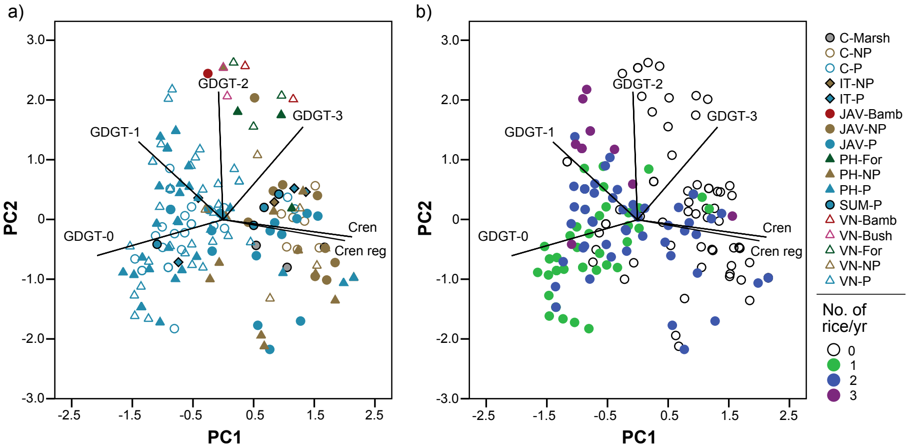

Figure 7. Principal component analysis (PCA) based on standardized relative abundances of six iGDGTs in 170 investigated soils. The first principal component (PC1) accounted for 53.9 % of the total variance and the second (PC2) for 29.9 %. **(a)** Symbols and colours denote different management forms. Abbreviations as in Fig. 2. **(b)** The sample site symbols are indicative of the number of rice cultivation cycles per year.

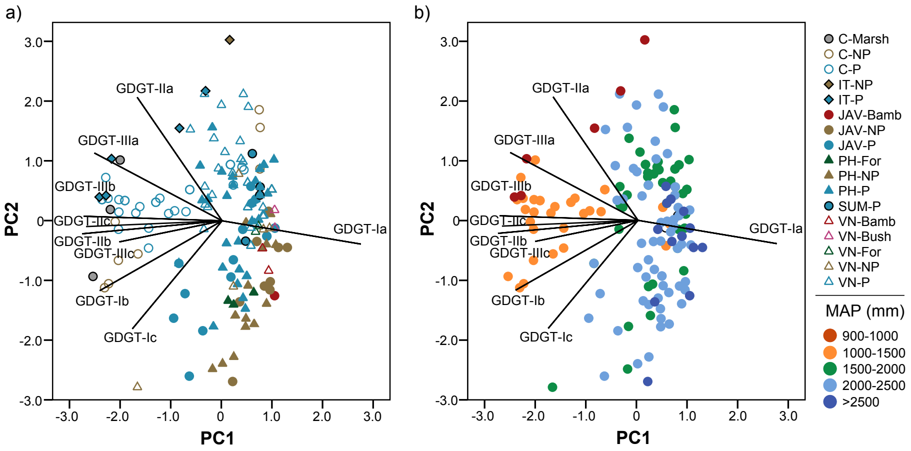

Figure 8. Principal component analysis (PCA) based on standardized relative abundances of nine brGDGTs in 170 investigated soils. The first principal component (PC1) accounts for 69.1 % of the variance and the second (PC2) for 14.3 %. **(a)** Symbols and colours denote different management forms. Abbreviations as in Fig. 2. **(b)** The sample site symbols are indicative of the mean annual precipitation.

