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Evolution of lipid abundance and molecular composition during the podzolisation of laterites in the upper Amazon basin

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Abstract In the upper Amazon basin, podzolisation involves the remobilization of large amounts of organic matter and chemical elements (Fe, Al, Si) previously accumulated in lateritic formations. In order to better understand the fate of organic matter in podzolic environments in this area, the evolution of lipid abundance and molecular composition were studied along a representative soil sequence showing the transition between a latosol and a well-developed podzol. Total solvent extracts were obtained from eight key soil samples from three profiles and their overlying litters, and enable us to follow both lateral and vertical evolutions. Lipid composition was determined by gas chromatography-mass spectrometry (GC-MS). Major compound classes include alkanes, alkanones, alkanols, alkanoic acids, ω-hydroxyacids, as well as aromatics, steroids and triterpenoids. Free lipids do not accumulate in the early stages of podzolisation but are abundant in well-developed podzolic horizons, possibly due to (i) combined acidity and waterlogging, (ii) limited amounts of complexing elements, (iii) a decreased microbial activity. The evolution of lipid composition is consistent with podzolisation mechanisms previously highlighted in the sequence. This paper provides further evidence for the occurrence of anoxic conditions in deep waterlogged podzolic horizons. It also shows that aromatic, phytotoxic compounds are stabilized in the well-developed podzol. This may play a role in the vegetation changes associated with podzolisation in the area.

Keywords Amazon basin · Podzols · Soil organic matter · Lipids

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Introduction

With an estimated stock of about $1{,}500 \times 10^{12}$ kg carbon, soil is the largest carbon reservoir in terrestrial ecosystems (e.g. Eswaran et al. 1993; Amundson 2001) and thus plays a major role in the global carbon cycle. Mechanisms of soil organic matter (SOM) stabilization are of great interest since they could lead to enhanced carbon sequestration and thus reduced CO_2 net emissions. Among SOM pools, lipids were

shown to be highly resistant to biodegradation in certain soils and horizons and are therefore likely to be stabilized in soils (e.g. Dinel et al. 1990). Their tendency to decrease soil fertility (e.g. Jambu et al. 1978) suggests that they may play a role in soil degradation mechanisms.

Soil lipids are mainly plant-derived, although macro- and microfauna can also contribute to this pool (e.g. Dinel et al. 1990). Free lipids are extracted from soil with organic solvents and comprise a wide variety of components like acids, alkanols, hydrocarbons, ketones, steroids and triterpenoids (Morrison 1969). Additional lipidic moieties occur either within macromolecules like cutin and suberin (Kolattukudy 1980) or bound to other mineral or organic soil constituents (e.g. Amblès et al. 1989a; Allard 2006). However, the release of bound lipids in the laboratory requires soil pretreatment and only free lipids will be considered in the present study.

Lipid evolution is affected by a wide range of factors such as pH (e.g. Jambu et al. 1985; Nierop et al. 2005), clay content (e.g. Amblès et al. 1989a), moisture and redox conditions (e.g. Jaffé et al. 1996) and microbial activity (e.g. Jambu et al. 1985). In turn, lipids can also affect soil properties and their accumulation is generally associated with low fertility (e.g. Jambu et al. 1978). Due to their hydrophobicity, their adsorption to soil surfaces can reduce aggregate stability or water retention (e.g. Jambu et al. 1978; Dinel et al. 1990). Some of them, in particular alkanoic acids, can also react with polyvalent cations (e.g. Dinel et al. 1990). Furthermore, they can be toxic towards soil microorganisms (e.g. Fustec-Mathon et al. 1975; Jambu et al. 1978) and inhibit seed germination and plant growth (e.g. Wang 1969). The study of soil lipids can thus provide information on the sources of SOM, microbial activity, the pathways of degradation and/or stabilisation of SOM, as well as a record of some soil physico-chemical characteristics. Free lipids have been reported to accumulate in acidic soils like podzols (e.g. Stevenson 1966; Jambu et al. 1978), and waterlogging may further increase their stabilization (Jambu et al. 1978). In such environments, they can represent up to 20% of SOM (Stevenson 1966).

In the Amazon basin, do Nascimento et al. (2004) recently described the development of waterlogged podzols, lying in depressions of low plateaux, at the expense of higher elevated and well drained clay-depleted laterites. They highlighted the occurrence of a localized transformation front between laterites and podzols. Organic matter in general plays a major role in podzol development (Lundström et al. 2000) and lipids in particular could take part in the podzolisation process (Jambu et al. 1978) due to their degrading effect on soil properties. Many studies have focused on the fate of lipids in podzols (e.g. Amblès et al. 1989a, b, 1993; Jambu et al., 1978, 1991, 1993; Naafs et al. 2004b; Quénéa et al. 2004, 2006). They enabled a better understanding of the sources and fate of lipids in podzolic environments. However, these studies deal with podzols developed under temperate climates and are generally restricted to surface horizons, although Naafs et al. (2004b) studied the vertical evolution of lipid composition along a whole podzolic profile. The site described by do Nascimento et al. (2004) therefore offers a unique opportunity to study for the first time the evolution of lipids (i) in tropical podzols, (ii) in the different steps of their development.

The present study focuses on free lipids extracted from eight key soil horizons from three soil profiles representative of the development of podzols in the upper Amazon basin, as well as their overlying leaf litter. Free lipid abundance and composition are assessed during the different stages of podzol development in order to elucidate their origin and fate during this evolution. Stabilization/destabilization mechanisms likely to influence lipid abundance and composition are analysed. The results are discussed in relation with the impact of podzol development on lipid dynamics and potential implications of lipids on the podzolisation process itself.

Materials and methods

Samples

A precise description of the investigated site can be found in do Nascimento et al. (2004). Briefly, it is located on the low elevation plateaux of the Jau national park (upper Amazon basin, Fig. 1a). It is preserved from human activity and has a hot humid tropical climate with mean annual temperature and precipitation of 26°C and 2,000 mm, respectively. The studied samples belong to a 200 m long and 2–3 m deep soil sequence along which podzolic soils

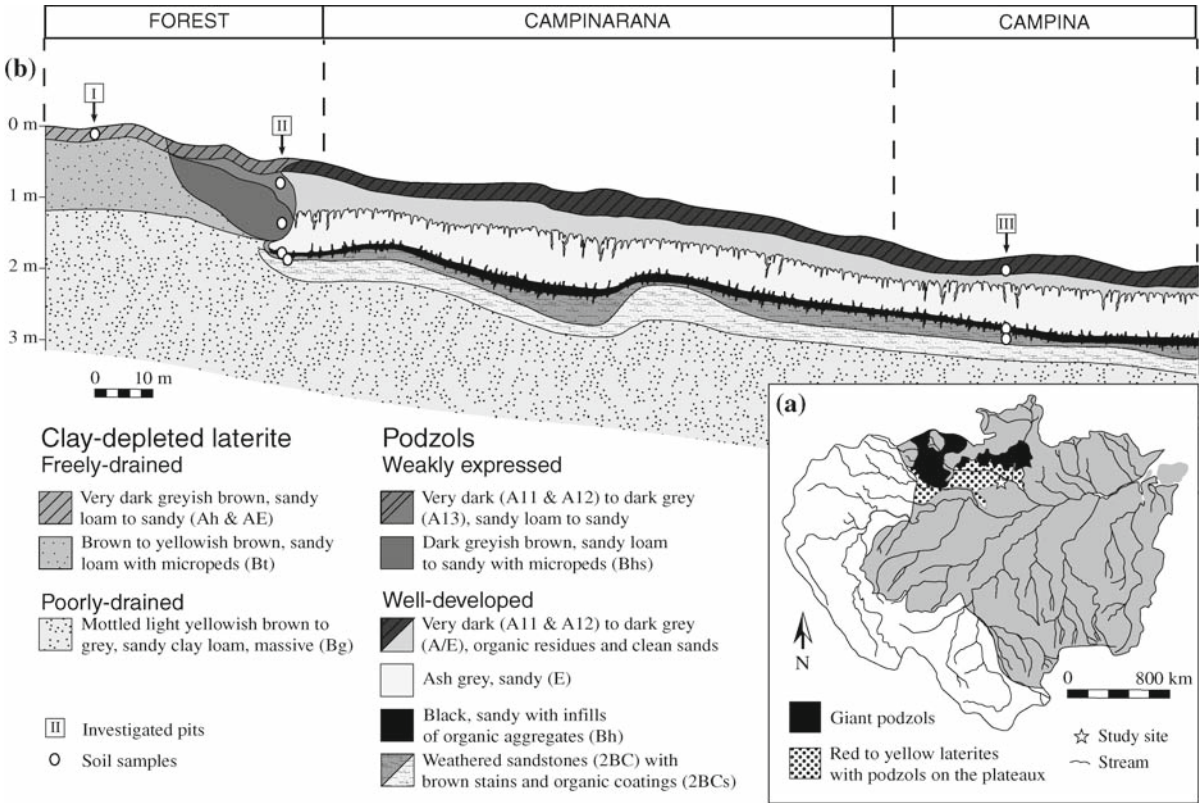

Fig. 1 (**a**) Site location (star) on a simplified soil map of the Amazon basin, (**b**) simplified representation of the soil catena from a high to low elevation point of the plateau with investigated horizons (white dots). Adapted from do Nascimento et al. (2004)

develop at the expense of yellow clay-depleted laterites (Fig. 1b). Podzols are located in a depression while laterites remain in higher positions.

Eight organic-rich horizons were selected in three profiles (I, II, III) along the sequence (Fig. 1b). They belong either to subsurface organo-mineral horizons (A) or deep illuviated horizons (B, BC) with accumulations of OM (suffix h) and/or metals (Fe and Al, suffix s). One of them (I AE) was sampled at the surface of the yellow clay-depleted laterite. Two (II A12, II Bhs) come from the upper part of pit II and belong to horizons of weakly expressed podzols at the margin of the depression. The other five (II Bh, II 2BCs, III A12, III Bh, and III 2BCs) are specific to horizons of well-expressed podzols, sampled at the bottom part of pit II and towards the centre of the depression on the whole profile of pit III. The density of roots is greatest in surface horizons and decreases rapidly with depth. Moreover, 2BCs horizons are indurated and thus less permeable than upper horizons. Soil samples were collected from the freshly cleaned faces of soil pits. They were air-dried, sieved through a 2-mm screen and stored in the dark in sealed glass jars prior to analyses.

A vegetation change is observed along the sequence. Pit I is overlain by evergreen forest, while vegetation types typical of sandy and periodically waterlogged soils of the Rio Negro basin (Anderson 1981) cover the rest of the sequence. Pit II is at the transition between evergreen forest and *Campinarana*, which consists of lower and very dense tree populations. At last, pit III is overlain by *Campina*, a shrub savannah including grasses and lichens. Decaying litter overlying each pit was additionally sampled and air-dried.

pH measurement

pH was measured in water with a 1:2.5 soil:water ratio.

