Predicting soil water repellency by hydrophobic organic compounds and their vegetation origin

J. Mao[1,2], K.G.J. Nierop[2], M. Rietkerk[1], and S.C. Dekker[1]

[1] Copernicus Institute of Sustainable Development- Environmental Sciences, Faculty of Geosciences, Utrecht University, Heidelberglaan 2, PO Box 80115, 3508 TC Utrecht, The Netherlands.

[2] Department of Earth Sciences-Organic Geochemistry, Faculty of Geosciences, Utrecht University, Heidelberglaan 2, PO Box 80115, 3508 TC Utrecht, The Netherlands.

Correspondence to: J. Mao (J.Mao@uu.nl)

Abstract

It is widely accepted that soil water repellency (SWR) is mainly caused by plant-derived hydrophobic organic compounds in soils; such hydrophobic compounds are defined as SWR-markers. However, the detailed influence of SWR-markers on SWR is yet unclear and the knowledge of their original sources is still limited. The aims of this study are to select important SWR-markers to predict SWR based on their correlation with SWR and to determine their origin. In our study, sandy soils with different SWR were collected, along with their covering vegetation, i.e. plant leaves/needles and roots. A sequential extraction procedure was applied to the soils to obtain three organic fractions: DCM/MeOH soluble fraction (D), DCM/MeOH insoluble fraction of IPA/NH_3 extract (AI) and DCM/MeOH soluble fraction of IPA/NH_3 extract (AS), which were subdivided into ten dominant SWR-marker groups: (D) fatty acid, (D) alcohol, (D) alkane, (AI) fatty acid, (AI) alcohol, (AI) ω-hydroxy fatty acid, (AI) α,ω-dicarboxylic acid, (AS) fatty acid, (AS) alcohol and (AS) ω-hydroxy fatty acid. Waxes and biopolyesters of the vegetation were also sequentially extracted from plants. The soils with higher SWR have significantly higher relative concentrations of (AS) alcohols. A number of indications suggest that (AS) alcohols are mainly derived from roots and most likely produced by microbial hydrolysis of biopolyesters (mainly suberins). In addition, the strong correlation between the biomarkers of plant tissues and SWR-markers in soils suggests that it is more accurate to predict SWR of topsoils using ester-bound alcohols from roots, and to predict SWR of subsoils using root-derived ω-hydroxy fatty acids and α,ω-dicarboxylic acids. Considering the sandy soils studied here , our relations obtained need to be tested for other types of soils. Our analysis indicates that plant roots have a primary role influencing SWR relative to plant leaves.

1. Introduction

Soil water repellency (SWR) is one of the important properties that can interrupt soil water infiltration and potentially lead to soil erosion, and occurs globally in a wide range of soil types under various kinds of vegetation (Franco et al., 1995, 2000; Doerr et al., 2000, 2005; Michel et al., 2001; Poulenard et al., 2004; Hansel et al., 2008; de Blas et al., 2010). SWR is caused by hydrophobic organic compounds in soils. These compounds originate from vegetation (McGhie and Posner, 1981; Bisdom et al., 1993; de Blas et al., 2010; Horne and McIntosh, 2000) or microorganisms (Bond and Harris, 1964; McGhie and Posner, 1980) and have been defined as SWR-markers by Mao et al. (2014). Different groups of SWR-markers have been isolated from water repellent soils by a number of extraction techniques with selective organic solvents and have been identified by using several types of analytical instruments in previous research (Ma'shum et al., 1988; Franco et al., 1995, 2000; Hansel et al., 2008; Atanassova and Doerr, 2010; de Blas et al., 2010; Mao et al., 2014).

Although numerous SWR-markers have been identified, the relation between these markers and the severity of SWR is still not clear. Significantly more organic matter was found in water repellent soils than in wettable soils, but there was no clear correlation between the extracted amounts of organic matter and SWR severity (Atanassova and Doerr, 2010; Mainwaring et al., 2004, 2013). Few studies have attempted to explain the possible relation between hydrophobic organic compounds and SWR. De Blas et al. (2013) found a significant correlation between the amount of free lipids and SWR; however, the amount of bound lipids did not correlate with soil hydrophobicity. Ester-bound biopolymers (in particular suberins) have been shown to lead to relatively stronger SWR compared to free lipids in sandy soils (Mao et al, 2014). Hence, it is clear that not only the amount but also the type of SWR-markers affect the severity of SWR (Contreras et al., 2008; de Blas et al., 2013).

The severity of SWR significantly varies depending on vegetation species and soil depths (Doerr et al., 2002, 2005; Buckzo et al., 2005; de Blas et al., 2010, 2013; Neris et al., 2012; Mao et al., 2014; Zavala et al., 2014). For instance, soil under eucalyptus always showed more severe water repellency than under pine during dry periods in northwest Spain (Rodríguez-Alleres and Benito, 2011, 2012). Morley et al. (2005) found large variation in SWR from extreme repellent to non-repellent sandy soil under grasses, at depths ranging from 0 to 40 cm. As vegetation is the primary input of organic matter in soils (Van Bergen et al., 1997; Kögel-Knabner, 2002), it is now well accepted that SWR is mainly the result of accumulated hydrophobic organic compounds in soils originally derived from vegetation (Bisdom et al., 1993; DeBano, 2000; Doerr et al., 2000; Horne and McIntosh, 2000; Hansel et al., 2008; de Blas et al., 2010, 2013) and to a smaller extent from microbes (Hallett and Young, 1999; Feeney et al., 2006).

In this paper we aim to predict SWR based on the occurrence of different types and amounts of SWR-markers in sandy soils and to understand and link the SWR-markers to their origin, i.e. the vegetation type (leaf or root). We therefore use sandy soils under different vegetation types similar to our previous study (Mao et al., 2014), in which the soils contain more than 100 different SWR-markers. Sandy soils have been chosen because they contain hardly any organo-mineral complexes, leading to negligible interactions between soil particles and organic matter, in contrast to clay or silt soils (Schulten and Leinweber, 2000; Kleber et al., 2007). To predict SWR from specific leaf/root biomarkers, we apply linear regression data analysis to the SWR-markers both as individual compounds and combined in compound groups from the three different fractions: DCM/MeOH soluble fraction (D), DCM/MeOH insoluble fraction of IPA/NH_3 extract (AI) and DCM/MeOH soluble fraction of IPA/NH_3 extract (AS), as analysed by Mao et al. (2014).

2. Materials and methods

2.1 Sampling

The sand dunes of the Zuid-Kennemerland National Park in The Netherlands were chosen as a sampling site. Soils and vegetation samples were collected along two perpendicular transects, with a variety of vegetation cover. All the soils were classified as Cambic Arenosols (FAO, 2006), and more details about the soil characteristics and transects are given in Mao et al. (2014). The soils were sampled from maximal three different soil horizons at spots under different types of vegetation (Table 1). The living plant leaves and roots were taken separately from each vegetation species, except for sheep fescue, of which the roots found in the filed were very fine and therefore the leaves and roots were decided to be collected together. All collected soils were oven-dried at 30°C for 48 hours, and passed a 1.4 mm diameter sieve to remove large leaf and root fragments. All vegetation samples were freeze-dried and stored in a dry place prior to further analysis.

2.2 Soil characteristics measurements

A 1:2.5 (w/w) soil to water ratio was used to determine soil pH value (Metson, 1956), which was measured by using a pH meter (Consort C830). To determine total organic carbon (TOC) and total nitrogen (TN), all soils were decalcified using 1 M HCl to remove inorganic carbon (Van Wesemael, 1955) and ground into fine powder by using planetary ball mills (Pulverisette®5, Fritsch). The TOC and TN contents of the soils were measured using a CNS analyser (Fisons Instruments NA1500).

