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Effects of development stage on organic matter transformation in Podzols

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ABSTRACT

Podzols are soils in which organic acid and mineral leaching results in the formation of a B horizon, which often contains a high amount of organic carbon. As Podzols cover large areas of the globe ($\pm 12\%$ in European forests), carbon stocks of Podzols are important in the context of climate change mitigation. However, the dynamics of carbon storage in Podzols are not yet fully understood. In this study pyrolysis-GC/MS was used to investigate organic matter (OM) transformation from leaf litter to stabilized OM in the B horizon. It was analysed how OM transformation differed for different stages of Podzol development (leaf litter > incipient > active > buried) and for different vegetation types (deciduous, coniferous, mixed) in a temperate climate. The consequences for carbon storage in Podzols were evaluated. Identified pyrolysis products (105) were assigned to different chemical groups (lignin phenols, aliphatics, etc.) and relative abundances were calculated. The relative abundance of (lignin) phenols decreased from 42 to 58% in leaf litter and fermentation material to 34–49% in A and B horizons of incipient Podzols, to 14–47% in active Podzols, and to 10–18% in buried Podzols. At the same time, the relative abundance of aliphatics increased from 10 to 14% in leaf litter and fermentation material to 19–27% in the A and B horizons of incipient Podzols, to 13–56% in active Podzols, to 27–63% in buried Podzols. Vegetation type did not cause large changes in the OM composition. Incipient Podzols had a soil OM composition similar to the illuvial dissolved OM (DOM) input, as the buildup of stabilized OM has just started. Concluding, the soil OM composition changes for different Podzol development stages (incipient > active > buried), and stabilization of aliphatics increases when the relative input of illuvial DOM, and thus of lignin phenols, decreases.

1. Introduction

Podzols are extensively studied soils characterized by an illuvial horizon enriched in organic matter (OM) and aluminium or iron (or both) that have eluted from overlying horizons (Lundström et al., 2000; Sauer et al., 2007). Current interest in Podzols mainly focusses on their carbon storage capacity (Lopes-Mazzetto et al., 2018; Olsson et al., 2009), as Podzol carbon stocks are important in the context of climate change mitigation. This is especially true for the boreal areas that are excessively impacted by climate change (Soja et al., 2007). Podzols are important for carbon storage, because they are among the soils with the highest carbon storage (136 t C ha⁻¹ in 0–30 cm) (Batjes, 2014), cover a large area ($\pm 12\%$ in European forests) (De Vos et al., 2015), and because carbon in Podzols may be more stabilized against microbial

decay. Microbial degradation of OM might be slowed down in Podzols due to a low pH and, only in highly developed Podzols, stagnating water on top of the impermeable B horizon.

The complex, interacting and sometimes ambivalent soil processes that result in the storage of carbon in Podzols are not fully understood. However, it is known that the formation of metal-organic complexes or precipitates plays an important role in the formation of the carbon rich and less permeable B horizons that are characteristic for Podzols (Jansen et al., 2005). The formation of these metal-organic complexes depends on environmental factors such as pH and metal/carbon (M/C) ratio (Jansen et al., 2002), on the availability of aluminium and/or iron cations, and on the OM composition (Scheel et al., 2007).

Previous works have studied the transition of OM from leaf litter towards the B horizon in Podzols, often using pyrolysis-gas

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chromatography/mass spectrometry (pyr-GC/MS). It was found that in incipient Podzols OM in the B horizon was predominantly derived from roots with no chemical resemblance to dissolved organic matter (DOM), whereas humus bands (fibres) under the Bh horizon had a chemical DOC signature in well-developed drained Podzols (Nierop, 1998; Nierop and Buurman, 1999, 1998). A more recent study (Lopes-Mazzetto et al., 2018) also reported major differences in molecular composition of the OM in Podzol profiles related to the contribution of DOM (phenol, acetic acid, benzofurans, pyridine, benzene and naphthalene) or roots (straight chain aliphatics and methoxyphenols from the biomacromolecules suberin and lignin). Rothstein et al. (2018) found that the organic horizons were the sources of the majority of DOM entering Podzol B horizons, with little contribution from desorbed SOM. Another study reported that in Podzol Bh horizons aromatic structures and also presumably labile structures like polysaccharides can be stabilized by organo-mineral associations (Schmidt et al., 2000). Lopes-Mazzetto et al. (2018) found that DOC derived B horizons were relatively enriched in aromatics. Long-chain lipids, sterols, carbohydrates, lignins and alkyl aromatics were found to accumulate in Podzol B horizons (Wilcken et al., 1997). These specific findings for Podzol B horizons are in line with the preferential precipitation of aromatic components with a high content of carboxylic groups reported for O horizon material at different pH levels and aluminium-to-carbon (Al/C) ratios (Scheel et al., 2008). However, Gonzalez-Perez et al. (2012) found that Podzol B horizons are variable in composition, and that local influences and SOM composition play an important role in podzolization processes, at least in warm climates.

In spite of the previous work done on the molecular characterization of OM in Podzols, the molecular transformation of OM during its passage from leaf litter to stabilized OM in the B horizon remains understudied. In particular, potential differences between vegetation types (coniferous, deciduous, mixed) and different stages of Podzol development (incipient, active, buried) have not yet (or only sparsely) been considered. Different stages of Podzol development differ in terms of the relative influence of surface organic horizons on stabilized OM in the B horizons. In incipient Podzols, the build-up of OM in the B horizon has just started, and the input of DOC from the surface is high. In active Podzols, the development of the B horizon has progressed further, but there is still an ongoing input of illuvial DOM. The buried Podzols are added as an extreme end stage of Podzol development, with no active input anymore from illuvial DOM and with stabilized OM in the B horizon that has persisted over time. These three different Podzol categories were selected to enable a comparison of the transformation from illuvial DOM to stabilized OM in the B horizon for different phases of podzolization (incipient, active and buried). The differences in OM composition between the different horizons of the different Podzol categories are used to analyse which part of the illuvial DOM is being stabilized in the B horizon and how this changes over time.

Information on preferential precipitation and/or stabilization of SOM is relevant for the debates on podzolization theory (Jansen, 2003) and SOM stabilization (Schmidt et al., 2011). Although different podzolization theories exist, the general opinion is that Podzols are formed by complexation of Al and Fe by illuvial DOM in the top (O, A, E) horizons and by immobilization of these complexes in the lower (B) horizons (Lundström et al., 2000). Molecular level information on the transition of OM from leaf litter to the B horizon can provide a better understanding of the changes in OM composition that occur during passage through the soil profile. This allows analysis of the OM characteristics that are important in Al-OM precipitation, which is an important stabilization mechanism for organic carbon in Podzols (Kögel-Knabner et al., 2008). The changes in OM composition along the soil profile are also relevant to investigate the paradigm that SOM stabilization is an ecosystem property (Schmidt et al., 2011). Certain groups of compounds may be stabilized preferentially in the B horizon, independent from the illuvial DOM input.

