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Lipid, sterol and saccharide sources and dynamics in surface soils during an annual cycle in a temperate climate region

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ABSTRACT

Multi-biomarkers were characterized in surface soils with different vegetation during an annual cycle in Oregon, U.S.A., to study the composition and dynamics of soil organic matter (SOM). The major compound classes identified include saccharides, steroids, terpenoids, and homologous series of aliphatic lipids (*n*-alkanoic acids, *n*-alkanols, and *n*-alkanes). Saccharides, *n*-alkanoic acids, and sterols were the most dominant compound groups identified in Ryegrass field soils, whereas *n*-alkanoic acids, *n*-alkanols, and sterols were dominant in soils under conifer and deciduous vegetation. Plant species, instead of microbial organisms, was found to be the primary source influencing the concentration and distribution of the major biomarker tracers in the studied surface soils. Over an annual cycle, concentrations of higher plant lipids such as monoacyl glycerides, sterols, *n*-alkanoic acids and total wax were higher during summer (especially June–August). During fall into winter, the concentrations of all compounds decreased to steady state levels due to cessation of *de novo* synthesis and concomitant biodegradation and remineralization of detritus. Sucrose and glucose reached maximum concentrations during spring (especially March–May), which could be related with plant growth, especially rootlets in the soils. Mycose, the microbial/fungal metabolite, maximized during late summer, suggesting the concomitant increase of microbial/fungal activity with the increasing primary production. The composition and variation of biomarkers observed over an annual cycle improved our understanding of SOM dynamics in temperate soils, which could also be linked to regional and global carbon cycles.

1. Introduction

Soil is a major component of terrestrial particles that can be transported to estuaries and oceans by the atmosphere and rivers. Soil erosion and transport occurs as a consequence of natural processes (e.g. desertification, wind scouring, landslides) and of anthropogenic activities (e.g. agricultural tilling and harvesting, construction) (Morgan, 2005). Wind transport of eroded and resuspended soil particles, with concomitant atmospheric chemistry and fallout to river drainage basins, are processes of global importance and environmental concern (e.g. Lal, 2003). As a consequence, there is a need to assess the nature and fate of soils, both *in situ* and as part of the particle burden in the rivers and the atmosphere (Nierop et al., 2003; Otto et al., 2005; Otto and Simpson, 2007; Rogge et al., 2007; Rushdi et al., 2009; Simoneit et al., 2004a; Simoneit, 2006). Soil organic matter (SOM) is a complex mixture of numerous organic components from both viable and detrital biomass that vary in constitution and reactivity. The content and composition of SOM is determined primarily by overlying plants, microorganisms (fungi, bacteria, algae) and minor animals (Gleixner et al., 2002; Otto et al., 2005). Thus, SOM quality is directly related to plant productivity and microbial

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activity (e.g. Fierer et al., 2005), which is important for regional and global environmental processes, such as carbon cycling, atmospheric transport, and climate change. In order to better link SOM to environmental processes, contents of bulk lipids and lipid classes have been characterized for numerous soil types. It has been reported that SOM usually contains substantial amounts of structural biopolymers and lipids comprised of hydrocarbons, phospholipids, fats, waxes, fatty acids, terpenoids and steroids (Kindler et al., 2009; Otto and Simpson, 2005). Once released into the environment, the lipids (e.g. hydrocarbons) and structural biopolymers (e.g. cellulose, hemicellulose, lignin, and cutin/suberin), in comparison with other organic compounds (e.g. protein, nucleic acid biopolymers, and saccharides), are mostly refractory and undergo limited microbial degradation. Thus, they can be identified in soils and sediments where they are partially degraded and preserved. Therefore, organic compounds characteristic of soil biomass may be applied as potential tracers for soil processes (Medeiros et al., 2006; Otto et al., 2005; Otto and Simpson, 2007; Rogge et al., 2007; Rushdi et al., 2009; Simoneit et al., 2004a).

Analyses of solvent-extractable organic matter from soil samples have aided in evaluating (1) soil fertility and productivity (Gleixner et al., 2002; Huguet et al., 2010; Medeiros et al., 2006; Miltner et al., 2009; Trendel et al., 2010; Weijers et al., 2006, 2007; Wiesenberg et al., 2008), (2) soil-derived organic compounds resuspended in atmospheric particulate matter across various environments (Simoneit et al., 2004a,b), and (3) levels of pesticides, PAHs, and microbiological contaminants (Al-Mutlaq, 2006; El-Boukari et al., 2008; Liu et al., 2010; Woodruff et al., 2009). As soil activity cycles from primary production to dormancy, the corresponding molecular biomarkers change (Medeiros et al., 2006). As such, there is a need to investigate the composition of SOM using a multi-biomarker approach over an annual cycle in order to better understand its dynamics.

Here we document the dominant multi-biomarkers of various soils from a temperate climate region, over an annual cycle. We aim to (1) identify and quantify the major organic compounds in surface soils of different types from Oregon, U.S.A., including Ryegrass fields and conifer and deciduous tree vegetation; (2) characterize the variations of the major organic compounds of the studied soils from primary production to dormancy seasons; and (3) compare the similarities and dissimilarities of multi-biomarkers between Oregon soils and Western Canada grassland and conifer forest soils. The purpose of this study is to elucidate the dynamics of soil organic compounds encompassing a wide range of polarities and susceptibility to degradation.

2. Experimental methods

2.1. Sample collection

One initial set of soil samples was taken at the end of each month from a 60 ha perennial Ryegrass field (*Lolium perenne* L.) located southwest of Corvallis, Oregon, USA from January 2004 to January 2005 (Medeiros et al., 2006). Four to five surface soils (0–3 cm depth) samples were collected in an approximate 20 m diameter area and homogenized to give one composited sample. Analyses of composited samples from four different parts of the field demonstrated that the spatial variability of the compound concentrations is one order of magnitude smaller than the variability between seasons over an annual cycle (Medeiros et al., 2006). The soil was classified as fine, smectitic, and mesic Typic Albaqualfs, with a pH range between 4.2 and 4.6 (1:2; soil:water suspension) and TOC = 4.1 ± 0.2% (dry combustion; WR12 Leco Carbon Analyzer, St. Joseph, MI). A second set of surface soils was sampled from an agricultural Ryegrass field northeast of Corvallis and from a public park and trail in the city for comparison (Al-Mutlaq, 2006). Sampling started in mid-October of 2004 and continued monthly to September of 2005. The grass was harvested in early July. This grass field is located in the Hyslop Research Laboratory Farm of Oregon State University, Corvallis. The public park is the Rose Garden in Avery Park, Corvallis, where rose bushes and conifers are surrounded by a grassy area; the trail is located along the Willamette River front in downtown Corvallis with vegetation characterized by a mixture of coniferous forests and deciduous woodlands, as well as flowering bushes. The top 3 cm of surface soil was collected from an area of ~0.5 m^2 at each location using a stainless steel scoop. All samples were collected in pre-cleaned glass jars with Teflon-lined caps and brought to the laboratory for analysis. Samples were air dried on pre-cleaned aluminum trays at room temperature, ground with a mortar and pestle and then sieved to obtain 5 g of fine particles (<125 μm) before organic matter extraction. Soil temperatures and precipitation levels were recorded at an automated weather station (OCS, 2005, 2006) located approximately 5 km from the sampling sites.

2.2. Extraction

Dry soil samples (5–10 g) were sonicated twice for 15 min in a 30 mL mixture of dichloromethane:methanol (DCM:MeOH, 3:1, v/v). The extract aliquots were combined, filtered and concentrated by rotary evaporator to about 2 mL, then further to about 500 μL using a stream of high purity nitrogen. Aliquots (20 μL) of the total extracts were converted to their trimethylsilyl (TMS) derivatives using *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) (Pierce) and pyridine (Pierce) for 3 h at 70 °C. Prior to analysis the excess reagent was evaporated by a stream of nitrogen and the product dissolved in an equivalent volume of hexane.

2.3. GC–MS analysis

Each silylated total extract of the soil samples was analyzed within 24 h using an HP (now Agilent) 6890 gas chromatograph interfaced with an HP 5973 mass selective detector (GC–MS). A DB5-MS capillary column (30 m × 0.25 mm i.d. and film thickness of 0.25 μm, Agilent) was used with helium as the carrier gas at a constant flow rate of 1.3 mL min^{-1}. The injector and MS ion source temperatures were maintained at 280 °C and 230 °C, respectively. The column temperature program consisted of injection at 65 °C and hold for 2 min, temperature increase of 6 °C min^{-1} to 300 °C, followed by an isothermal hold at 300 °C for 15 min. The MSD was operated in the electron impact mode with an ionization energy of 70 eV. The scan range was set from 50 to 650 Da at 1.27 scan s^{-1}. The samples were analyzed in the splitless mode (splitless time: 30 s).

The data were acquired and processed with the HP (Agilent) Chemstation software. Individual compounds were identified by comparison of mass spectra with literature and library data, comparison of mass spectra and GC retention times with those authentic standards and/or interpretation of mass spectrometric fragmentation patterns. Compounds were quantified using total ion current (TIC) peak area and converted to compound mass using calibration curves of external standards (perdeuterotetracosane for *n*-alkanes, hexadecanoic acid for fatty acids and esters, hexacosanol for *n*-alkanols, sitosterol for steroids and triterpenoids, dehydroabietic acid for diterpenoids, glucose for monosaccharides, and sucrose for disaccharides). Procedural blanks were run in sequence to soil samples, presenting no significant background interferences.

Saccharides were analyzed as freely soluble saccharides and recoveries of standards were already published elsewhere (Medeiros and Simoneit, 2007, 2008), varying from 70% to 119%.

3. Results and discussion

The relative normalized concentrations of the lipid compounds in soils from the Oregon region are shown in Tables S1 and S2 (Supplementary Material) and summarized in Table 1. The mean percentages of total EOM (extractable organic matter) for the organic compound classes in these soils are given in Table 2. The percentage of total EOM to total organic carbon (TOC) contents ranged from 0.05 to 0.45% for the Ryegrass soils, and from 0.31 to 1.14% for the Rose Garden and River Park soils. Solvent extractable organic matter represents a minor fraction of TOC; however, the biomarkers are source specific and representative of seasonal changes in SOM composition due to production/exudation by plants and microbial degradation, providing key information on plant-microbe dynamics in soils. Examples of the typical GC–MS total ion current (TIC) traces and key ion traces for the samples are shown in Figs. 1–3 and S1. The total extracts show the distributions and relative abundances of the major organic constituents which consist primarily of saccharides, sterols, monoacyl glycerides, and the homologous compound series of *n*-alkanoic acids, *n*-alkanols, *n*-alkanes, α,ω-alkanedioic acids, and minor terpenoids.