Solvent extraction, lipid separation and derivatization

In the present study, the term "free lipids" refers to the pool of OM extracted from soil with a dichloromethane:methanol mixture without pre-treatment, as described hereafter. Visible roots were hand-removed prior to extraction. Litter samples were crushed in a mortar using liquid nitrogen. Litter (5 g) and soil (50 g) samples were stirred with dichloromethane:methanol (2:1, v:v) at room temperature, using 6 mL of solvent per gram litter/soil. The supernatant was separated from the residues by centrifugation at 3,000 rpm for 15 min. The extraction was repeated three times (first overnight and then for 2 h). The extracts were combined, passed through Millipore HF filters, and concentrated first with a rotary evaporator and eventually under a stream of dry nitrogen gas. Soil extractions were duplicated. Solvent extracts were weighed and separated into four aliquots.

Lipid composition of every aliquot was analyzed by GC-MS, with or without further pretreatment, as described below. The first aliquot was analyzed without further pretreatment. In the second aliquot, apolar (hydrocarbons) and poorly polar (ketones) lipids were separated by alumina column chromatography using 2 g (II Bhs, II Bh, II 2BCs), or 20 g (I AE, II A12, III A12, III Bh, III 2BCs) of activated alumina (activity II) and elution with heptane (22 resp. 220 mL, apolar fraction) and toluene (8 resp. 80 mL, poorly polar fraction). Carboxylic acids of the third aliquot were derivatized to their corresponding methyl esters by refluxing for 15 min in methanol with a few drops of acetyl chloride. In the fourth aliquot, carboxylic acid and free hydroxyl groups were derivatized to their corresponding trimethylsilyl (TMS) esters and ethers, respectively, using chloromethylsilane and hexamethyldisilane in pyridine (Sweeley et al. 1963).

Gas chromatography-mass spectrometry (GC-MS) analysis

Lipid compositions were analysed on an Agilent 6890N gas chromatograph coupled with an Agilent 5973N mass spectrometer with electron impact at 70 eV. The GC was equipped with a DB5MS column (30 m × 0.25 mm, film thickness 0.5 μm) with He as a carrier gas. The samples were injected splitless, with the injector temperature at 280°C. The oven temperature was programmed from 100 to 300°C (isothermal for 30 min) at 4°C min^{-1}. These experimental conditions do not allow satisfactory detection of compounds with more than about 33 carbon atoms. Compound identification was based on comparison with published data and the NIST mass spectral library.

Results

Mass balance

The amounts of lipids extracted from the different litters are comparable and range from 56 to 69 mg g^{-1} dried litter (Table 1). They are intermediate between the amounts of lipid extracted by Fustec et al. (1985) from deciduous trees (39–53 mg g^{-1} oven dry mass) and conifers (117–159 mg g^{-1}). However, to the best of our knowledge, there are no such references for tropical species.

Amounts of lipids extracted from the different soil horizons exhibit a wider variability, ranging from 0.06 to 3.28 mg g^{-1} soil (Table 1 and Fig. 2). In the surface horizon of the latosol (I AE), lipids represent 3.4% of SOM. In the transition profile (pit II), very low amounts of free lipids were extracted (less than 1 mg g^{-1} soil, accounting for less than 1.3% of

Table 1 Organic matter and lipid contents of the investigated samples

Horizon	SOM[a] (g kg^{-1} soil)	Solvent extracts (mg g^{-1} soil/litter)	Solvent extracts (% SOM)
I Litter	ND	56.1	ND
I AE	32.2	1.12 ± 0.05	3.4 ± 0.2
II Litter	ND	69.3	ND
II A12	70.2	0.93 ± 0.07	1.3 ± 0.1
II Bhs	86.8	0.35 ± 0.04	0.4 ± 0.05
II Bh	33.4	0.28 ± 0.02	0.8 ± 0.05
II 2BCs	59.2	0.06 ± 0.03	0.1 ± 0.05
III Litter	ND	64.1	ND
III A12	24.8	3.28 ± 0.18	13.2 ± 0.7
III Bh	43	1.85 ± 0.25	4.3 ± 0.6
III 2BCs	149.4	2.97 ± 0.30	2.0 ± 0.2

ND: not determined

[a] Considering that in forest soils, OM content is twice as much as organic C content (Duchaufour 2001)

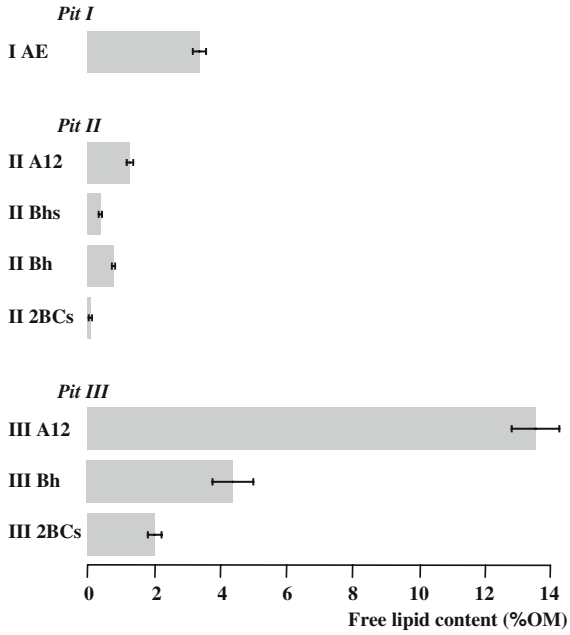

Fig. 2 Evolution of soil organic matter lipid content with depth in pit I (latosol), pit II (transition) and pit III (well-developed podzol)

SOM). They decrease with depth but the same trend is not observed when expressed as a percentage of SOM. They represent a higher proportion of SOM in II A12 and II Bh than in II Bhs and II 2BCs. In contrast, relatively large amounts of free lipids were extracted from the well-developed podzol (pit III). They are most abundant in the surface horizon III A12, where they account for up to 13.2% of SOM, while they represent 4.3% and 2.0% of SOM in III Bh and III 2BCs, respectively. The amounts of free lipids extracted from surface horizons of the three pits are between 1% and 14% of SOM, that is to say in the range of values reported in temperate podzol or acidic soil surface horizons (e.g. Stevenson 1966; Fustec-Mathon et al. 1975; Amblès et al. 1991, 1994a; Nierop et al. 2005). However, the amount of lipids extracted from III A12 is much higher than in I AE and II A12. Moreover, the lipid enrichment of SOM in the former shows that these compounds are stabilized with respect to other SOM under certain circumstances. A decreased pH is known to favor lipid accumulation (e.g. Morrison 1969). Soil pH in pit III is lower than in pit II throughout (Table 2) and could partly explain such a difference. Another major

Table 2 pH of the different soil horizons

Horizon	pH
I AE	4.8
II A12	4.8
II Bhs	4.8
II Bh	4.2
II BCs	5.0
III A12	4.0
III Bh	3.8
III BCs	3.6

difference between pit II and pit III is that the latter is waterlogged over a longer period throughout the year (do Nascimento et al. 2008). The combination of both acidity and waterlogging could explain the high accumulation of lipids as underlined by Jambu et al. (1978). It must be noted that lipids extracted from pit III are characterized by a dark-brown color and a high solubility in methanol. Lipids with such properties, referred to as "soil bitumen", have been described by Morrison (1969). They appeared to be characteristic for peats, and Fustec-Mathon et al. (1975) showed that such lipids inhibit the growth of microbial populations. Dubroeucq and Volkoff (1998) reported the development of peat blankets on top of well-developed podzols in the upper Rio Negro basin. Such a peatification process may be ongoing in the soil sequence investigated in the present study and lead to the accumulation of these compounds. Anyway, the dark-brown lipids are most likely macromolecular compounds (Amblès et al. 1991), which are not GC-amenable, and thus will not be analyzed in the present study.

The variation of SOM lipid content with depth displays different features according to the degree of podzol development. A decrease in lipid contribution to SOM with depth has been reported by several authors (e.g. Dinel et al. 1990). This is not the case in pit II, where fewer lipids are extracted from II Bhs and II 2BCs than from II A12 and II Bh. Naafs et al. (2004b) have observed that roots could account for an important part of lipid input in podzol Bh horizons where roots often accumulate. However, since a denser rooting was not observed in II Bh as compared to the other deep horizons, a larger input of lipids by roots in II Bh seems unlikely. However, in a previous study, Bardy et al. (2007) have shown that SOM is highly complexed with aluminum in pit II, especially

in II Bhs and II 2BCs. In these horizons, lipids may thus also occur as organo-metallic complexes and therefore be transferred to the bound lipid pool, as observed by Amblès et al. (1985) after addition of Fe. Besides, a transfer of colloidal or particulate organic matter is suggested from surface to deep horizons through sandy and highly porous subsurface AE and E horizons (Fig. 1). As lipids are poorly soluble in water, and II 2BCs is rather impervious, they could be transferred from surface horizons and accumulate in II Bh, on top of the less permeable II 2BCs, in which only more soluble and lipid-depleted organic matter would penetrate. In pit III, the contribution of free lipids to SOM decreases with depth. In this pit, where there are less organo-metallic complexes than in pit II (Bardy et al. 2007), the classically observed decreased amount of free lipids with depth may be assigned to several factors such as (i) a decreased rooting and thus a lower input of lipids with depth, (ii) a low solubility of lipids in water and thus their low illuviation, (iii) the incorporation of lipids into macromolecules, (iv) a higher degradation of lipids as compared with other SOM. Although III 2BCs is indurated, it contains significant amounts of lipids. However, field observation of III 2BCs reveals the occurrence of macrovoids filled with organic matter, which is similar to that of III Bh.

Lipid composition of leaf litters

Total lipid extracts of litters are dominated by the same compounds along the soil sequence (Fig. 3; Table 3, Appendix 1). Linear lipids consist mostly of long-chain *n*-alkanes in the C_{27}–C_{33} range, with prominent contributions of the C_{29} and C_{31} homologues and odd-over-even predominance associated with CPI[1] ranging from 5.7 to 9.1 (Fig. 3). Such alkanes are well-known constituents of higher plants (Kolattukudy et al. 1976). From litter I to litter III, the relative abundance of *n*-alkanes tends to decrease regarding that of steroids and triterpenoids (compounds no. 1–13) discussed below. Linear lipids also comprise short-chain *n*-alkanoic acids ranging from C_{14} to C_{18}, with a maximum at C_{16} and even-over-odd predominance. They include the unsaturated