The aim of this study was to investigate how the molecular SOM

composition changes during its passage from leaf litter to the B horizon in temperate region Podzols, and to evaluate the potential consequences of these changes in OM composition for the stabilization of carbon in Podzols. Pyrolysis-GC/MS was used to answer the following questions: (i) How does the SOM composition change along the soil profile (from leaf litter to stabilization in the B horizon) in different phases of podzolization (incipient, active, buried)? (ii) What is the effect of a different vegetation input (deciduous, coniferous, mixed) on the transformation of OM from leaf litter to B horizon?, (iii) What is the molecular composition of the water extractable organic matter (WEOM) fraction, and how does it compare to the OM composition of the original leaf litter and fermentation layer material?, and (iv) How do potential differences in OM transformation from leaf litter to the B horizon between Podzols in a different development stage or with a different vegetation input affect the stabilization of carbon in temperate region Podzols?

2. Materials and methods

2.1. Soil profiles and sampling

Eight soil profiles were selected in the provinces of Noord-Brabant and Limburg in The Netherlands (Table 1, Suppl. Mat. Tables S1/S2/S3). All profiles were classified as Podzols or, in the case of the incipient Podzols, had clear signs of podzolization. Three profiles (Herperduin, Bedafse Bergen and Boshoverheide) were palaeo-Podzols developed in cover sand deposited in the ice ages and buried beneath drift-sands (1200 CE and/or 1800 CE) (Table 1). Current vegetation is a planted pine forest at Herperduin and Boshoverheide, while vegetation is absent at the Bedafse Bergen site. Three other profiles were not covered by drift-sand and are referred to as active Podzols (Maashorst, Weerterbergen and Schaykse Heide) (Table 1). Vegetation input at the active Podzols was deciduous, coniferous or mixed. A mixed oak (*Quercus robur*), birch (*Betula verrucosa*) forest is found at Maashorst, a pine (*Pinus nigra*) plantation at Weerterbergen, and a mixed oak (*Quercus robur* and *Quercus rubra*), birch (*Betula verrucosa*), pine (*Pinus nigra*) forest at Schaykse Heide. Two soil profiles were sampled that are not official Podzols yet (following FAO guidelines), but show signs of incipient podzolization (Rakt and Nabbegat) (Table 1). The climate at the Podzol sites is temperate oceanic (Cfb according to the Köppen classification), with a mean annual temperature of 9–10 °C, and a mean annual precipitation of 773–795 mm (KNMI, 2019). Rainfall is well distributed throughout the year. All sampling sites are on Pleistocene sands deposited during the last glacial. Mineral soil samples were taken with Kopecky rings (100 cm³; ø 53 × 50 mm) from all pedogenic horizons (A, B, E and C) for the eight profiles. Leaf litter was collected at the active and incipient Podzol sites.

2.2. Soil analyses

Mineral soil samples were freeze dried and sieved (< 2mm). Soil moisture content was determined by weighing before and after freeze drying. Bulk density was determined using Kopecky density rings. Subsamples of milled soil material were dried for one night at 105 °C before measuring total nitrogen and carbon with dry combustion on a VarioEL elemental analyser (Elementar). Both pH (H₂O) and electrical conductivity (EC) were determined from a filtered (< 0.45 µm) 1:2.5 wt-to-volume soil/water solution. Leaf litter and fermentation samples were dried at 40 °C, shredded and milled. Total nitrogen and carbon were determined for these organic samples similar as described for the mineral samples.

2.3. Water extractable organic matter (WEOM)

Field moist leaf litter (L) and fermentation (Of) material collected at Herperduin (coniferous; same species as Weerterbergen), Rakt

Table 1
Chemical properties of the selected mineral samples of the 8 profiles.

Horizon	Thickness /cm	BD /g*cm ⁻³	Moisture /%	pH H ₂ O	EC /μS*cm ⁻¹	C /g*kg ⁻¹	N /g*kg ⁻¹
Profile 1. Maashorst [MH], (Carbic) Podzol, Deciduous							
AEp	12	1.23	4.71	4.14	58.4	29.6	1.3
Bh1	23	1.00	5.90	3.85	33.8	16.6	0.6
Bh2	6	1.23	7.54	3.99	26.7	14.3	0.6
Bs	19	1.17	6.14	4.04	22.5	5.6	0.2
Profile 2. Weerterbergen [WB], Podzol, Coniferous							
2AEp	20	1.16	6.81	3.22	99.2	33.6	1.0
2Bh(s)	6	0.99	13.23	3.58	84.7	78.1	2.2
2B/C	16	1.21	4.85	4.21	29.6	12.0	0.4
Profile 3. Schaykse Heide [SH], Podzol, Mixed							
AEp	22	1.16	17.14	2.97	108.7	42.8	2.1
Bhs	10	1.27	17.81	3.26	45.9	23.2	1.0
Profile 4. Herperduin [HD], Buried (Cambic) Podzol							
3Ah	2	1.53	3.20	3.94	16.1	11.3	0.2
3Bh	13	0.97	11.61	4.07	24.3	48.3	1.6
3Bs	7	1.17	4.41	3.93	25.4	6.4	0.2
Profile 5. Bedafse Bergen [BB], Buried (Carbic) Podzol							
2Ah	5	0.82	27.31	3.69	35.1	73.4	2.3
2AE	5	1.24	15.73	3.53	35.7	31.4	1.3
2Bh	3	1.09	26.30	3.56	40.4	48.4	1.5
2Bs	9	1.12	18.71	3.96	28.5	21.0	0.7
Profile 6. Boshoverheide [BH], Buried Podzol							
3Ah	2	1.26	7.66	3.35	43.9	26.9	0.8
3Bh	2	1.14	9.71	3.40	70.8	33.2	1.0
3Bs	5	nd	nd	4.10	80.9	nd	nd
Profile 7. Rakt [RA], Cambic Arenosol							
A Eh	4	nd	nd	3.08	167.0	nd	nd
Bw	8	1.40	3.63	3.75	76.1	4.2	0.2
Profile 8. Nabbegat [NG], Cambic Arenosol							
AE	5	1.03	12.66	3.30	104.1	48.7	2.5
Bw	12	1.36	4.86	3.01	69.7	5.5	0.3

BD = Bulk Density, EC = Electrical Conductivity, nd = not determined.

(deciduous; same species as Maashorst) and Schaykse Heide (mixed deciduous/coniferous) was used to study the water extractable organic matter (WEOM) input at the Podzol sites. An amount of 100 mL distilled water was added to 10 g of oven dried (40 °C) leaf litter or fermentation material (plant milled < 1 mm; sample-solution weight ratio 1:10). Solutions were decanted after 24 hr shaking and 30 min centrifuging (2200 g). The residue was shaken for 2 hr with distilled water before centrifuging (2200 g). The combined solutions were filtered over 0.45 μm (mixed cellulose ester membrane filters, Whatman) and freeze dried.