3.1. Saccharides

Plants produce saccharides by photosynthesis for energy, and when in excess, saccharides are stored as sucrose for respiration during night time when plants cannot photosynthesize. Saccharides can be also derived from the degradation of cellulose and hemicellulose biopolymers, which are mainly responsible for plant structural strength. A cellulose molecule is a long-chain, linear polymer made up of 7000 to 12,000 D-glucose monomers, while a hemicellulose molecule is a 100–200 sugar monomer polysaccharide mixture of glucose, mannose, galactose, xylose, arabinose, 4-*O*-methylglucuronic acid and galacturonic acid (Parham and Gray, 1984). In soils, these complex carbohydrate biopolymers undergo oxidative, enzymatic and hydrolytic degradation into simple sugars. Thus, saccharides are a major fraction of SOM and also common components in atmospheric aerosols due to wind resuspension of soil particles (Gleixner et al., 2002; Simoneit et al., 2004a).

Saccharides occur in all samples throughout the year (Tables S1 and S2), and the primary saccharides include mycose (a.k.a. trehalose, I, the chemical structures cited in the text are shown in Appendix I), sucrose (II) and α- and β-glucose (III) (e.g. Fig. S1h). These same saccharides were previously identified as the major sugars in temperate climate agricultural soils from the San Joaquin Valley, California (Rogge et al., 2007; Simoneit et al., 2004a) and from the Ryegrass field south of Corvallis, Oregon (Medeiros et al., 2006). Saccharides are a major organic compound class in the total EOM of Ryegrass field soils (21.5%) and a minor class in Rose Garden (2.1%) and River Park (0.9%) soils (Table 2; Figs. 1 and 2). In a comparable study, saccharides were previously also identified as a major class in the total solvent extracts of the mineral horizons of conifer forest soil (22.6%) and grassland soils (6.2%) from Western Canada (Otto and Simpson, 2005).

The total saccharide concentrations in these Ryegrass field and other soils reached a maximum during April and July of the annual cycle from Jan 2004 to Jan 2005 and then decreased to lower concentrations during the remainder of the year (Tables S1 and S2; Figs. 1 and 2). Mycose was the predominant saccharide throughout the year and it peaked in July (Fig. 4b). It is a microbial metabolite, serves as a carbon and energy source for bacteria, and functions as a cell protectant against abiotic stresses such as desiccation, frost and heat (Lordachescu and Imai, 2011). Sucrose and, to a lesser extent, glucose levels in the soils were also highest during March and April, the active primary productivity months. Glucose reached a maximum concentration during July, the warmest month (Fig. 4a and S2). Levoglucosan, the tracer for cellulose in biomass burning emissions (Simoneit et al., 1999), was not detectable in any of these soil samples.

3.2. Sterols

Sterols are ubiquitous and distinctive constituents of all biota, except bacteria. Because these compounds are relatively stable and distributed characteristically in different biota, the analysis of sterols can provide a means of determining the origins of organic materials in the environment (Volkman, 1986). Sterols can be utilized as indicators for source inputs of organic matter to soils. For instance, the C_{28}–C_{29} phytosterols (mainly campesterol, IV, R = CH_3; stigmasterol, V; and sitosterol, IV, R = C_2H_5), which are components of plant lipid membranes, organs and waxes, are used as tracers in soils for plant sources (Sinsabaugh et al., 1997; Volkman, 1986). Although, there is evidence that cholesterol (C_{27}, IV, R = H) is a sterol present in the surface lipids of higher plant leaves and fruits (Noda et al., 1988), it is considered as a major animal sterol and used as a biomarker for faunal input to soils (Puglisi et al., 2003; Rogge et al., 2006). Ergosterol (VI) is a fungal metabolite and has been applied as a biomarker tracer for fungi in soils (Ruzicka et al., 2000).

Sterols are ubiquitous in environmental samples such as aerosol particles, sediments, desert dust, soils, etc. (e.g. Al-Mutlaq et al., 2002, 2007; Rogge et al., 2006, 2007; Rushdi et al., 2005; Simoneit et al., 2004b). However, the sterol contents of agricultural soils are affected by biological activity in the system and farming practices (Rogge et al., 2006; Sinsabaugh et al., 1997). Soil bacteria and fungi can alter sterols or utilize them as substrates (e.g. Ahmad et al., 1991; Otto et al., 2005; Ruzicka et al., 2000). It was also found that soil properties such as pH, moisture content and other factors can affect the microbial metabolism of sterols (Casalicchio and Lercker, 1974). The ratio of cholesterol to the phytosterols may be an indicator of the dominant detrital input sources in a soil, despite microbial degradation.

The sterol levels in the soils from this study are summarized in Table 1, S1 and S2 and an example of their distribution is shown in Figure S1e. The sterols are a major organic compound class of total EOM in River Park (19.7%), Ryegrass field (17.5%) and Rose Garden (12.1%) soils (Table 2). In a comparable study, steroids were also previously identified as a major organic compound class in the total solvent extracts of the mineral horizons of grassland soils (30.9%) and conifer forest soil (29%) from Western Canada, and included sitosterol, stigmasterol, campesterol and ergosterol (Otto and Simpson, 2005).

The sterol contents of these soils differ among the sites and over the annual cycle. The changes in sterol distributions for each soil type are shown in Figs. 1 and 2, and illustrate the time variations as relative concentrations in the total EOM. Generally, the level of sitosterol is the highest at all sites, followed by stigmasterol then campesterol. Ergosterol was not detected in any of these surficial soil samples, indicating that its formation must occur in deeper horizons as reported by Otto and Simpson (2005). These distributions were also affected by time in the case of the Ryegrass field, as the levels of these compounds were highest in June–July and similar in the other months of the study period (Fig. 4d). Nevertheless, the sterol distribution pattern can be

Table 1
Major organic groups and individual compounds in soils from temperate locations over an annual cycle (2004–2005).

Group Individual compound	Ryegrass field ng/g (min–max)	Rose Garden ng/g (min–max)	River Park ng/g (min–max)
Saccharides			
Mycose	1200–17800	370–9200	600–1198
Sucrose	150–2950	30–4630	160–220
α-+β-Glucose	95–2240	80–3120	240–300
Total	1790–23090	560–11454	1060–1658
Percent of total EOM (min–max)	7.0–40	0.30–5.7	0.80–0.90
Month (min/max)	Jan/Jul	Feb/Jul	Jan/Aug
Steroids			
Sitosterol	1802–12850	9020–43700	19900–22400
Campesterol	131–5430	2020–9670	5000–5600
Stigmasterol	370–3420	380–1680	1080–1400
Cholesterol	106–2142	980–3500	2000–2880
Total	2968–22540	13430–58250	28580–31680
Percent of total EOM (min–max)	7.6–24	9.0–16	17–22
Month (min/max)	Sep/Jul	Oct/Jun	Jan/Aug
Acyl glycerides			
1-Tetracosyl glyceride	780–6188	5100–10250	3010–3850
1-Hexacosyl glyceride	114–3570	330–2270	506–708
2-Tetracosyl glyceride	442–2140	12–860	20–40
Total	3045–17586	10331–17466	5486–6708
Percent of total EOM (min–max)	7.7–25	3.3–10	3.6–4.3
Month (min/max)	Jan/Jun	Feb/Jun	Jan/Aug
***n*-Alkanoic acids**			
n-Hexadecanoic acid	408–18770	1040–5750	2440–7200
n-Tetracosanoic acid	10–5474	19,450–63800	5000–19200
n-Hexacosanoic acid	6–4930	8200–23100	1600–5800
Total	608–57122	43773–154685	18895–49454
Percent of total EOM (min–max)	2.9–32	24–37	15–27
Month (min/max)	Nov/Jul	Nov/Jul	Jan/Aug
***n*-Alkenoic acids**			
Octadecenoic acids	40–2710	n.d.–2650	242–320
Hexadecenoic acid	n.d.–1840	140–3500	100–2060
Octadecadienoic acid	n.d.–248	n.d.–240	n.d.–135
Total	43–3698	194–3340	420–2437
Percent of total EOM (min–max)	0.20–10	0.10–1.6	0.30–1.3
Month (min/max)	Nov/Jul	Nov/Jun	Jan/Aug
Other acids			
1,23-Tricosanedioic acid	n.d.–3670	960–4350	n.d.–1000
Benzoic acid	96–1900	80–250	20–1080
1,21-Heneicosanedioic acid	n.d.–1800	n.d.–4250	n.d.–1200
Total	160–7840	2205–11410	20–3880
Percent of total EOM (min–max)	0.80–20	1.1–5.1	0–2.1
Month (min/max)	Nov/Jul	Feb/Jul	Jan/Aug
***n*-Alkanols**			
n-Hexacosanol	280–24700	2550–23950	4630–7160
n-Tetracosanol	18–1830	9300–42800	12600–14360
n-Docosanol	54–1190	5150–32400	9020–10800
Total	1676–35543	36100–134510	39050–42740
Percent of total EOM (min–max)	5.1–23	22–30	23–31
Month (min/max)	Mar/Jul	Nov/Jul	Jan/Aug
***n*-Alkanes**			
n-Hentriacontane	n.d.–2990	1220–9350	1380–2480
n-Nonacosane	1–2964	860–6250	2770–4060
n-Tritriacontane	n.d.–1073	120–1500	460–1380
Total	3–10523	3557–34720	14480–22390
Percent of total EOM (min–max)	0.010–8.4	2.2–16	11–12
Month (min/max)	Apr/Jul	May/Jun	Jan/Aug
Alkyl ferulates			
Docosyl ferulate	n.d.	640–9860	710–1196
Tetracosyl ferulate	n.d.	49–1330	236–492
Docosyl dihydroferulate	n.d.	25–650	n.d.–77
Total	–	2152–11604	1147–2327
Percent of total EOM (min–max)	–	1.1–7.1	0.90–1.3
Month (min/max)	–	Apr/Feb	Jan/Aug
Diterpenoids (resins)			
Dehydroabietic acid	12–131	4050–36250	10200–13100
Isopimaric acid	n.d.	1040–1900	2440–3040
Abietic acid	n.d.	402–1750	400–720
Total	12–131	7060–42690	16590–17380
Percent of total EOM (min–max)	0.020–0.40	4.6–12	8.9–14
Month (min/max)	May/Feb	Dec/Jul	Aug/Jan
Triterpenoids			
α- + β-Amyrins	551–2268	650–6160	1460–5650