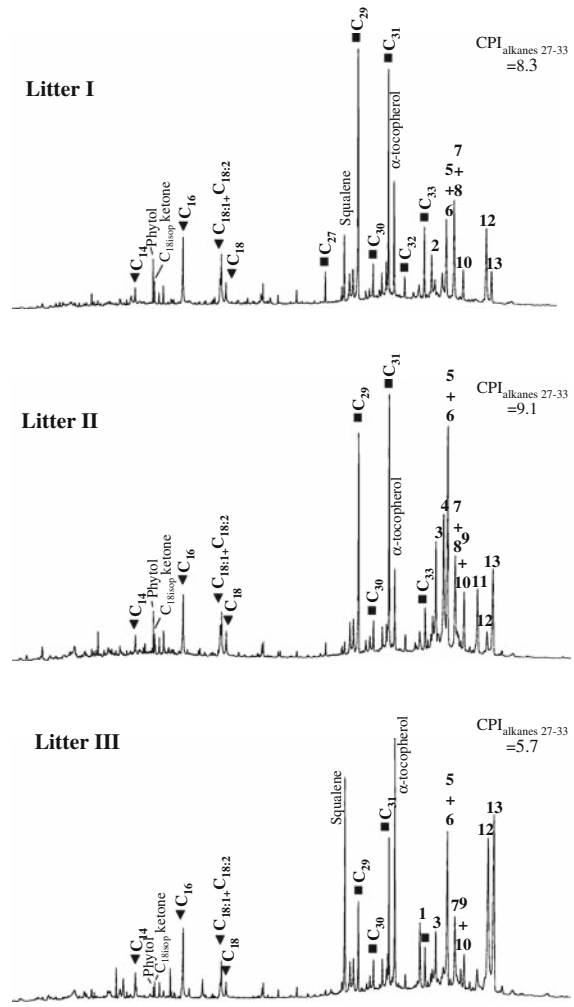

Fig. 3 GC/MS trace of litter TLEs, without derivatization. Legend: (■) *n*-alkanes, (▼) alkanoic acids; $C_{x:y}$: *x* indicates chain length and when necessary, *y* indicates the number of insaturations; C_{18isop} stands for 6,10,14-trimethyl-2-pentadecanone (C_{18} isoprenoid ketone); numbers refer to compounds in Table 3 and Appendix 1

counterparts $C_{16:1}$, $C_{18:1}$ and $C_{18:2}$. These alkanoic acids only occur in small amounts as free lipids in higher plants (e.g. Kolattukudy et al. 1976). However, C_{16}, $C_{16:1}$, $C_{18:1}$ and $C_{18:2}$ alkanoic acids are released during decomposition of plant triacylglycerols (e.g. van Bergen et al. 1997). Although long-chain alkanoic acids are abundant in higher plant epicuticular waxes (Kolattukudy et al. 1976), Nguyen Tu et al. (2001) have already observed that they were scarce in leaf litter.

Low contributions from phytol and C_{18} isoprenoid ketone (6,10,14-trimethyl-2-pentadecanone) are

[1] Carbon preference indexes (CPI) calculation was adapted from Allan and Douglas (1977):

$$CPI_{23-31} = \frac{(C_{23}+C_{25}+C_{27}+C_{29})+(C_{25}+C_{27}+C_{29}+C_{31})}{2(C_{24}+C_{26}+C_{28}+C_{30})}$$

Table 3 Mass spectral characteristics of steroids and triterpenoids detected in total lipid extract of litter samples without derivatization (no. 1–13) and additional compounds detected after silylation (no. 14 and 15, as TMS derivatives)

no.	Compound	Characterstic fragment ions	M^+
1	Friedoolean-6-ene	95,109,121,137,177,191,205,218,231,395	410
2	Stigmast-5-en-3β-ol *(β-sitoserol)*	145,213,231,255,273,303,329,396	414
3	Olean-12-en-3-one*(β-amyrone)*	189,203,218,409	424
4	Olean-12-en-3β-ol *(β-amyrin)*	189,203,218,411	426
5	Ursan-12-en-3-one *(α-amyrone)*	189,203,218,409	424
6	Lup-20(29)-en-3-one	189,205,218,313,409	424
7	Ursan-12-en-3β-ol *(α-amyrin)*	189,203,218,411	426
8	Lup-20(29)-en-3β-ol *(lupeol)*	189,207,218,315,411	426
9	Olean-12-en-3β-ol acetate *(β-amyrin acetate)*	189,203,218,453	468
10	Stigmast-4-en-3-one	124,229,289,370	412
11	Ursan-12-en-3β-ol-acetate *(α-amyrin acetate)*	189,203,218,453	468
12	Friedooleanan-3α-ol	69,81,96,109,125,137,165,206,231,257,275,395,413	428
13	Friedooleanan-3one *(friedeline)*	69,81,96,109,125,205,273,302,411	426
14	Unknown	73,75,95,109,123,135,147,177,197,237,347,395,410,485	500?
15	Unknown triterpenoic acid[a]	73,133,189,203,279,307,320,482,585	600

[a] Nierop et al. 2005

detected in the three litter samples. They probably derive from the oxidation of the chlorophyll C_{20} phytyl chain (Ikan et al. 1975). Additionally, squalene and α-tocopherol are abundant, especially in litter III. The latter has already been observed in vegetation total lipid extracts, including tropical species (e.g. van Bergen et al. 1997; Pereira et al. 2002). Nguyen Tu et al. (2001) additionally observed that leaf litter from *Ginkgo biloba* was enriched in α-tocopherol compared with fresh or senescent leaves. Moreover, series of high molecular weight compounds ($M > 410$) are detected in the three samples (Table 3). They are either derived from sterols (**2**: stigmast-5-en-3β-ol, **10**: stigmast-4-en-3-one) or triterpenes with friedelene/friedelane (**1**: friedoolean-6-ene, **12**: friedooleanan-3α-ol, **13**: friedooleanan-3-one), oleanene (**3**: β-amyrone, **4**: β-amyrin, **9**: β-amyrin acetate), ursene (**5**: α-amyrone, **7**: α-amyrin, **11**: α-amyrin acetate) or lupene (**6**: lup-20(29)-en-3-one, **8**: lup-20(29)-3β-ol) structures. Despite similar mass spectra, ursene and oleanene structures can be differentiated due to longer retention times of compounds with ursene skeletons (Rullkötter et al. 1994). The latter are coeluted with lupene structures, in a similar way as their unsaturated counterparts (Rullkötter et al. 1994). These compounds are classically found in higher plant lipids (e.g. Bull et al. 2000). The relative abundances of the four groups of triterpenoids vary among the litter samples. Litter I is dominated by ursene and lupene structures, while oleanene ones are virtually absent. In litter II, major contributions arise from oleanene, ursene and lupene structures. In litter III, friedelene skeletons are the most abundant ones.

Lipid extract silylation additionally enabled detection of low amounts of alkanols in the C_{26}–C_{32} range with predominantly even chain lengths and maximizing at C_{28} or C_{30} (not shown) as well as two high molecular weight triterpenol and/or triterpenoic acids (Table 3, compounds **14** and **15**). Based on mass fragmentation, one of them seems to be similar to a triterpenoic acid also detected in soil lipid extracts by Nierop et al. (2005).

Taken together, virtually the same compounds were extracted from litters overlying pit I, II and III. However, they occur with different relative intensities. This may be due to differences in the nature of the covering vegetation and in microbial populations and/or activity. Triterpenoids are easily degraded in conditions favourable to microbial activity (e.g. Amblès et al. 1993; van Bergen et al. 1997) and their high relative abundance in litter III could be due to a decreased microbial activity associated with waterlogging in the well-developed podzol, although, for example, lipids

from sycamore litter are dominated by triterpenoids (Bull et al. 2000).

Molecular composition of soil lipids

Figure 4 illustrates the main lipid classes extracted from horizon II A12. These lipid classes are observed in every investigated soil sample. Only low amounts of alkanes and alkan-2-ones were extracted, although higher proportions of alkanes are found in deep horizons. On the other hand, chromatograms are dominated by alkanoic acids and alkanols. ω-Hydroxyacids are also detected, especially in surface horizons, whereas only traces of α,ω-alkanedioic acids were found. This is in agreement with general trends observed in acidic soils, namely that acids are usually more abundant than alkanols, whose contribution in turn is greater than those of ketones and alkanes (e.g. Amblès et al. 1989b; Naafs et al. 2004a, b; Nierop et al. 2005). It can be noted that sugars were also extracted during the procedure, which is not surprising due to their solubility in dichloromethane:methanol mixtures (e.g. Simoneit et al. 2004). Simoneit et al. (2004) identified sugars in total solvent extracts of Amazonian soils. Based on mass spectra and retention times, comparison with their data shows that the three sugar-derived compounds present on Fig. 4 are likely, from low to high retention times, α-glucose, β-glucose and mycose.

The distributions of these compound classes in the investigated samples are presented below and discussed in terms of lipid origin. The evolution with podzol development is considered. In order to determine alkane and ketone distributions, these fractions were separated from the total extract on an alumina column, and the distributions were determined using selective ion detection (SID) at $m/z = 57$ for alkanes and 59 for ketones. Furthermore, alkanoic acids and alkanols were derivatized to their corresponding methyl esters and trimethylsilyl ethers, respectively, in order to improve their detection. Their distributions were determined using SID at $m/z = 74$ for methylated alkanoic acids, and $m/z = 75$ for silylated alkanols.

Alkanes

As reflected in Fig. 5, *n*-alkanes range from C_{15} to C_{33}, with longer chains up to C_{36} detected in I AE, and have a bimodal distribution. In the C_{15}–C_{20} range, short-chain *n*-alkanes with maxima at C_{16}–C_{17} show no odd or even predominance, in agreement with a microbial origin (Jambu et al. 1985). An unresolved complex mixture (UCM) is additionally observed in this range. Mass spectra indicate that it consists of a mixture of isomers of branched alkanes. UCM are usually assigned to contaminations by petroleum hydrocarbons (e.g. Frysinger et al. 2003). However, the investigated site lies in a national park preserved from human activity, no engine was used in the field, and the purity of the solvents was checked. This UCM, which only consists of short-chain

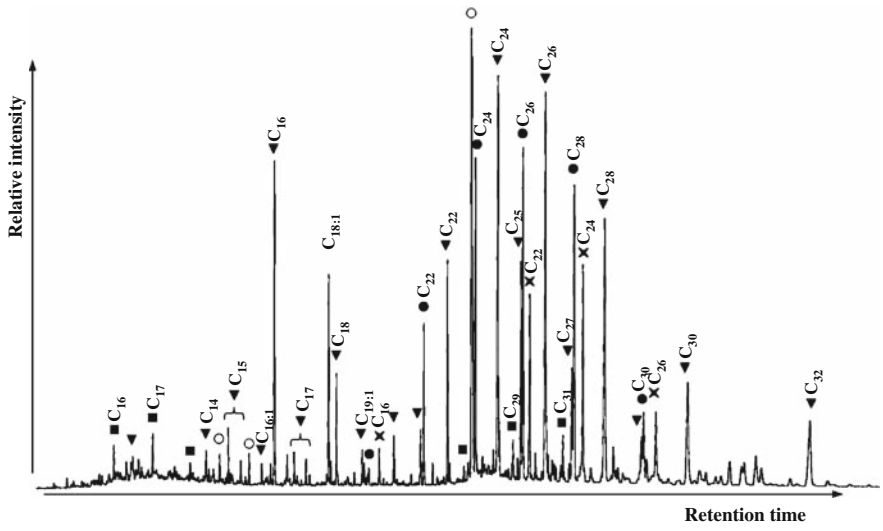

Fig. 4 GC/MS trace of II A12 lipid extract after silylation. Legend: (○) sugars, (■) *n*-alkanes, (●) *n*-alkanols, (▼) alkanoic acids, (×) ω-hydroxyacids. Alkanones and α,ω alkanedioic acids are not presented on the figure due to their low abundance. $C_{x:y}$: x indicates chain length and when necessary, y indicates the number of double bonds. Alkanoic acids and alkanols are detected as their TMS esters and ethers, respectively