2.4. Mineral soil samples

In order to obtain reliable chromatograms and mass spectra upon pyrolysis (See 2.5) the organic carbon content of the mineral soil samples (A and B horizons) was increased by removing the sand following the procedure described earlier by Nierop and Buurman (1998). For each sample 5 g of freeze-dried soil material was shaken with 25 mL NaOH (0.05 M) for 2 hr under nitrogen and then allowed to stand for 1 min. Sand sank to the bottom, while the solution with dissolved and particulate OM remained in suspension at the top. The supernatant was collected in a plastic bottle. These steps were repeated until the solution was colourless. The combined supernatants were then acidified to pH 2–3 by adding HCl (1 M). Also 1 mL concentrated HF was added to dissolve silicates and increase the organic carbon content. The acid mixtures were shaken for 36 hr. Excess salts were removed by dialysis of the acid mixtures against distilled water using Visking dialysis membranes (pore diameter: 12 000–14 000; Medicell International, London). After dialysis solutions were freeze dried. Nierop and Buurman (1998) reported that with above steps less than 5% of the originally present OM was lost during dialysis and that the residues (sand) contained < 0.005% organic carbon (Nierop and Buurman, 1998). In this study, the average carbon losses (data not shown) due to

the combined pre-treatment steps were comparable to the losses as reported by Nierop and Buurman (1998).

2.5. Pyrolysis-GC/MS

Samples were analysed in duplicate using a multi-shot furnace pyrolyser (EGA/Py-3030D; Frontier Lab, Japan), coupled to a Thermo Scientific Trace 1300 Gas Chromatograph (Milan, Italia) with a Rxi-1 ms fused silica column (Restek: 30 m; 0.25 mm i.d.) coated with dimethyl poly-siloxane (film thickness: 0.50 μm). Samples were introduced to the pyrolyser by an AS-1020E Auto-shot Sampler (Frontier Lab, Japan). The amount of pyrolysed material was approximately 200 μg for the majority of the samples (including all mineral soil samples), and 100–200 μg for some of the other samples to prevent overloading of the chromatographic peaks. Pyrolysis temperature was set at 600 °C (0.8 min) and helium was used as a carrier gas (constant flow: 1 mL/min). The injection temperature of the gas chromatograph (GC) (operated in 100:1 split mode) was set at 250 °C and the pyrolysis interface had a temperature of 300 °C. Initial temperature of the GC oven was set at 40 °C (hold time: 1 min, heating rate: 7.0 °C/min) and final temperature was 320 °C (hold time: 10 min). The GC was coupled to a Thermo Scientific ISQ 7000 Single Quadrupole Mass Spectrometer (Milan, Italia) (*m/z*: 47–500; ionization energy: 70 eV). Pyrolysis products were identified using the NIST MS search 2.3 library.

Pyrolysis-GC/MS was used as it is an efficient tool to reveal molecular transformations in OM and is often applied to investigate chemical transformation of soil organic matter (SOM) (Gonzalez-Perez et al., 2012; Lopes-Mazzetto et al., 2018; Rothstein et al., 2018). In pyrolysis, chemical bonds are cleaved by heating, releasing a wealth of molecules. Analysis of these molecules allows reconstruction of the chemical structure of the starting material (Derenne and Quéneá, 2015). Advantages of pyrolysis are (i) that it is less selective than most other chemical analytical techniques, resulting in a larger view of the

chemical structure of SOM, and (ii) that it is a popular technique, which allows comparison with earlier studies (Derenne and Quénéa, 2015). Drawbacks of pyrolysis are (i) that only pyrolysis products that are GC-amenable are detected, (ii) that quantification is difficult, (iii) that artefacts can be formed, and (iv) that N-containing compounds are poorly detected (Derenne and Quénéa, 2015). Pre-treatment with HF (See 2.4) is often used for organic-poor samples as a demineralization step, to prevent extensive retention of pyrolysis effluents by the mineral matrix (Derenne and Quénéa, 2015).

2.6. Data analysis

The pyrolysis-GC/MS data was analysed using Chromeleon Consol and Chromeleon Chromatography Studio software (Thermo Scientific, USA; version 7.2.9). Data analysis largely followed an earlier described procedure (Schellekens et al., 2017). Dominant products were identified in the different sample types (WEOM, leaf litter/fermentation material, and mineral soil material), resulting in a list of 105 compounds (Suppl. Mat. Table S4). Identification was based on the selection of a quantifying ion (Suppl. Mat. Table S4) and two or more confirming ions. Peak integration was checked manually. For each sample, the sum of all peak areas of the quantifying ions, was set at 100% and relative amounts were calculated with respect to this sum. 5 α -Androstane was used as internal standard (IS) and quality control check of the pyrograms, but was not used for quantitative purposes. 5 α -Androstane was ignored in the summation of the peaks. In addition, another compound, most likely D-Allose, was ignored in the summation of the quantified peaks because of the skewed broad peaks, which would have resulted in an over-interpretation of the relative percentage of polysaccharides. All samples were measured in duplicate, and pyrolysis products were only taken into account when identified in both duplicate measurements. This resulted in the removal of 16 products, all below the detection limit. Mean values were calculated for the peak areas of the duplicate measurements. All pyrolysis products were divided over eight chemical groups, largely similar to the groups used by Schellekens et al. (2017). These groups were: N = nitrogen containing compounds, Ps = polysaccharides, Al = aliphatics, B = benzenes, Ph = phenols, Lg = lignin phenols, Bf = benzofurans, and PAH = polyaromatic hydrocarbons. A principal component analysis (PCA) was performed in R to find correlations between the different chemical groups and to analyse clustering for different grouping variables and data subsets (PCA plots). The grouping variables were: sample type (total L/Of, WEOM L/Of, incipient, active, buried), vegetation type (deciduous, coniferous, mixed), Podzol site (SH/WB/MH, BB/HD/BH, NG/RA: See Table 1), and soil horizon (L/Of, A, B). The different OM samples were the objects. The PCA was based on a correlation matrix and the data was zero centred. The PCA was used to explore the shifts in the relative abundances of the different chemical groups for the analysed soil horizons of the different Podzol groups (incipient, active, buried) and the different vegetation types. Pyrograms of the analysed samples can be found in the supplementary material (Figures S1, S2, S3).

3. Results

3.1. Leaf litter and fermentation layer material

Differences in the relative abundances of the different chemical groups were small between total leaf litter (L) and material of the fermentation horizon (Of) and between the different vegetation types (Table 2). Phenols (30–37%) and lignin phenols (13–22%) were the groups with the highest relative abundance for all L/Of samples. Mixed Of had a lower relative abundance of lignin phenols and a higher relative abundance of benzenes than the other L/Of samples. Principal component analysis (PCA) showed only minor shifts in the chemical group distribution from the L to the Of horizon (Suppl. Mat. Figure S4, top graphs). The largest L/Of shift was found for mixed vegetation

along the PC1 axis (explaining 65.7% of the variation), reflecting a decrease in phenols and lignin phenols and an increase in benzenes.