Table 1 (*continued*)

Group Individual compound	Ryegrass field ng/g (min–max)	Rose Garden ng/g (min–max)	River Park ng/g (min–max)
Total	551–2268	650–6160	1460–5650
Percent of total EOM (min–max)	1.4–4.0	0.40–2.1	1.1–3.0
Month (min/max)	Sep/Jul	Feb/Jul	Jan/Aug
Pesticides			
Oxadiazon	n.d.	160–1480	n.d.
Total	–	160–1480	–
Percent of total EOM (min–max)	–	0.10–0.60	–
Month (min/max)	–	Oct/Jun	–
Total all compounds (EOM; μg/g)	21.00–176.2	122.5–456.3	128.0–185.5
Month (min/max)	Nov/Jul	Nov/Jul	Jan/Aug

Abbreviations: max = maximum; min = minimum; n.d. = not determined; EOM = extractable organic matter.

Table 2
Mean percentages of EOM for major organic compound groups in soils from temperate locations.

Compound group	Ryegrass field	Rose Garden	River Park	Grasslands[a]	Conifer Forest[a]
Saccharides	**21.5**	2.1	0.9	6.2	22.6
Steroids	17.5	12.1	19.7	**30.9**	**29**
Acyl glycerides	14.7	7.2	4.0	2.0	0
n-Alkanoic + alkenoic acids	20.0	**33.1**	21.5	21.7	19.9
Other acids	7.2	2.4	1.1	3.5	0
n-Alkanols	14.4	25.9	**26.7**	27.0	12.5
n-Alkanes	2.4	6.1	11.7	5.4	0.8
Alkyl ferulates	0	2.9	1.1	0	0
Diterpenoids (resins)	0.1	7.3	11.1	0	12
Triterpenoids	2.5	0.9	2.1	3.0	0.8
Pesticides	0	0.2	0	0	0
Total	**100**	**100**	**100**	**99.7**	**97.6**

EOM = extractable organic matter; numbers in bold are the maximum abundances.
[a] Data from Otto and Simpson (2005).

influenced by the crop (Rogge et al., 2007), but sitosterol is typically dominant. Cholesterol is found at low levels throughout the annual cycle (Tables S1 and S2) indicating an origin from algal lipid detritus (Rogge et al., 2007). Another source could be higher order fauna from application of manure fertilizer, which was not the case for these soils, where synthetic or no fertilizers were used.

3.3. Monoacyl glycerides

Monoacyl glycerides are major constituents of plant and microbial membranes and are part of the storage lipid (fats) pool (Harwood and Russell, 1984; Tulloch, 1976). They are common compounds in grassland soils (Feng and Simpson, 2007; Otto et al., 2005; Otto and Simpson, 2005), and are found in all Oregon region soils (e.g. Fig. S1i, S1j, Tables S1 and S2). The monoacyl glycerides are a significant compound class in the total EOM of Ryegrass field soil (14.7%) and a minor class in Rose Garden (7.2%) and River Park (4%) soils (Table 2). In a comparable report, monoacyl glycerides were also identified as minor components in the total extracts of the mineral horizons of grassland soils (2%) (Otto and Simpson, 2005).

The monoacyl glycerides had a carbon number range from C_{16} to C_{28}, C_{max} at 24, and even/odd carbon number predominances of the fatty acid ligands (Tables S1 and S2). The 1-monoacyl glycerides (VII) were more abundant than their 2-monoacyl glyceride (VIII) isomers. In Ryegrass field soils, the monoacyl glyceride concentrations reached a minor maximum in February and a major maximum during summer (June–August), with lower and fluctuating concentrations in the other months of the annual cycle (Fig. 4c, Table S1). For the Rose Garden and River Park soils, the monoacyl glyceride concentrations were similar, both maximizing between June and August (Fig. 5c, Table 1 and S2).

Although ω-hydroxyalkanoic acids were not found in any of these soils samples, the glyceryl esters of two homologs are significant components of only the grass field soils. These compounds are the 2-alkan-ω-olyl glycerides (IX, n = 18 and 20, Fig. 1 and S1a) and occur at highly variable concentrations (Table S1).

3.4. n-Alkanoic acids

The *n*-alkanoic acids are basic units of plant fats, oils and phospholipids. Since free *n*-alkanoic acids are relatively minor plant wax components and intermediary in the production of other wax constituents, their concentrations in soils may be influenced significantly by biochemical processes occurring in plant sources and by the bacterial degradation of wax esters, which can also be hydrolyzed to *n*-alkanoic acids and *n*-alkanols (Tulloch, 1976).

The *n*-alkanoic acids are a major organic compound class in all Oregon region soil samples (e.g. Fig. S1d, Table 1, S1 and S2). The *n*-alkanoic acids are the most abundant organic compound class in the total EOM of Rose Garden soil (32.5%), and a major class in River Park (20.7%) and Ryegrass field (17.6%) soils (Table 2). The *n*-alkanoic acids were also identified as major compounds in total extracts of deeper horizons in grassland (21.7%) and conifer forest (19.9%) soils (Otto and Simpson, 2005).

In the Ryegrass field soils, the *n*-alkanoic acids range from C_{12} to C_{30}, with C_{max} primarily at 16, and a strong even/odd carbon number predominance (CPI = 5.8 to 107). In comparison, the range and C_{max} are both similar to the *n*-alkanoic acid distribution in Ryegrass wax, which ranges from C_{16} to C_{32} and a C_{max} at 16, suggesting this plant wax as the source for these compounds (Oros et al., 2002, 2006). The *n*-alkanoic acid concentrations reached a minor maximum during February and a major maximum during

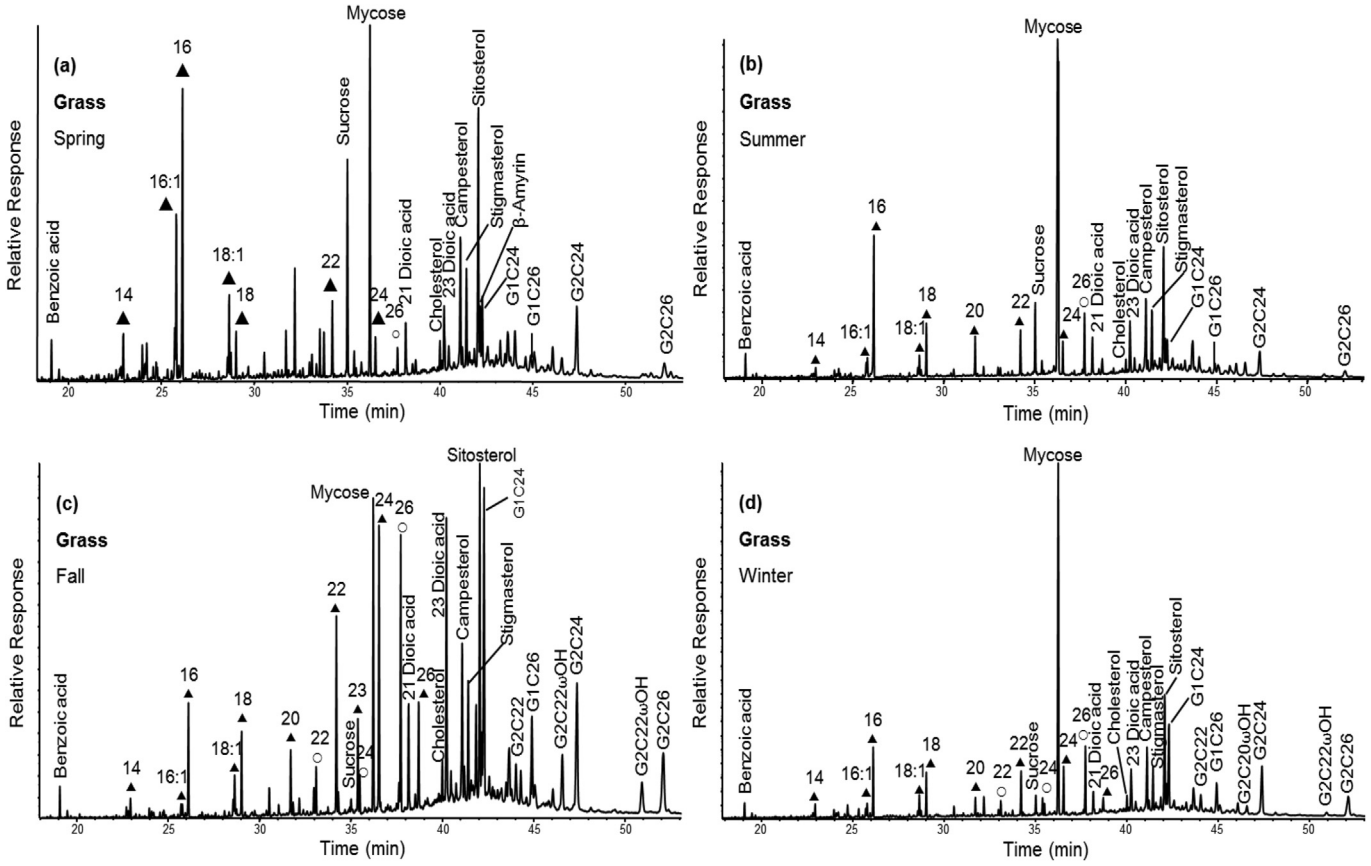

Fig. 1. Salient features of the GC–MS data of total extracts from grass field soils: (a) Total ion current (TIC) trace during spring season, (b) TIC trace during summer season, (c) TIC trace during fall season, (d) TIC during winter season. The symbols over the peaks indicate homologous series (◦ = *n*-alkanol, Δ = *n*-alkanoic acid) and the numbers are the compound carbon chain lengths (G1 = 1-Acyl glycerides; G2 = 2-Acyl glycerides; G2w = Alkan-G2C20wOH and G2C22wOH = 2-Alkan-ω-olyl glycerides).

summer (June–August) for the Ryegrass soils (Fig. 4c; Table S1). The Rose Garden soils had a similar *n*-alkanoic acid distribution, range, CPI and C_{max} as the Ryegrass field, but higher concentrations (Table S2). They have a maximum *n*-alkanoic acid level during summer (Fig. 4c). For the River Park soil, the *n*-alkanoic acid concentrations were greater in July than in January (e.g. Fig. 4c). In addition, all the Oregon region soil samples show minor contributions from unsaturated fatty acids including $C_{16:1}$, $C_{18:1}$ and $C_{18:2}$, which represent primary unweathered lipids. The ratio of low ($<C_{20}$) to high ($\geq C_{20}$) molecular weight *n*-alkanoic acids (L/H) was used to assess microbial inputs to the soil samples (Tables S1 and S2). The low L/H ratio for the Ryegrass field soils (0.1) and higher L/H (1.0–9.7) for the other soils reflect greater microbial lipid remnants in the Rose Garden and River Park soils, and this is more prominent during winter.