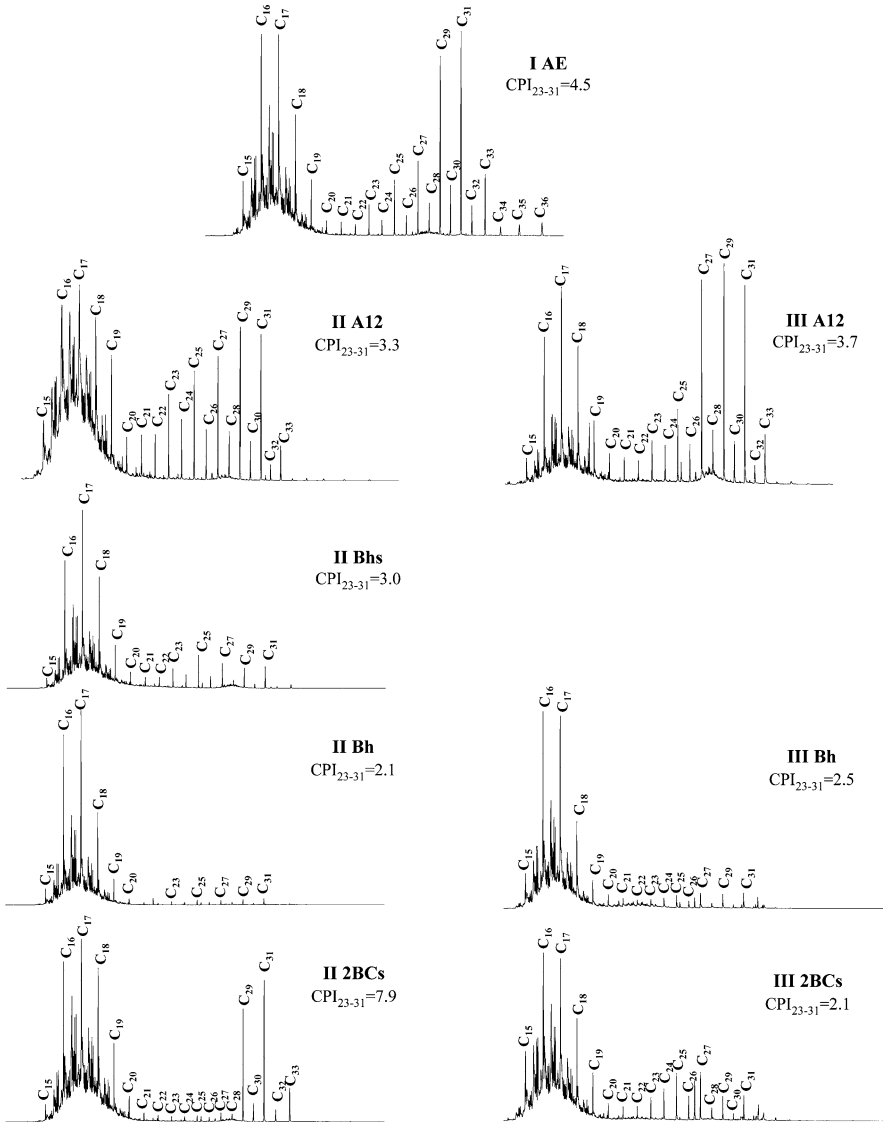

Fig. 5 Partial chromatograms ($m/z = 57$) showing the distribution of alkanes in the heptane fraction of soil lipid extracts

branched alkanes may be attributed to microbial reworking, as suggested by Han and Calvin (1969), Dachs et al. (1998) and Quénéa et al. (2006). As branched hydrocarbons are degraded less readily than *n*-alkanes (Amblès et al. 1989b), this can explain the persistence of the UCM with depth. Anyway, this UCM only represents a very small proportion of the total lipid extracts. Indeed, although it accounts for a high proportion of alkanes in II A12 (Fig. 5), Fig. 4 shows that it is only minor with respect to total lipid extract. In the C_{23}–C_{33} range, long-chain alkanes show a strong odd-over-even predominance with maxima at C_{29}–C_{31}, pointing to a vegetal origin, as long chain, odd carbon numbered *n*-alkanes are typical components of higher plant epicuticular waxes (Eglinton and Hamilton 1967) and C_{29} and C_{31} homologues are the major alkanes found in litter samples (Fig. 3).

A large contribution of long-chain alkanes is classically observed in soil surface horizons (e.g. Jambu et al. 1991). Most authors have not observed large amounts of long-chain *n*-alkanes in plant roots (e.g. Nierop et al. 2005; Quénéa et al. 2006). However, Jansen et al. (2006) have recently reported that some tropical species had more long-chain *n*-alkanes in their roots than in their leaves, still with

a marked odd-over-even predominance. In the present study, the distribution of *n*-alkanes observed in surface horizons thus reflects the input of leaf litter-derived lipids in these horizons, which is consistent with the predominance of C_{29} and C_{31} alkanes in the litter lipid extracts, with a possible additional input from decaying roots. However, as long-chain alkanes cover a wider range and have a lower CPI than those extracted from litter samples (Fig. 5), additional sources like bacteria or fungi are also likely (e.g. Dinel et al. 1990). In deeper horizons, long-chain *0n*-alkanes are generally less abundant than short-chain ones, and have a slightly lower CPI, except in II 2BCs. The lower CPI observed in II Bh, III Bh and III 2BCs can first be explained by a higher degree of degradation of alkanes, which tends to reduce odd predominance. As organic matter eluviation is a key mechanism in podzolisation (Lundström et al. 2000), small amounts of *n*-alkanes without odd-over-even predominance may also have been leached from surface horizons (Amblès et al. 1998), in particular in Bh and III 2BCs horizons. On the other hand, a high abundance of C_{29} and C_{31} *n*-alkanes and an elevated CPI are measured in the II 2BCs horizon. It shows that poorly-decomposed plant material has probably been transported down to II 2BCs as particulate organic matter through the sandy and porous horizons of the podzol, probably prior to the induration of the horizon, and is preserved there.

Alkanones

Low amounts of *n*-alkan-2-ones were detected in the samples, as usually reported in soils (e.g. Amblès et al. 1993). Their distributions are observed through GC analysis of the poorly polar fraction separated by alumina column chromatography. Most are long-chain moieties ranging from C_{23} to C_{35} with an odd-over-even predominance (Fig. 6). The C_{17} alkan-2-one is additionally extracted from III 2BCs. Two main patterns are observed. In I AE and II A12, the distributions are dominated by C_{29} while in the other horizons, a shift towards shorter chain lengths is observed, with a decreased contribution at C_{31} and a maximum shifting towards C_{27}, except in II Bh, were C_{27} and C_{29} co-dominate. Except low amounts of C_{25} and C_{27} homologues in *Sphagnum* (Baas et al. 2002), *n*-alkan-2-ones have not been reported as plant constituents but long-chain moieties are commonly extracted from sediments (e.g. Cranwell et al. 1987; Rieley et al. 1991), senescent leaves (Nguyen Tu et al. 2007) and soils (e.g. Amblès et al. 1989b, 1993; Jaffé et al. 1996; Naafs et al. 2004b; Quénéa et al. 2004, 2006). Although their formation pathways have not been entirely elucidated, several authors (e.g. Morrison 1969; Cranwell et al. 1987; Amblès et al. 1989b; Rieley et al. 1991) suggest that they may result from (i) subterminal oxidation of alkanes or (ii) from β-oxidation and subsequent decarboxylation of alkanoic acids. These pathways would respectively lead to chain length distributions (i) identical to *n*-alkanes as observed by Amblès et al. (1993); Jaffé et al. (1996) or Naafs et al. (2004b) or (ii) similar to that of alkanoic acids, minus one carbon atom. Amblès et al. (1993) further suggest that the oxidation of *n*-alkanes to *n*-alkan-2-ones decreases with chain length, and that the decrease is inversely correlated with microbial activity. When comparing the distributions of *n*-alkanes (Fig. 5) and *n*-alkan-2-ones (Fig. 6) in surface horizons, we can observe virtually identical distributions of long-chain compounds in I AE and II A12, and a *n*-alkan-2-ones distribution shifted to shorter chain lengths in III A12. In surface horizons, *n*-alkan-2-ones could thus result from oxidation of *n*-alkanes. This would point to a decreased microbial activity in pit III, which is likely, because of the development of acidity (Table 2) and waterlogging in this profile. However, the discrepancies observed between I AE, II A12 and III A12 could also be due to differences in the overlying vegetation. In deep horizons, no correlations can be observed (see Figs. 5 and 8 for alkanes and alkanoic acid distributions), so that *n*-alkan-2-ones are certainly formed through a combination of different pathways. In pit III, the same pattern is observed in the whole profile, whereas in pit II, the abundances of C_{29} and C_{31} *n*-alkan-2-ones are particularly reduced in II Bhs and II 2BCs. Amblès et al. (1989b) showed that C_{29} and C_{31} *n*-alkan-2-ones tend to be more associated than shorter ones with mineral phases. This may explain their reduced contribution in II Bhs and II 2BCs, where Bardy et al. (2007) showed that there are abundant organo-metallic complexes.

A low contribution from the C_{18} regular isoprenoid ketone (6,10,14-trimethylpentadecan-2-one) was detected as well, as shown on Fig. 6. It has been

