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SOILS, SEC # • RESEARCH ARTICLE

Free fatty acids in Lake Aydat catchment soils (French Massif Central): sources, distributions and potential use as sediment biomarkers

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Abstract

Purpose: Eighteen soils were sampled in the Lake Aydat catchment in order to analyse free fatty acid (FA) content; FAs are considered to be among the most amenable biomarkers to mobilisation by runoff waters. The majority of the study area has soil cover consisting of grasslands or forest since the 2nd World War, although some covers having changed more recently.

Material and methods: The soil studied all developed on volcanic rocks (andisols). The bulk organic matter (OM) content of the samples was characterized by Rock-Eval (RE) pyrolysis. The FAs were determined by gas chromatography-mass spectrometry (GC-MS) analysis of isolated and derivatized (methylation and trimethylsilylation) FA fractions.

Results and discussion: Few low molecular weight compounds (LMW; i.e., $<C_{20}$) were detected; FA distributions were dominated by even numbered-carbon high molecular weight (HMW; $\geq C_{20}$) normal FAs and difunctionalized FAs that included: dicarboxylic acids (diFAs), n-alkylcarboxylic acids (nFAs), and α- and ω-hydroxycarboxylic acids (αHOFAs and ωHOFAs). The distributions and abundances of HMW terms of all families (which can be all considered as representative of terrestrial OM source) displayed only slight differences. These differences were rationalized by the following ratios: $(C_{26:0}+C_{28:0})/\Sigma C_{even}$ nFAs, C_{22}/C_{24} di-FAs, and C_{20-}/C_{20+}ω-HOFAs). Soils from areas that had changed use recently consistently displayed intermediate ratio values

typical of their double inheritance. All grassland soils and some samples from intermediate areas contained notable amounts of the bile acid deoxycholic acid that testifies to their present or recent use for cattle breeding.
Conclusions: Despite the variety and the abundance of all HMW FAs in soils, work done previously on Lake Aydat sediments found only nFAs (Stefanova, M. and Disnar, J. R. 2000. Composition and early diagenesis of FAs in lacustrine sediments, Lake Aydat (France). Org Geochem 31, 41-55). These results suggest we should question the importance of the watershed contribution, the source (plant or soil) and mode of transportation of the FAs to the lake sediments.

Keywords: Biomarkers • Conifer • Fatty acids • French Massif Central • Grassland • Sediments • Soils

1 Introduction

Fatty acids (FAs) are major components of the lipids of living organisms. They mostly occur: (i) in the form of esters (of alkanols, sterols and glycerol) if they are components of the cell membranes of bacteria and eukaryotes; (iia) as polyesters in the protective tissues of higher plants (namely cutin in leaves and suberin in barks and roots); and also (iib) in the free or combined state (waxes) at the outer surface of leaves (Feng et al. 2010 and references therein). Similar to other lipid compounds, FAs have been extensively studied by organic geochemists as tracers of plant input to marine and lacustrine sediments (Cranwell 1977, 1978, 1981; Meyers and Ishiwatari 1993; Ho and Meyers 1994; Prartono and Wolff 1998; Ficken et al. 2000; Fisher et al. 2003; Jacob et al. 2007). While the FAs incorporated into phospholipids have received considerable attention as specific tracers of soil microorganisms (Zelles 1997, 1999; Ruess and Chamberlain 2010 and references therein), soil lipids, including FAs, have been little investigated. This paucity of data was pointed out by Bull et al. (2000a), and still remains fully valid, despite the publication of a few papers in the meantime (see below). Most papers on soil lipids in general and FAs in particular deal with the fate or turnover of lipid components of the soil organic matter (SOM) in cultivated or uncultivated soils (Dinel et al. 1998; Nierop and Verstraten 2005; Otto and Simpson 2006; Wiesenberg and Schwark 2006; Wiesenberg et al. 2008, 2010; Amelung et al. 2008; Feng et al. 2010 and references therein). Only very few papers consider FAs as plant source indicators (Almendros et al. 1996; van Bergen et al. 1997; Bull et al. 2000b; Gleixner et al. 2001; Marseille et al. 1999). Both these objectives are considered together in studies in which lipids are used for tracking changes in soil use (Lichtfouse et al. 1994; Wiesenberg et al. 2004; Quénea et al. 2006).

As soil scientists, sediment geochemists usually base the identification of the source organisms of FAs (and other lipid compounds) on the composition of the putative living organism (e.g., Cranwell 1974; Rieley et al. 1991). The possibility that original FA distributions might be altered during compound transfer from plant source to downstream sediment trap (lake or sea) – and especially in the soil where they can remain for a rather long time – is generally overlooked (e.g., Kusch et al. 2010).

A few years ago, Stefanova and Disnar (2000) published a study on the free and bound FA content in the recent sediments of Lake Aydat (> ca. 1950). This lake is located in the French Massif Central, in an area covered by grasslands and forests. It is presently eutrophic and, accordingly, the previous authors evidenced only a minor organic contribution from the watershed to the lake sediment as per the results of their FA study. The present study deals with the analysis of the free FAs extracted from 18 representative soils in relation to the different

vegetation cover and topographic conditions (orientation and slope) in the lake catchment. This work has a threefold interest: 1) to evaluate the variations in the content and natural composition of free FAs, 2) to check their ability to differentiate the vegetation covers as a source of FAs and 3) their possible use as biomarkers from catchment. To answer these questions we selected soils under different plant cover (i.e., grass and trees) and over a range of environmental factors (soil characteristics, elevation, slope, etc.). Some of the studied soils that have experienced changes in land use during the last century should also allow us to assess the persistence of FAs from historic land uses and, accordingly, to test the potential of lipids to track such changes.

2 Setting

Soil samples were taken from the catchment of Lake Aydat, located in the French Massif Central, about 25 km SW of Clermont-Ferrand (Fig. 1). The catchment is at an altitude ranging from 825 m (lake level) to about 1300 m above sea level. The highest points are volcanoes of the Chaîne des Puys. Between the volcanic domes flows the Veyre River, the major tributary of Lake Aydat. The Lake Aydat catchment comprises rather shallow soils developed on recent volcanic rocks (i.e. younger than 70 000 years, one of the latest manifestations of the volcanic activity being the basaltic flow that dammed the Veyre river valley about 8600 years ago, giving birth to Lake Aydat). The area was most certainly covered by forest until its intensive exploitation for the development of agriculture, from the middle of the first millennium (Michelin 1996). Nowadays, in the Aydat catchment, the areas of greatest slope are no longer used as pasture and are covered by forest or by shrubby meadows (Table 1 and Fig. 1). Here, the areas designated as “intermediate” were used as grasslands until the end of the 1940’s and are presently abandoned (namely S05, S28, S33 and S34; Institut Géographique National, 1946).

The volcanoes are presently covered by forests (mainly *Picea sp.*), most of them being recent plantations, whereas the rest of the catchment is covered by pastures (grasslands) and, in lesser abundance, by shrubs. In total, the present watershed comprises 70% grasslands, 15% forest, with the rest being urbanized areas. The geological substratum is mostly basaltic, accompanied by basaltic trachyandesite and Quaternary alluvium near the Veyre River. Aydat soils are andisols, constituted by lightly-textured basic lava. Sand-silt constituted the only horizon (A, organo-mineral) above the C horizon. These soils are well drained and slightly acidic. The abundance of worm casts and molehills indicates a high degree of biological activity.