2.3 Water repellency assessment

The water drop penetration time (WDPT) test is widely accepted and used to evaluate the extent of SWR (Van't Woudt, 1959; Krammes and DeBano, 1965; Wessel, 1988; Dekker and

Ritsema, 1994; Doerr et al., 2005). To obtain the WDPT of all oven-dried soils before extraction, the WDPT value of each soil was determined based on the average penetration time of twenty individual water droplets. Based on the WDPT method, the severity of SWR was classified as follows: wettable (<5 s), slightly repellent (5-60 s), strongly repellent (60-600 s), severely repellent (600-3600 s) and extremely repellent (>3600 s) (Bisdom et al., 1993; Dekker and Ritsema, 1996). The repellency classes of all the soils are presented in Table 1.

2.4 Soil and vegetation extraction

To investigate different fractions of SWR-markers, sequential extraction methods have been applied to all the soils (see for details Mao et al. (2014)) and vegetation samples. To isolate free lipids from the soils and the plants, the oven-dried soils, leaves and roots were weighed and extracted by dichloromethane/methanol (DCM/MeOH (9:1, v:v)) by using a Soxhlet apparatus for 24 hours to give the D fraction (Bull et al., 2000; Nierop et al., 2005; Jansen et al., 2006). The residual soils were air-dried and extracted using a Soxhlet apparatus containing *iso*-propanol/ammonia solution (IPA/NH_3, 7:3 (v:v), 32% ammonia solution) for 48 hours. The soils became wettable after IPA/NH_3 extraction. The soluble lipids (AS fraction) were separated from the dried IPA/NH_3 extracts by DCM/MeOH (9:1), and the residues resulted into so-called AI fractions, which involved ester bonds.

All the D and AS fractions of the soils and DCM/MeOH extracts of the plants were methylated using diazomethane (CH_2N_2). The AI fractions and the lipid-free air-dried leaves and roots were depolymerised by trans-methylation using BF_3-MeOH at 70 ℃ for 16 hours (Riederer et al., 1993). Prior to analysis, all the aliquots were eluted through a small silicagel 60 column (0.063-0.2 mm diameter, 79-230 mesh) with ethyl acetate and silylated using N,O-*bis* (trimethylsilyl) trifluoroacetamide (BSTFA) in pyridine at 60℃ for 20 min.

2.5 Gas Chromatography (GC) and GC- Mass Spectrometry (MS) analysis

A HP 6890 Series GC fitted with a flame ionisation detector (FID) was used to analyse derivatised extracts. A CP-Sil 5 CB capillary column (Agilent Technologies, 30 m length × 0.32 mm diameter, 0.10 µm film thickness) was used to separate compounds, using helium as carrier gas with a constant pressure at 100 kPa. The oven heating programme started with an initial temperature of 70 ℃, increased to 130 ℃ at 20 ℃ min^{-1}, then heated from 130 ℃ to 320 ℃ at 4 ℃ min^{-1}, and finally held at 320 ℃ for 20 min.

GC-MS analysis of extracts was performed on a Thermo Trace GC Ultra GC connected to Finnigan Trace DSQ mass spectrometer with a mass range of *m/z* 50-800, using helium at a 1.0 ml min^{-1} flow rate as the carrier gas. The GC-MS was equipped with a similar capillary column as the GC-FID, and the same oven temperature mode was used as for the GC-FID analysis.

Based on GC-FID and GC-MS analyses, the relative response factors of compound groups (alkanes, alcohols, fatty acids, ω-hydroxy fatty acids and α,ω-dicarboxylic acids) were rather similar and hardly discriminating between various types of compounds. Therefore, a known amount of squalane as an internal standard was added to extracts to quantify compounds by peak area integration from GC-MS chromatograms to correct for possible co-eluting compounds. Both for GC-FID and GC-MS analyses, 1 µl of derivatised extracts were injected onto the column. Compound identification was conducted on mass spectra using a NIST library or by interpretation of the spectra, and combined with their retention times or by comparison with literature data.

2.6 Statistical data analysis

163 The correlation between SWR-markers and SWR can be clearly interpreted by linear
164 regression analysis. Here we applied simple linear regression between measured SWR value
165 (i.e. the WDPT) at log scale (log (s)) to the concentrations of individual SWR-markers and
166 each compound group. To assess both the quantitative and qualitative effects, we carried out
167 regression analysis on the absolute amount (μg g^{-1}soil) and the relative amount (μg g^{-1}TOC)
168 of SWR-markers. In our study the quantity of every compound group was defined as absolute
169 amount (μg g^{-1}soil) and the quality as the ratio of the concentrations of two different
170 compound groups (Group1/Group2, [-]). We will distinguish these functional compound
171 groups, based on the extraction type (D, AI and AS) and their compound types, i.e. alkanes,
172 fatty acids, alcohols, ω-hydroxy fatty acids or α,ω-dicarboxylic acids.

3. Results

3.1 Single compounds analysis

3.1.1 Single SWR-markers from soils

For all soils, the majority of compounds had negative but no significant correlations between their relative concentrations (μg g^{-1}TOC) and SWR. In Table 2 only the significant correlations between relative concentrations of individual markers and SWR are given, in which we analysed this for 1) all soils, 2) topsoils and 3) subsoils, respectively.

For all soils (n=15), in the D fraction we only found that C_{24} alcohol significantly positively related to SWR (log_{10} WDPT; Table 2; r=0.575, p=0.025). For the AS fraction, three even-numbered alcohols (C_{20}, C_{24} and C_{30}) and C_{20} ω-hydroxy fatty acid had significant positive relations with SWR. Other, in general short-chain fatty acids, alcohols and alkanes from different fractions exhibited significant negative relations with SWR (Table 2).

For all the topsoils (n=10) the longer chain AS-alcohols (C_{20}, C_{24} and C_{30}), which had significant relations with SWR for all soils, were no longer significant in the topsoils. Only negatively related compounds were found for the topsoils. For the AI-fraction, similar significant negatively correlated markers for the topsoils were found as compared to all soils. For the AS fraction C_{22}, C_{23} and C_{24} fatty acids had significant negative correlations with SWR for all the topsoils, which could not be found for all soils. In contrast, AS alcohols did not show significant relations with SWR for the topsoils. For all the subsoils (n=5), short-chain alcohols (C_{16} and C_{18}) in the D fraction and fatty acids (C_{18} and C_{21}) in the AI fraction showed negatively significant correlations with SWR, while none of the compounds in the AS fraction had a significant correlation with SWR.

3.1.2 Single biomarkers from vegetation

The compound groups fatty acids, alcohols and alkanes were identified in DCM/MeOH extracts from plant leaves and roots (Fig. 1a-c). Besides these three main groups mentioned above, β-sitosterol was abundantly present in all the leaves and roots, but was found in soils with much lower abundance and had an insignificant correlation with SWR, as similar as other identified sterols (e.g. stigmasterol in mosses). Other typical biomarkers were found in leaves and roots of one or more species but hardly found in all soils, for instance, dehydroabietic acid in black pine needles, in the leaves of oak and sea-buckthorn, therefore those biomarkers were not taken into account as an SWR marker to predict SWR.

For the fatty acids in all leaves and roots a strong even-over-odd preference was found, in which chain lengths of most plant extracts ranged between C_{16}-C_{32}. The sheep fescue and hypnum moss clearly showed the largest range of abundant fatty acids, in which C_{28} was most abundant for both species. For sea-buckthorn and hawthorn, roots had more different kinds of fatty acids than the leaves. C_{30} was most abundant in leaves of hawthorn, C_{24} in roots of hawthorn, C_{22} in both leaves and roots of sea-buckthorn. For pine needles, C_{16} and C_{18} fatty acids were the only fatty acids found, while the pine roots contained a large range with C_{24} as dominating one. Long-chain even-numbered fatty acids were more abundant in the leaves (with C_{20} as most dominant) than in the roots of common oak, with C_{16} as most dominant. In summary the number of different fatty acids found in roots was larger than in leaves, with highest concentrations in sea-buckthorn roots and oak leaves.