3.5. Alkanedioic acids

Series of α,ω-alkanedioic acids with a range from C_{21} to C_{27}, C_{max} at 23, and an odd/even carbon number predominance are present as a minor organic compound class in all Oregon region soil samples (e.g. Fig. S1g, Tables S1 and S2). In the Ryegrass field soils, the α,ω-alkanedioic acid concentrations reached maxima during February and June–July, with lower concentrations during the other months of the year. For the Rose Garden and River Park soils, the α,ω-alkanedioic acid concentrations were highest in summer.

Alkanedioic acids have previously been identified from a variety of sources and in the environment (Abas et al., 1995; Gogou et al., 1996; Hildemann et al., 1994; Mazurek and Simoneit, 1984; Otto et al., 2005; Rogge et al., 1993; Simoneit and Mazurek, 1982; Simoneit, 1989; Stephanou, 1992; Stephanou and Stratigakis, 1993). The α,ω-alkanedioic acids ($>C_{16}$) with mainly an even/odd carbon predominance were previously reported in soils and identified as typical biomarkers from suberin (Nierop et al., 2003, 2005; Winkler et al., 2005; Otto and Simpson, 2006). Suberin is a biopolymer containing aromatics and polyesters of predominantly long chain (C_{20}–C_{32}) aliphatic acids, diacids and ω-hydroxy acids (Bernards, 2002), and comprises the periderm of roots and bark, functioning as a barrier for underground parts, wound surfaces and internal organs (Kolattukudy, 1980; Winkler et al., 2005).

This unusual odd carbon chain length predominance of these alkanedioic acids has not been reported before and there appears to be one precedent for their formation in these soils. The microbial metabolism of alkan-2-ones to ultimately alkanedioic acids has been demonstrated in culture by hydrocarbon-utilizing mycobacteria (Lukins and Foster, 1963; Patzelt, 2007). Alkan-2-ones (o/e predominance) are common constituents in soil lipids and derive from plant wax (hydrocarbon) metabolism by microbes (e.g. Rushdi et al., 2005; Rogge et al., 2007; Trensel et al., 2010). Thus, we propose the source of these odd carbon chain alkanedioic acids is from alkanes via alkan-2-ones, which are at trace levels in these soils, mediated by the soil microbiota.

3.6. n-Alkanols

The *n*-alkanols are a predominant organic compound class in all the soil samples (e.g. Fig. S1c, Tables S1 and S2). *n*-Alkanols are the

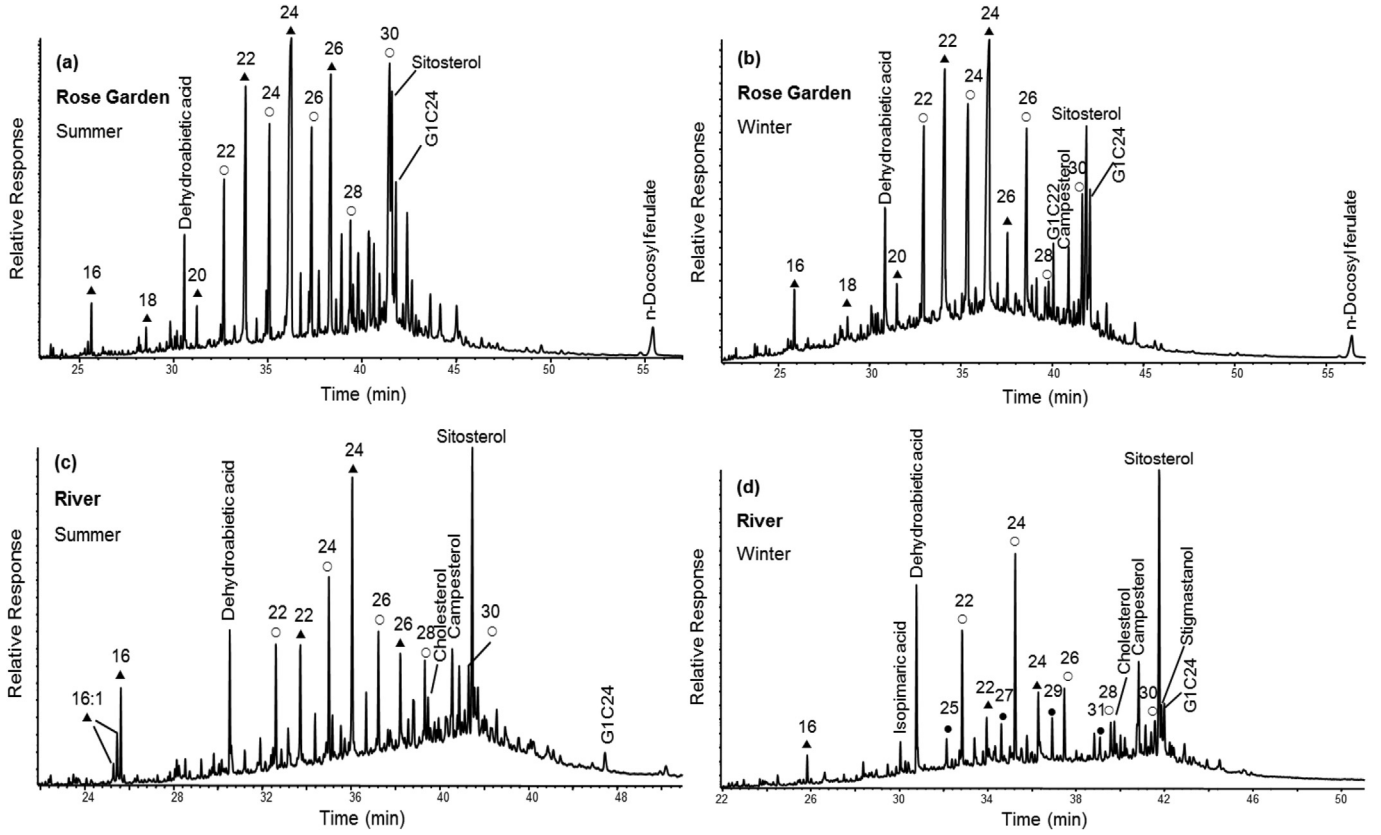

Fig. 2. Salient features of the GC–MS data of total extracts from (a and b) Rose Garden soil and (c and d) River Park soil: TIC for (a) summer season, (b) winter season, (c) summer season, and (d) winter season. The symbols over the peaks indicate homologous series (• = *n*-alkane, ◦ = *n*-alkanol, Δ = *n*-alkanoic acid) and the numbers are the compound carbon chain lengths (G1 = 1-Acyl glycerides; G2 = 2-Acyl glycerides; DHA = dehydroabietic acid)

most abundant compound class in the total EOM of the River Park soil (26.7%), and they are major in the Rose Garden (25.9%) and Ryegrass field (14.4%) soils (Figs. 1 and 2, Table 2). The *n*-alkanols were reported as major constituents in total extracts of the mineral horizons in grassland (27.0%) and conifer forest (12.5%) soils (Otto and Simpson, 2005).

In the Ryegrass field soils, the *n*-alkanols range from C_{18} to C_{32}, with a C_{max} at 26, and strong even/odd carbon number predominance. In comparison, the range and C_{max} are both similar to Ryegrass wax, which shows *n*-alkanols as the predominant compound class ranging from C_{22} to C_{28}, a C_{max} at 26, and an even carbon number predominance, confirming that this plant wax is a direct source for these compounds (Oros et al., 2002, 2006). In the Ryegrass field and Rose Garden soils, the *n*-alkanol concentrations reached a maximum during May to August and fluctuated over the other months of the annual cycle (Tables S1 and S2). The *n*-alkanol concentrations were greater in August than in January for the River Park soils (Table 1 and S2; Fig. 2c, d).

The *n*-alkanol distribution can be influenced by degradation of wax esters, which can hydrolyze to *n*-alkanols and *n*-alkanoic acids (Tulloch, 1976). However, low molecular weight *n*-alkanols ($<C_{20}$) were not detected, which suggests that lower plants, fungi, spore waxes, and wax esters are not significant contributors of *n*-alkanols to these soil samples.

3.7. *n*-Alkanes

The presence of *n*-alkanes in soils indicates a significant input from epicuticular waxes of terrestrial plants (Tables S1 and S2). The *n*-alkanes were a significant organic compound class in the total EOM from River Park soil (11.7%) and a minor class in Rose Garden (6.1%) and Ryegrass field (2.4%) soils (Table 2). In another report, *n*-alkanes had similar levels and distributions in total extracts of grassland (5.4%) and conifer forest (0.8%) soils (Otto and Simpson, 2005).