3 Materials and methods

3.1 Sampling, soil characterization and slope calculation

Eighteen soil monoliths, representative of the diversity of soil present in the catchment of Lake Aydat, were sampled in autumn 2008. The location and context of the eighteen sites are described in Fig. 1 and the vegetation cover and the main characteristics of the selected soils are listed in Table 1. Slope calculations were performed according to Kasel and Bennett (2007). Samples of the top of superficial organo-mineral horizon (2–4 cm) were dried in an oven (40°C), crushed and sieved at 2 mm. The < 2 mm fractions were analysed.

3.1.1. pH and granulometry

Soil pH was determined as described in Margesin and Schinner (2005). Granulometry was performed on air-dried samples on the < 2 mm fraction from one sample within each of the three land uses. The size distribution of particles was determined using the pipette method after dispersion with 1M NaOH (Embrapa 1997).

3.1.2. Rock-Eval analyses

Approximately 60 mg of dried and crushed soils were used for RE analysis. The RE parameters used in this study were: (i) Total Organic Carbon (TOC; %) that accounts for the quantity of OC present in the soil; (ii) the Hydrogen Index (HI, in mg hydrocarbons.g^{-1} TOC), which is the amount of HC released during pyrolysis, normalized to TOC and (iii) the Oxygen Index (OI, in mg CO_2. g^{-1} TOC) that corresponds to the oxygen content of the OM released during pyrolysis, normalized to TOC (Espitalié et al. 1985; Lafargue et al. 1998; Disnar et al. 2003).

3.2. Lipid extraction and analysis by Gas Chromatography–Mass Spectrometry (GC-MS)

Lipids were extracted from ca. 2 g of dried and crushed soil samples using accelerated solvent extraction with CH_2Cl_2:MeOH (1:1 v/v; ASE 200 Dionex®) at 100°C and 1000 psi for 5 min in 3 cycles (5 ml cells, 60% flush volume). The total extract was dried under N_2 and then fractionated into neutral and acidic compounds using solid phase extraction on Aminopropyl Bond Elute© phase according to Jacob et al. (2005). Acid fractions were dried under N_2 and methylated by adding a mixture of anhydrous MeOH and acetyl chloride kept at room temperature for 1 hour. The obtained methyl esters were then further derivatized by reacting with 125 µl N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) in 250 µl pyridine at 60°C during 1 hour. Standard (5α-cholestane) was added prior to GC-MS analysis.

Esterified and silylated acid fractions were analyzed by GC-MS with a Polaris TRACE-GCQ. The chromatograph was fitted with an Rtx-5MS column (30 m, 0.25 mm i.d., 0.25 µm film thickness). The GC operating conditions were: 40°C (hold 1 min) ramping from 40°C to 120°C at 30°C.min^{-1}, then from 120°C to 300°C at 5°C.min^{-1}, hold 30 min. The samples (2.0µl) were injected automatically in splitless mode, with the injector temperature set at 280°C. Helium was the carrier gas (1 ml.min^{-1}). The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV and scanned from 50 to 650 m/z. Identifications were based on GC retention times and comparison of mass spectra with published data. Because of possible coelution, the concentrations were estimated by measuring peak areas on ion specific chromatograms. Acid concentrations were estimated after calculating a correction factor between the peak area on the ion specific chromatogram and the peak area on the Total Ion Current (TIC) and then reported to the area of standard peak (5α-cholestane) on the TIC. The Pearson product moment correlation was used to test for correlation with Statistica (Statsoft 2008). The level of significance of all tests was set at $P<0.05$.

4 Results

The samples analysed were separated into three groups depending on their present and past vegetation cover: forests, grasslands and intermediate areas that have changed occupation during the past century. In most cases these intermediate areas correspond to abandoned grasslands that were colonized by shrubs and/or trees (mostly conifers).

4.1 Soil samples main characteristics (Table 1)

All the samples are rich in TOC, with the range being between 5.2 %, the value obtained for grassland soil S14, up to 38.2 % in the forest sample S26 (Table 1). Grassland soils in general exhibited lower TOC values (average

= 10.8%, SD = 5.6%) than both intermediate site soils (average = 16.1%, sd = 6.9%) and forest soils, except for site S12 (25.7%) that was located in a swampy area. Slope values were low to moderate, ranging from 0.5 to 16.6°. The largest slope gradients were reached in forest soils (average = 15.8°) whereas grasslands developed on lower slopes (average = 6.9°, SD = 4.5). OI values were relatively higher in forest soil samples (e.g. sample S26, has the high OI value but also the highest HI, the greatest slope and the lowest pH value: 4.2). Granulometry revealed a gradient from grassland to forest soils, characterized by a decreasing amount of silts compensated by an increase in sand, accompanied by a slight decrease in pH (Table 1).

4.2 Identification, composition and distribution of lipids in the acid fraction of soil samples

The free FA fraction of the soil total lipid extract (TLE) contained the following groups of aliphatic compounds: nFAs, diFAs, ω- and α-HOFAs. Total fatty acids (TFA) concentrations varied between 823 and 6794 µg/g TOC for grassland soils, between 1639 and 6636 µg/g TOC for intermediate soils, and between 833 and 23346 µg/g TOC in forest soils (Table 1). Characteristic chromatograms of the acid extractable fractions from grassland and forest soils are shown in Fig. 2.

4.2.1 n-alkylcarboxylic acids (nFAs)

The total abundance of nFAs ranged from 396 to 6318 µg/g TOC/sample, making it the most abundant family of free FAs in grassland and intermediate soils (53 to 68% of TFA). Fig. 3 summarizes the distributions of nFAs from each group of vegetation cover studied. In all cases, nFAs ranged from *n*-$C_{16:0}$ to *n*-$C_{34:0}$ and displayed an even-over-odd predominance. In grassland samples (Fig. 3a; 3b), nFAs showed a monomodal distribution, with a maximum at *n*-$C_{26:0}$. In forest soils and sample S34 (intermediate vegetation; Fig. 3d), nFAs showed similar concentrations of *n*-$C_{22:0}$, *n*-$C_{24:0}$, *n*-$C_{26:0}$ and *n*-$C_{28:0}$ (Fig. 3e; 3f).

4.2.2 ω-hydroxycarboxylic acids (ωHOFAs)

ωHOFAs represented between 34 to 65% of the TFA for forest soils. In grassland and intermediate soils this compound family was less abundant than the nFAs and represented up to 28% of the TFA. All samples presented a homologous series of compounds ranging from C_{12}-ωHOFA to C_{29}-ωHOFA with an even-over-odd predominance. The distribution was monomodal in grassland soils and bimodal in intermediate and forest soils. High abundances of the C_{22}-ωHOFA and C_{24}-ωHOFA homologues were recorded in grassland and intermediate soils (Fig. 4a; 4d), with higher concentrations than the *n*-$C_{22:0}$ and *n*-$C_{24:0}$ nFAs, respectively. Forest soil samples (Fig. 4e; 4f) exhibited an exceptionally high abundance of C_{12}, C_{14} and C_{16}-ωHOFA. Intermediate soil sample S34 (Fig. 4d) showed the characteristics of grassland and forest soils, the major compounds being C_{22}, C_{24} and C_{16}-ωHOFA, respectively.

4.2.3 α-Hydroxycarboxylic acids (αHOFAs)

α-Hydroxycarboxylic acids (αHOFA) represented between 8 and 22% of aliphatic acids in grassland soil TFAs, between 11 and 23% in intermediate soils and between 5 and 12% in forest soils. Homologous series ranged from C_{20} to C_{30}. In all samples, C_{24}-αHOFA was the dominant homologue, followed by notable and comparable levels of all homologues from C_{22} to C_{26}, including odd-numbered chains (Fig. 5).