In contrast to fatty acids, the alcohols observed in plants ranged between C_{16}-C_{32} and were only even-numbered (Fig. 1b). The most abundant alcohol in sheep fescue and hypnum moss was C_{26}. C_{22} was the most dominating in sea-buckthorn leaves while in their roots C_{18}, C_{22} and C_{26} alcohols had similar predominance. For hawthorn, C_{26} was most the abundant in leaves and C_{24} in roots. C_{24} alcohol was predominant in pine needles and oak leaves while their roots showed a more uniform distribution (C_{18}-C_{24} and C_{18}-C_{26}, respectively). To

summarise, the number of different alcohols found in roots was larger than in the leaves, which is similar as found for the fatty acids, but abundance of the alcohols in the leaves was much higher.

Only long-chain odd-numbered alkanes (C_{21}-C_{31}) were observed in the leaves, except for pine needles in which no alkanes were found (Fig. 1c). C_{27} dominated oak leaves, C_{29} dominated all the other leaves and roots except sea-buckthorn roots that were dominated by C_{21} and had a larger range of alkanes than all other plant tissues. Fatty acids, alcohols, ω-hydroxy fatty acids, and α,ω-dicarboxylic acids were released from the ester-bound lipids (cutin and suberin) upon BF_3-MeOH hydrolysis of all leaves and roots (Fig. 2 a-d). In addition, several di- and trihydroxy fatty acids, common cutin and suberin monomers, were identified, but as they were hardly or not found in our soils (Mao et al., 2014) they do not play a major role in our correlation analysis. Therefore, we limited ourselves to the previously mentioned compound groups.

The even-over-odd-numbered fatty acids (C_{16}-C_{30}) dominated all leaves and roots (Fig. 2a). Interestingly, C_{16} fatty acid was the most dominating ester-bound fatty acid for all above-ground plant tissues in relative high concentrations, in contrast to the roots. All roots had a large range of fatty acids, dominated by C_{24}, except for hawthorn that contained only C_{20} and C_{22} fatty acids.

Compared to leaves, a larger number of ester-bound alcohols in greater abundance were found in the roots. For sheep fescue, C_{20} alcohol was the dominant one, while C_{18} was the only one found in hypnum moss (Fig. 2b). No ester-bound alcohol was found in sea buckthorn and hawthorn leaves. Pine needles only showed C_{24}, while oak leaves showed only C_{20}. The most dominant ester-bound alcohol in the roots of sea-buckthorn and pine was C_{16}, while in those of hawthorn and oak C_{24} and C_{20} were, respectively.

Sheep fescue showed a large range of ω-hydroxy fatty acids dominated by $C_{18:1}$ (Fig. 2c), whereas hypnum moss contained only C_{16}. The roots of sea-buckthorn had the widest range of ω-hydroxy fatty acids, from C_{16} to C_{28}, while the roots of hawthorn had the narrowest range from C_{16} to C_{22} excluding $C_{18:1.}$ C_{24} was most dominant for sea-buckthorn roots while in hawthorn roots C_{20} was most abundant. C_{12} and C_{14} ω-hydroxy fatty acids were only observed in pine needles, whereas longer-chain ones (> C_{18}) were present only in its roots maximising at C_{22}. $C_{18:1}$ ω-hydroxy fatty acid predominated in both oak leaves and roots.

Even-numbered α,ω-dicarboxylic acids (C_{16}-C_{28}) as typical suberin-derived biomarkers were only found in the plant roots (Fig. 2d). No α,ω-dicarboxylic acids were found in sheep fescue and hypnum moss while in the roots of the other species the dominating α,ω-dicarboxylic acid differs: sea buckthorn ($C_{18:1}$), hawthorn (C_{16}), oak (C_{16}) and pine (C_{22}).

3.1.3 Soil-vegetation link based on single compounds

Compared to leaves, roots contained a larger number of different extractable and ester-bound biomarkers, except for the alkanes. The concentrations of most extractable lipids in roots were lower than in leaves, while the opposite was generally true for ester-bound lipids.

Comparing the D fraction with extractable lipids of plants, C_{16}, C_{17} and C_{18} fatty acids in the D fraction of soils are negatively related to SWR for all soils and the topsoils (Table 2), which were most abundant in sheep fescue (Fig. 1a). The oak leaves contained the highest concentration of C_{24} alcohol, which in the D fraction was the only compound that positively related to SWR. Alcohols C_{20} and C_{24} in the ester-bound lipids of the hawthorn roots were most abundant and can clearly be related to C_{20} and C_{24} alcohols in the AI fraction of soils.

3.2 Compound groups analysis

3.2.1 SWR-marker groups from soils

To get a more general view on the relation between certain compounds and SWR, we have analysed compound groups (i.e. sum of all compounds of the same type). For all soils, the absolute total amounts of the main compound groups in the D, AI and AS fractions ranged from 1.61 to 63.80 mg g^{-1}soil, from 0.84 to 62.18 mg g^{-1}soil and from 0.27 to 40.24 mg g^{1}soil, respectively. For all soils, all compound groups, i.e. (D) fatty acid, (D) alcohol, (D) alkane, (AI) fatty acid, (AI) alcohol, (AI) ω-hydroxy fatty acid, (AI) α,ω-dicarboxylic acid, (AS) fatty acid, (AS) alcohol and (AS) ω-hydroxy fatty acid, had significant positive relations between quantity (log_{10} (μg g^{-1}soil)) and SWR (log_{10} WDPT) (Table 3). For all the topsoils, all compound groups significantly correlated to SWR except (AI) α,ω-dicarboxylic acid and (AS) fatty acid. For all the subsoils less compound groups had significant relations with SWR. For the high TOC soils, no group had a significant correlation with SWR, while for the low TOC soils, all groups significantly related to SWR except (AI) fatty acid and (AS) ω-hydroxy fatty acid.

As absolute values highly correlate with organic matter content and therefore with SWR, relative amounts are more interesting to understand the importance of one component over the other. For all soils, the relative total amounts of the main compound groups in the D, AI and AS fractions ranged from 0.74 to 2.74 mg g^{-1}TOC, from 0.48 to 2.01 mg g^{-1}TOC and from 0.24 to 1.43 mg g^{-1}TOC, respectively. To this end the correlation between the relative concentrations (log_{10} (μg g^{-1}TOC)) of compound groups and SWR was analysed. Only (AS) alcohol group had a positive significant correlation for all soils and the subsoils (Table 3). The other groups either had a negative or positive relation with SWR but not significant. No compound group significantly related to SWR for the topsoils.

3.2.2 Vegetation biomarker groups

Considering the biomarker groups of extractable lipids of sea-buckthorn, hawthorn, pine and oak, oak leaves had much more abundant fatty acids and alcohols than the leaves of other plants (Table 4). The roots of sea-buckthorn were richer in fatty acids and alcohols than the other roots. Alkanes were observed in all leaves except pine needles, whereas a relatively small amount of alkanes was found in pine roots. The leaves of hawthorn had the highest amount of alkane while no alkanes were found in its roots. Sea-buckthorn was the only plant species containing alkanes in both its leaves and roots.

Ester-bound fatty acids and ω-hydroxy fatty acids occurred in all leaves and roots, whereas the leaves and roots of hawthorn had the highest abundance of fatty acids of all leaves and the highest ω-hydroxy fatty acids of all roots (Table 4). Much less ester-bound alcohols were observed in leaves than in roots. The roots of hawthorn had the most abundant alcohol group. As expected, no α,ω-dicarboxylic acids were present in leaves but only in roots.