Vascular plants synthesize epicuticular waxes containing odd carbon number *n*-alkanes, usually in the range from C_{25} to C_{33}, with C_{27}, C_{29} or C_{31} as dominant homologs (Eglinton and Hamilton, 1967), which often contribute up to 90% of all hydrocarbons found in plant waxes. Short chain *n*-alkanes ($<C_{20}$) with an even/odd carbon number preference have been reported for algal and bacterial detritus, and higher plants and soils (Kuhn et al., 2010; Simoneit et al., 1979). The minor *n*-alkanes are determined by the mass fragmentogram of the *m*/*z* 85 key ion in GC–MS data (Fig. S1b). The *n*-alkanes in the Ryegrass field soils ranged from C_{21} to C_{33}, C_{max} at 29 or 31, with a strong odd/even carbon number predominance (Table S1). The CPI varied from 4.4 to 23. This is also evident in the distribution of the *n*-alkanes previously reported for Ryegrass wax, which ranged from C_{25} to C_{33}, with C_{max} at 31, and a strong odd/even carbon number predominance (CPI = 27) (Oros et al., 2002). The lower CPI in the Ryegrass field soils indicates that the *n*-alkanes may have undergone some degradation. The *n*-alkane concentrations for both the Ryegrass field and Rose Garden soils maximized during June to August and fluctuated during the other months of the annual cycle (Table 1, S1 and S2). The *n*-alkane concentrations were highest in summer for the River Park soils (Table S2).

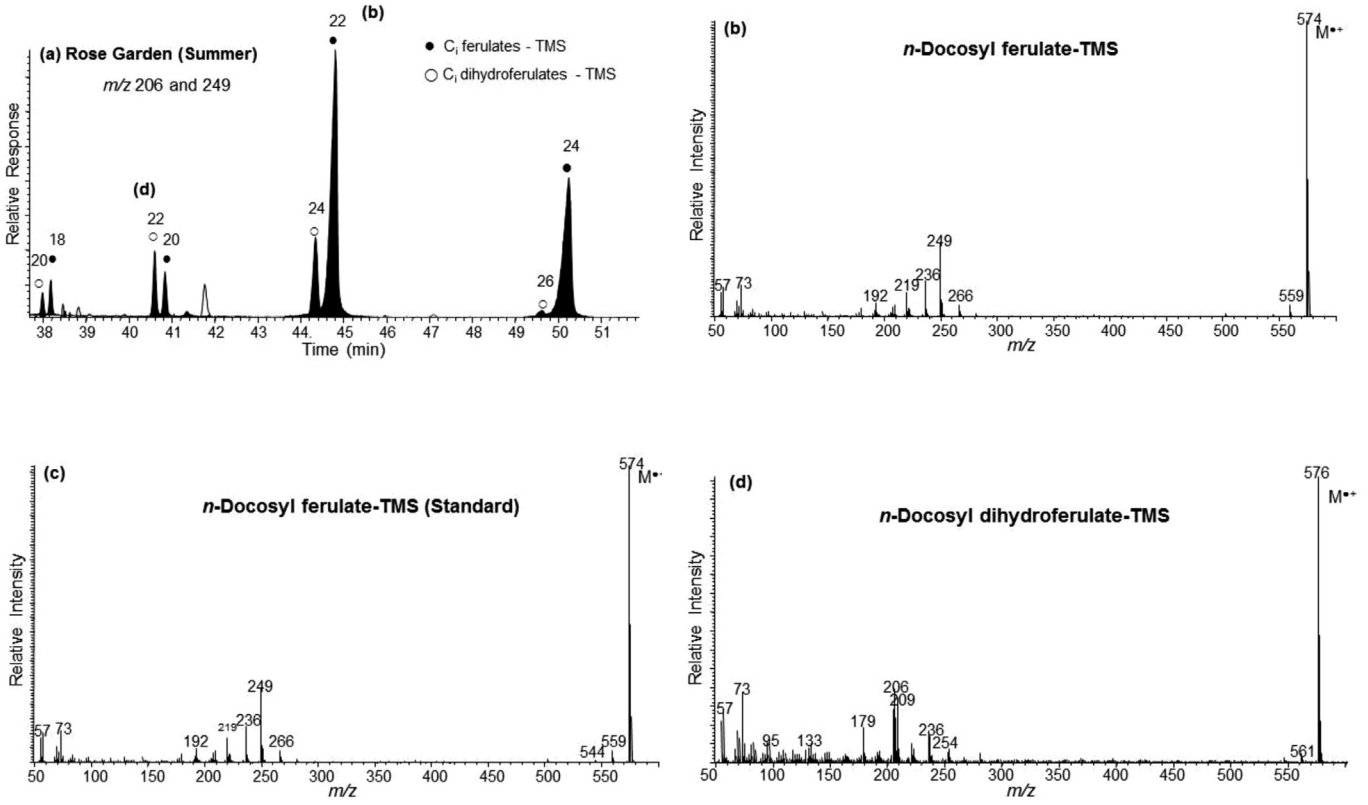

Fig. 3. Salient features of the GC–MS data of total extract from Rose Garden soil during summer: (a) mass fragmentogram for *m*/*z* 206 and 249 (key ions for *n*-alkyl dihydroferulate-TMS and *n*-alkyl ferulate-TMS, respectively), (b) mass spectrum of *n*-docosyl ferulate-TMS, (c) mass spectrum of *n*-docosyl ferulate-TMS standard for comparison purposes, and (d) mass spectrum of *n*-docosyl dihydroferulate-TMS.

3.8. Other compounds

Phenylpropanoid esters are incorporated in suberins and cutins, and occur as wax esters in epicuticular wax of numerous plants (e.g. Cefarelli et al., 2005; del Río et al., 2004; Griffiths et al., 1999; He et al., 2015; Jetter et al., 2002; Lee et al., 2004; Whitaker et al., 2001). They can be phenylpropanoid acid esters (e.g. coumaric acid, ferulic acid, caffeic acid) or phenylpropanoid alcohol esters (e.g. coumaryl alcohol, ferulyl alcohol, caffeyl alcohol) coupled to the respective fatty alcohol or fatty acid. These compounds have been reported in various plants and they are of current interest to natural product chemists due to their potential physiological properties such as antimicrobial or antioxidant activities in food, cosmetic and pharmaceutical formulations (e.g. Cefarelli et al., 2005; He et al., 2015; Lee et al., 2004).

We find series of alkyl ferulates (X) and alkyl dihydroferulates (XI) with the alcohol moieties of C_{20}, C_{22} and C_{24} for both in these soils (Table S2, Fig. 3). Only the *trans* (E) isomers of the ferulates are detected. These compounds occur during all seasons in the total EOM of the Rose Garden (2.9%) and River Park (1.1%) soils, but not in the Ryegrass soil samples (Tables 1 and 2). Similar alkyl *p*-coumarates have been reported in epicuticular wax from *Rosa rugosa* (Hashidoko et al., 1992), but were not detectable in these samples.

The alkyl ferulates were confirmed by comparison with the *n*-docosyl ferulate standard and its TMS derivative (Fig. 3c). *n*-Docosyl dihydroferulate and its TMS derivative both have molecular ions ($M^{\bullet+}$) as base peaks, unlike the mass spectra reported for dihydrocoumaryl docosanoate and its TMS derivative, which have $M^{\bullet+}$ at 1% relative intensity and *m*/*z* 206 as base peak (Jetter et al., 2002). Based on the homolog distributions, the minor alkyl dihydroferulate series is probably derived from the ferulates and both series are natural product tracers in soil from incorporation in this case of rose plant detritus.

The major triterpenoids (C_{30} compounds) found in the all the soil samples were α-amyrin (XII) and β-amyrin (XIII) (e.g. Fig. S1f). Triterpenoids are present as minor components comprising up to 2.5% of total EOM in the Oregon region soil samples (Table 2). In comparison, triterpenoids comprised only 0.8% of the total extracts of conifer forest soils from Western Canada (Otto and Simpson, 2005). Triterpenoids are important biomarker constituents of many higher plants, especially of angiosperms and gramineae, in their waxes, gums or mucilages (Ghosh et al., 1985; Rickling and Glombitza, 1993). They were previously identified as major components in Ryegrass waxes (Oros et al., 2002), which indicates those waxes as the primary source for these natural compounds in the Ryegrass field soil samples.

Several key diterpenoids (C_{20} compounds) in the samples included dehydroabietic acid (XIV), pimaric acid (XV), isopimaric acid (XVI), abietic acid (XVII), and abieta-8,11,13,15-tetraenoic acid (XVIII) (e.g. Fig. 2). Diterpenoids are important biomarker constituents of many higher plants, especially of conifer (gymnosperms) resins and waxes (Mazurek and Simoneit, 1997; Simoneit, 1986, 1998; Simoneit et al., 1993). Diterpenoids in resins often bleed from conifer branches and needles and are unavoidably adsorbed to epicuticular waxes. Dehydroabietic acid, which was found in the highest abundance, is an alteration product of both abietic acid and pimaric acid. Dehydroabietic acid has been regarded both as a partially altered environmental oxidation product and a pyrolysis product of resin acids (Mazurek and Simoneit, 1997; Simoneit, 1977, 1986). It was previously identified as a candidate tracer compound