4.2.4 Dicarboxylic acids (diFAs)

All samples displayed a homologous series of diFAs extending from C_{20} to C_{26} with a marked even-over-odd predominance. DiFA distributions showed a maximum at C_{24}, with high C_{22}-diFA proportions in grassland and intermediate soils (Fig. 6a; 6d). In forest soil samples, diFA distributions were dominated by C_{22}-diFA, followed by C_{24} and C_{20}-diFAs (Fig. 6e,f).

4.2.5 Other compounds

In the Aydat catchment area, traces of nC_{22}, nC_{24} and nC_{26} alkanols were observed in some soil samples regardless of the vegetation cover. These compounds represented a simple and modest contamination of the FA fraction by dominant compounds of the neutral lipid fraction (ca. 0.04% of the TFA). Deoxycholic acid, a bile acid, was found at notable levels in all grassland soils but one (from a shrubby area), and in most of those from intermediate areas (Fig. 8).

5 Discussion

5.1 Abundance and preservation of SOM and FAs in catchment soils

With TOC contents between 5% and 38.2 %, all the studied samples were rich in OM irrespective of their vegetation cover (grassland S12: 25.7 %; forest S26: 38.2 %; intermediate S33: 29.7% TOC; Table 1). This richness provides preliminary evidence for a rather long residence time of SOM and consequently for good OM preservation. More direct indications were provided by RE parameters (HI and OI values). For example, samples S26 and S33, which were among the richest in OM, also presented relatively high HI and low OI values (namely in the 360-380 $mgHC.g^{-1}TOC$ and 170-250 $mgCO_2.g^{-1}TOC$ ranges; Table 1). Such HI and OI values that are common for forest litter in temperate areas are also typical for well-preserved type III OM (Disnar et al. 2003). In contrast, sample S36, which also originated from a forest soil and which contained only 8% TOC, presented lower HI and higher OI values (i.e. 220 $mgHC.g^{-1}TOC$ and 378 $mgCO_2.g^{-1}TOC$, respectively; Table 1) that constituted a clear indication of a more intensive OM alteration than the other samples. Despite this alteration, sample S36 had an extremely high FA content that suggests a better preservation of these compounds than bulk SOM, in agreement with general knowledge on the greater resistance of lipids compared to other biochemical compounds to (bio-)degradation (namely proteins and polysaccharides; Tissot and Welte 1984).

At the molecular scale, the overall good FA preservation is first evidenced by high even-over-odd compound predominance in the four compound families examined (Zelles 1997; Jandl et al. 2005; Disnar et al. 2005). The low contents of odd C numbered FAs strongly suggests that there has been no significant contribution from products of the oxidative degradation of alkanols or *n*-alkanes, *via* methyl ketones (Amblès et al. 1994; Bull et al. 2000b). From a general point of view, soil lipids can indeed be affected by chemical processes such as hydrolysis and transesterification of lipid esters and further by oxidation and reduction. The latter processes are dependent on soil pH and moisture, but also on other environmental factors such as the clay content, the nature of the microbial biomass, and the vegetation types (van Bergen et al. 1997). In the present case, two of these factors might immediately be suspected of having played a notable role in the preservation of FAs, and more generally of SOM. The first one is acidity since, as has long been observed, the preservation of soil lipids is primarily favored by a low pH (Moucawi et al. 1981; Jambu et al. 1985, 1987; van Bergen et al. 1998), although acidity favours the hydrolysis of biopolymers (Nierop et al. 2005) and the selective preservation of certain types of FAs,

especially aliphatic compounds (Bull et al. 2000a; Nierop and Verstraten 2003). The second factor is the volcanic nature of the soil parent material that might have given rise to abundant non-crystalline minerals. These are thought to be capable of forming stable organo-mineral complexes that might favour physical protection of SOM (Torn et al. 1997). In fact, this hypothesis has been contradicted by recent work (Buurman et al. 2007) and thus remains to be confirmed. Nevertheless, the role played by minerals in OM preservation is a generally accepted concept (e.g., Six et al. 2002).

5.2 Acid compounds as potential biomarkers in catchment soils

First, it is worth noting the low proportion of LMW nFAs $C_{16:0}$ and $C_{18:0}$, and above all the absence of their unsaturated counterparts such as *n*-$C_{18:1}$ and/or *n*-$C_{18:2}$ (i.e., linoleic acid). The latter compounds are frequently detected at variable concentrations in plant lipids, for example in the TLE as well as in the hydrolysate of the residue of the grass *Holcus latanus* (Bull et al. 2000b). In contrast, both these compounds and especially *n*-$C_{18:2}$ were only present at low levels in the soil where this grass grew. This is consistent with the high biodegradability of the LMW saturated and unsaturated FAs (Marseille et al. 1999).

With the exception of the LMW ωHOFAs that are particularly abundant in soil sample S36 (cf. section 5.1; Fig. 4), all Aydat catchment soils display similar or at least comparable FA distributions, whatever their plant cover or the compound family considered (Figs 3–6).

Among all the compound families examined, nFAs display the widest distribution of homologues, at least from *n*-$C_{16:0}$ to *n*-$C_{34:0}$ (Fig. 3). This family of compounds is usually divided into LMW and HMW compounds [i.e. *n*-C_{20-} and *n*-C_{20+} (including *n*-C_{20})], which is consistent with the reputed origin of these two sub-groups: the cellular membrane for the former and epicuticular waxes for the latter (Kolattukudy 1980). In contrast to the former that are ubiquitous and rather easily biodegraded as a result of their biological location and of their rather low molecular weight (e.g., Marseille et al. 1999), the latter are quite resistant and are thus frequently used as plant source indicators in sediment studies. However, in such cases they are generally considered as “markers of higher plants” without any further detail (Tissot and Welte 1984; Baudin et al. 2010), disregarding the fact that compound distributions are also known to vary depending on the species studied (e.g., Rieley et al. 1991), but also on the age of the plant (Martins et al. 1999; Lecomte 2009), and many abiotic factors such as light, temperature, osmotic stress, etc (Shepherd and Griffiths 2006).

Among the various other FA families observed in the studied samples, ωHOFAs were frequently present at high concentration levels, i.e. almost identical to those of nFAs (Fig. 2). As is particularly well exemplified by the altered forest sample S36 (cf. previous section), this compound family presents a bimodal distribution similar to that of nFAs, with a first mode in the LMW range (i.e., at C_{16}) and a second mode in the HMW range, at C_{22} (Fig. 4). Based on early studies (Eglinton and Hunneman 1968; Holloway 1982), authors usually assume that ωHOFA are cutin and/or suberin derivatives, irrespective of whether the ωHOFAs were found in sediment samples (e.g., Huang et al. 1996; Wakeham 1999; Stefanova and Disnar 2000) or soils (van Bergen et al. 1998; Naafs et al. 2004; Bull et al. 2000b). In fact, the “long chain” [as designated by Eglinton and Hunneman (1968)] HOFAs constitutive of cutin are almost exclusively C_{16} and/or C_{18} mono, di and trihydroxy FAs (Espelie and Kolattukudy 1979; Holloway 1982; Goni and Hedges 1990; Järvinen 2010). Here, such LMW ωHOFA are present in all samples but especially in soils developed under forest. The absence of the C_{18} HOFA was also consistent with the distribution of ωHOFAs of two spruce species, including *P. abies*, the dominant tree species

in the study area (Priigelt and Lognay 1996). This source assignment did not hold for the HMW ωHOFA (C_{20+}). However, in contrast to cutin, which comprises only LMW FAs ($\leq C_{18}$), suberin contains notable proportions of heavier terms. For example, Matzke and Riederer (1991) compared the chemical constitution of cutin and suberin from the leaves and the periderm (bark) of three major tree species (*Picea abies L.*, *Quercus robur L.* and *Fagus sylvatica L.*), and found that the suberin-rich periderm from stems and branches of the three species (plus roots of *Picea*) yielded notable proportions of $\geq C_{20}$ ωHOFAs (up to *n*-$C_{24:0}$ for *Picea* and to *n*-$C_{26:0}$ for *Fagus* and *Quercus*). These results strongly suggest that the HMW ωHOFAs (C_{20+}) in Aydat soils probably originated from the suberin of twigs, branches and roots of trees and/or grasses.