3.2.3 Soil-vegetation link based on compound groups

Fig. 3 shows the relative concentrations of the compound groups subdivided between top- and subsoils. Interestingly, although the composition within each compound group is different, there is almost no significant difference between the concentrations of compound groups in top- and subsoils. The relative abundance of (AI) α,ω-dicarboxylic acids in the topsoils was significantly higher than in the subsoils ($p=0.013$), while such compounds only derive from roots. There was no significant difference between relative abundances of all other summed compound groups between top- and subsoils. Although more extractable fatty acids were found in leaves than in roots, except for sea-buckthorn (Table 4), no clear differences for (D) fatty acids were observed between top- and subsoils (Fig. 3). The amounts of (D) alkanes in top- and subsoils were almost equal, while leaves had much more alkanes

than roots. Comparing the AI fraction, AI-fatty acids was equal in the topsoils and subsoils (Fig. 3) while the ester-bound fatty acids were more abundant in leaves than in roots (Table 4). The ω-hydroxy fatty acids were slightly lower in the topsoils than in the subsoils, whereas the concentration of this group was lower in leaves than in roots.

3.3 Quality relation of two compound groups to SWR

From the above analysis, individual compound groups in absolute concentrations (μg g^{-1}soil) were in general able to understand the SWR behaviour, while using the relative amounts (μg g^{-1}TOC) were not. As a next step, we analysed the ratio of two different compound groups reflecting a quality parameter of SWR markers in relation to SWR. To understand if this quality factor is able to describe the SWR, the linear correlation of such a ratio and SWR was analysed. For all soils, (AS) alcohol was essential for a significant combination (Table 5). When (AS) alcohol was the numerator, the correlation between the ratio of two groups and SWR was positive, otherwise, it was negatively correlated. Also for the topsoils and the subsoils, (AS) alcohol occurred in all significant combinations and had a positive relation when (AS) alcohol was the numerator. In contrast to all soils, for the topsoils, not all the groups that combined with (AS) alcohol showed a significant relation. Among those significant combinations, all three compound groups from the D fraction were included; however, (AI) alcohol was the only group from the AI fraction, while (AS) fatty acid was the only one from the AS fraction. For the subsoils it is interesting that significant combinations coincided with all AI compound groups except (AI) alcohol. None of the significant combinations were the same for the topsoils and subsoils. All the significant combinations for the top-/subsoils were also obtained in those for all soils. Similar to all soils, (AS) alcohol as the numerator achieved positive correlations between the quality ratios and SWR for the topsoils.

For the topsoils, all the groups from the D fraction were included in the significant combinations. Linking those groups to the extractable lipids of the plant leaves, oak leaves had the highest concentrations of both fatty acids and alcohols. All the D fraction groups were abundantly present in the roots of sea-buckthorn. The leaves and the roots of hawthorn had the highest abundances of ester-bound alcohols. For the subsoils, among the significant combinations, all three AI groups, i.e. fatty acid, ω-hydroxy fatty acid and α,ω-dicarboxylic acid, occurred in the ester-bound lipids of vegetation. The ester-bound fatty acids were most abundant in the leaves of hawthorn and the roots of sea-buckthorn, respectively (Table 4). Hawthorn roots were richer in ω-hydroxy fatty acids than the other plant roots, whereas pine needles had the highest ω-hydroxy fatty acids for all leaves. α,ω-Dicarboxylic acids were richest in oak roots.

4. Discussion

4.1 Single SWR-markers

As known, the extracted SWR-markers are all hydrophobic (Hansel et al., 2008; Atanassova and Doerr, 2010; de Blas et al., 2013); however, still significant negative correlations have been shown as relative abundances. For all soil categories, compared to long-chain compounds, the short-chain ones showed more negative linear relations with SWR. Atanassova and Doerr (2010) also detected more abundant short-chain dicarboxylic acids in less water repellent soils. Mainwaring et al. (2004) mentioned low molecular weight polar compounds diffuse quickly through soil water. Referring to that, a possible explanation of those more negative relations is that the short-chain compounds are supposed to be more mobile and less hydrophobic, inducing a relative lower SWR. Since the measured SWR is an average value reflecting the contribution of all components, the contribution of the short-chain compounds to cause SWR is apparently relatively smaller than the average contribution induced by all SWR-markers resulting in negative relations. In addition, it also implies that other long-chain compounds have a relatively larger contribution to SWR, which is supported by the positive relations. Soil organic matter composition and hence SWR-markers differ between soils under various vegetation. From either ecological or chemical point of view, the influence of single SWR-markers on SWR cannot be accurately quantified, and thus, single compounds are not good SWR-markers to predict the extent of SWR well.

4.2 Role of compound groups

Since single SWR-markers may not be capable to predict SWR, we analysed the possible correlations between compound groups and SWR. We are the first to discuss about the quantity and quality of SWR-markers to predict SWR. For all soils, the positive relations between the absolute amounts of all the compound groups and SWR follow the significant

positive relation between TOC and SWR shown by Mao et al. (2014). Therefore, it is not surprising that the absolute quantity of the single SWR-marker groups showed its potential of predicting SWR. However, the quality of compounds is more important than the quantity by influencing SWR (Lozano et al., 2013). Regarding the relative concentrations of SWR-marker groups, (AS) alcohol was the only group to show a significant relation with SWR for all soils and the subsoils, respectively. In addition, alcohols have been detected in water repellent soils and associate with SWR (Mainwaring et al., 2004; Hansel et al., 2008; Atanassova and Doerr, 2010). As (AS) alcohol does not comprise an abundant group in all AS extracts, the relation between compound groups and SWR might not be simply explained only by a single compound group. Therefore, the ratio of two different groups, namely the quality of the compound groups in our study, was used to demonstrate the significant combinations predicting SWR for different soil categories.

For the topsoils, there are fewer groups from AI and AS fractions combined with (AS) alcohol that significantly related to SWR than for all soils. For instance, α,ω-dicarboxylic acids in the AI fraction and ω-hydroxy fatty acids in both AI and AS fractions in combination with (AS) alcohols did not predict SWR well in topsoils. It is reasonable that those combinations were no longer significant because of the different original sources of SWR-markers. The main source of SWR-markers in the topsoils is most likely plant leaves (Bull et al., 2000a; Naafs et al., 2004a), whereas both α,ω-dicarboxylic acids and ω-hydroxy fatty acids are typically derived from roots (Kolattukudy et al., 1981, 2001; Pollard et al., 2008). For the subsoils, the entire D fraction originating from leaf waxes were not involved in the significant combinations with (AS) alcohol, suggesting little contribution of organic compounds to the sandy subsoils is from leaves (Nierop and Verstraten, 2004). All three groups that successfully combined with (AS) alcohol are from the root-derived AI fraction

405 revealing that the primary source of organic matter in subsoils is roots (Bull et al., 2000b;
406 Nierop et al., 2006) and those combinations could well predict the subsoil SWR.
407 (AI) alcohol was not on the list of significant group combinations for the subsoils but was
408 the only AI group present in one significant combination for the topsoils, potentially
409 implying that (AI) alcohol combined with (AS) alcohol can be a good predictor of SWR in
410 the topsoils. Based on the analysis of the significant combinations of the top- and subsoils,
411 the original source of SWR-markers probably plays a vital role on selecting best
412 combinations to predict soil SWR. However, the relations observed between SWR-marker
413 groups and SWR may not be directly applicable to other types of soils with different soil
414 texture, structure and vegetation cover (Bisdom et al., 1993; Doerr et al., 2000; De Blas et al.,
415 2010).
416
417 **4.3 Role of the AS fraction**
418 Interestingly, only (AS) alcohol positively related to SWR significantly. It implies that SWR
419 is higher when the soil organic matter contains relatively more (AS) alcohol. In addition,
420 (AS) alcohol was most frequently appearing in significant group combinations. Although the
421 AS fraction seems an important SWR fraction, compared to the other two fractions, the AS
422 fraction contained the least amount of extracted SWR-markers, the AS fraction as such and
423 its origin is poorly understood. Mao et al. (2014) speculated that the AS fraction physically
424 blocked by the suberin-derived AI fraction are mainly from leaves and a smaller part from
425 roots. However, in this paper:
426 1. As observed earlier, there were no alkanes occurring in the AS fractions (Mao et al.,
427 2014), while in the present study alkanes was one of the main groups present in leaves while
428 hardly or not in roots, suggesting a negligible leaf signal in the AS fraction.