3.2. Water extractable organic matter (WEOM)

Some differences in the relative abundances of the different chemical groups were found between leaf litter (L) and fermentation layer (Of) material for the WEOM fraction (Table 3). The largest differences were: (i) a higher relative abundance of polysaccharides for Of (27–46 vs. 9–12%), (ii) a higher relative abundance of benzenes for L (15–27 vs. 10–13%), and (iii) a higher combined relative abundance of phenols and lignin phenols for L (39–47 vs. 26–34%). PCA revealed clear shifts in the OM composition from the L to the Of horizon for all vegetation types, mainly reflecting an increase in the relative abundance of polysaccharides (Fig. 1, Suppl. Mat. Figure S4: bottom graphs). There were only minor differences between the different vegetation types (Table 3).

3.3. Comparison of total and WEOM leaf litter and fermentation layer material

The largest differences between WEOM and total L/Of were (Tables 2 and 3): (i) a lower relative abundance of phenols and lignin phenols for WEOM (26–47 vs. 42–58%), (ii) a higher relative abundance of N containing compounds for WEOM (10–24 vs. 4–11%), (iii) a higher relative abundance of benzenes (10–27 vs. 7–16%) for WEOM, especially for L samples, and (iv) a higher relative abundance of polysaccharides for WEOM Of samples (27–46 vs. 10–13%). WEOM and total L/Of formed separate clusters in a PCA plot with all samples sorted on sample type and soil horizon (Fig. 1). However, the distinction was much clearer for the WEOM Of samples, whereas the WEOM L samples were close to the cluster of total L and Of samples (Fig. 1). WEOM and total L/Of samples were only separated along the PC2 axis (explaining 22.8% of the variation), which mainly reflected a higher relative abundance of polysaccharides for the WEOM samples (especially the WEOM Of samples).

3.4. Incipient Podzols: From leaf litter to B horizon

The chemical group distribution was similar for the different soil horizons and for the two studied incipient Podzols (RA, NG) (Table 4). The most abundant chemical groups were phenols (29–38%) and aliphatics (19–27%). The changes along the soil profiles were similar for the two incipient Podzols (RA, NG) as revealed by PCA (Fig. 2). The relative abundance of polysaccharides increased, whereas the relative abundance of phenols and lignin phenols decreased from leaf litter (L) to fermentation layer (Of) material (WEOM fractions) (Fig. 2: arrow 1). Then, from the Of layer to the A horizon, the relative abundance of polysaccharides decreased and the relative abundance of aliphatics and phenols increased (also of lignin phenols, but less strong) (Fig. 2: arrow 2). Changes in the relative abundances of the chemical groups were very small from the A to the B horizon in both incipient Podzols (Fig. 2: arrow 3).

3.5. Active Podzols: From leaf litter to B horizon

We found some differences in the relative abundance of the chemical groups between the soil horizons of the active Podzols (Table 4). Most importantly a higher relative abundance of aliphatics was found for the A horizons than for the B horizons (35–57 vs. 13–35%), except for the Bs horizon of the Maashorst (MH) profile. The changes along the soil profiles were similar for the three active Podzols (MH, WB, SH) which each had a different vegetation input (Fig. 3). Analogous to the incipient Podzols, PCA revealed an increase in polysaccharides from leaf litter (L) to fermentation layer (Of) material (WEOM fractions) (Fig. 3: arrow 1). Again, similar to the trend observed for the incipient Podzols, from the Of layer to the A horizon of the active Podzols the

Table 2
Relative abundance of chemical groups for the litter and fermentation material.

Total L/Of	N (%)	Ps (%)	Al (%)	B (%)	Ph (%)	Lg (%)	Bf (%)	PAH (%)
L (dec)	9.1	9.1	12.5	7.3	33.5	21.8	6.6	0.2
Of (dec)	10.9	9.6	11.3	7.5	34.2	21.8	4.5	0.2
L (con)	3.8	13.5	12.4	10.6	31.5	19.2	8.6	0.4
Of (con)	8.0	13.0	9.6	7.7	35.9	19.9	5.8	0.1
L (mix)	4.2	11.5	10.5	7.9	36.8	21.3	7.6	0.3
Of (mix)	8.6	11.4	13.5	15.6	29.5	12.8	8.4	0.2

L = Leaf litter, Of = Fermentation material. Vegetation sources: dec = deciduous, con = coniferous, mix = mix of deciduous and coniferous. Chemical groups: PAH = polyaromatic hydrocarbons, N = nitrogen containing compounds, Bf = benzofurans, B = Benzenes, Al = aliphatics, Ps = carbohydrates (polysaccharides), Lg = lignin phenols, and Ph = phenols (after Schellekens et al. 2017).

Table 3
Relative abundance of chemical groups for the water extractable organic matter (WEOM).

WEOM	N (%)	Ps (%)	Al (%)	B (%)	Ph (%)	Lg (%)	Bf (%)	PAH (%)
L (dec)	17.8	11.9	7.4	14.6	32.4	14.4	1.3	0.2
Of (dec)	23.5	27.4	5.4	13.2	23.2	6.5	0.8	0.1
L (con)	9.8	8.6	10.3	26.8	26.3	12.6	4.6	1.1
Of (con)	11.3	38.7	4.7	10.5	25.9	8.0	0.8	0.2
L (mix)	11.1	10.8	7.6	23.3	33.6	10.0	2.8	0.7
Of (mix)	12.1	45.8	4.9	10.2	21.7	4.5	0.7	0.1

L = Leaf litter, Of = Fermentation material. Vegetation sources: dec = deciduous, con = coniferous, mix = mix of deciduous and coniferous. Chemical groups: PAH = polyaromatic hydrocarbons, N = nitrogen containing compounds, Bf = benzofurans, B = Benzenes, Al = aliphatics, Ps = carbohydrates (polysaccharides), Lg = lignin phenols, and Ph = phenols (after Schellekens et al. 2017).

relative abundance of aliphatics increased, whereas the relative abundance of polysaccharides decreased (Fig. 3: arrow 2). Different from the incipient Podzols, also changes were observed from the A to the B horizons of the active Podzols, with a small increase in the relative abundance of phenols, lignin phenols and polysaccharides and a decrease in the relative abundance of aliphatics (Fig. 3: arrow 3).

3.6. Buried Podzols: From A to B horizon

The relative abundances of the chemical groups were found to be very similar for the three buried (palaeo) Podzols and for most soil horizons within these soils (Table 4). Only in the Herperduin (HD)

profile some differences were found between the soil horizons: (i) a higher relative abundance of aliphatics (63 vs. 40–44%) for the Ah horizon, and (ii) a lower relative abundance of benzenes (11 vs. 16–22%) and polysaccharides (7 vs. 17–19%) for the Ah horizon. Changes from the A to the B horizon were similar for the three buried Podzols (HD, BB, BH) (Fig. 4). Only the transition from the A to the B horizon is shown, because the buried Podzols were not developed with the current vegetation input. Buried (palaeo) Podzols were included in this study, because of the focus on OM stabilization. From the A to the B horizon there was a decrease in the relative abundance of aliphatics and an increase in the relative abundance of benzenes (HD, BB) and/or polysaccharides (HD, BH) (Fig. 4).