Among the various families examined, diFAs present the smallest number of homologues (namely, even-numbered carbon chain diFA from C_{20} to C_{26}; Fig. 6 and Fig. 7c). An even smaller distribution of diFAs (i.e., C_{22}diFA + C_{24}diFA only) was found in the grass *Holcus lanatus* and the underlying soil by Bull et al. (2000b). Among the plant samples analysed by Bull et al. (2000b) the almost exclusive presence of diFAs in the hydrolysates of roots and lipid extract of aerial parts of grasses substantiate their contribution to plant constitutive polymers, and especially to the suberin of roots. In addition, the absence of such compounds in non-hydrolysed plant samples and their presence in the soil provides clear evidence that the original polymers only start to undergo degradation (i.e., hydrolysis) once they have been incorporated in soils. According to Amblès et al. (1994) diFAs may well be formed by oxidation of ωHOFAs. However, the similarity in chain length of the dominant components in both families would in this case cause little alteration in component distribution. Suberin was probably also the source for the αHOFAs (Matzke and Riederer 1991). In addition to the case of trees, which has been well documented (see refs here above), C_{16} to C_{24}-αHOFAs have also been found in the roots and leaves of the herbaceous angiosperm *Arabidopsis thaliana* (Franke et al. 2005). As schematized in Fig. 5, all the samples, whether they were taken in grassland or forest, showed a similar distribution of αHOFAs with notable amounts of even-carbon-numbered components in the C_{22}-C_{26} range, and a maximum at C_{24}.

5.3 Differentiating source materials in catchment soils

The greatest differentiation between grassland and forest is provided by the ωHOFAs and especially by the abundance of the LMW terms (Fig. 7), even in the absence of extensive alteration such as that experienced by sample S36. In forest soils, the importance of the annual needle litterfall (notwithstanding the contribution of rather resistant suberin-rich branches and roots) could explain the dominance of LMW ωHOFA (i.e. C_{12} to C_{16}-ωHOFA; Fig. 4). In contrast, in grassland and intermediate area soils, the abundance of HMW ωHOFA (i.e. C_{24}-ωHOFA and C_{22}-ωHOFA; Fig. 7a) might underline a significant contribution of grass root suberin to SOM. In the latter case, most of the cutin-rich aerial plant production is either harvested (to make hay) or grazed by cattle. Although the residual matter can return to the soil after a transit through the cattle gut, either directly or due to manuring practices, the contribution of cutin from aerial parts of grasses to SOM might be minor when compared to suberin from roots. This distinction between cutin and suberin and their biomarkers is probably the most marked in an area such as that of Lake Aydat where forest litters that are prone to mobilisation by running waters are rich in leaves and/or needles (and consequently in cutin) whereas, in contrast, the suberin from plant roots of grasslands probably contributes predominantly to SOM formation, most of the cutin-rich aerial plant production being either grazed by the cattle or harvested (see here above).

The major differences between grasslands and forests have been tentatively rationalized by the following ratios:

(n-$C_{26:0}$+n-$C_{28:0}$)/ΣC_{even} nFAs, C_{22}/C_{24} di-FAs, and C_{20-}/C_{20+} ω-HOFAs (Fig. 7). For all of these ratios, a gradient between these two vegetation types emphasizes the characteristics of the intermediate area, sometimes close to grasslands, sometimes to forests. n-$C_{26:0}$, which constitutes the mode of nFA distributions in grassland soils, is also accompanied by n-$C_{24:0}$ in intermediate soils. In contrast, spruce forest soils do not display clear modal distributions, the even C numbered FAs homologues being all present at similar levels in the n-$C_{22:0}$-n-$C_{28:0}$ range. Accordingly, the (n-$C_{26:0}$+n-$C_{28:0}$)/Σn_{even} nFA ratio values decreased from an average of 0.65 in grassland soils (n = 12; Fig.7b) to 0.50 in intermediate soils (n = 4) and down to 0.32 in forest soils (n = 2). Grasslands and intermediate soils presented higher concentrations of C_{24}diFA followed by C_{22}diFA, while forest soils had higher concentrations of C_{22}diFA followed by C_{20}diFA and C_{24}diFA homologues. This allows us to propose the C_{22}/C_{24} diFA ratio as a simple tool to differentiate grassland and intermediate soils from those of forest, in the Aydat catchment. The dominant ωHOFA homologues were C_{12}, C_{14} and C_{16} in forest soils, and C_{24} and C_{22} in grassland soils (Fig. 7a). In intermediate area soils, the relatively high abundance of C_{16}-ωHOFA, C_{22}-ωHOFA and C_{24}-ωHOFA, expressed as the C_{20-}/C_{20+}ωHOFA ratio (Fig. 7d), denotes their mixed grassland/forest influence.

5.4 FA signatures as biomarkers for identifying land use change

Carbon accumulation in soils depends on many factors, both anthropogenic and environmental (Kasel and Bennett 2007 and references therein). The Aydat catchment has been used by humans for forest exploitation and agriculture since at least the fifth century (Michelin 1996). A large part of the area currently predominated by grasslands or even forests was extensively used for agriculture for a period after the 2nd World War. A general problem in evaluating the impacts of land-use change is that the landscape is not used at random but with a preferential selection of soil types or positions best adapted for particular uses (e.g. Powers and Veldkamp 2005). Changes in vegetation cover affect soil properties, with consequential modifications on the OM content and molecular composition, which have long term impacts on the plant cover, e.g. plant communities developed after the afforestation of abandoned lands differ from ancient forests depending on the related modification of the soil properties (Glatzel 1991; Compton and Boone 2000; Heim et al. 2010). This behaviour has been shown to control vegetation diversity in forests (Foster 1992; Hermy 1994; Koerner et al. 1997) even 300 years after afforestation, and it has even been suggested that this situation could persist indefinitely (Dupouey et al. 2002). Finally, even if the relevant factors (soil characteristics, elevation, slope) do not allow a very clear discrimination, plant-derived organic acids permit some distinction of soils based on their respective uses (Fig. 7 and Table 1). In contrast, deoxycholic acid, the major bile acid excreted in the faeces of bovines, clearly identifies grasslands used as pastures and/or for manure spreading at present and in the recent past in the Aydat catchment (Fig. 8). This compound was found in notably high levels in almost all grassland soils and intermediate areas except two of these, which were probably more or less abandoned, as denoted by a rather dense shrub cover (S10 and S33; Fig. 8). The persistence of relatively high levels of deoxycholic acid in areas that have been abandoned for five to six decades is fully consistent with the previous statement that this biomarker might even be preserved over thousands of years in soils and sediments (Bull et al. 2002, 2003).

In addition to land-use, the slope of the soil could also play an important role in the accumulation of carbon and acid compounds. However, at Aydat, no significant correlation could be deduced from the comparison of slopes (Fig. 1 and Table 1) with TOC values (all $P>0.05$, $R = 0.26$) or slopes with soil FA contents ($P>0.05$, $R = 0.19$).