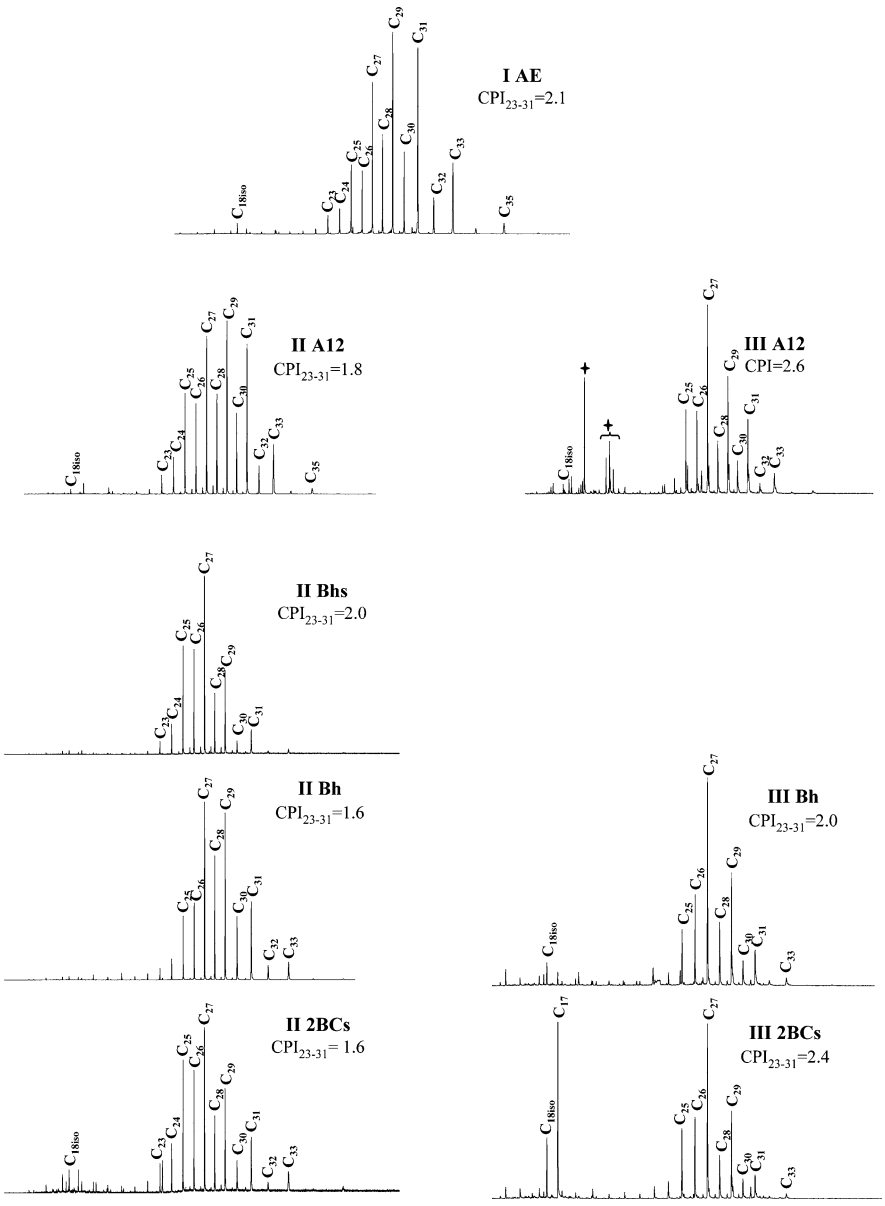

Fig. 6 Partial chromatograms ($m/z = 59$) showing the distribution of alkanones in the toluene fraction of soil lipid extracts. C_{18iso} stand for C_{18} regular isoprenoid ketone. +: methylesters

detected in sediments (e.g. Brooks et al. 1978), aquatic environments (e.g. Jaffé et al. 2006) and soils (e.g. Naafs et al. 2004b; Quénéa et al. 2004, 2006), and is extracted from leaf litter in the investigated site (Fig. 3).

Alkanols

After derivatization of alkanols to TMS ethers, series of *n*-alkan-1-ols ranging from C_{16} to C_{30} are observed in the three profiles (Fig. 7). Except in II 2BCs, they are dominated by long-chain compounds and have a strong even-over-odd predominance (CPI < 0.2) and a maximum at C_{26} or C_{28}. In II 2BCs, the C_{16} and C_{18} homologues are most abundant and C_{24}, C_{26}, C_{28} and C_{30} *n*-alkan-1-ols are present in equal amounts. However, based on TLE TIC traces (not shown), the apparent abundance of short-chain homologues in II 2BCs with respect to other horizons results more from the virtual lack of long-chain alkanols in this

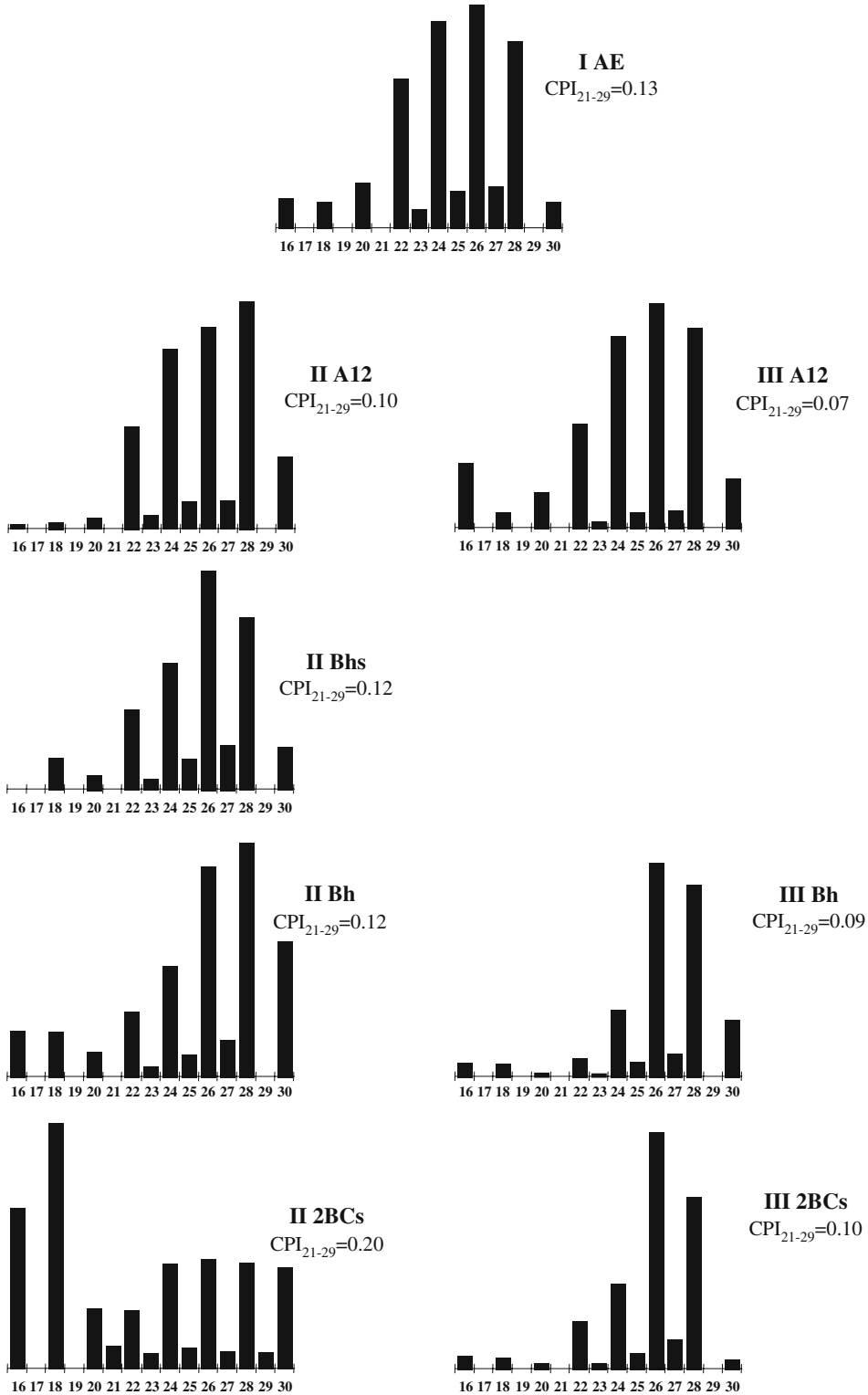

Fig. 7 Free alkanol distribution in the total lipid extracts. Numbers indicate chain length

horizon than from an enrichment in short-chain homologues. Long-chain compounds with even-over-odd predominance and maximum chain lengths of C_{26} and C_{28} are typical components of higher plant leaf waxes (e.g. Kolattukudy 1980). They are commonly detected in soils, with maxima between C_{22} and C_{28} (e.g. Jambu et al. 1993; Naafs et al. 2004a, b; Quénéa et al. 2004, 2006; Nierop et al. 2005). Even carbon numbered *n*-alkan-1-ols can also be formed by fatty acid reduction (Jambu et al. 1993) while odd carbon numbered ones are intermediates in the terminal oxidation of *n*-alkanes to *n*-alkanoic acids (Amblès et al. 1985, 1989b). As for short-chain *n*-alkan-1-ols ($<C_{20}$), they are usually associated with a microbial origin (Amblès et al. 1998), although C_{18} and C_{20} alkanols can also derive from roots (Nierop et al. 2005). The distributions observed point to major contributions of plant-derived primary alkanols. The oxidation of *n*-alkanes is certainly a minor process given the low amounts of odd numbered *n*-alkanols. Moreover, *n*-alkanols do not appear to be exclusively derived from fatty acid reduction given the differences observed in their distributions (see Fig. 8).

In surface horizons, the differences in *n*-alkanol distributions must be influenced by the overlying vegetation. They present decreased CPI with further podzol development, which suggests reduced organic matter decomposition related to a decreased microbial activity. In pit II, their distribution does not show a regular evolution with depth. In II A12 and II Bh, the C_{28} homologue is most abundant and their CPI are close (Fig. 7), while in II Bhs, the maximum is shifted towards C_{26} and in II 2BCs the contributions of long-chain homologues (C_{24}–C_{30}) have similar intensities. CPI is also slightly higher in II 2BCs (Fig. 7). Amblès et al. (1989b) showed that, unlike *n*-alkan-2-ones, alkanols with relatively short chains (C_{22} and C_{24}) are predominantly associated with mineral phases. Amblès et al. (1998) also showed that alkanols preferentially leached from a podzol are homologues with chain-length shorter than the maximum observed in soil (C_{24} vs. C_{28}), with a preservation of even predominance. As a consequence, alkanols in II Bh could be derived from those in II A12 through migration associated with particulate organic matter, thus keeping the same distribution, while those in II Bhs could be more soluble counterparts. In II 2BCs, the low abundance of long-chain alkanols can be associated with the poor decomposition of organic matter, consistent with *n*-alkane distribution, leading to a low release of plant-derived lipids, and the poor permeability of this horizon, preventing the illuviation of poorly soluble long-chain alkanols. In pit III, the distribution of long-chain alkanols is virtually preserved with depth, except for a decreased abundance of C_{22} and C_{24} homologues. As organic matter is probably exported from these horizons towards the drainage network, these homologues may be leached in the soluble form, as previously described by Amblès et al. (1989b), more intensely than in II Bhs and II Bh, where such decrease is also observed but to a lesser extent.

Alkanoic acids

Alkanoic acids are detected in the samples after derivatization into their corresponding methyl esters (Fig. 8). This fraction is dominated by a bimodal distribution of saturated *n*-alkanoic acids ranging from C_{12} to C_{32} with an even-over-odd predominance. Short-chain acids ($<C_{20}$) are dominated by the C_{16} homologue, while C_{24}, C_{26} and/or C_{28} are the most abundant long-chain counterparts ($>C_{20}$). Such bimodal distributions are commonly found in soil lipid extracts (e.g. Jambu et al. 1985; Amblès et al. 1994a; Bull et al. 2000; Naafs et al. 2004a, b; Nierop et al. 2005; Otto and Simpson 2005).

Short-chain *n*-alkanoic acids, and especially C_{16} and C_{18}, are ubiquitous in the environment, which means that in soils they can have a vegetal or a microbial origin (e.g. Dinel et al. 1990). However, *n*-alkanoic acids synthesized by bacteria usually have chain length shorter than C_{20} (e.g. Haack et al. 1994), and *n*-alkanoic acids of fungal origin have been reported to range from C_{10} to C_{24} (e.g. Weete 1974). There is only little variation in the distributions of short-chain *n*-alkanoic acids in the sequence, which can be explained both by their ubiquity and their high solubility (Amblès et al. 1998) that can lead to their redistribution within the profiles.