2. The ω-hydroxy fatty acids in the AS fraction were mainly C_{22} and C_{24}, which are typical of suberin-derived compounds from roots (Kolattukudy et al., 1980; Nierop et al., 2006; Spielvogel et al., 2014).

3. For the subsoils, only the ratios of (AS) alcohol/ (AI) compounds had significant positive relations with SWR. Here (AI) compounds included (AI) fatty acid, (AI) ω-hydroxy fatty acid and (AI) α,ω-dicarboxylic acid, which are suberin-derived compounds (Mao et al., 2014). Those significant combinations suggest that the origin of (AS) alcohol may be relevant to the origin of the (AI) fraction, namely roots. (AS) alcohol/(AI) alcohol was the only ratio of AS alcohol/AI compounds that did not predict SWR in the subsoil well, implying that (AI) alcohol is different to some degree from the other (AI) groups when it is associated with (AS) alcohol.

4. For the topsoils, the ratio of (AS) alcohol/ (AI) compounds (except (AI) alcohol) did not have strong correlations with SWR. (AI) compounds mainly originate from roots, demonstrating that roots-derived compounds possibly do not respond to the SWR of the topsoils. For the topsoils, the ratio of (AS) alcohol/ (AI) alcohol significantly related to SWR, implying that the relation between (AS) alcohol and (AI) alcohol is unique and different than the relations between (AS) alcohol and other (AI) compounds.

5. ω-Hydroxy fatty acid group in the AI fraction had a positive significant relation ($r=0.58$, $p=0.02$) with (AS) alcohol, but none of the compound groups in the D fraction well correlated to (AS) alcohol. As previously pointed out, the D fraction and AI fraction are mainly derived from leaf-waxes and roots, respectively (Mao et al., 2014). The correlations reflect that the (AS) alcohol did not have the same original source as (D) compounds but probably originate from the same source as (AI) compounds. All arguments together suggest that roots are the likely main original source of the AS fraction.

As described in our previous study, the AS fraction does not directly have contact with water in soils as it is physically blocked by the AI fraction by definition (Mao et al., 2014). The DCM-MeOH insoluble, larger ester-bound components in the AI fraction can be turned into an AS fraction by microbial hydrolysis producing monomeric compounds that are extractable (Fernando et al., 1984; Martins et al., 2014). Kolattukudy (2001) proposed a structure of suberin, in which ω-hydroxy fatty acids and α,ω-dicarboxylic acids are ester bonded to form (linear) polymers. Possessing only one functional group, alcohols are likely bound on the edge of such large molecules. Upon degradation, these alcohols could be hydrolysed easier to become monomers than ω-hydroxy fatty acids and α,ω-dicarboxylic acids which both contain two functional groups that occur more inside the polymers. α,ω-Dicarboxylic acids were not found in the AS fraction, which may imply that their position within the suberin polymers is apparently different from that of the ω-hydroxy fatty acids through which they are less easily hydrolysed than the other groups.

We speculate that an AI fraction is turned into an AS fraction by microbial hydrolysis. The more microbial activity in soils, the more decomposed of organic matter becomes (Schnürer and Rosswall, 1982), and as a result a larger amount of a given AI fraction could be transformed into an AS fraction. Consequently, according to linear regression analysis, the larger the AS fraction, the stronger SWR gets. Over time, when the AI fraction decreases by microbial hydrolysis, the amount of the AS fraction increases, the SWR is raising until the remaining AI fraction becomes too small to cover the whole AS fraction. As such, the ratio of AS/AI fractions becomes a tipping point to indicate the optimal SWR. Once part of the AS fraction is not blocked anymore by the AI fraction and becomes directly extractable by DCM-MeOH, it automatically becomes part of the D fraction. Before that, the role of AS fraction may be a kind of catalyst that binds (and is blocked by) the predominantly root-

derived AI fraction to mineral soil particles meanwhile inducing SWR. The proportion of the AS fraction in soil organic matter may be an important predictor of SWR.

If we extrapolate this from the molecular level to the level of young soils, their amount of organic matter is small. Therefore, the microbial activity is also small and only a small amount of (AS) fraction can be produced, and thus SWR is relatively small. When the soil becomes more developed, there is more organic matter, and also more time to produce a larger AS fraction, the SWR also becomes higher. Over time, when organic matter input and output is in equilibrium, the size of the AS fraction may also become stable; the level of SWR for that particular soil may become stable as well. As the AS fraction is mainly derived from roots and is produced upon microbial hydrolysis of the predominantly root-derived AI fractions, we expect plants with larger root biomass in older, more developed soils will lead to highest SWR. Compared to shrubs and trees, smaller plants such as grasses and mosses which have smaller and thinner root systems and produces smaller organic matter contents will likely cause smaller SWR.

4.4 Plant signals in soils

Soil organic matter composition of different soils varies largely due to differences in vegetation cover (Van Bergen et al, 1997; Nierop, 2001; Kögel-Knabner, 2002). In this study, the main groups of the extractable and ester-bound lipids present in the leaves and roots were, in general, all identified in D, AS and AI fractions of the soils under the given vegetation. No significant difference between the summed relative abundances of the groups (except (AI) α,ω-dicarboxylic acid) in the top- and subsoils was found in our study. This means that the signals of leaves and roots are mixed in both top- and subsoils potentially due to a mixed cover of vegetation sources or vegetation succession at the field site. In such a situation, (AI)

501 α,ω-dicarboxylic acids still showed significantly higher concentrations in the subsoils than in
502 the topsoils, strongly reflecting the root contribution to the subsoils.
503 The covering plants are the main sources of the SWR-markers and the extractable and
504 ester-bound lipids in soils reflect, therefore, the leaf and root signals of these plants (Nierop
505 et al., 2003; Naafs et al., 2004a). Within the extractable lipids, alkanes and alcohols are more
506 suitable than fatty acids to indicate the origin of the soil lipids, since fatty acids are not
507 sufficiently specific to be used as biomarkers (Van Bergen et al., 1997; Jansen et al., 2006).
508 The C_{27} and C_{29} alkanes are the dominating alkanes in all soils analysed (Mao et al., 2014);
509 they were also the major alkanes found in most of our vegetation leaves, strongly suggesting
510 a close relation between the soil alkanes and those occurring in plant leaves (Bull et al.,
511 2000a; Naafs et al., 2004a; Nierop et al., 2006). Since C_{26} alcohol is typical of grass (Walton,
512 1990; Van Bergen et al., 1997), which predominated both the sheep fescue and the soils
513 under sheep fescue (Mao et al., 2014), implying that C_{26} alcohol in the soils most likely
514 indeed originated mainly from grasses. Similarly, C_{24} alcohol, which is an indicator of oak
515 leaves (Bull et al., 2000), was abundantly present in the soils under oak. Regarding the
516 alcohol group, more alcohols were observed in leaves than in roots and more alcohols were
517 found in the topsoils than in the subsoils, suggesting a large contribution of extractable lipids
518 from plant leaf waxes to the directly underlying (top)soils.
519 The ester-bound lipid biomarkers represent the cutin and suberin-derived compounds in the
520 plant leaves/needles and roots, respectively. α,ω-Dicarboxylic acids are typically derived
521 from suberins (Kolattukudy, 2001), which were only found in roots, and similar to the ester-
522 bound alcohols and ω-hydroxy fatty acids, they were more enriched in subsoils rather than in
523 topsoils, implying that the organic matter in the sandy subsoils well reflects a root origin (e.g.
524 Nierop et al., 2006). The small amounts of α,ω-dicarboxylic acids in the topsoils may derive
525 from shallow roots plants such as grasses providing suberins to the topsoils. An alternative

source may be bark which also contains suberins albeit their contribution to soils is smaller than that of roots (Preston et al., 1994). As aforementioned, most likely the AS fraction has mainly the same root origin as the AI fraction.