5.5 FAs as potential indicators of terrestrial input to the sedimentary record

Lake Aydat is eutrophic, with seasonally abundant algal production (diatoms and cyanobacteria). Consequently, the amount of OM produced in the lake water body is certainly much more abundant than that provided by the catchment, thus strongly diluting the latter. A previous study on Aydat lacustrine sediments investigated the major free and bound lipid compounds recently deposited (> 1950) in the center of the lake (Stefanova and Disnar 2000). Among the compounds discussed here, only HMW nFAs (i.e. C_{20+}) were ascribed to higher plants of the watershed. FA distributions of all the other families examined were highly dominated by LMW terms (i.e., C_{20-}). Beginning with the highly dominant nFAs in *n*-$C_{16:0}$ and *n*-$C_{18:0}$, all these LMW compounds were attributed either to autochthonous lacustrine production or to microorganisms. In soil samples, only *n*-$C_{16:0}$ was found and in much lower proportions than HMW nFAs. This is consistent with the previously mentioned high biodegradability of these light ends (Marseille et al. 1999). In the sediment, diFAs ranging between C_{16} and C_{22} and maximizing at C_{16} were interpreted as originating from diatoms. A microbial source was also considered for the LMW αHOFAs (C_{20-}) that were found in notable proportions in the sediment albeit not in the free fraction but in bound form. This origin was also confirmed by the presence of *iso* and *anteiso* forms of these components. Without going into further detail, this brief comparison between FA soil and sediment markers clearly demonstrated that despite favorable factors such as high contents of SOM in a generally good state of preservation, a rather wet mountainous climate and relatively steep slopes, few terrestrial plant markers were transported by runoff waters and finally accumulated in the lake sediments.

6 Conclusions

As depicted by high TOC contents and relatively high and low HI and OI RE index values, respectively, Lake Aydat catchment soils that are presently covered by either grassland or forest (spruce dominant), are all rich in well preserved OM. The soils' free FA content is globally dominated by various HMW (C_{20+}) compounds: nFAs, diFAs, αHOFas and ωHOFAs; however, none of these compound families are specific to grasses or trees and consequently can consistently all be used as indicators of terrestrial OM as a whole, without any further distinction (as most authors usually do). Nevertheless, the forest soils are particularly rich in LMW ωHOFAs probably inherited from the cutin of needles and/or leaves. The abundance of these compounds, which increases with OM alteration, also denotes their relative stability with regard to that of the bulk OM. As generally admitted, HMW nFAs are mostly derived from plant leaf and needle cuticular waxes, and all the other oxygenated HMW compounds (αHOFAs and diFAs) very likely from the suberin of roots and/or twigs and branches. Differences in the abundance of these various compounds between grasslands and forests soils has allowed us to propose the following molecular ratios: $(C_{26:0}+C_{28:0})/\Sigma C_{even}$ nFAs, C_{22}/C_{24} di-FAs, and C_{20-}/C_{20+}ω-HOFAs to discriminate between soil samples. Consistently, grassland soils contained notable amounts of the bile acid deoxycholic acid. The preservation of this compound in soils that have changed use (e.g., from grassland to forest) witnesses their past use as pastures much more clearly than plant-derived FAs. Despite the abundance of a variety of HMW FAs, saturated nFAs were the only ones that had been previously found in sediments taken at the center of the lake (Stefanova and Disnar 2000). The exclusive presence of these compounds strongly suggests that: (i) there is only a very small delivery of FAs from these catchment soils to the lake and consequently (ii) these nFAs were most probably introduced directly by leaves and/or needles brought to the lake by the wind or runoff waters. Results

showed here question the importance of other processes that are generally overlooked, beginning with the mode of transportation of the FAs from the soils to the lake sediments.

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Table 1 Edaphic and topographic characteristics of soil samples of Lake Aydat catchment with Rock Eval pyrolysis data and FA concentrations. IH values are expressed in mg HC.g^{-1} TOC and OI in mg CO_2. g^{-1} TOC

Site	Vegetation (humus type)	Geological substratum	Granulometry Sand (%)	Silt (%)	Clay (%)	Slope (°)	Elevation (m)	pH_{CaCl2}	TOC (%)	HI	OI	FA conc. (µg.g $soil^{-1}$)	FA conc. (µg.g TOC^{-1})
S08	grassland	Basaltic				3.4	1096	5.27	12.5	310	178	186	1491
S09	grassland	Basaltic				9	1081	5.48	14.3	322	230	150	1048
S10	grassland (+ shrubs)	Basaltic				13.2	1061	4.96	13.7	257	188	113	823
S11	grassland (+ shrubs)	Basaltic				13.4	1047	4.66	11.2	267	197	145	1303
S12	grassland	Basaltic				9.3	1034	5.78	25.7	322	209	317	1230
S13	grassland	Basaltic				2.4	1023	5.26	6.6	327	176	120	1813
S14	grassland	Basaltic				9.8	1032	5.53	5.2	271	209	63	1210
S15	grassland	Basaltic				10.4	1045	5.24	6.2	262	255	312	5029
S17	grassland	Basaltic				3.4	1075	5.52	7.1	286	182	485	6794
S02	grassland	Quat. Alluv.				0.5	956	5.54	10.6	285	206	322	3025
S03	grassland	Basaltic				2.4	957	5.27	6.6	218	207	236	3583
S20	grassland	Basaltic	22	75	4	5.7	975	5.76	9.4	271	192	146	1561
S05	intermediate	Doreit				2.4	1268	4.52	16.2	352	167	843	5216
S28	intermediate	Basaltic				8.7	1055	5.32	7.5	236	208	501	6636
S33	intermediate	Basaltic				4	1038	5.01	29.7	378	176	486	1639
S34	intermediate	Basaltic	49	47	4	11	980	5.2	10.8	232	211	370	3418
S26	forest	Basaltic				16.6	1075	4.2	38.2	364	248	317	833
S36	forest	Basaltic	58	40	2	14.9	995	5.45	8	220	378	1877	23349

Legend: Quat. Alluv. = Quaternary Alluvion, HI = hydrogen index, OI = oxygen index.

FIGURE CAPTIONS

Fig. 1 Location of lake Aydat catchment area (French Massif Central). Soil sampling sites are represented by white circles. The profile shows the topography of a transect from S08 to S17 sites.

Fig. 2 Partial GC-MS chromatograms (TIC) of the methylated and silylated acid fractions of soil lipid extracts from Lake Aydat catchment. S14: grassland soil sample; S26: forest soil sample.

Fig. 3 Histograms showing the distributions of nFAs in lipid extracts of soil collected in grassland (S09 and S14), intermediate (S33 and S34) and forest regions (S26 and S36) of the Lake Aydat catchment.