3.7. Comparison of Podzol development stages

The Podzol samples clustered for the different development stages (Fig. 1). The PCA plot showed a changing relative contribution of the different chemical groups from incipient Podzols, to active Podzols, to buried Podzols. Analysis of the loadings showed that this change reflected a decrease in phenols and lignin phenols, and an increase in aliphatics and polysaccharides with increasing Podzol development (incipient > active > buried) (Fig. 1). The following differences were found in the relative abundances of the chemical groups for the different Podzol development stages (Table 4): (i) the relative abundances of the chemical groups of the incipient Podzols were (much) more similar to the leaf litter and fermentation material than the active and buried Podzols, (ii) the relative abundance of lignin phenols and phenols decreased, whereas the relative abundance of aliphatics, benzenes and polysaccharides increased from incipient to active to buried Podzols, and (iii) the relative abundances of the chemical groups were

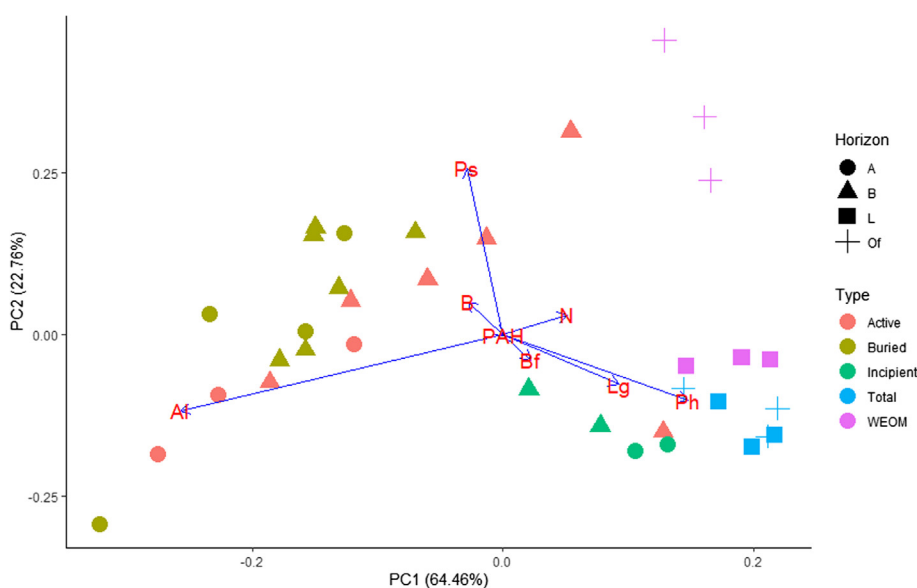


Fig. 1. PCA plot with loadings including all samples sorted on sample type (total L/Of, WEOM L/Of, active Podzols, buried Podzols, incipient Podzols) and soil horizon (A, B, L and Of). Chemical groups: PAH = polyaromatic hydrocarbons, N = nitrogen containing compounds, Bf = benzofurans, B = Benzenes, Al = aliphatics, Ps = polysaccharides, Lg = lignin phenols, and Ph = phenols (after Schellekens et al. 2017).

Table 4
Relative abundance of chemical groups for all soil samples.

Podzol	Site	Horizon	N (%)	Ps (%)	Al (%)	B (%)	Ph (%)	Lg (%)	Bf (%)	PAH (%)
Active	MH	AEp	3.1	18.7	50.2	10.2	13.3	2.7	1.6	0.2
		Bh1	5.9	24.8	22.1	24.6	19.9	1.7	0.8	0.2
		Bh2	6.4	35.1	12.8	22.1	21.8	1.1	0.5	0.2
		Bs	6.4	14.4	43.9	20.2	13.5	0.8	0.7	0.2
	WB	2 AEp	2.2	13.3	56.5	11.3	11.9	2.8	1.9	0.2
		2 Bh(s)	2.8	23.9	28.9	21.2	20.0	2.7	0.4	0.2
		2B/C	4.9	21.2	34.7	21.8	15.2	0.9	1.1	0.2
	SH	AEp	3.7	15.8	35.1	26.0	16.0	1.8	1.3	0.3
		Bhs	4.6	10.4	19.1	17.1	44.0	3.2	1.4	0.2
	Buried	HD	3 Ah	1.8	7.4	63.1	11.0	11.6	1.8	3.0
3 Bh			5.2	16.9	39.8	22.0	14.3	1.2	0.6	0.1
3 Bs			3.6	19.3	43.6	15.6	15.7	1.1	0.9	0.2
3 Bf			2.8	21.2	40.0	16.9	14.9	1.6	2.4	0.3
BB		2 AE	2.5	29.6	33.4	18.5	13.3	1.3	1.2	0.2
		2 Bh(s)	3.4	27.4	27.6	22.7	16.8	1.6	0.4	0.1
		2 Bs	3.4	21.2	34.3	26.1	13.7	0.7	0.3	0.1
		3 Ah	2.5	25.2	47.2	12.5	8.9	1.4	2.0	0.2
BH		3 Bh	2.7	31.2	35.9	16.4	12.1	1.2	0.3	0.1
		3 Bs	3.4	31.4	37.0	13.7	12.8	1.3	0.4	0.1
		3 Bf	6.4	10.3	19.3	10.7	37.7	11.4	4.1	0.1
		3 Bw	8.9	14.2	27.0	14.2	29.4	4.8	1.3	0.2
Incipient	RA	AEh	6.4	10.3	19.3	10.7	37.7	11.4	4.1	0.1
		Bw	8.9	14.2	27.0	14.2	29.4	4.8	1.3	0.2
	NG	AE	6.3	10.1	21.9	9.9	37.8	7.6	6.3	0.2
		Bw	6.8	12.1	23.7	11.9	36.3	6.1	3.0	0.2

Sites: MH = Maashorst, WB = Weerterbergen, SH = Schaykse Heide, HD = Herperduin, BB = Bedafse Bergen, BH = Boshoverheide, RA = Rakt, and NG = Nabbe gat. Chemical groups: PAH = polyaromatic hydrocarbons, N = nitrogen containing compounds, Bf = benzofurans, B = Benzenes, Al = aliphatics, Ps = carbohydrates (polysaccharides), Lg = lignin phenols, and Ph = phenols (after Schellekens et al. 2017).

similar for the soil horizons within the soil profiles of the incipient and buried Podzols, but differed between the A and the B horizons of the active Podzols (Fig. 5).