On the other hand, long-chain alkanoic acids with even carbon number are typical constituents of higher plant epicuticular waxes (Kolattukudy et al. 1976). Long-chain alkanoic acids are poorly soluble in water (Amblès et al. 1998), and they are unlikely to derive from *n*-alkanol or *n*-alkane oxidation (Amblès et al. 1994b) given their respective distributions (see

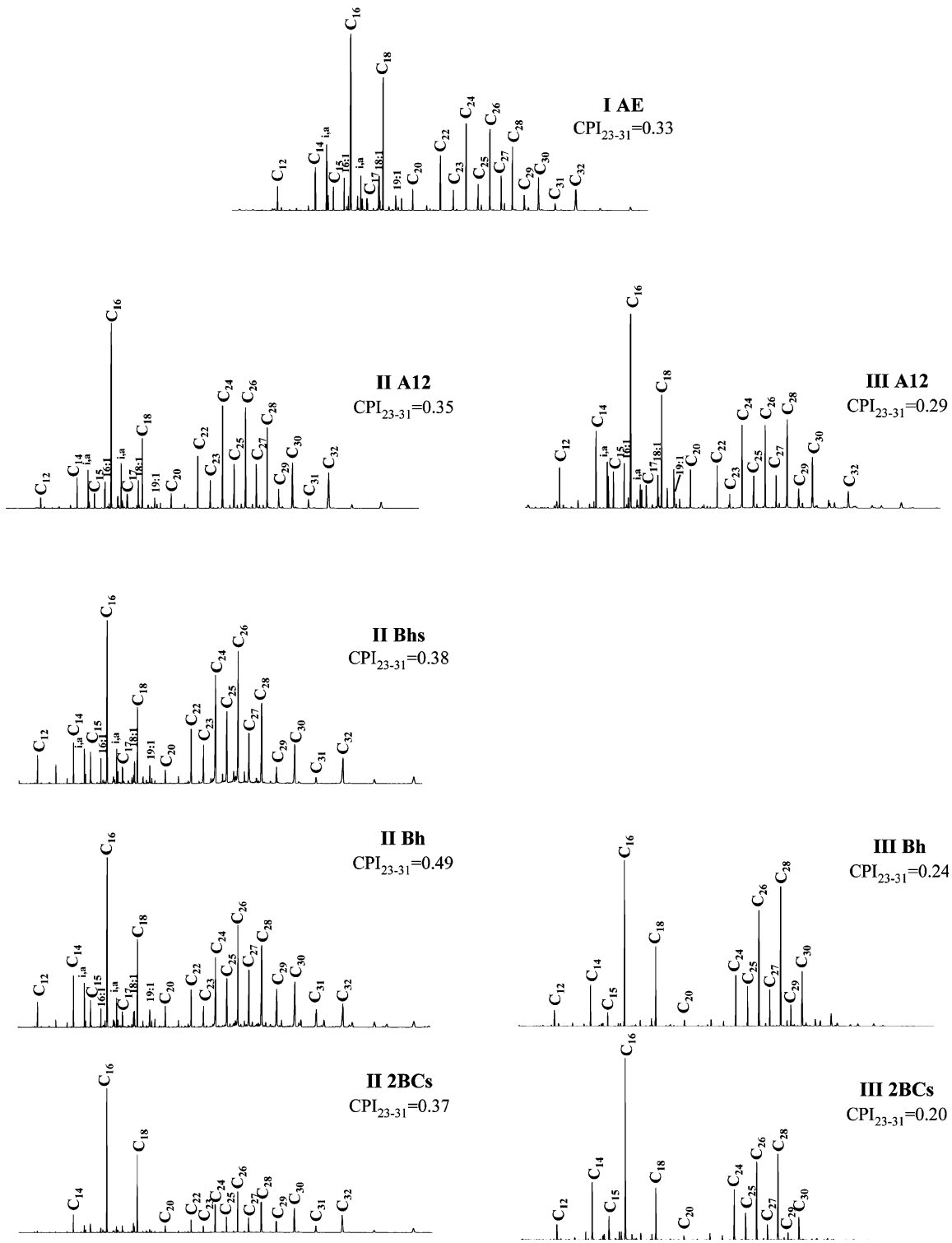

Fig. 8 Partial chromatograms ($m/z = 74$) showing the distribution of alkanoic acids (as methyl esters) in the total lipid extracts. C_x: *x* indicates the carbon number of the alkanoic acids; 16:1, 18:1 and 19:1 are monounsaturated homologues; a and i stand for *anteiso-* and *iso-*

Figs. 5, 7 and 8). As a consequence, long-chain alkanoic acids certainly mainly originate from the in situ decomposition of plant-derived organic matter in the investigated soil sequence. In surface horizons, their distributions are quite similar, except for a slightly higher contribution of C_{28} in III A12 likely to reflect a different vegetal cover. In pit II, their distribution remains similar with depth, except in II 2BCs, which lacks long-chain homologues, as previously observed for *n*-alkanols. The low relative abundance of long-chain homologues in II 2BCs would thus again reflect a low input of free lipid through organic matter decomposition. In pit III, significant differences are observed in III Bh and III 2BCs with respect to III A12. The main difference is that in these deep horizons, long-chain alkanoic acids only range from C_{24} to C_{30}. The virtual absence of the C_{20} and C_{22} acids in these two horizons is remarkable. It can be anticipated that these compounds have a fungal origin. Fungi are known to develop under acidic conditions (e.g. Dinel et al. 1990), and are thus likely to account for an important part of the soil microflora in the present study. However, they require an aerobic environment. As emphasized below, anoxic conditions seem to happen in III Bh and III 2BCs due to intense waterlogging (do Nascimento et al. 2008), and may lead to a decrease of fungal biomass. As for CPI, they are relatively constant in pit I and pit II (0.33–0.49), and somewhat higher in pit III, where they decrease with depth (0.29–0.20). This points to a lower decomposition of alkanoic acids in pit III.

The occurrence of *iso*- and *anteiso*- branched C_{15} and C_{17} alkanoic acids points to bacterial contributions to the free alkanoic acid pool (e.g. Jambu et al. 1985; Haack et al. 1994; Jaffé et al. 1996; Zelles 1999). The contributions of these branched acids relative to their corresponding linear homologues decreases with podzol development (from pit I to pit III), and is hardly detected in II 2BCs, III Bh and III 2BCs. This tends to suggest a decreased bacterial activity with podzol development and points to a very low activity in III Bh, III 2BCs and II 2BCs, in agreement with the detection of undecomposed plant material in the latter.

Monounsaturated alkanoic acids $C_{16:1}$, $C_{18:1}$ and $C_{19:1}$ are also detected in the samples. $C_{16:1}$ and $C_{18:1}$ are classically detected in soil lipid extracts (e.g. van Bergen et al. 1997) and can either be derived from plants through hydrolysis of triglycerides (e.g. van Bergen et al. 1997) or from microbial communities (e.g. Haack et al. 1994). These compounds were detected in the litter layer, together with $C_{18:2}$, which is absent in soil samples. This either means that in soils, $C_{16:1}$ and $C_{18:1}$ are not derived from a higher plant input, or more likely that the $C_{18:2}$ is rapidly degraded, as usually observed for polyunsaturated acids (e.g. Mouçawi et al. 1981). The occurrence of the $C_{19:1}$ fatty acid in soils is unusual. To the best of our knowledge, only Wiesenberg et al. (2004) reported it in a soil total lipid extract. Robinson and Eglinton (1990) detected it in a microbial mat and Haack et al. (1994) reported its presence in cultures of isolates of natural soil bacteria. Since this compound occurs simultaneously with *iso*- and *anteiso*- branched C_{15} and C_{17} alkanoic acids, a microbial origin is likely.

ω-Hydroxyacids

A series of ω-hydroxyacids with even chain length equal to C_{16} and C_{20}–C_{28} (Fig. 9) was detected in surface horizons and to a lesser extent in II Bhs and II Bh. Only traces were found in the other horizons. The distributions maximize at C_{24} in I AE, II A12 and II Bhs, and C_{26} in III A12 and II Bh. No unsaturated ω-hydroxyacids were detected. Long-chain ω-hydroxyacids are commonly found in acidic soils (van Bergen et al. 1998; Naafs et al. 2004a, b; Nierop et al. 2005; Jaffé et al. 2006). Even carbon numbered ω-hydroxyacids mainly originate from the hydrolysis of cutin and suberin biopolyesters (Kolattukudy 1980), dominant in leaves and roots, respectively. Cutin is associated with short-chain (C_{16}–C_{18}) ω-hydroxyacids while suberin can provide a wider range of homologues (C_{16}–C_{26}). An alternative source of ω-hydroxyacids would be the terminal oxidation of fatty acids (Naafs et al. 2004a) but in the present study, it must be a minor mechanism, since this process would lead to distributions similar to those of alkanoic acids, hence the presence of odd chain numbered homologues (Fig. 8). Accordingly, ω-hydroxyacids are mainly released from suberin and cutin during decomposition of plant remains. Although in soils, maximum chain length is usually C_{22} or C_{24} as found in I AE, II A12 and II Bhs (van Bergen et al. 1998; Naafs et al. 2004a, b; Nierop et al. 2005), Jaffé et al. (2006) reported a dominant

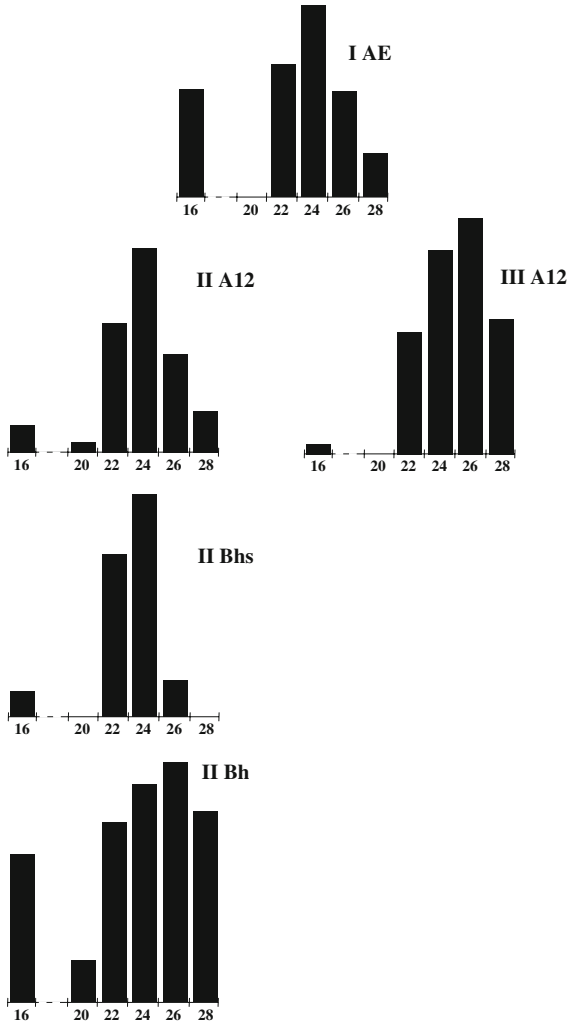

Fig. 9 Free ω-hydroxyacids distribution in the total lipid extracts. Numbers indicate chain length

contribution from the C_{28} homologue in a peat lipid extract. The absence of ω-hydroxyacids in II 2BCs, III Bh and III 2BCs could be assigned either to a low root density or to a limited organic matter decomposition in these horizons, so that ω-hydroxyacids are not released in the free lipid pool.