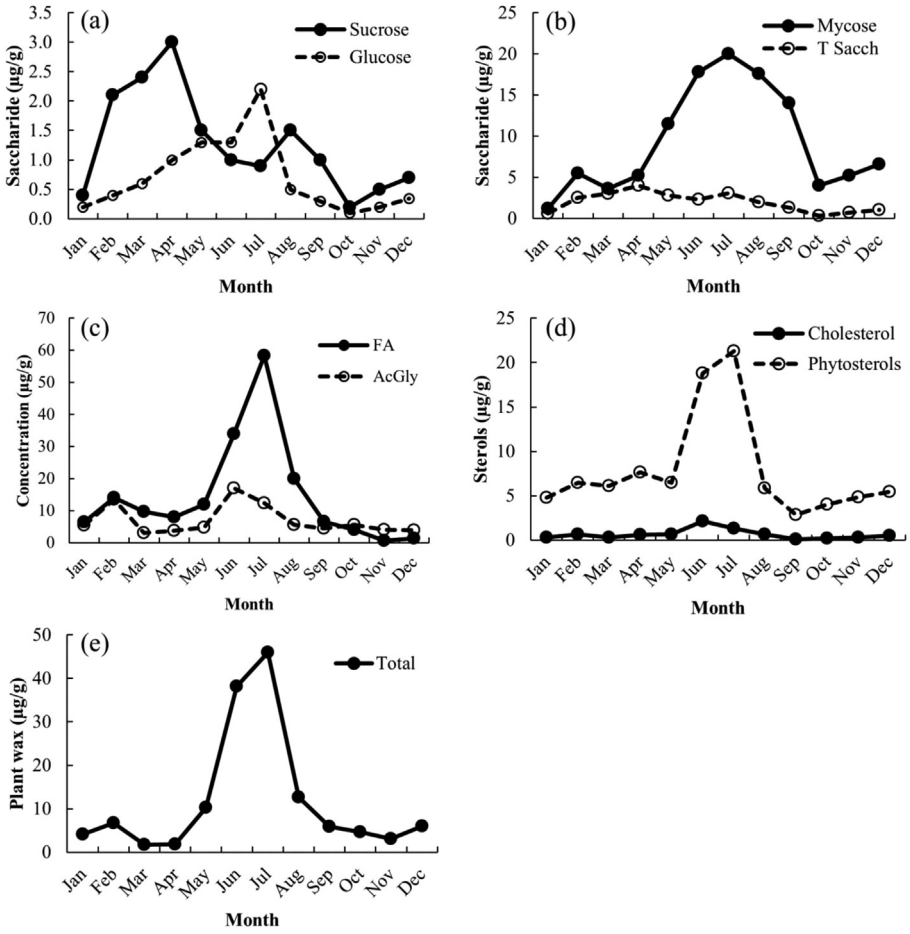

Fig. 4. Seasonal variations of: (a) glucose and sucrose, (b) total saccharides and mycose, (c) acyl glycerides and *n*-alkanoic acids, (d) phytosterols and cholesterol, and (e) plant wax in the Ryegrass field soils.

for coniferous wood combustion (Rogge et al., 1998; Simoneit et al., 1993; Standley and Simoneit, 1994). The alteration products including abieta-8,11,13,15-tetraenoic acid and isopimaric acid can derive from oxidative and microbial degradation processes or as products of burning of conifer wood (Oros and Simoneit, 2001). The minor presence of diterpenoids in the total EOM of Ryegrass field soil (0.1%; Table 2) is likely due to atmospheric transport of conifer waxes found in pollen and conifer smoke from burning. In contrast, their larger presence in the total EOM from River Park (11.1%) and Rose Garden (7.3%) soils suggests a direct input of conifer plant materials (resins, waxes and needles) into these soils (Tables 1 and 2). These diterpenoids were also reported as major components (12%) in total extracts of conifer forest soils from Western Canada (Otto and Simpson, 2005).

Synthetic chlorinated compounds are common constituents in agricultural soils due to their widespread application as pesticides and strong ability to persist in the environment. The single chlorinated compound identified as a minor component in Rose Garden soil was Oxadiazon ($C_{15}H_{18}Cl_2N_2O_3$), which is an herbicide used for pre-emergent control of annual grasses and broad leaf weeds (Table 2, 0.2% of total EOM).

4. Temperate soil dynamics

The seasonal variation of the ambient air temperatures and the soil temperatures recorded in the Corvallis region close to the sampling sites for January 2004 to December 2005 are shown in Figure S2 (data from OCS, 2005, 2006). The lowest soil temperatures were during winter at 5.6 ± 3.3 °C and maximized during summer (July–August) at 29.8 ± 9.6 °C. Precipitation was highest in winter and essentially lowest during summer. It should be noted that the soil temperatures are generally up to 10 °C warmer than the ambient air in summer.

The peak contributions of organic matter in Ryegrass field and Rose Garden soils occurs mainly in June through August as shown by the maximal concentrations of higher plant lipid components such as acyl glycerides, fatty acids, sterols, and waxes (Figs. 4 and 5). Sucrose and to a lesser extent glucose have maximum concentrations during spring (March–May), reflecting the onset of plant growth, especially rootlets in the soils (Figs. 4a and 5a). The microbial/fungal metabolite, mycose, also peaks later in summer, which suggests a soil microbial/fungal response to the increased ambient temperature of the soils with increasing primary production (Figs. 4b and 5b). It should be noted that ergosterol, the fungal steroid tracer, was not detectable in any of these surface soils. During fall into winter the concentrations of all compounds decrease to steady state levels due to cessation of *de novo* synthesis and concomitant biodegradation and remineralization of detritus. However, the Oregon soils are not fully dormant, as was observed for soils from Hokkaido, Japan, where the saccharides were not detectable during winter (Simoneit et al., 2004a). In that case, the soil was frozen solid for typically a three month cold period

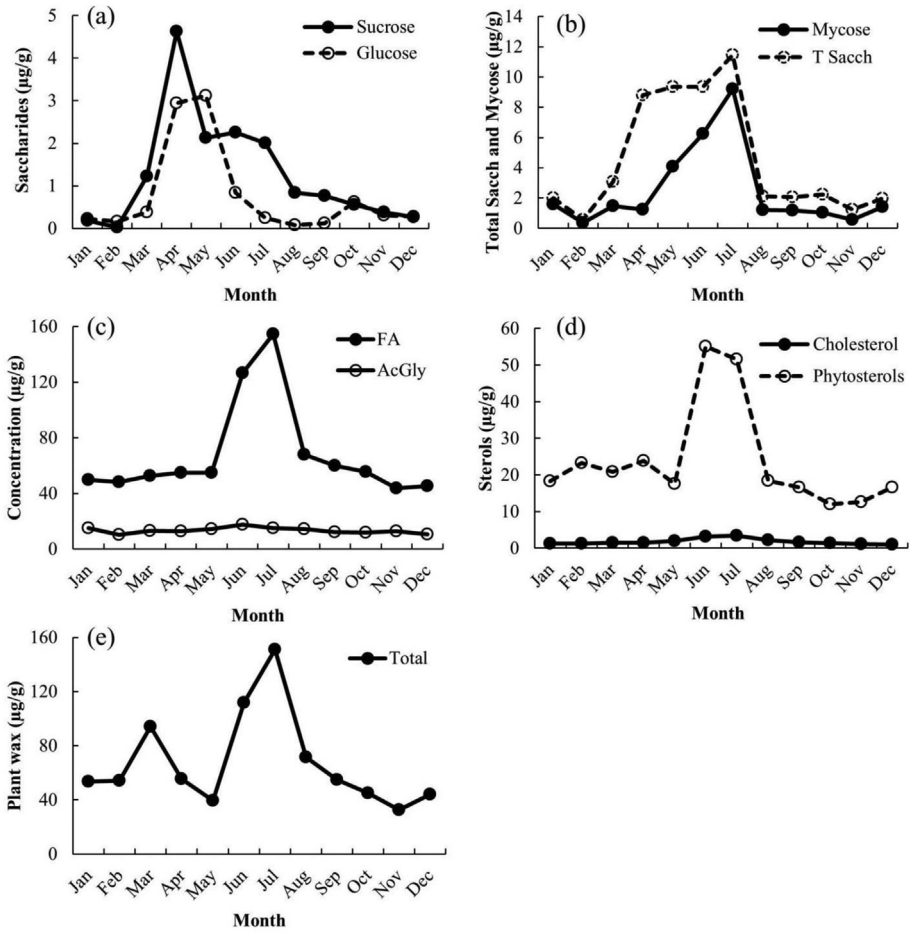

Fig. 5. Seasonal variations of: (a) glucose and sucrose, (b) total saccharides and mycose, (c) acyl glycerides and *n*-alkanoic acids, (d) phytosterols and cholesterol, and (e) plant wax in the Rose Garden soils.

resulting in essentially complete biological dormancy.

Both the Rose Garden and River Park soils are under open stands of conifers (e.g. Douglas Fir) and thus incorporate resin with leaf/branch detritus. Diterpenoid diagenesis of pimaric, isopimaric and abietic acids (DT) to dehydroabietic acid (DHA) can be discerned (Simoneit, 1977); however, diagenesis does not seem a significant process for organic compound alteration in the studied soils. The highest DHA/DT ratio is observed during June and July with an annual mean of 3.7, indicating that the alteration of diterpenoid acids to DHA occurs throughout the annual cycle with a maximum during the warm season. Above all, the organic component concentrations and distributions in the soils are influenced mainly by their origin from the various plant species, the primary producers, and less so by the extent of physical, chemical, and biological alteration or the environmental conditions.

In summary, the major organic components imparted to Oregon region soils were identified as saccharides, phytosterols, terpenoids, and homologous series of *n*-alkanoic acids, *n*-alkanols, and *n*-alkanes, which are similar compared with grassland soils and conifer forest soil from Western Canada. The organic component concentrations and distributions in the soils are influenced primarily by their plant species origin, and less so by the extent of physical, chemical, and biological alteration and the environmental conditions. In addition, as soil activity cycles from primary production to dormancy the corresponding biomarkers, especially their concentrations, change.

Since soils could enter into aquatic systems by rain erosion of surficial particles from fields and surface water runoff, and into the atmosphere by wind scouring of particles, the variations in biomarker concentrations observed between seasons (primary production season vs. dormancy season) and sources (e.g. higher plants vs. microbial organisms) may have a large impact on local carbon cycles in temperate areas. The analysis of biomarker tracers coupled with homologous compound series provides chemical fingerprints that improves our understanding of SOM origins and dynamics and the linkage of SOM to regional and global environmental processes such as carbon cycling, atmospheric transport, and climate change.