4. Discussion

4.1. The effect of Podzol development stage on the OM composition from leaf litter to B horizon

Changes in the OM composition (Fig. 5) from leaf litter to the B horizon in Podzols of different development stages (incipient > active > buried) can provide insight into the podzolization process (Buurman et al., 2013). In the incipient Podzols, in which podzolization has just started, the SOM composition of the investigated soil horizons (A and B) is still very similar to the OM composition of the leaf litter and fermentation layer material (Tables 2–4). In the active Podzols,

where there is ongoing podzolization and an active input of illuvial DOM, the SOM composition of the investigated soil horizons (A and B) has become different from the composition of the illuvial DOM (Fig. 5; Tables 2–4). Possible reasons for the observed changes of the OM composition of the A and B horizons compared to the composition of the illuvial DOM are preferential precipitation and/or stabilization of certain compound groups due to selective degradation by micro-organisms and/or differences in solubility and therefore transportability. Lastly, in the buried Podzols, the input of fresh leaf litter derived DOM to the well-developed Podzols has been cut off due to burial by drift sand. Although, in some of the studied profiles podzolization has started again in these sands, the podzolization process in the buried Podzols has ended due to a negligible input of illuvial DOM. Nevertheless, the similarity of the SOM composition of the mineral A and B horizon to the composition of the original leaf litter derived DOM has decreased even further (Fig. 5; Tables 2–4). This is probably due to

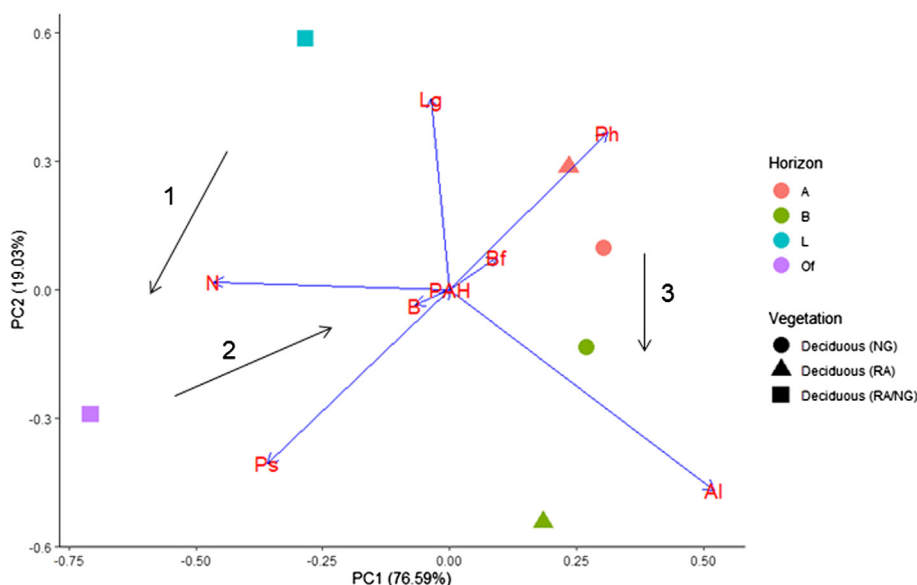


Fig. 2. PCA plot with loadings (blue arrows) for the incipient Podzols: RA = Rakt (deciduous input) and NG = Nabbe gat (also deciduous input) (See Table 1 for detailed site info). The transformation of OM along the soil profiles is highlighted with (black) arrows: (1) from leaf litter (L) to fermentation layer (Of) material, (2) from Of to A horizon, and (3) from A to B horizon. Chemical groups: PAH = polyaromatic hydrocarbons, N = nitrogen containing compounds, Bf = benzofurans, B = Benzenes, Al = aliphatics, Ps = polysaccharides, Lg = lignin phenols, and Ph = phenols (after Schellekens et al. 2017).

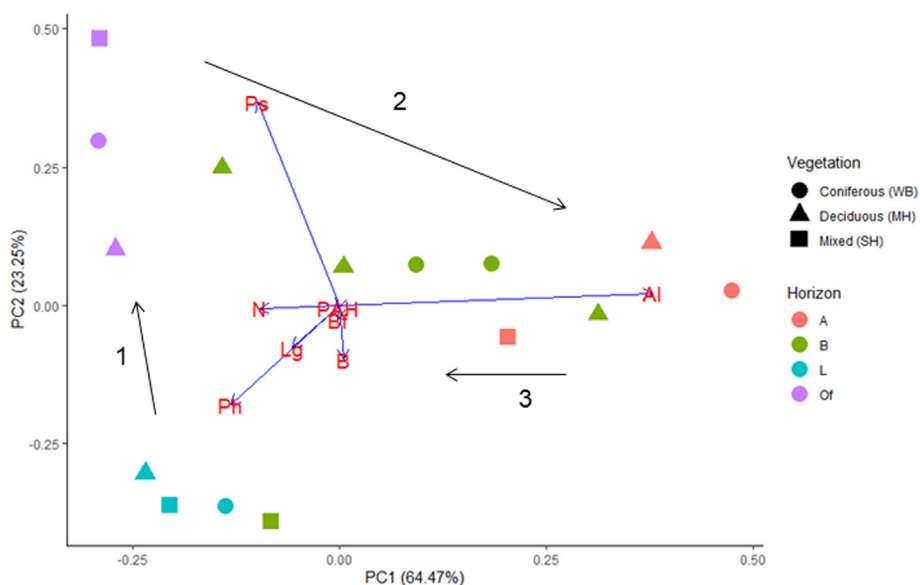


Fig. 3. PCA plot with loadings (blue arrows) for the active Podzols: MH = Maashorst (deciduous input), WB = Weerterbergen (coniferous input), and SH = Schaykse Heide (mixed input) (See Table 1 for detailed site info). The transformation of OM along the soil profiles is highlighted with (black) arrows: (1) from leaf litter (L) to fermentation layer (Of material), (2) from Of to A horizon, and (3) from A to B horizon. Chemical groups: PAH = polyaromatic hydrocarbons, N = nitrogen containing compounds, Bf = benzofurans, B = Benzenes, Al = aliphatics, Ps = polysaccharides, Lg = lignin phenols, and Ph = phenols (after Schellekens et al. 2017).