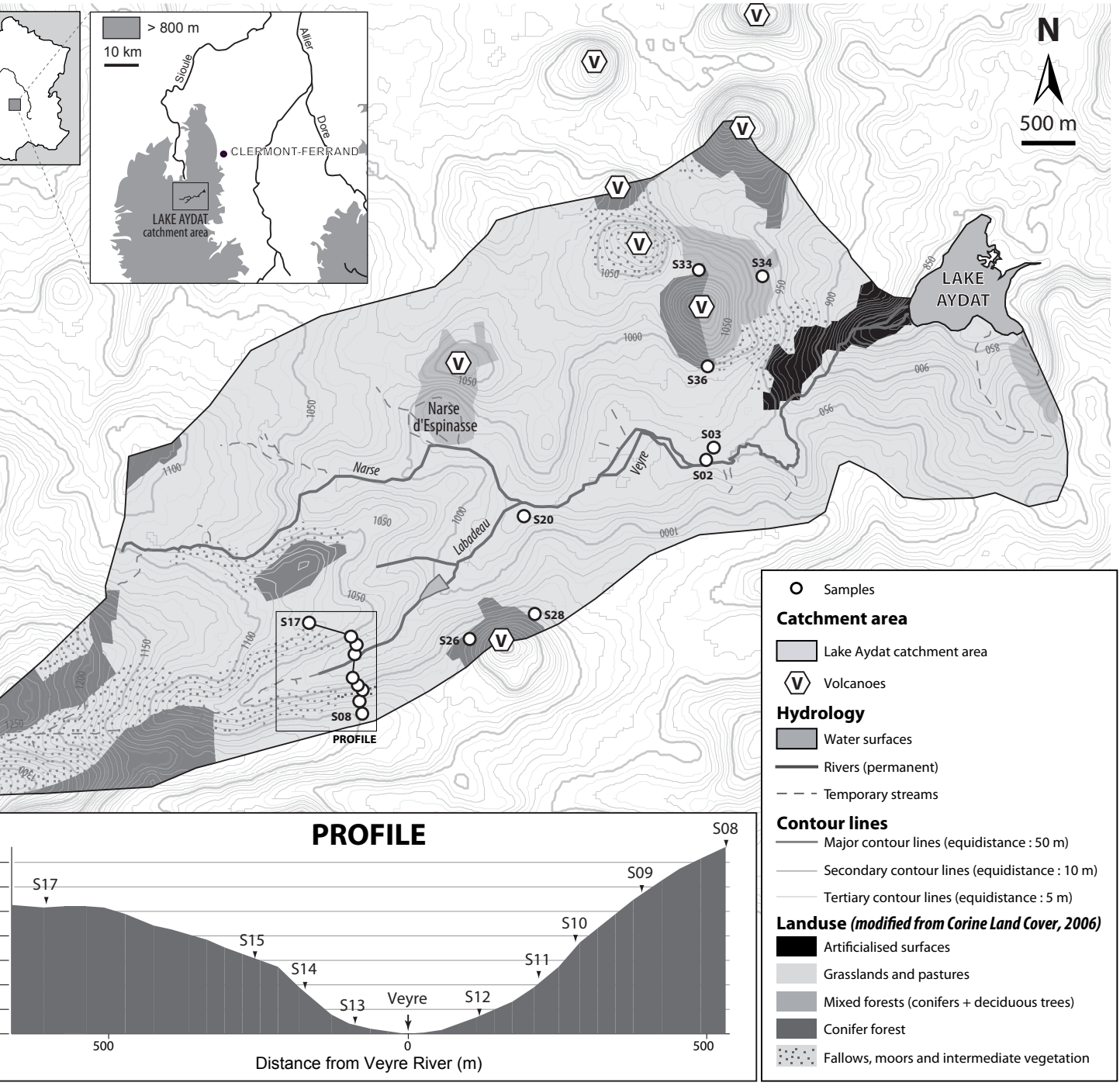
Fig. 4 Histograms showing the distributions of ωHOFAs in lipid extracts of soil collected in grassland (S09 and S14), intermediate (S33 and S34) and forest regions (S26 and S36) of the Lake Aydat catchment soils.

Fig. 5 Histograms showing the distributions of αHOFAs in lipid extracts of soil collected in grassland (S09 and S14), intermediate (S33 and S34) and forest regions (S26 and S36) of the Lake Aydat catchment.

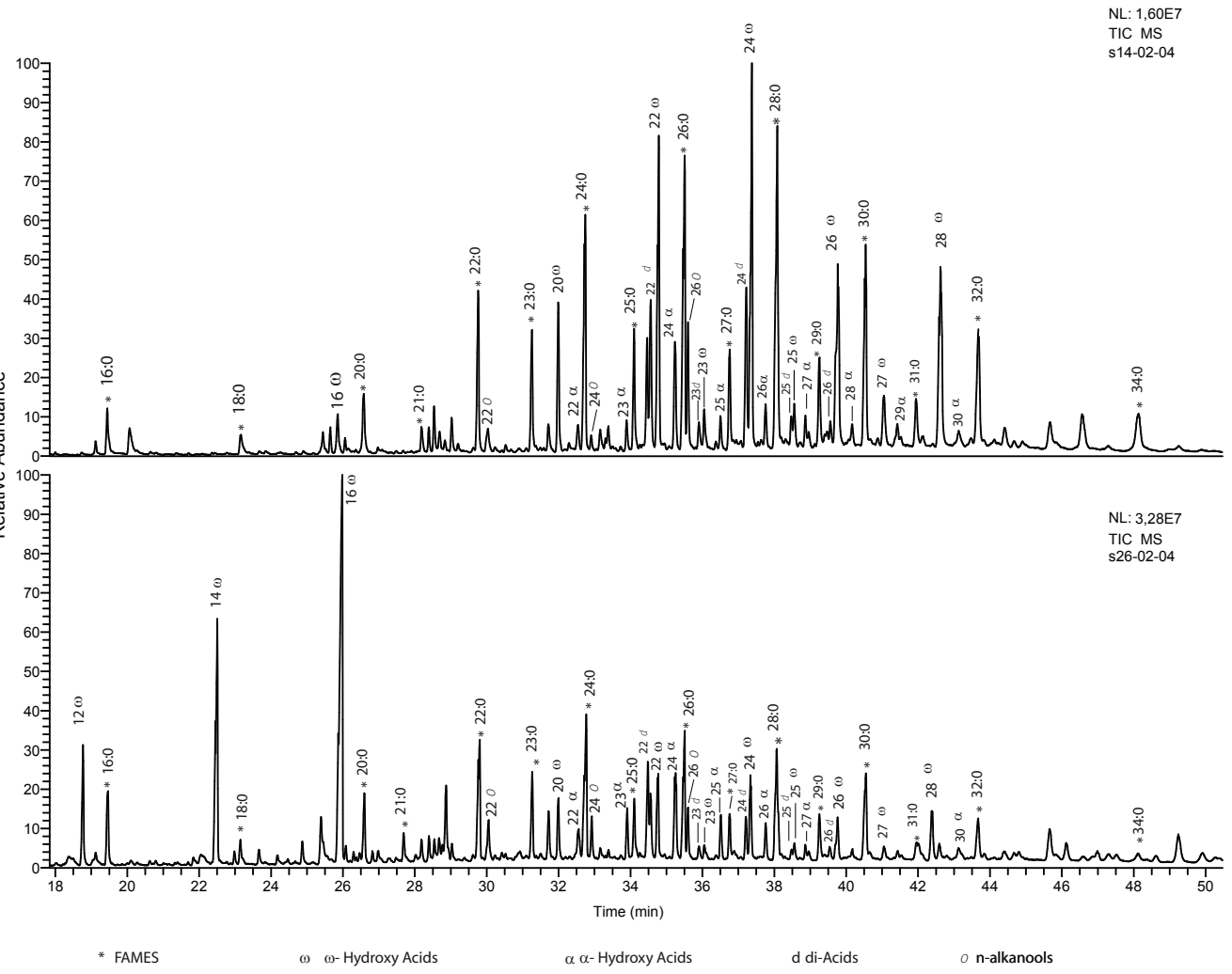
Fig. 6 Histograms showing the distributions of diFAs in lipid extracts of soil collected in grassland (S09 and S14), intermediate (S33 and S34) and forest regions (S26 and S36) of the Lake Aydat catchment.