Aromatic acids

Aromatic acids were extracted from deep horizons of the well-developed podzol III Bh and III 2BCs (Fig. 10, Appendix 2).

Aromatic acids released from III Bh and III 2BCs are dominated by *p*-hydroxybenzoic acid (**B_1**) and 3,4-dihydroxybenzoic acid (**B_3**), also called protocatechuic acid, while vanillic (**B_2**) and syringic (**B_4**) acids are present in lower proportions. **B_2** and **B_4** are probably lignin-derived. The presence of these two acids is in agreement with an angiosperm vegetation. As for **B_1** and **B_3**, they can be derived from lignin through decarboxylation or from other plant-derived polyphenolic compounds (Filley et al. 2006). **B_3** was also reported as an intermediate in vanillic acid aerobic (Filley et al. 2002) or anaerobic degradation (Young and Frazer 1987). To the best of our knowledge, high amounts of such compounds have seldom been detected in soil lipid extracts, although they were extracted from fungi-infected shoots (Nguyen Tu et al. 2000). Moreover, Jalal and Read (1983) reported the extraction of *p*-hydroxybenzoic, vanillic and syringic acids from a Calluna dominated heathland, while Jaffé et al. (2006) extracted vanillic acid from a peat sample. On the other hand, they occur as building blocks of macromolecules and are often released upon pyrolysis or CuO oxidation of SOM (e.g. Nierop and Buurman 2007; Dickens et al. 2007) but their stabilization as free compounds is uncommon. Several studies (e.g. Zhu and Mallik 1994) have shown that these compounds are phytotoxic. Their presence in an unbound state in well-developed podzols therefore seems to indicate that they are poorly degraded or poorly incorporated into macromolecular structures in the conditions prevailing in deep horizons of the well-developed podzol. Owing to their phytotoxicity, they could thus play a role in the vegetation change observed along the sequence.

Triterpenoids

In addition to aromatic compounds, important contributions of pentacyclic triterpenoids are also detected in deep horizons of the well-developed podzol III Bh and III 2BCs (Fig. 10, Appendix 3).

Hopanes and pentacyclic triterpenoids are classical biomarkers for respectively microbial and higher plant inputs to sediments (e.g. Garrigues et al. 1986). Such compounds have also been detected in soil lipid extracts (Ries-Kautt 1986; van Bergen et al. 1997; Jaffé et al. 1996; Bull et al. 2000; Naafs et al. 2004a, b). Most pentacyclic triterpenoids found in soil are derived from leaves or roots (e.g. van Bergen et al. 1997; Nierop et al. 2005). In soils, they are usually easily degraded or incorporated in the bound lipid

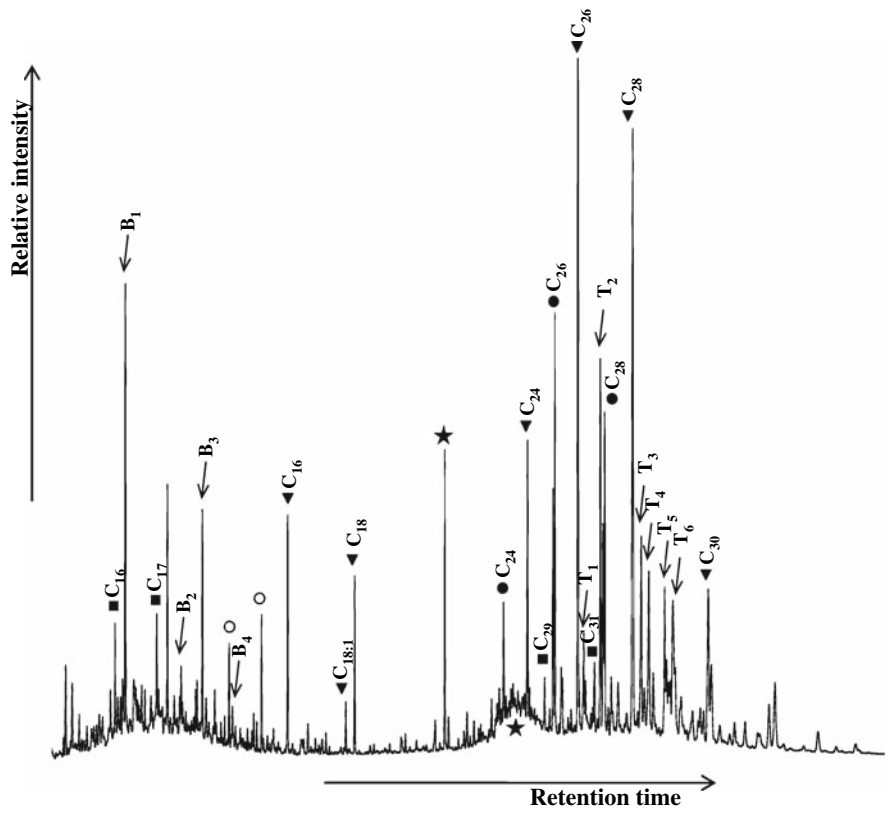

Fig. 10 GC/MS trace of III Bh lipid extract after silylation. Legend: (○) sugars, (■) n-alkanes, (●) *n*-alkanols, (▼) alkanoic acids, (★) phthalates. $C_{x:y}$: *x* indicates chain length and when necessary, *y* indicates the number of double bonds. Polar compounds are measured as TMS esters and/or ethers. Structures of B_x and T_x compounds are presented in Appendix 2 and Appendix 3, respectively

fraction (Gobé et al. 2000), so that their concentration decreases rapidly with depth (van Bergen et al. 1997), unless an important input by roots occurs, as observed by Naafs et al. (2004a) in a podzol Bh horizon. Ries-Kautt (1986) and Jaffé et al. (1996) have reported the occurrence of mono- to tetraaromatic triterpenoids in peats and flooded rain forest soils, respectively. Aromatization is one of the pathways suggested for the degradation of triterpenes (Trendel 1985). Such compounds have been observed in recent sediments, for example in the Amazon basin (Laflamme and Hites 1979; Gomes and Azevedo 2003; Jacob et al. 2007) and are therefore likely to be formed over short periods in the range of decades. Jaffé et al. (1996) and Jacob et al. (2007) additionally suggested that aromatization only occurs in anoxic environments.

Lipid extracts from III Bh and III 2BCs comprise pentacyclic triterpenoids. Six of them ($\mathbf{T_1}$ to $\mathbf{T_6}$ on Fig. 10) contribute significantly to the total lipid extract. Five were identified. They exhibit various levels of unsaturation and one includes an oxygen atom. $\mathbf{T_3}$ is a taraxerol methyl ether (NIST Library). Although uncommon, the occurrence of pentacyclic triterpene methyl ether has been reported recently in Brazilian lake sediments by Jacob et al. (2005). The authors suggest that they are relatively stable in early stages of diagenesis. $\mathbf{T_4}$ is a 17α(H), 21β(H)-homohopane with 31 carbon atoms (Philp 1985; Ries-Kautt 1986). According to van Dorsselaer (1975), it is likely to derive from the oxidation and subsequent reduction of polyhydroxyhopanes with a C_{35} skeleton. $\mathbf{T_4}$ has already been detected as a major compound in sediments (e.g. Sinninghe-Damsté et al. 1995) and in deep horizons of two different peats (Quirk et al. 1984; Ries-Kautt 1986). Under specific conditions, this compound thus seems to be stabilized, although these conditions have not been elucidated. $\mathbf{T_1}$ and $\mathbf{T_2}$ are monoaromatic pentacyclic triterpenoids. The former most likely has a oleanene or ursene structure, while the latter has a oleanane, ursane or lupane skeleton (Ries-Kautt 1986; Jacob et al. 2007). They are most likely derived from the loss of the oxygenated function in C3 position and

subsequent aromatization of the abundant α- and β-amyrin or lupeol derivatives observed in leaf litters (Fig. 3, Table 3). **T_6** is a tetraaromatic triterpene. Its structure is uncertain, as isomers with the ethyl group at the 1′ and 3′ positions have the same mass spectra (Chaffee and Johns 1983). The 1′ isomer would likely derive from the ring A to ring D aromatization of lupeol (Laflamme and Hites 1979) while Greiner et al. (1977) suggested that the 3′ isomer would originate from the ring D to ring A aromatization of a hopanoid precursor. The detection of **T_2**, with a possible lupane structure, and of trace amounts of the triaromatic intermediate **T_7** suggests that **T_6** is the isomer with the ethyl chain in 1′ position.

The detection of these compounds in III Bh and III 2BCs only point to specific SOM degradation pathways, leading to aromatization of triterpenoids, in these horizons. The abundance of aromatic triterpenoids suggests the occurrence of anoxic microenvironments in this waterlogged profile. To the best of our knowledge, such compounds have never been reported in podzols before.

Lipids and the podzolisation process

The present study shows that there are both vertical and lateral variations in free lipid content and composition within the investigated soil sequence, representative of the development of waterlogged podzols in the upper Amazon basin. The different pits of the soil sequence correspond to successive stages in the development of podzols at the expense of clay-depleted laterites (pit I):

i. The formation of a shallow, poorly-differentiated podzol (Bhs) in pit II, with a high abundance of organo-metallic complexes (mainly with Al) (Bardy et al. 2007);
ii. The differentiation at greater depth of separate Bh and 2BCs horizons in pit II, probably formed through the illuviation of less soluble organic matter from surface horizons for the former, and the translocation of soluble or colloidal organic matter from II Bhs for the latter (Bardy et al. 2008);
iii. The further evolution of the well-differentiated podzol as revealed by pit III, apparently associated with a decreased microbial activity (Bardy et al. 2008) and the remobilization and exportation of previously accumulated organic matter from deep Bh and 2BCs horizons (Bardy 2008).

In the following, the evolutions in free lipid abundance and composition are discussed in relation with the processes going on in the investigated soil sequence and the evolution of total SOM, as studied by do Nascimento et al. (2004) and Bardy et al. (2007, 2008). New data inferred from the present study and adding to the comprehension of the processes are eventually emphasized.

There are few free lipids in pit II. In II Bhs and II 2BCs, it can be noted that their virtual absence is consistent with the low abundance of aliphatic chains observed by Bardy et al. (2008) on the ^{13}C CP/MAS NMR spectra of OM in these horizons. It is also interesting to note that in these two horizons, which have the lowest lipid contents, Bardy et al. (2007) detected the highest amounts of organo-metallic complexes in the whole sequence. The low abundance of free lipids in pit II may thus at least in part be due to the fact that many lipids, especially polar ones, are not free in this pit, but complexed with metallic cations like Al^{3+}.

In pit III, free lipids accumulate insofar as they represent a higher percentage of OM than in pit II. In the surface horizon, they even account for up to 13%, that is to say a significant part, of SOM. The previous studies on this sequence, in agreement with the literature, suggest that the following conditions are likely to favor their stabilization in pit III in comparison with pit II: (i) a combination of a higher acidity and higher waterlogging (do Nascimento et al. 2008), (ii) a depletion of complexing elements like Al (Bardy et al. 2007) and (iii) a decreased microbial activity (Bardy et al. 2008).