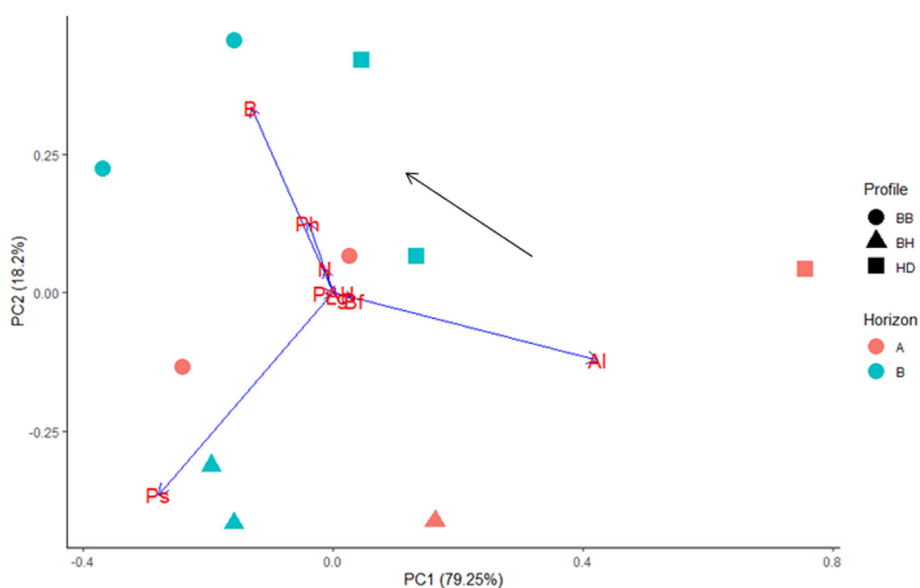


Fig. 4. PCA plot with loadings (blue arrows) for the buried Podzols: HD = Herperduin, BB = Bedafse Bergen, and BH = Boshoverheide (See Table 1 for detailed site info). The transformation of OM from the A to the B horizon is highlighted with a (black) arrow. Chemical groups: PAH = polyaromatic hydrocarbons, N = nitrogen containing compounds, Bf = benzofurans, B = Benzenes, Al = aliphatics, Ps = polysaccharides, Lg = lignin phenols, and Ph = phenols (after Schellekens et al. 2017).

ongoing leaching of OM compound groups most prone to be transported and due to ongoing degradation of OM compound groups that may be preferred by the microbial soil community. Thus, the OM composition is transformed from the original leaf litter derived DOM to the SOM in incipient Podzols, to the SOM in more well-developed active Podzols, and finally to the SOM that is stabilized in well-developed buried Podzols (Fig. 5).

The decrease in the relative abundance of phenols and lignin phenols and increase in the relative abundance of aliphatics with increasing Podzol development (Table 4) suggest that aliphatics are being stabilized over time, whereas phenols and lignin phenols, which are dominant in the leaf litter and fermentation layer material (Tables 2 and 3), are degraded with increasing Podzol development. An earlier study also reported a strong decrease in the relative abundance of lignin-derived products in the mineral soil horizons compared to the organic layers (Girona-García et al., 2019).

In the incipient Podzols differences in the OM composition between the A and the Bw horizons are still small (Table 4). In the active Podzols, podzolization is an active process and the clearest differences between the A and the B horizons were found; from the A to the B horizon a decrease in aliphatics and an increase in phenols, benzenes

and polysaccharides were observed. A high abundance of aliphatics in the Podzol A horizon has been found before in a warmer climate (Gonzalez-Perez et al., 2012). In the buried Podzols, where there is no direct link anymore with the leaf litter input, the differences between the A and the B horizons have largely disappeared, and the OM composition of both the A and the B horizons is similar to that of the active Podzol A horizons. The findings show that the molecular OM composition changes with increasing Podzol development, and these changes seem to be related to the amount of illuvial DOM input received from the surface. OM transformation starts in the leaf litter on the surface, which undergoes changes towards the fermentation layer and finally towards a water extractable fraction that enters the soil as illuvial DOM input. In the incipient Podzols the buildup of OM in the B horizon is relatively little compared to more well-developed older soils, therefore the illuvial DOM signal is stronger. This explains why in the incipient Podzols, the OM composition is still similar to the illuvial DOM input with a relatively large abundance of phenols and lignin phenols and a relatively small abundance of aliphatics (Tables 3 and 4). The active Podzols still receive a lot of illuvial DOM, but podzolization has changed the OM composition, with an increase in the relative abundance of aliphatics and a decrease in the relative abundance of phenols

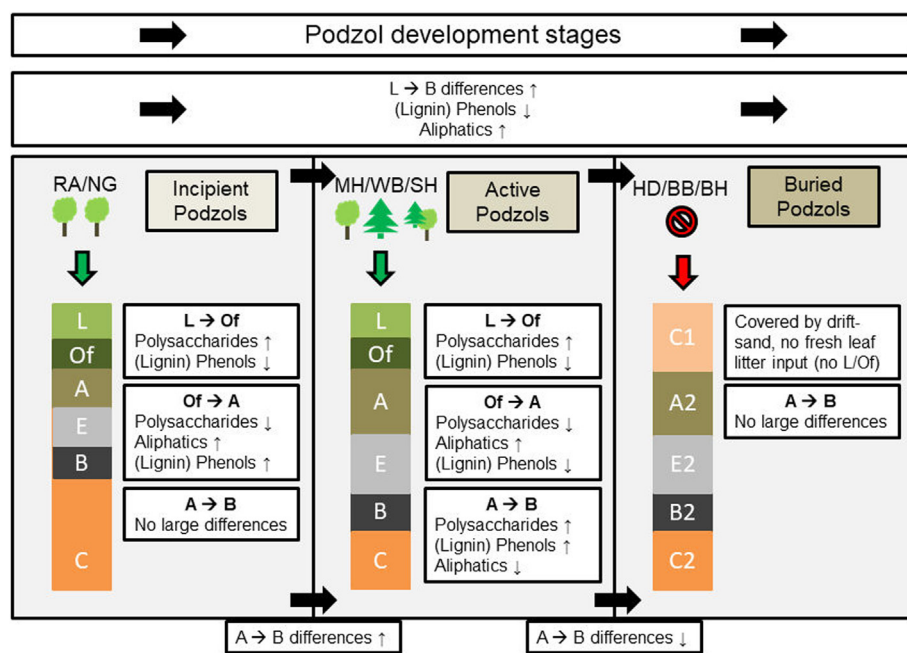


Fig. 5. Visualization of the changes in OM composition from leaf litter to the B horizon for incipient, active and buried Podzols. Changes in OM composition are highlighted between the studied soil horizons and between the different Podzol groups. Vegetation input was deciduous in both incipient Podzols (RA/NG), deciduous (MH), coniferous (WB) or mixed (SH) in the active Podzols, and there was no vegetation input in the buried Podzols (HD/BB/BH). L = leaf litter, Of = fermentation layer, A/E/B/C are the mineral soil horizons. RA = Rakt, NG = Nabbegat, MH = Maashorst, WB = Weerterbergen, SH = Schaykse Heide, HD = Herperduin, BB = Bedafse Bergen, BH = Boshoverheide (See Table 1 for detailed site info).

and lignin phenols (Tables 3 and 4). The transformation of OM seems to start in the topsoil, as the changes in OM composition are more prominent in the A horizons of the active Podzols. Preferential leaching, precipitation and/or degradation of specific compound groups may explain these differences between the A and B horizons in the active Podzols. Lastly, in the buried Podzols, the input of illuvial DOM from the surface has ended or is negligible, but the transformation of OM continues. The changes (increase in aliphatics, decrease in phenols) occur mainly in the B horizons of the buried Podzols, and the OM composition of these horizons becomes more similar to that of the A horizons (Table 4).