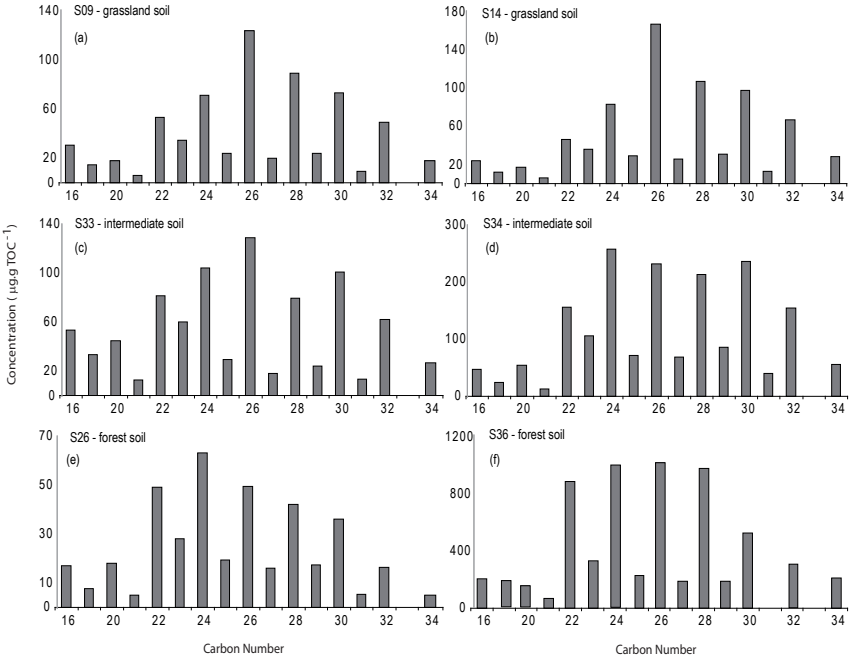
Fig 7 Summary of the most informative parameters yielded by the analysis of free lipids extracted from soils developed in the catchment of Lake Aydat. (a) Distribution of nFAs, ωHOFAs, αHOFAs and diFAs homologues according to the type of soil. Darker greys indicate the predominance of distinct homologues (b) Distribution of selected parameters [$(C_{26:0}+C_{28:0})/\Sigma C_{even}$ nFAs, (c) C_{22}/C_{24} diFAs, and (d) C_{20-}/C_{20+}ω-HOFAs] depending on soil type.

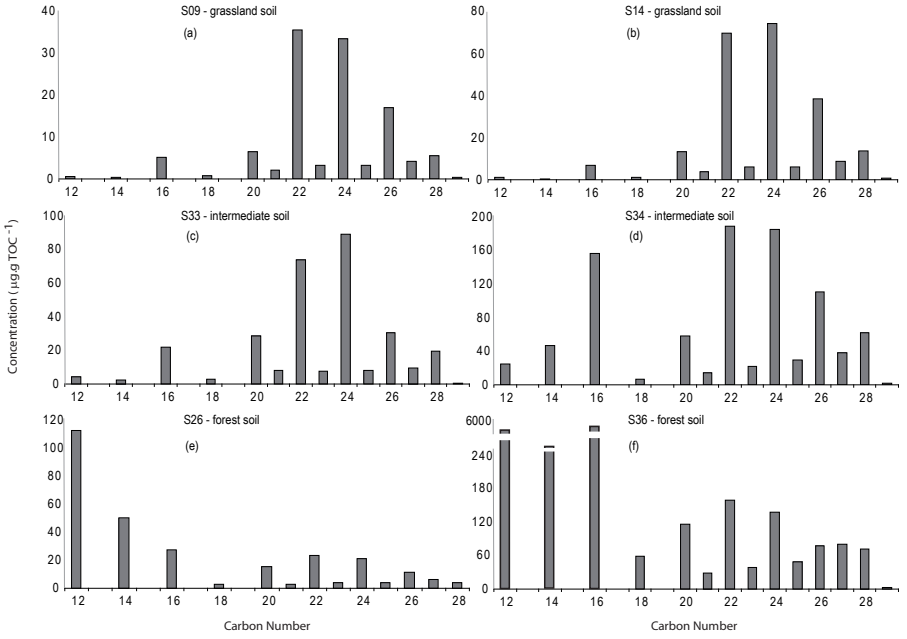
Fig. 8 Concentrations in deoxycholic acid in grassland, intermediate and forest soil samples from Lake Aydat catchment.

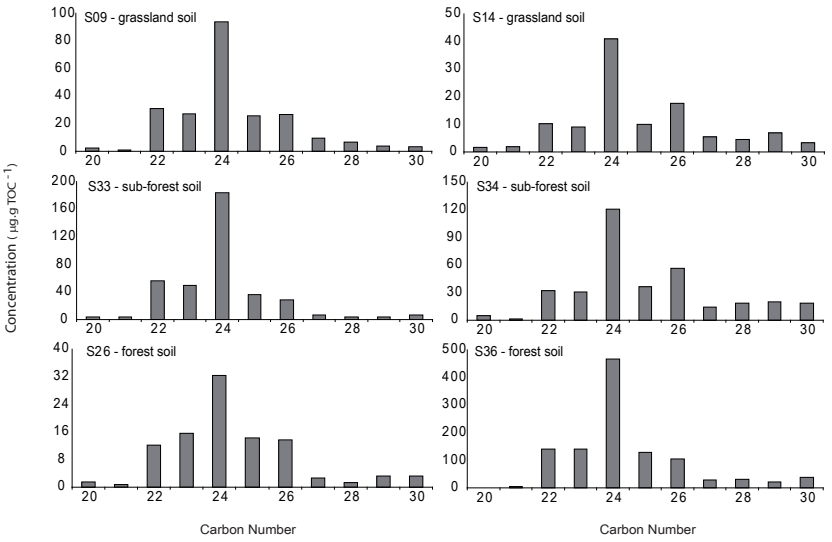

> 800 m
10 km
Sioule
Allier
Dore
CLERMONT-FERRAND
LAKE AYDAT
catchment area
N
500 m
LAKE
AYDAT
Narse
d'Espinasse
Narse
Veyre
Labadeau
S33
S34
S36
S03
S02
S20
S28
S26
S17
S08
PROFILE
Samples
Catchment area
Lake Aydat catchment area
Volcanoes
Hydrology
Water surfaces
Rivers (permanent)
Temporary streams
Contour lines
Major contour lines (equidistance : 50 m)
Secondary contour lines (equidistance : 10 m)
Tertiary contour lines (equidistance : 5 m)
Landuse (modified from Corine Land Cover, 2006)
Artificialised surfaces
Grasslands and pastures
Mixed forests (conifers + deciduous trees)
Conifer forest
Fallows, moors and intermediate vegetation

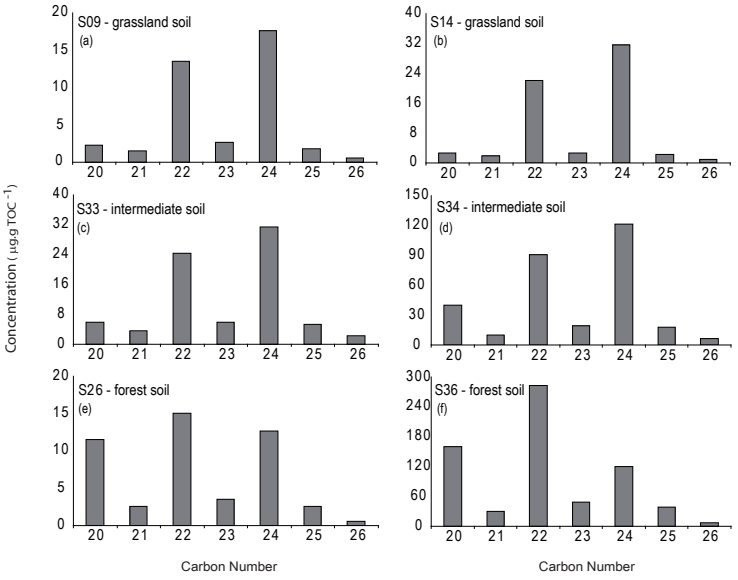
PROFILE
S17
S15
S14
S13
Veyre
S12
S11
S10
S09
S08
500
0
500
Distance from Veyre River (m)