5. Conclusion

The prediction of SWR from the quantity of the SWR-markers follows the relation between soil TOC and SWR. The relative amounts of the most single short-chain SWR-markers negatively relate to SWR, while the long-chain markers have positive but insignificant relations with SWR. It implies that a single SWR-marker is not suitable to explain and predict the behaviour of SWR. The analysis of the quality of SWR-marker groups suggests that (AS) alcohol combined with suberin-derived ω-hydroxy fatty acids and α,ω-dicarboxylic acids can well predict the SWR of subsoils. For the topsoils, the combination (AS) alcohol/ (AI) alcohol is a good predictor of the SWR. The relatively more (AS) alcohol a soil contains, the more water repellent it becomes. The relations between the SWR of sandy soils and SWR-markers may not be entirely suitable for other types of soils, as soil textures and structures may impact it differently. A combined number of indications suggest that in this study the AS fraction is mainly root-derived and likely produced by microbial hydrolysis of ester-bound lipids. Together, roots produce markers that induce SWR stronger than above-ground plant tissues, and root-derived compounds more sufficiently predict SWR. To what extent this holds for other soil types with different texture and structure needs further research.

Acknowledgements

This study is funded by the Earth and Life Science and Research Council (ALW) with financial aid from the Netherlands Organization for Scientific Research (NWO) (Grant 821.01.004). The authors thank PWN for permitting our research in the Zuid-Kennemerland National Park and Jos A. Hageman for helping with the geostatistical analysis of data.

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737
738 Table 1. Soil profile and vegetation description

Profile	Sample label	Sampling depth (cm)	Horizon	pH	TOC (mg g^{-1} soil)[c]	TN (mg g^{-1}soil)	C/N ratio	WDPT (s)	log_{10} WDPT (s)	Repellency class	Vegetation	Vegetation sampled
1	WRC-1[a]	0 – 7	A	8.79	0.76	0.16	4.82	0	-1.00	wettable	*Festuca sp.* (sheep fescue)	Leaves combined with roots
	WRC-2	7 - 14	Ahb[b]	8.33	4.83	0.51	9.54	35	1.55	slight	*Festuca sp.*	
	WRC-3	14 - 20	B	8.72	1.40	0.25	5.66	0.3	-0.48	wettable	*Festuca sp.*	
2	WRC-6	0 – 1	A	8.26	3.47	0.38	9.20	1	0.00	wettable	Algae	None
3	WRC-8	0 – 5	Ah	7.87	5.49	0.49	11.15	148	2.17	strong	*Hypnum Laconosum* (hypnum moss)	Whole moss plants
	WRC-9	5 – 10	B	8.70	1.57	0.25	6.21	2	0.36	wettable	*Hypnum Laconosum*	
4	WRC-10	0 – 10	Ah	6.92	26.80	2.00	13.42	18	1.25	slight	*Hypnum Laconosum*	
5	WRC-13	0 – 16	Ah	5.84	14.98	1.01	14.80	240	2.38	strong	*Pinus nigra* (black pine)	Green needles and roots
6	WRC-14	0 – 9	Ah	7.09	31.08	2.40	12.96	417	2.62	strong	*Crataegus sp.* (hawthorn)	Leaves and roots
	WRC-15	9 – 15	B	7.55	5.02	0.53	9.49	550	2.74	strong	*Crataegus sp.*	
7	WRC-25	0 – 7	Ah	7.66	10.22	0.82	12.47	4786	3.68	extreme	*Hippophae rhamnoides* (sea-buckthorn)	Leaves and roots
	WRC-26	7– 12	B	8.10	4.77	0.45	10.57	331	2.52	strong	*Hippophae rhamnoides*	
8	WRC-30	0 – 2	Ah1	5.76	87.44	6.35	13.77	1905	3.28	severe	*Quercus robur* (common oak)	Leaves and roots
	WRC-31	2 - 4.5	Ah2	5.79	20.71	1.59	13.04	2512	3.40	severe	*Quercus robur*	
	WRC-32	4.5 – 20	B	8.08	2.46	0.27	9.05	14	1.14	slight	*Quercus robur*	

739
740 [a] WRC-1 consisted of a top soil, which was formed by wind-blown sand deposition at a grass covered soil.
741 [b] WRC-2 consisted of a dark brownish Ah horizon with grass roots, which was buried by wind-blown sand deposition.
742 [c] Soil TOC had a significant positive correlation (r=0.76, p=0.001) with SWR (Mao et al., 2014): $log_{10}WDPT(s) = 1.96* log_{10}TOC+ 0.01$

Table 2. The relative concentrations (log (μg g^{-1}TOC)) of single SWR-markers significantly related to SWR

SWR-marker[a]	Soil category					
	All soils (n=15)		Topsoils (n=10)		Subsoils (n=5)	
	Coef.[b]	Sig.[c]	Coef.	Sig.	Coef.	Sig.
(D)C_{16} fatty acid	-0.811	0	-0.905	0		
(D)C_{17} fatty acid	-0.612	0.015	-0.73	0.017		
(D)C_{18} fatty acid	-0.768	0.001	-0.811	0.004		
(D)C_{21} fatty acid	-0.555	0.032				
(D)C_{15} alcohol	-0.741	0.002	-0.873	0.001	-0.94	0.017
(D)C_{16} alcohol	-0.675	0.006	-0.662	0.037		
(D)C_{17} alcohol	-0.729	0.002	-0.756	0.011		
(D)C_{18} alcohol	-0.581	0.023			-0.951	0.013
(D)C_{24} alcohol	0.575	0.025				
(D)C_{20} alkane	-0.797	0.000	-0.819	0.004		
(D)C_{23} alkane	-0.571	0.026				
(D)C_{24} alkane	-0.67	0.006	-0.713	0.021		
(AI)C_{16} fatty acid	-0.547	0.035	-0.659	0.038		
(AI)C_{18} fatty acid	-0.733	0.002	-0.668	0.035	-0.909	0.033
(AI)C_{21} fatty acid	-0.773	0.001	-0.726	0.018	-0.925	0.025
(AS)C_{22} fatty acid			-0.687	0.028		
(AS)C_{23} fatty acid			-0.639	0.047		
(AS)C_{24} fatty acid			-0.653	0.040		
(AS)C_{20} alcohol	0.596	0.019				
(AS)C_{24} alcohol	0.613	0.015				
(AS)C_{30} alcohol	0.532	0.041				
(AS)C_{20} ω-hydroxy fatty acid	0.524	0.045				

[a]D, AS and AI refers to DCM/MeOH soluble fraction, DCM/MeOH soluble fraction of IPA/NH_3 extract and DCM/MeOH insoluble fraction of IPA/NH_3 extract, respectively. [b]linear correlation coefficient. [c]significance;

Table 3. Correlation coefficients of single SWR-marker groups significantly (< 0.05) related to SWR

Soil catergory	Absolute amount (log (μg g^{-1}soil))			Relative amount (log (μg g^{-1}TOC))		
	SWR-marker[a]	Coef.[b]	Sig.[c]	SWR-marker	Coef.	Sig.
All soils	(D) fatty acid	0.797	0.000	(AS) alcohol	0.706	0.003
	(D) alcohol	0.777	0.001			
	(D) alkane	0.778	0.001			
	(AI) fatty acid	0.694	0.004			
	(AI) alcohol	0.758	0.001			
	(AI) ω-hydroxy fatty acid	0.701	0.004			
	(AI) α,ω-dicarboxylic acid	0.650	0.009			
	(AS) fatty acid	0.624	0.013			
	(AS) alcohol	0.821	0.000			
	(AS) ω-hydroxy fatty acid	0.543	0.037			
Top soils	(D) fatty acid	0.796	0.006	None		
	(D) alcohol	0.780	0.008			
	(D) alkane	0.779	0.008			
	(AI) fatty acid	0.688	0.028			
	(AI) alcohol	0.740	0.014			
	(AI) ω-hydroxy fatty acid	0.675	0.032			
	(AS) alcohol	0.786	0.007			
	(AS) ω-hydroxy fatty acid	0.691	0.027			
Subsoils	(D) fatty acid	0.937	0.019	(AS) alcohol	0.904	0.035
	(D) alcohol	0.907	0.034			
	(D) alkane	0.882	0.048			
	(AI) fatty acid	0.903	0.036			
	(AI) alcohol	0.917	0.029			
	(AS) alcohol	0.969	0.006			