4.2. The effect of vegetation input on the OM composition from leaf litter to B horizon

The most important finding regarding the differences in vegetation input, was the absence of large differences in chemical group abundances between deciduous, coniferous and mixed leaf litter and fermentation material (Table 2). This is in line with our earlier findings of a similar chemical compound class distribution for deciduous, coniferous and mixed leaf litter derived DOM using liquid-chromatography coupled to quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) (Brock et al., 2019). A study by Nierop et al. (1999) reported that a direct relation between vegetation input and DOM derived from the humus layer was only found under pine forest (Nierop et al., 1999). Others found no difference between forest types (deciduous and coniferous) in the quantity of carbon delivered to Podzol B horizons (Rothstein et al., 2018). Rothstein et al. (2018) also found a greater similarity of B horizon SOM to DOM in the deciduous forest, which was not found in our study. This difference is probably due to local differences in tree species, climate and microbial processing. Microbial processing of the DOM inputs, which appears to be important in the formation of SOM (Rothstein et al., 2018), may also explain the absence of large vegetation input differences by homogenizing the OM input. Our results indicate that the stage of Podzol development is a more important factor than vegetation type for a direct relation between vegetation input and OM of the mineral soil horizons (Tables 2, 3 and 4). In the active and buried Podzols the SOM presumably includes more older, decomposed material, whereas in the incipient Podzols the high similarity of the SOM composition with the illuvial DOM input suggests

a more direct link with the fresh litter input. This may also imply that differences in the illuvial DOM input from different types of vegetation may only play a role in the beginning phase of podzolization, but not in the later phase in which long term stabilization of carbon takes place. It would be interesting to study this in more detail in future studies.

Phenols and especially lignin phenols have a relatively low water solubility compared to most other chemical groups (e.g. polysaccharides and benzenes): e.g. guaiacol, a lignin phenol, found in both deciduous and coniferous leaf litter, has a solubility of 23.3 g/L (in water, 25 °C), phenol, has a higher solubility of 83.3 g/L (in water, 20 °C), whereas polysaccharides (sugars) have in general a relatively high water solubility. These differences in water solubility probably explain the strong decrease in the relative abundance of phenols and lignin phenols and increase in polysaccharides that was observed when comparing the water extractable organic matter (WEOM) fraction with the total leaf litter and fermentation layer material (Tables 2 and 3).

We observed a difference in the OM composition between leaf litter and fermentation layer material in the WEOM samples, which was not observed for the total leaf litter and fermentation layer samples (Tables 2 and 3). We found a reduced abundance in phenols, lignin phenols and benzenes, and an increased abundance of polysaccharides from the leaf litter to the fermentation layer. This is in line with the lower relative abundance of lignin compounds and higher relative abundance of carbohydrates (which include polysaccharides) for fermentation layer material compared to leaf litter that we observed (not yet published) using LC-QTOF-MS (Brock et al., 2019). The absence of clear differences in the relative chemical group abundances for total L/Of (Table 3) could mean that the changes in solubility causing the L/Of differences, which appear after water extraction, are happening within the chemical groups. Some compounds might be more soluble than others, probably due to microbial processing.

4.3. Carbon stabilization in Podzols

This study showed that the OM composition changes from fresh leaf litter to the fermentation layer, to incipient Podzols, to active Podzols, to buried (palaeo) Podzols (Fig. 1). It was already discussed that the buried Podzols have no or a negligible input of illuvial DOM from fresh litter and that the B horizons of these soils have a substantial carbon stock that has been formed over time due to podzolization processes

(e.g. metal–organic precipitation). Studying the OM composition of the B horizons in buried Podzols and comparing it to the OM composition in much younger soils and in fresh litter input, may show if certain compound groups (e.g. aliphatics) are preferentially stabilized over time.

We found Podzol B horizons in the studied Podzols to be rich in aliphatics, polysaccharides, benzenes and phenols, while lignin phenols were almost absent (Table 4). However, these were general trends and local influences and SOM composition may explain variations in Podzol B composition, as described before for warmer climates (Gonzalez-Perez et al., 2012). Although, Gonzalez-Perez et al. (2012) also reported a relatively low abundance of lignin in three studied B horizons, their lignin abundances are still (much) higher (3–43%) than our values (1–6%). However, the large range in values also makes it likely that local differences (SOM composition, climate etc.) play an important role. Nevertheless, the finding that lignin phenols were almost absent in Podzol B horizons (decreasing rel. abundance: incipient > active > buried), is in line with the previous finding that lignin is not necessarily less degradable (and thus more stabilized in B horizons) (Schmidt et al., 2011). The decrease in lignin phenols may also be caused by the fact that plant litter is the only source for lignin, whereas for the other compound groups microbes are an important source as well. Our finding of significant relative abundances of polysaccharides in the B horizons, supports earlier findings that showed that also presumably labile (and more microbial-derived) structures like polysaccharides can be stabilized by organo-mineral associations in Podzol Bh horizons (Schmidt et al., 2000). Our study shows that local influences (e.g. vegetation input) may play a less important role in podzolization in a more temperate climate compared to earlier findings for warmer climates (Gonzalez-Perez et al., 2012) and that the stage of Podzol development has a larger influence on the OM composition in Podzols and thus on carbon stabilization. For the management of temperate region Podzols and soil conservation practices the findings of this study highlight that it is important to take into account the development stage or age of Podzols as it affects the composition and amount of stabilized carbon, and to beware that selecting a specific vegetation type to stimulate carbon storage may only have a limited and short-term effect in Podzols.

In future studies, it would be interesting to study the effect of a different vegetation input on the OM composition not only in active Podzols, but also in incipient Podzols. Furthermore, the limitations of analytical pyrolysis as mentioned in the methods section, may be partially overcome in future works when applying computational tools (Almendros et al., 2013; De La Rosa et al., 2013), which can potentially show additional characteristics such as aromaticity and the extent of lignin degradation instead of just the relative abundances of chemical compound groups.

5. Conclusion

The OM composition from leaf litter derived DOM to the B horizon changes with ongoing podzolization (incipient > active > buried) in temperate region Podzols. Long term stabilization of OM is dominated by aliphatics, whereas lignin phenols in illuviating DOM turn over more rapidly. The observed shift from lignin phenols to aliphatics reflects the balance between illuvial DOM input and accumulation of stabilized OM. The largest differences in OM composition between the A and the B horizons were found in active Podzols, where podzolization is most active. Differences in OM composition between Podzols with a different vegetation input (deciduous, coniferous, mixed) were small, suggesting a limited effect of vegetation type on the SOM composition. In the incipient Podzols, the SOM composition of both the A and B horizon still has a relatively large similarity with the illuvial DOM input, as the buildup of OM in the B horizons is relatively little compared to the older active and buried Podzols. Concluding, the SOM composition changes for different Podzol development stages (incipient > active >

buried), and stabilization of aliphatics increases when the relative input of illuvial DOM, and thus of lignin phenols, decreases. For the management of temperate region Podzols and soil conservation practices the findings of this study highlight that it is important to take into account the development stage or age of Podzols as it affects the composition and amount of stabilized carbon, and to be aware that selecting a specific vegetation type to stimulate carbon storage may only have a limited and short-term effect in Podzols.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2020.114625>.

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