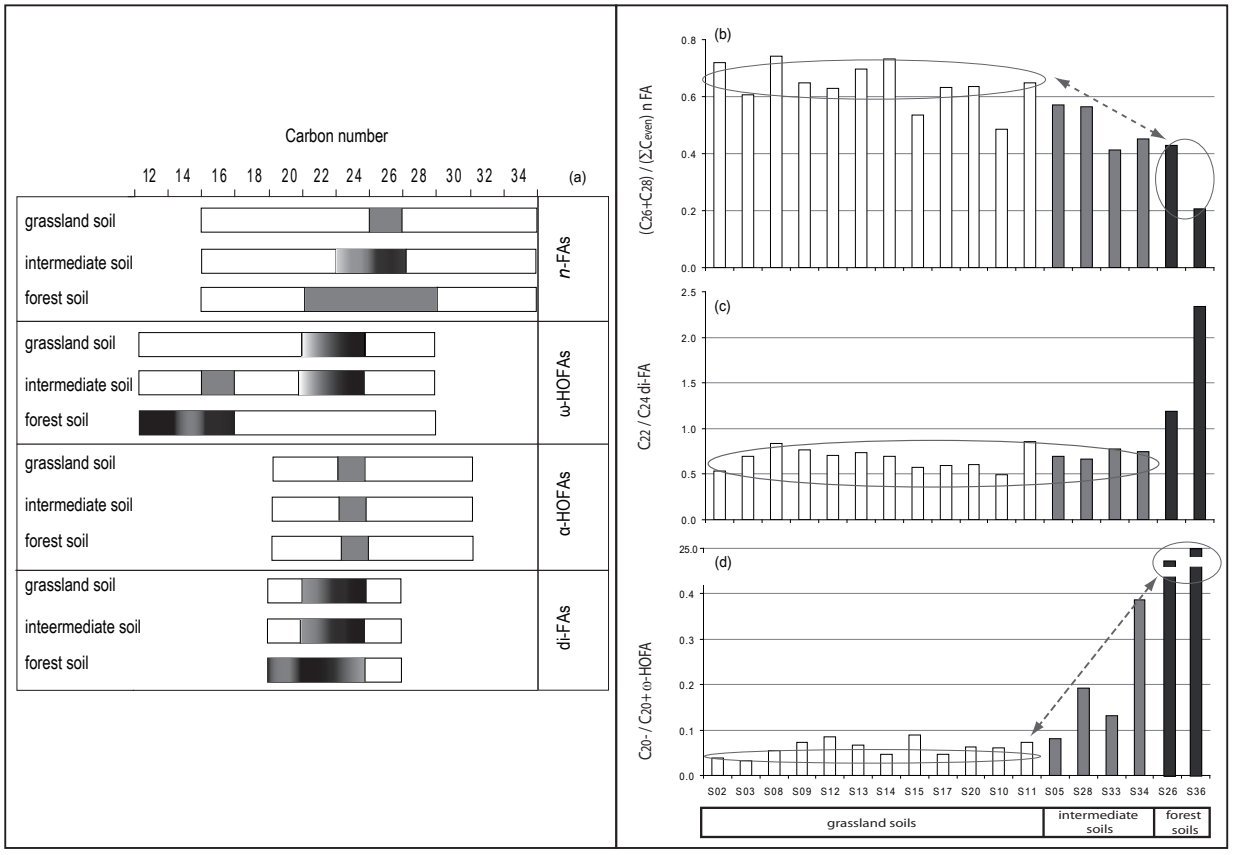

NL: 1,60E7
TIC MS
s14-02-04
NL: 3,28E7
TIC MS
s26-02-04
Relative Abundance
Time (min)
* FAMES
ω ω- Hydroxy Acids
α α- Hydroxy Acids
d di-Acids
0 n-alkanools

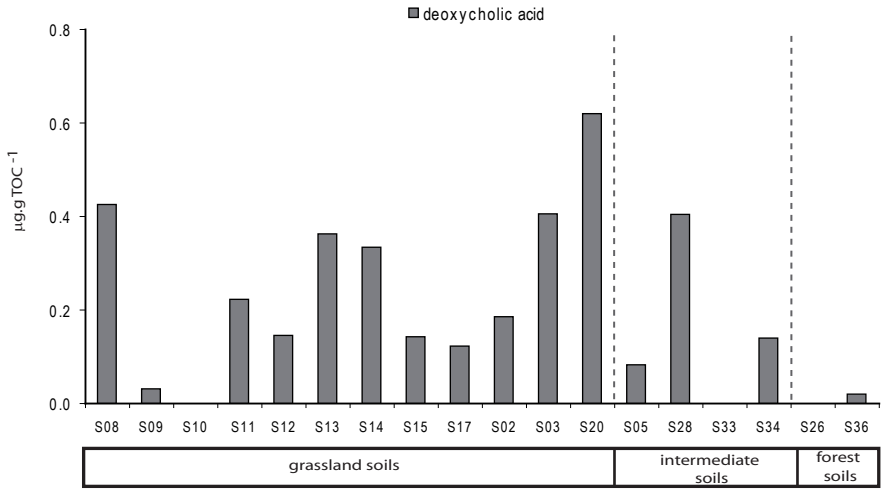

S09 - grassland soil
(a)
S14 - grassland soil
(b)
S33 - intermediate soil
(c)
S34 - intermediate soil
(d)
S26 - forest soil
(e)
S36 - forest soil
(f)
Concentration (μg.g TOC^{-1})
Carbon Number
Carbon Number


S09 - grassland soil
(a)
S14 - grassland soil
(b)
S33 - intermediate soil
(c)
S34 - intermediate soil
(d)
S26 - forest soil
(e)
S36 - forest soil
(f)
Concentration (μg.g TOC -1)
Carbon Number
Carbon Number


S09 - grassland soil
S14 - grassland soil
S33 - sub-forest soil
S34 - sub-forest soil
S26 - forest soil
S36 - forest soil
Concentration (μg.g TOC⁻¹)
Carbon Number
Carbon Number


S09 - grassland soil
(a)
S14 - grassland soil
(b)
S33 - intermediate soil
(c)
S34 - intermediate soil
(d)
S26 - forest soil
(e)
S36 - forest soil
(f)
Concentration (μg.g TOC -1)
Carbon Number
Carbon Number


Carbon number
12 14 16 18 20 22 24 26 28 30 32 34
(a)
grassland soil
intermediate soil
forest soil
n-FAs
grassland soil
intermediate soil
forest soil
ω-HOFAs
grassland soil
intermediate soil
forest soil
α-HOFAs
grassland soil
inteermediate soil
forest soil
di-FAs
(b)
(C26+C28) / (ΣCeven) n FA
(c)
C22 / C24 di-FA
(d)
C20- / C20+ ω-HOFA
S02 S03 S08 S09 S12 S13 S14 S15 S17 S20 S10 S11 S05 S28 S33 S34 S26 S36
grassland soils
intermediate soils
forest soils


deoxycholic acid
µg.g TOC -1
0.8
0.6
0.4
0.2
0.0
S08
S09
S10
S11
S12
S13
S14
S15
S17
S02
S03
S20
S05
S28
S33
S34
S26
S36
grassland soils
intermediate soils
forest soils