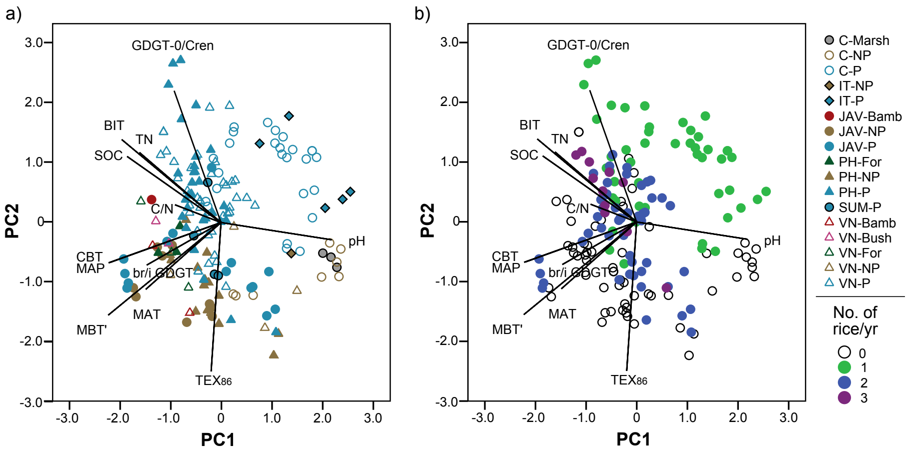

Figure 9. Principal component analysis (PCA) based on commonly used indices and ratios for the 170 investigated soils. The first principal component (PC1) accounts for 33.5 % of the variance and the second (PC2) for 21.4 %. **(a)** Symbols and colours denote different management forms. Abbreviations as in Fig. 2. **(b)** The sample site symbols are indicative of the number of rice cultivation cycles per year.

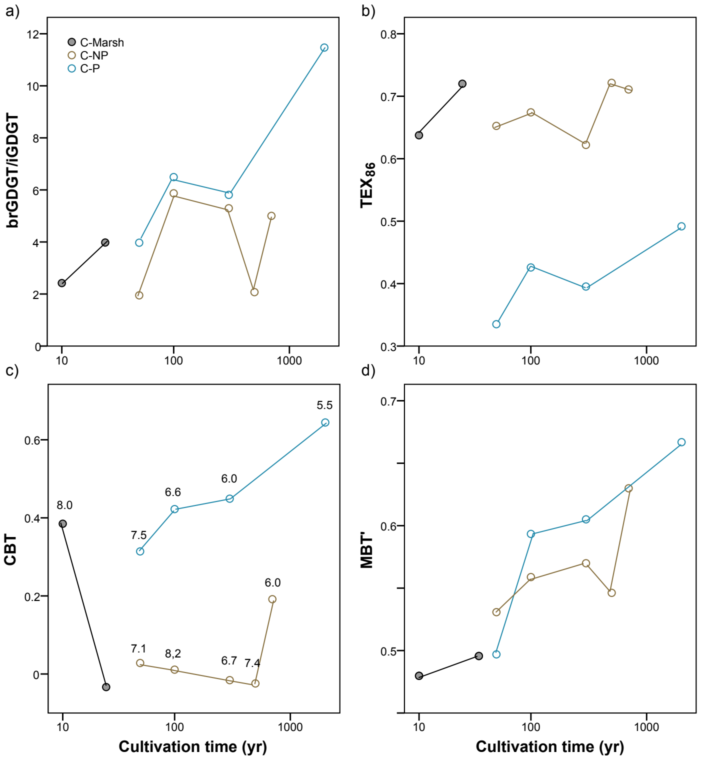

Figure 10. Time plots of various GDGT ratios and indices in soils of the Chinese Cixi region: **(a)** ratio of branched vs. isoprenoid GDGTs, **(b)** the TEX_{86}, **(c)** the CBT and **(d)** MBT′. Note logarithmic scale for the cultivation time. Numbers in plot **(c)** reflect soil pH values.