As for the distributions of the different compound classes in the sequence, only that of alkanols seems to give information on illuviation mechanisms, which are consistent with those suggested by do Nascimento et al. (2004) and Bardy et al. (2008) and discussed above. The similarity of the distributions of alkanols in II A12 and II Bh on the one hand, and III A12, III Bh and III 2BCs on the other hand, suggests the occurrence of illuviation of poorly soluble OM from surface to deep, relatively porous horizons. Furthermore, the reduced abundance of C_{24} chains in III Bh and III 2BCs is consistent with

an exportation of OM from these horizons to the river network.

Another point on which the study of lipids is informative and in agreement with previous micromorphological and spectroscopic observations is the evolution of microbial activity along the sequence. It is revealed by the presence of lipidic biomarkers such as branched fatty acids and ω-hydroxyacids, along with the evolution of CPI of most lipid classes, which tend to show that microbial activity decreases with podzol lateral evolution, from pit I to pit III. Accordingly, in surface horizons, Bardy et al. (2008) observed through ^{13}C NMR that the extent of decomposition of carbohydrates is lower with further podzol development. The data also suggest a decrease of microbial activity with depth, with the lowest activities in II 2BCs, III Bh and III 2BCs. These horizons correspond to those in which OM micromorphology is monomorphic (Bardy et al. 2008), that is to say poorly reworked by microbial activity. In these horizons, it is thus consistent that hardly any C_{15i} or C_{15a} branched alkanoic acids are detected, nor any ω-hydroxyacids released during the decomposition of plant tissues. In the II 2BCs horizons, lipidic biomarkers even evidence the presence of undecomposed plant remains.

The patterns observed for lipid contents and distributions are thus in general agreement with the podzolisation process. The present study additionally brings new information. First, in the early stages of podzolisation (pit II), free lipids only make up a small part (less than 2%) of total SOM. This suggests that in the investigated area, the accumulation of free lipids does not play an important role in the initiation of the podzolisation process, contrary to what Jambu et al. (1978) had hypothesized. Then, the present study shows that waterlogged conditions lead to the formation of anoxic microenvironments in pit III deep horizons, as reflected by the particular evolution of triterpenoids through aromatization. The distribution of alkanoic acids further suggests subsequent changes in the microflora, with a probable decrease in fungal biomass in III Bh and III 2BCs horizons. Finally, the present study highlights the stabilization of simple aromatic acids in pit III, known for their phytotoxicity. Although nothing has been proven so far, these compounds could have a role in the vegetation change observed along the sequence. In that case, the modification of the vegetal cover, and the associated changes in evapotranspiration may lead to further soil degradation.

Conclusion

The evolution of lipid content and composition was investigated in key samples of a soil sequence at the transition between latosol and podzol in the upper Amazon basin as well as in the overlying litter. This study enables a better understanding of the fate of free lipids in waterlogged podzols of the upper Amazon basin. The results are consistent with those obtained previously concerning the podzolisation mechanisms and the changes in organic matter structure in the same soil sequence. The present study also adds to our understanding of the podzolisation process. In particular, it highlights that free lipids do not accumulate in the first stages of the podzolisation process, but that they are abundant in well-developed waterlogged podzols. It also indicates that anoxic conditions occur in deep horizons of well-developed podzols, and that phytotoxic compounds are stabilized in these environments. It thus suggests that lipids may play a role in the vegetation changes observed on top of well-developed podzols in the upper Amazon basin.

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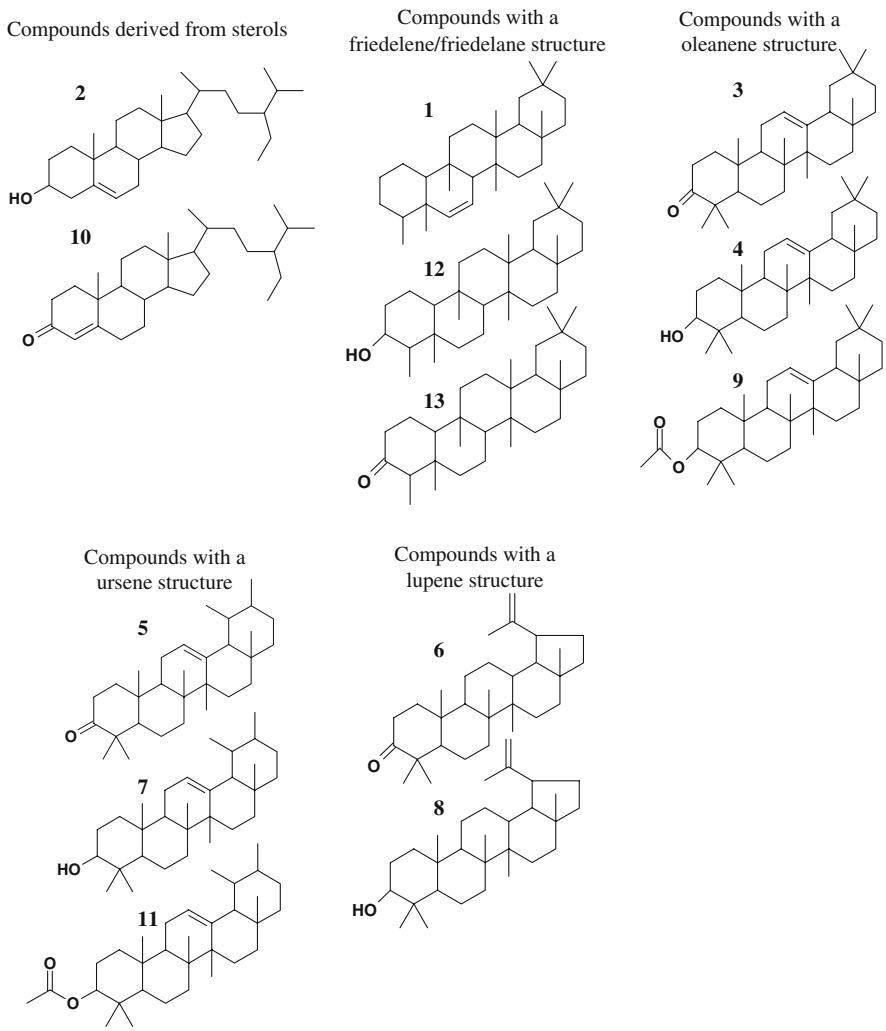
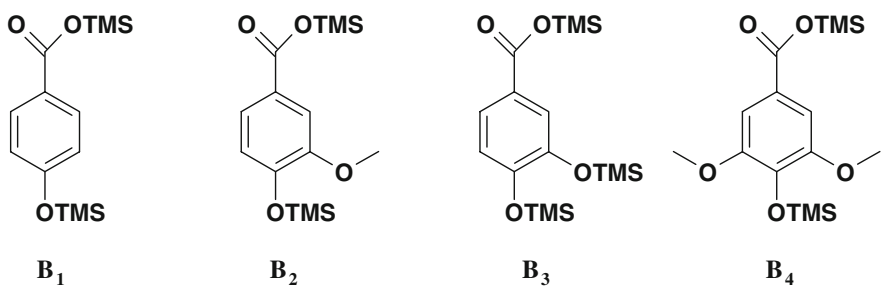
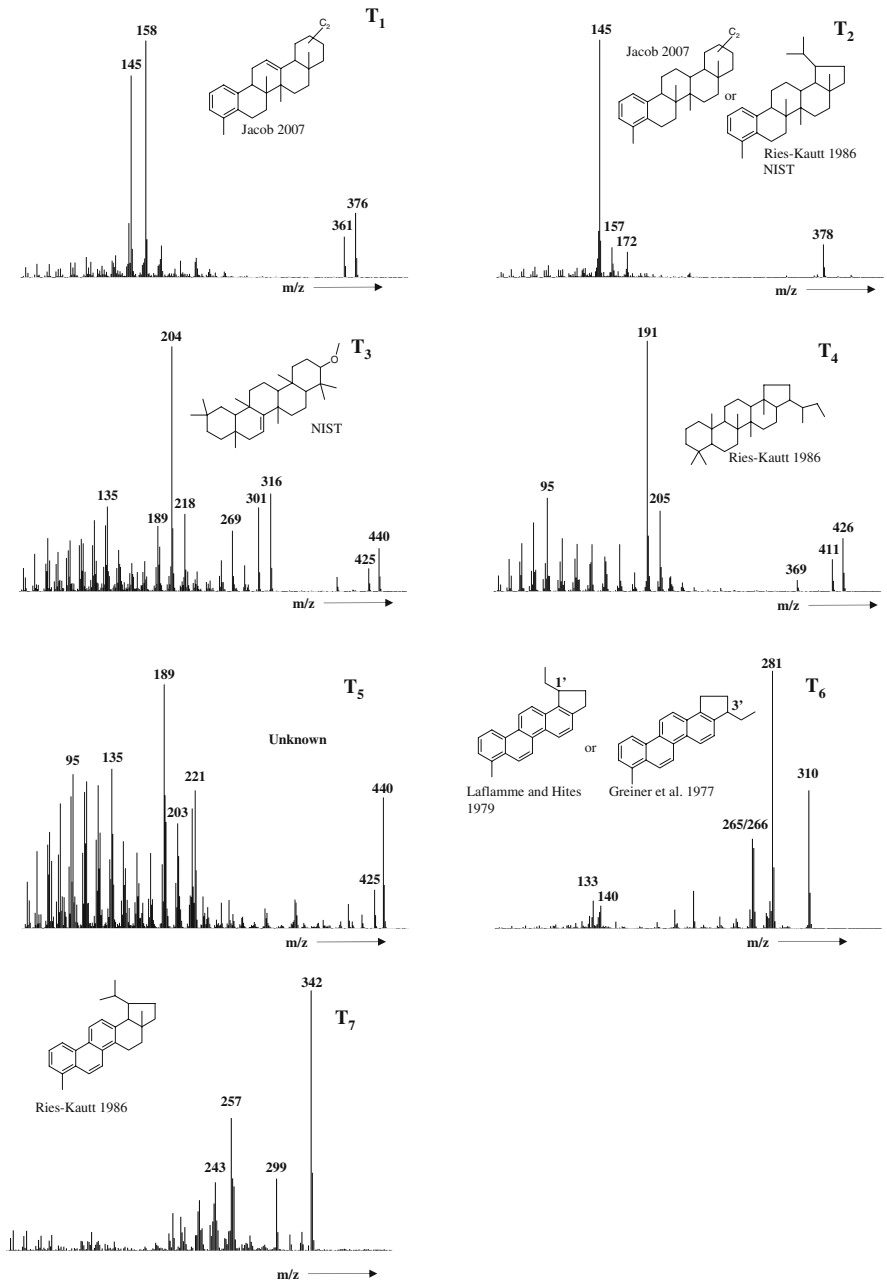
Appendix



Appendix Fig. 1 Structures of polycyclic compounds observed in litter TLEs (Fig. 3)



Appendix Fig. 2 Structures of benzoic acid derivatives (B_x compounds on Fig. 10) observed in the silylated extracts of III Bh and III 2BCs



Appendix Fig. 3 Mass spectra and suggested structures of triterpenic derivatives (T_x compounds on Fig. 10) observed in the silylated extracts of III Bh and III 2BCs

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