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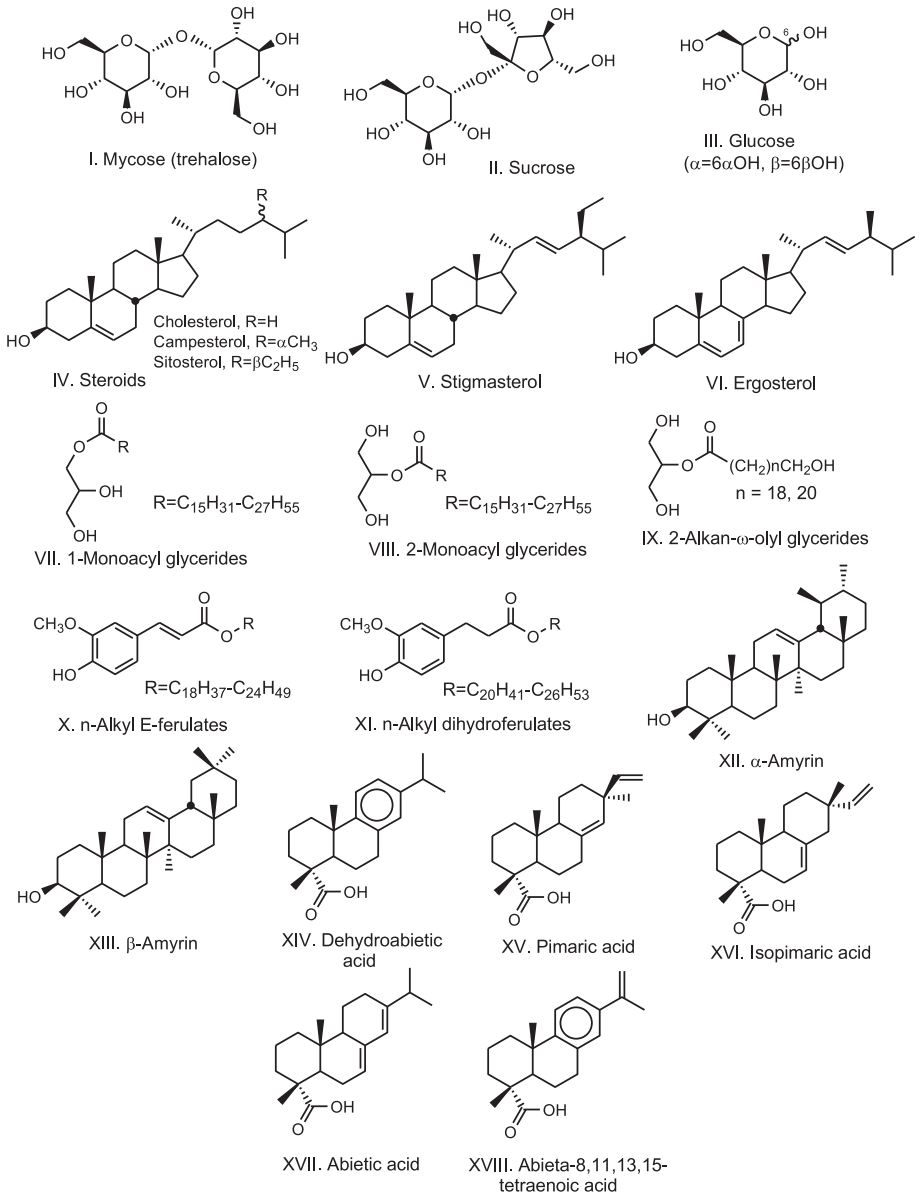
Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2015.11.007.

Appendix I. Chemical structures cited in the text



References

Abas, M.R., Simoneit, B.R.T., Elias, V., Cabral, J.A., Cardoso, J.N., 1995. Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. Chemosphere 30, 995–1015.

Ahmad, S., Roy, P.K., Khan, A.W., Basu, S.K., Johri, B.N., 1991. Microbial transformation of sterols to C_{19}-steroids by *Rhodococcus equi*. World J. Microbiol. Biotechnol. 7, 557–561.

Al-Mutlaq, K.F., 2006. Characteristics and alteration of pesticide residues in surface soils of agricultural fields and public parks. Environ. Geol. 51, 493–497.

Al-Mutlaq, K., Rushdi, A.I., Simoneit, B.R.T., 2002. Characteristics and sources of organic matter in desert sand samples from the Riyadh and Al-Qasim areas of Saudi Arabia. Preliminary results. Arab. Gulf J. Sci. Res. 20, 141–155.

Al-Mutlaq, K., Rushdi, A.I., Simoneit, B.R.T., 2007. Organic compound tracers in fine soil and sand particles during summer in the metropolitan area of Riyadh, Saudi Arabia. Environ. Geol. 52, 559–571.

Bernards, M.A., 2002. Demystifying suberin. Can. J. Bot. 80, 227–240.

Casalicchio, G., Lercker, G., 1974. Composition of the soil lipid fraction. VI. Status and dynamics of some sterols in profiles of natural soils and in arboreal vegetation. Agrochimica 18, 528–537.

Cefarelli, G., D'Abrosca, B., Fiorentino, A., Izzo, A., Monaco, P., 2005. Isolation, characterization, and antioxidant activity of E- and Z-*p*-coumaryl fatty acid esters from cv. Annurca apple fruits. J. Agric. Food Chem. 53, 3525–3529.

del Río, J.C., Rodríguez, I.M., Gutiérrez, A., 2004. Identification of intact long-chain *p*-hydroxycinnamate esters in leaf fibers of abaca (*Musa textilis*) using gas chromatography/mass spectrometry. Rapid Commun. Mass Spectrom. 18, 2691–2696.

Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322–1335.

El-Boukari, H., Aassiri, A., Morillo, J., Khaddor, M., Ouassini, A., 2008. Pesticides and lipid occurrence in Tangier agricultural soil (northern Morocco). Appl. Geochem. 23, 3487–3497.

Feng, X., Simpson, M.J., 2007. The distribution and degradation of biomarkers in Alberta grassland soil profiles. Org. Geochem. 38, 1558–1570.

Fierer, N., Jackson, J.A., Vilgalys, R., Jackson, R.B., 2005. Assessment of soil microbial community structure by use of taxon-specific quantitative PCR assays. Appl. Environ. Microbiol. 71, 4117–4120.

Ghosh, A., Misra, S., Dutta, A.K., Choudhury, A., 1985. Pentacyclic triterpenoids and sterols from seven species of mangrove. Phytochemistry 24, 1725–1727.

Gleixner, G., Poirier, N., Bol, R., Balesdent, J., 2002. Molecular dynamics of organic matter in a cultivated soil. Org. Geochem. 33, 357–366.

Gogou, A., Stratigakis, N., Kanakidou, M., Stephanou, E.G., 1996. Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. Org. Geochem. 25, 79–96.

Griffiths, D.W., Robertson, G.M., Shepherd, T., Ramsey, G., 1999. Epicuticular waxes and volatiles from faba bean (*Vicia faba*) flowers. Phytochemistry 52, 607–612.

Hashidoko, Y., Tahora, S., Mizutani, J., 1992. Long chain alkyl esters of 4'-hydroxycinnamic acids from leaves of *Rosa rugosa*. Phytochemistry 31, 3282–3283.

Harwood, J.L., Russell, N.J., 1984. Lipids in Plants and Microbes. George Allen and Unwin, London.