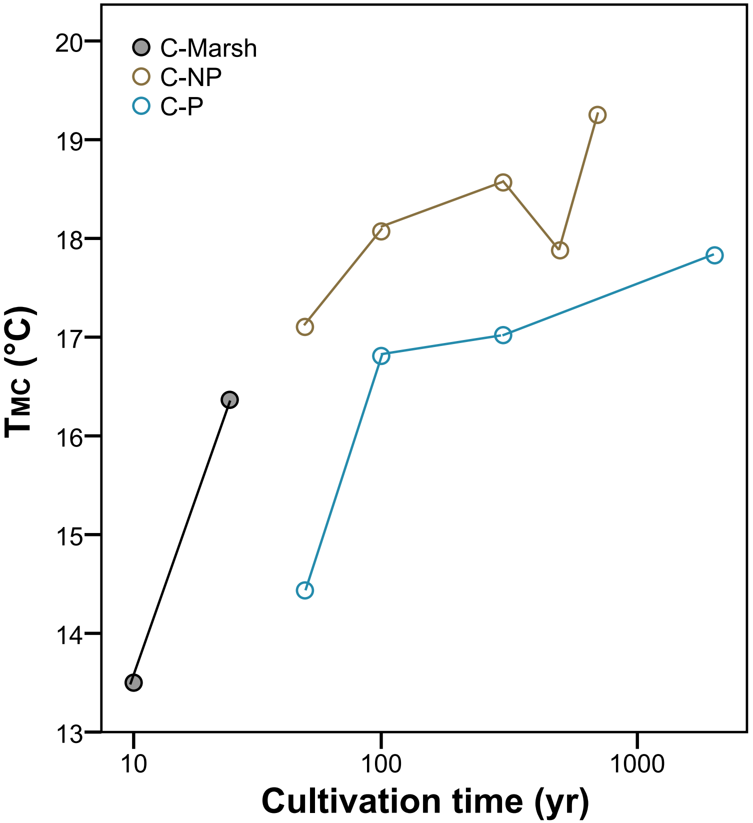

Figure 11. Time plot of MBT′-CBT derived temperatures (T_{MC}) in soils of the Chinese Cixi. Note logarithmic scale for cultivation time.

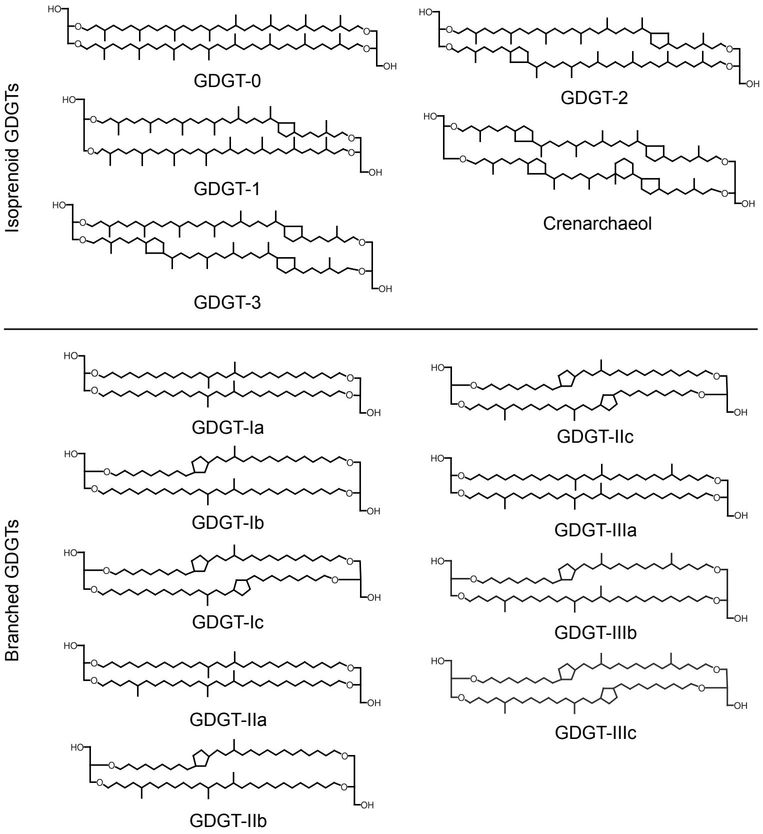

Figure A1. Chemical structures of branched GDGTs (brGDGTs) and isoprenoid GDGTs (iGDGTs) investigated in this study.