[a]D, AS and AI refers to DCM/MeOH soluble fraction, DCM/MeOH soluble fraction of IPA/NH_3 extract and DCM/MeOH insoluble fraction of IPA/NH_3 extract, respectively. [b]linear correlation coefficient. [c]significance;

Table 4. The group abundances of both DCM/MeOH extractable lipids and ester-bound lipids upon BF3-MeOH hydrolysis of leaves and roots (μg g^{-1} dried material)

Lipid type	Compound name	Vegetation species									
		Festuca ovina (sheep fescue)	*Hypnum Lacunosum* (hypnum moss)	*Hippophae rhamnoides* (sea-buckthorn)		*Crataegus sp.* (hawthorn)		*Pinus nigra* (black pine)		*Quercus robur* (common oak)	
		Leaves+ roots	whole plants	leaves	roots	leaves	roots	needles	roots	leaves	roots
Extractable	fatty acid	771.5	103.1	125.3	902.4	49.2	145	35.2	27.8	598	109.6
	alcohol	632.6	55.7	413.7	236.9	394.7	53.3	65.6	25.7	1105.6	47.6
	alkane	109.3	18.0	284.3	84.9	2263.1	0.0	0.0	2.7	50.8	0.0
Ester-bound	fatty acid	1170.2	927.4	336.5	994.9	1320.6	128.7	566.8	327.2	574.1	97.4
	alcohol	37.9	3.7	0.0	544.4	0.0	851.8	51.0	201.8	2.5	455.1
	ω-hydroxy fatty acid	1382.6	51.1	39.8	821.6	274.0	1369.2	2053.6	229.4	161.6	1037.2
	α,ω-dicarboxylic acid	0.0	0.0	0.0	175.3	0.0	284.2	0.0	25.5	0.0	414.7

Table 5. Correlation coefficients and significance levels of combinations of two SWR-marker groups significantly (< 0.05) related to SWR based on the quality factor (Group1/Group2)

Soil category	Group1 [a]	Group2	Coef.[b]	Sig.[c]
All soils	(D) fatty acid	(AS) alcohol	-0.710	0.003
	(AS) alcohol	(D) alcohol	0.658	0.008
	(AS) alcohol	(D) alkane	0.645	0.010
	(AS) alcohol	(AI) fatty acid	0.681	0.005
	(AS) alcohol	(AI) alcohol	0.689	0.050
	(AS) alcohol	(AI) ω-hydroxy fatty acid	0.631	0.012
	(AS) alcohol	(AI) α,ω-dicarboxylic acid	0.654	0.008
	(AS) alcohol	(AS) fatty acid	0.607	0.016
	(AS) ω-hydroxy fatty acid	(AS) alcohol	-0.579	0.024
Top soils	(D) fatty acid	(AS) alcohol	-0.680	0.030
	(AS) alcohol	(D) alcohol	0.661	0.037
	(AS) alcohol	(D) alkane	0.637	0.048
	(AS) alcohol	(AI) alcohol	0.664	0.036
	(AS) alcohol	(AS) fatty acid	0.642	0.045
Subsoils	(AS) alcohol	(AI) fatty acid	0.993	0.001
	(AS) alcohol	(AI) ω-hydroxy fatty acid	0.955	0.011
	(AS) alcohol	(AI) α,ω-dicarboxylic acid	0.925	0.024

[a]D, AS and AI refers to DCM/MeOH soluble fraction, DCM/MeOH soluble fraction of IPA/NH_3 extract and DCM/MeOH insoluble fraction of IPA/NH_3 extract, respectively.
[b] linear correlation coefficient. [c]significance;

Figure Captions

fig 01. Chain length distribution of DCM/MeOH extractable lipids (μg g^{-1} dried material) of vegetation leaves and roots. a: fatty acids; b: alcohols; c: alkanes.

fig 02. Chain length distribution of ester-bound lipids (μg g^{-1}dried material) upon BF_3-MeOH hydrolysis of vegetation leaves and roots. a: fatty acids; b: alcohols; c: ω-hydroxy fatty acids; d. α,ω-dicarboxylic acids.

fig 03. The relative average concentrations (μg g^{-1}TOC) of compound groups in the top- and subsoils. Error bars represent standard deviations of concentrations for compound groups. * means significant differences between top- and subsoils.

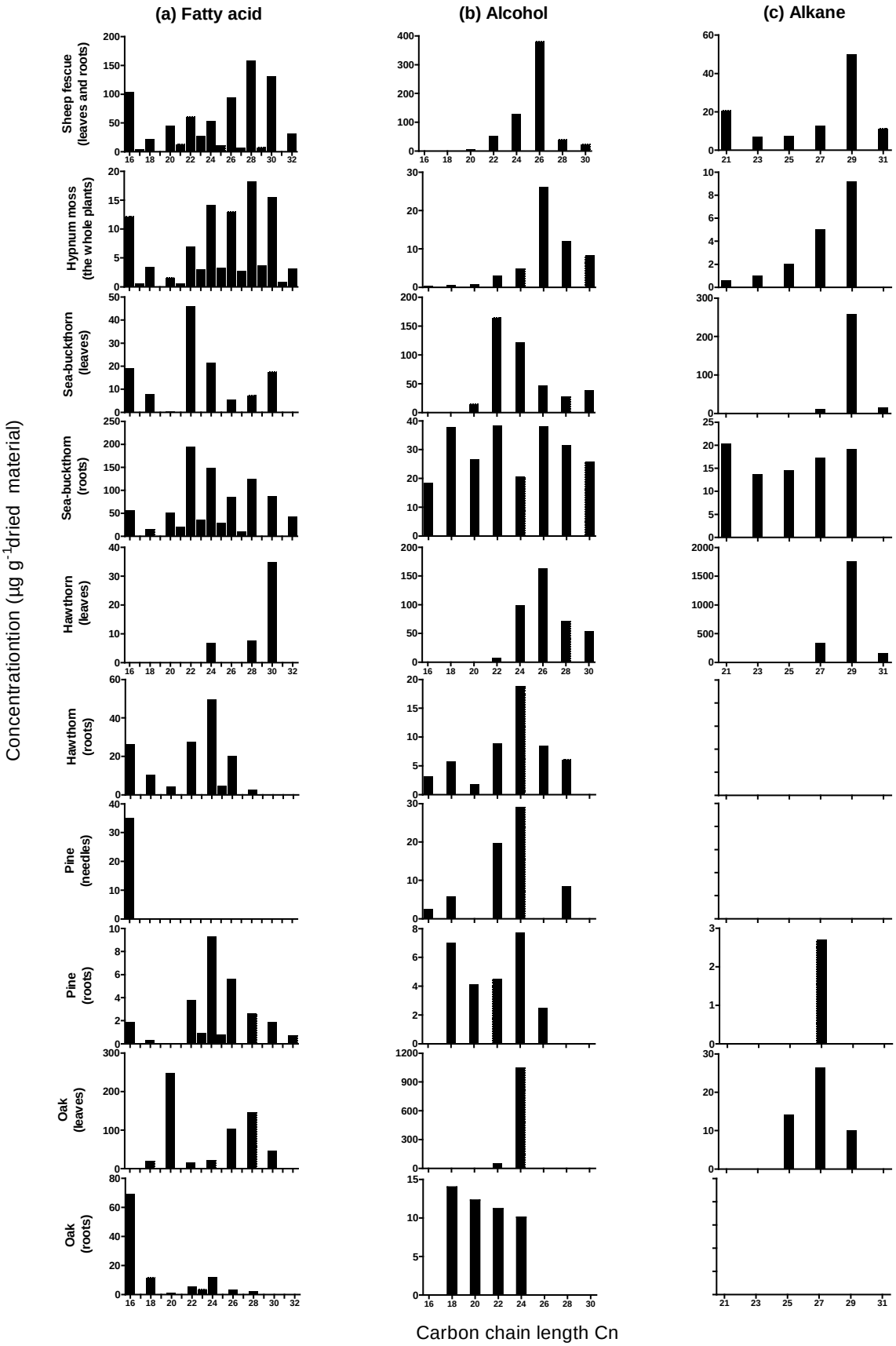
(a) Fatty acid
(b) Alcohol
(c) Alkane
Sheep fescue (leaves and roots)
Hypnum moss (the whole plants)
Sea-buckthorn (leaves)
Sea-buckthorn (roots)
Hawthorn (leaves)
Hawthorn (roots)
Pine (needles)
Pine (roots)
Oak (leaves)
Oak (roots)
Concentrationtion (μg g-1dried material)
Carbon chain length Cn