He, D., Simoneit, B.R.T., Jara, B., Jaffé, R., 2015. Gas chromatography mass

spectrometry based profiling of alkyl coumarates and ferulates in two species of cattail (*Typha domingensis* P., and *Typha latifolia* L.). Phytochem. Lett. 13, 91–98. http://dx.doi.org/10.1016/j.phytol.2015.05.010.
Hildemann, L., Klinedinst, D.B., Klouda, G.A., Currie, L.A., Cass, G.R., 1994. Sources of urban contemporary carbon aerosol. Environ. Sci. Technol. 28, 1565–1576.
Huguet, A., Fosse, C., Metzger, P., Fritsch, E., Derenne, S., 2010. Occurrence and distribution of extractable glycerol dialkyl glycerol tetraethers in podzols. Org. Geochem. 41, 291–301.
Jetter, R., Klinger, A., Schäffer, S., 2002. Very long-chain phenylpropyl and phenylbutyl esters from *Taxus baccata* needle cuticular waxes. Phytochemistry 61, 579–587.
Kindler, R., Miltner, A., Thullner, M., Richnow, H.H., Kästner, M., 2009. Fate of bacterial biomass derived fatty acids in soil and their contribution to soil organic matter. Org. Geochem. 40, 29–37.
Kolattukudy, P.E., 1980. Biopolyester membranes of plants: cutin and suberin. Science 208, 990–1000.
Kuhn, T.K., Krull, E.S., Bowater, A., Grice, K., Gleixner, G., 2010. The occurrence of short chain *n*-alkanes with an even over odd predominance in higher plants and soils. Org. Geochem. 41, 88–95.
Lal, R., 2003. Soil erosion and the global carbon budget. Environ. Int. 29, 437–450.
Lee, J.Y., Yoon, J.W., Kim, C.T., Lim, S.T., 2004. Antioxidant activity of phenylpropanoid esters isolated and identified from *Platycodon grandiflorum* A. DC. Phytochemistry 65, 3033–3039.
Liu, Y., Chen, L., Zhao, J.F., Wei, Y.P., Pan, Z.Y., Meng, X.Z., Huang, Q.H., Li, W.Y., 2010. Polycyclic aromatic hydrocarbons in the surface soil of Shanghai, China: concentrations, distribution and sources. Org. Geochem. 41, 355–362.
Lordachescu, M., Imai, R., 2011. Trehalose and abiotic stress in biological systems. In: Shanker, A. (Ed.), Abiotic Stress in Plants - Mechanisms and Adaptations. Tech Publishing Co., Rijeka, Croatia, pp. 215–234.
Lukins, H.B., Foster, J.W., 1963. Methyl ketone metabolism in hydrocarbon-utilizing mycobacteria. J. Bacteriol. 85, 1074–1087.
Mazurek, M.A., Simoneit, B.R.T., 1984. Characterization of biogenic and petroleum derived organic matter in aerosols over remote, rural and urban areas. In: Keith, L.H. (Ed.), Identification and Analysis of Organic Pollutants in Air. Ann Arbor Science/Butterworth Publishers, Woburn, MA, pp. 353–370 (Cited in Tables S1 and S2).
Mazurek, M.A., Simoneit, B.R.T., 1997. High molecular weight terpenoids as indicators of organic emissions from terrestrial vegetation. In: Eganhouse, R.P. (Ed.), Molecular Markers in Environmental Geochemistry, Amer. Chem. Soc. Symp. Series 671. ACS, Washington, DC, pp. 92–108.
Medeiros, P.M., Simoneit, B.R.T., 2007. Analysis of sugars in environmental samples by gas chromatography-mass spectrometry. J. Chromatogr. A 1141, 271–278.
Medeiros, P.M., Simoneit, B.R.T., 2008. Source profiles of organic compounds emitted upon combustion of green vegetation from temperate climate forests. Environ. Sci. Technol. 42, 8310–8316.
Medeiros, P.M., Fernandes, M.F., Dick, R.P., Simoneit, B.R.T., 2006. Seasonal variations in sugar contents and microbial community behavior in a ryegrass soil. Chemosphere 65, 832–839.
Miltner, A., Kindler, R., Knicker, H., Richnow, H.H., Kästner, M., 2009. Fate of microbial biomass-derived amino acids in soil and their contribution to soil organic matter. Org. Geochem. 40, 978–985.
Morgan, R.P.C., 2005. Soil Erosion and Conservation, third ed. Blackwell Science Ltd., Blackwell Publishing, Oxford, UK, p. 320.
Nierop, K.G.J., Naafs, D.F.W., Verstraten, J.M., 2003. Occurrence and distribution of ester-bound lipids in Dutch coastal dune soils along a pH gradient. Org. Geochem. 34, 719–729.
Nierop, K.G.J., Naafs, D.F.W., van Bergen, P.T., 2005. Origin, occurrence and fate of extractable lipids in Dutch coastal dune soils along a pH gradient. Org. Geochem. 36, 555–566.
Noda, M., Tanaka, M., Seto, Y., Aiba, T., Oku, C., 1988. Occurrence of cholesterol as a major sterol component in leaf surface lipids. Lipids 23, 439–444.
OCS 2005, 2006. 2013 Oregon Climate Service. Oregon State University. http://www.ocs.oregonstate.edu.
Oros, D.R., Simoneit, B.R.T., 2001. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 1. Temperate climate conifers. Appl. Geochem. 16, 1513–1544.
Oros, D.R., Mazurek, M.A., Baham, J.E., Simoneit, B.R.T., 2002. Organic tracers from wild fire residues in soils and rain/river wash-out. Water Air Soil Poll. 137, 203–233.
Oros, D.R., bin, Abas, M.R., Omar, N.Y.M.J., Rahman, N.A., Simoneit, B.R.T., 2006. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: part 3. Grasses. Appl. Geochem. 21, 919–940.
Otto, A., Simpson, M.J., 2005. Degradation and preservation of vascular plant-derived biomarkers in grassland and forest soils from Western Canada. Biogeochemistry 74, 377–409.
Otto, A., Simpson, M.J., 2006. Sources and composition of hydrolysable aliphatic lipids and phenols in soils from western Canada. Org. Geochem. 37, 385–407.
Otto, A., Simpson, M.J., 2007. Analysis of soil organic matter biomarkers by sequential chemical degradation and gas chromatography-mass spectrometry. J. Sep. Sci. 30, 272–282.
Otto, A., Shunthirasingham, C., Simpson, M.J., 2005. A comparison of plant and microbial biomarkers in grassland soils from the Prairie Ecozone of Canada. Org. Geochem. 36, 425–448.
Parham, R.A., Gray, R.L., 1984. Formation and structure of wood. In: Rowell, R. (Ed.), Chemistry of Solid Wood, Adv. Chem. Series 207. American Chemical Society, Washington, DC, pp. 3–56.
Patzelt, H., 2007. Hydrocarbon metabolism. eLS. http://dx.doi.org/10.1002/9780470015902 a90000473.
Puglisi, E., Nicelli, M., Capri, E., Trevisan, M., Del Re, A.A.M., 2003. Cholesterol, β-sitosterol, ergosterol, and coprostanol in agricultural soils. J. Environ. Qual. 32, 466–471.
Rickling, B., Glombitza, K.W., 1993. Saponins in the leaves of birch? Hemolytic dammarane triterpenoid esters of *Betula pendula*. Planta Med. 59, 76–79.
Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol: 2. Non-catalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27, 636–651.
Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1998. Sources of fine organic aerosol: 9. Pine, oak, and synthetic log combustion in residential fireplaces. Environ. Sci. Technol. 32, 13–22.
Rogge, W.F., Medeiros, P.M., Simoneit, B.R.T., 2006. Organic marker compounds for soil and fugitive dust from open lot dairies and cattle feedlots. Atmos. Environ. 40, 27–49.
Rogge, W.F., Medeiros, P.M., Simoneit, B.R.T., 2007. Organic marker compounds in surface soils of crop fields from the San Joaquin Valley fugitive dust characterization study. Atmos. Environ. 41, 8183–8204.
Rushdi, A.I., Al-Mutlaq, K., Simoneit, B.R.T., 2005. Sources of organic compounds in fine soil and sand particles during winter in the metropolitan area of Riyadh, Saudi Arabia. Arch. Environ. Contam. Toxicol. 49, 457–470.
Rushdi, A.I., Al-Mutlaq, K.F., Simoneit, B.R.T., Al-Azri, A., DouAbul, A.A.Z., Al-Zarban, S., Al-Yamani, F., 2009. Characteristics of lipid tracer compounds transported to the Arabian Gulf by runoff from rivers and atmospheric dust transport. Arab. J. Geosci. 3, 113–131.
Ruzicka, S., Edgerton, D., Norman, M., Hill, T., 2000. The utility of ergosterol as a bioindicator of fungi in temperate soils. Soil Biol. Biochem. 32, 989–1005.
Simoneit, B.R.T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acta 41, 463–476.
Simoneit, B.R.T., 1986. Cyclic terpenoids of the geosphere. In: Johns, R.B. (Ed.), Biological Markers in the Sedimentary Record. Elsevier, Amsterdam, pp. 43–99.
Simoneit, B.R.T., 1989. Organic matter of the troposphere. V: application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. J. Atmos. Chem. 8, 251–275.
Simoneit, B.R.T., 1998. Biomarker PAHs in the environment. In: Neilson, A. (Ed.), The Handbook of Environmental Chemistry, vol. 3. Springer Verlag, Berlin, pp. 175–221. Part I.
Simoneit, B.R.T., 2006. Atmospheric transport of terrestrial organic matter to the sea. In: Volkman, J.K. (Ed.), The Handbook of Environmental Chemistry, Vol. 2, Part N, Marine Organic Matter: Biomarkers, Isotopes and DNA. Springer Verlag, Berlin, pp. 165–208.
Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere - II. Natural background of biogenic lipid matter in aerosols over the rural Western United States. Atmos. Environ. 16, 2139–2159.
Simoneit, B.R.T., Mazurek, M.A., Brenner, S., Crisp, P.T., Kaplan, I.R., 1979. Organic geochemistry of recent sediments from Guaymas Basin, Gulf of California. Deep Sea Res. 26, 879–891.
Simoneit, B.R.T., Rogge, W.F., Mazurek, M.A., Standley, L.J., Hildemann, L.M., Cass, G.R., 1993. Lignin pyrolysis products, lignans and resin acids as specific tracers of plant classes in emissions from biomass combustion. Environ. Sci. Technol. 27, 2533–2541.
Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos. Environ. 33, 173–182.
Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, K., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., Didyk, B.M., 2004a. Sugars – dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. Environ. Sci. Technol. 38, 5939–5949.
Simoneit, B.R.T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M.H., Lim, H.J., Turpin, B.J., Komazaki, Y., 2004b. Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. J. Geophys. Res. Atmos. 109, 1–22. http://dx.doi.org/10.1029/2004JD004598. D19S10.
Sinsabaugh, R.L., Antibus, R.K., Jackson, C.R., Karpanty, S., Robinson, M., Liptak, M., Franchini, P., 1997. A β-sitosterol assay for fine-root mass in soils. Soil Biol. Biochem. 29, 39–44.
Standley, L.J., Simoneit, B.R.T., 1994. Resin diterpenoids as tracers for biomass combustion aerosols. J. Atmos. Chem. 18, 1–15.
Stephanou, E.G., 1992. α,ω-Dicarboxylic acid salts and α,ω-dicarboxylic acids. Naturwissenschaften 79, 128–131.
Stephanou, E.G., Stratigakis, N., 1993. Oxocarboxylic and α,ω-dicarboxylic acids: photo-oxidation products of biogenic unsaturated fatty acids present in urban aerosols. Environ. Sci. Technol. 27, 1403–1407.
Trendel, J.M., Schaeffer, P., Adam, P., Schwartz, D., 2010. Molecular characterization of soil surface horizons with different vegetation in the Vosges Massif (France). Org. Geochem. 41, 1036–1039.
Tulloch, A.P., 1976. Chemistry of waxes of higher plants. In: Kolattukudy, P.E. (Ed.), Chemistry and Biochemistry of Natural Waxes. Elsevier, Amsterdam, pp. 235–287.
Volkman, J.K., 1986. A review of sterol markers from marine and terrigenous organic matter. Org. Geochem 9, 83–99.
Weijers, J.W.H., Schouten, S., Spaargaren, O.C., Sinninghe Damsté, J.S., 2006.

Occurrence and distribution of tetraether membrane lipids in soils: implications for the use of the TEX86 proxy and the BIT index. Org. Geochem. 37, 1680–1693.
Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Sinninghe Damsté, J.S., 2007. Environmental controls on bacterial tetraether membrane lipid distribution in soils. Geochim. Cosmochim. Acta 71, 703–713.
Whitaker, B.D., Schmidt, W.F., Kirk, M.C., Barnes, S., 2001. Novel fatty acid esters of *p*-coumaryl alcohol in epicuticular wax of apple fruit. J. Agric. Food Chem. 49, 3787–3792.
Wiesenberg, G.L.B., Schmidt, M.W.I., Schwark, L., 2008. Plant and soil lipid modifications under elevated atmospheric CO_2 conditions: I. Lipid distribution patterns. Org. Geochem. 39, 91–102.
Winkler, A., Haumaier, L., Zech, W., 2005. Insoluble alkyl carbon components in soils derive mainly from cutin and suberin. Org. Geochem 36, 519–529.
Woodruff, L.G., Cannon, W.F., Eberl, D.D., Smith, D.B., Kilburn, J.E., Horton, J.D., Garrett, R.G., Klassen, R.A., 2009. Continental-scale patterns in soil geochemistry and mineralogy: results from two transects across the United States and Canada. Appl. Geochem. 24, 1369–1381.