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# Occurrence and distribution of extractable and non-extractable GDGTs in podzols: implications for the reconstruction of mean air temperature

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Glycerol dialkyl glycerol tetraethers (GDGTs) are complex lipids of high molecular weight, present in cell membranes of archaea and some bacteria. Archaeal membranes are formed predominantly by isoprenoid GDGTs with acyclic or ring-containing biphytanyl chains. Another type of GDGTs with branched instead of isoprenoid alkyl chains was recently discovered in soils. Branched tetraethers were suggested to be produced by anaerobic bacteria and can be used to reconstruct past air temperature and soil pH. Lipids preserved in soils can take two broad chemical forms: extractable lipids, recoverable upon solvent extraction, and non-extractable lipids, linked to the organic or mineral matrix of soils. Moreover, within the extractable pool, core (i.e. "free") lipids and intact polar (i.e. "bound") lipids can be distinguished. These three lipid fractions may respond to environmental changes in different ways and the information derived from these three pools may differ. The aim of the present work was therefore to compare the abundance and distribution of the three GDGT pools in two contrasted podzols: a temperate podzol located 40 km north of Paris and a tropical podzol from the upper Amazon Basin. Five samples were collected from the whole profile of the temperate podzol including the litter layer. Five additional samples were obtained from three profiles of the tropical soil sequence, representative of the transition between a latosol and a well-developed podzol. Vertical and/or lateral variations in GDGT content and composition were highlighted. In particular, in the tropical sequence, GDGTs were present at relatively low concentrations in the early stages of podzolisation and were more abundant in the well-developed podzolic horizons, where higher acidity and increased bacterial activity may favour their stabilization. Concerning the temperate podzol, GDGT distribution was shown to vary greatly with depth in the soil profile, the methylation degree of bacterial GDGTs being notably higher in the surficial than in the deep soil horizons. Bacterial GDGTs were also detected in the litter layer of the temperate podzol, suggesting the presence of branched-GDGT producing bacteria in the litter, probably in anoxic microenvironments. Last, we showed for the first time that substantial amounts of non-extractable GDGTs could be released after acid hydrolysis of solvent-extracted soils, since non-extractable lipids represented in average ca. 25% of total (i.e. extractable + non-extractable) bacterial GDGTs and ca. 30% of total archaeal GDGTs in podzol samples. In addition, we observed that extractable and non-extractable GDGTs could present different distribution patterns. Thus, the average methylation degree of bacterial GDGTs was higher in the extractable than in the non-extractable lipid fraction in three soil horizons of the temperate podzol. Consequently, different mean air temperature values could be derived from extractable and non-extractable bacterial GDGT distributions, suggesting that data obtained from the extractable lipid fraction have to be interpreted with care. MAT values derived from non-extractable GDGTs were shown to be more consistent with MAT records, implying that MAT estimates obtained from the non-extractable pool might be more reliable.