fig 01

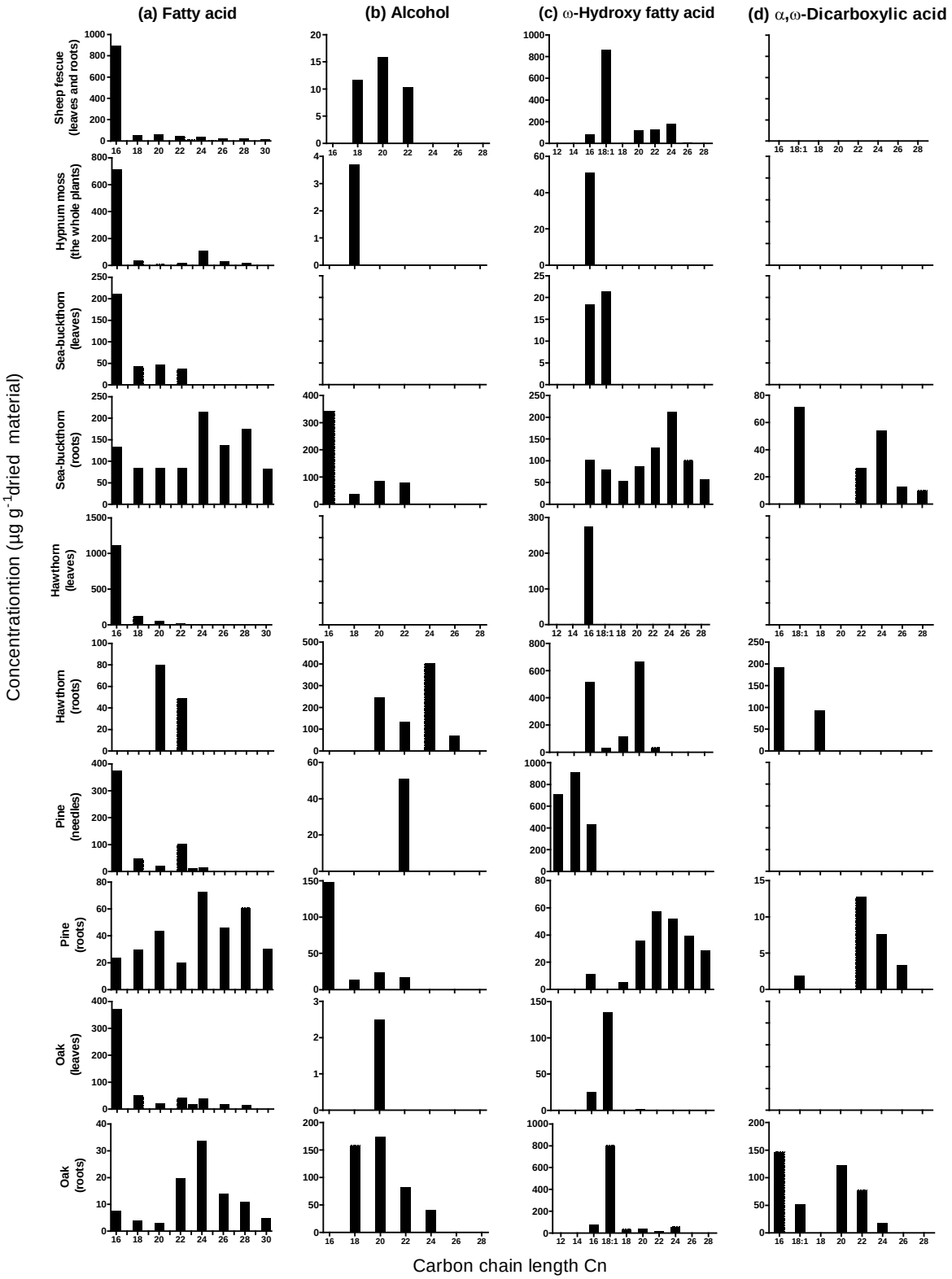
(a) Fatty acid
(b) Alcohol
(c) ω-Hydroxy fatty acid
(d) α,ω-Dicarboxylic acid
Sheep fescue (leaves and roots)
Hypnum moss (the whole plants)
Sea-buckthorn (leaves)
Sea-buckthorn (roots)
Hawthorn (leaves)
Hawthorn (roots)
Pine (needles)
Pine (roots)
Oak (leaves)
Oak (roots)
Concentrationtion (μg g-1dried material)
Carbon chain length Cn

fig 02

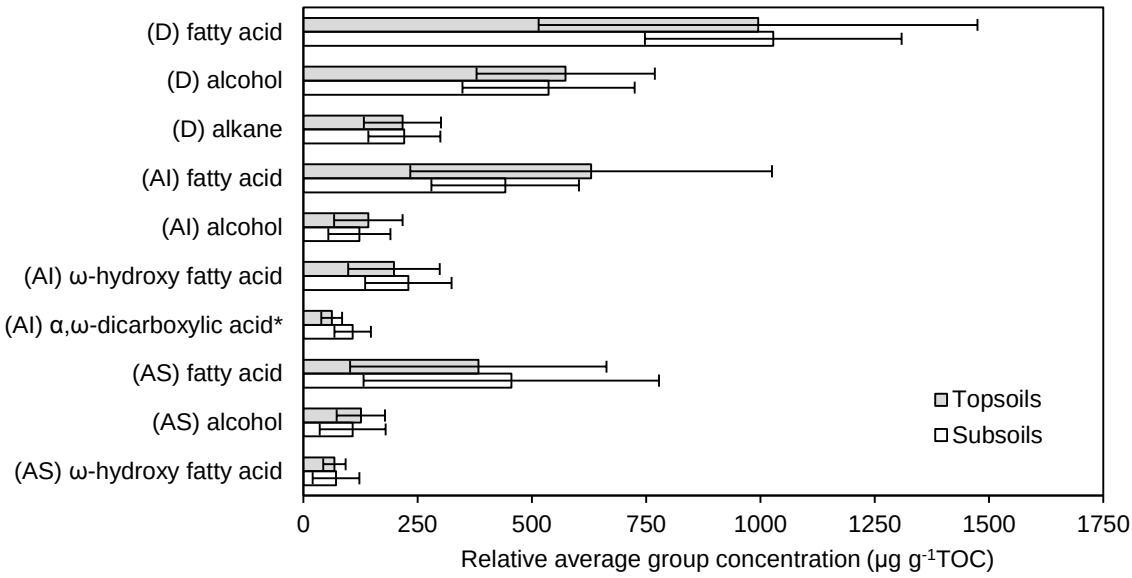
(D) fatty acid
(D) alcohol
(D) alkane
(AI) fatty acid
(AI) alcohol
(AI) ω-hydroxy fatty acid
(AI) α,ω-dicarboxylic acid*
(AS) fatty acid
(AS) alcohol
(AS) ω-hydroxy fatty acid
Topsoils
Subsoils
0
250
500
750
1000
1250
1500
1750
Relative average group concentration (µg g-1TOC)

fig 03