

# Determinants of soil organic matter chemistry in maritime temperate forest ecosystems

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## Abstract

The influences of ecosystem properties on the chemical complexity of soil organic matter (SOM) remain poorly understood. This study addresses the composition of NaOH-extracted SOM from maritime temperate forest sites in Flanders (Belgium) by pyrolysis-GC/MS. Pyrolysis-products were correlated to site variables including dominant tree species, management of the woody biomass, site history, soil properties, total carbon stocks and indicators for microbial activity. Despite a typical high inter-correlation between these site variables, the influence of the dominant tree species is prominent, as is a strong correlation to available nutrients. In nutrient-poor forests with low litter quality, the decomposition of relatively recalcitrant compounds appears hampered. Former heathland vegetation still had a profound influence on extractable-SOM chemistry of young pine forests.

## Key Words

Soil organic matter composition, temperate forest soils, pyrolysis-GC/MS, environmental factors.

## Introduction

While the influence of climate, vegetation, management and abiotic site factors on total C budgets and turnover is intensively assessed, high-resolution studies that elaborate on the general relations between these ecosystem properties and the chemical composition SOM are much more scarce. Determining factors of SOM chemistry remain poorly understood (von Lützow *et al.* 2006). This knowledge however is vital in understanding SOM stability under different soil conditions and global C sequestration. This work aims to establish a reconnaissance study in relating environmental factors to differences in NaOH-extractable SOM composition within a similar climatic context, i.e. maritime temperate forests in Belgium.

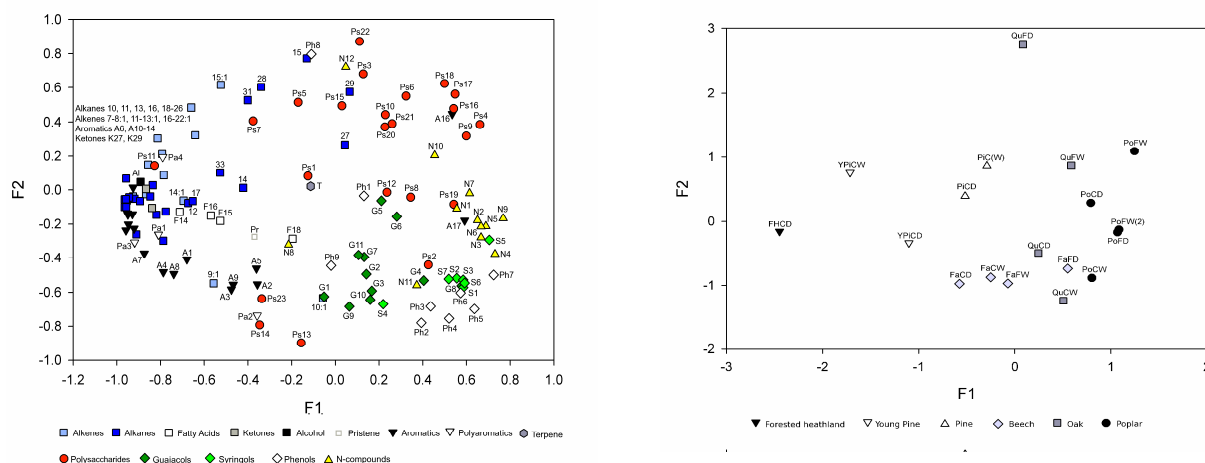
## Methods

Nineteen forest sites were considered dominated by common European tree species, i.e. Scots pine (*Pinus sylvestris* L.), European beech (*Fagus sylvatica* L.), Pedunculate oak (*Quercus robur* L.) and hybrid poplar (*Populus* spp.). Two young pine forests on historical heathland and a recently forested heathland were also included. Samples were taken over the entire depth of the A-horizon and were given a code reflecting the dominant tree species of the sampling site (i.e. Pi, Fa, Qu or Po and FH for Forested Heathland), the soil-texture class (C for sandy loam and coarser or F for silt loam and finer) and the soil-moisture-regime class (depth of the highest ground water level being either deeper than 50 cm (D) or shallower (W)). Site variables included vegetation and standing biomass management, litter layer characteristics, total soil C and basic soil properties (Table 1). The hot water carbon (HWC) fraction and soil CO<sub>2</sub> respiration were evaluated as an indication for microbial contribution to the SOM. SOM was extracted by NaOH (0.1 M), yielding between 41 and 92% of the total C<sub>org</sub>. The extract was acidified, dialyzed and freeze dried (Kaal *et al.* 2008). Freeze-dried samples were pyrolysed using a Curie-point pyrolyser GC-MS. Spectra were semi-quantified according to Buurman *et al.* (2009) and analysed by factor analysis. Spearman  $\rho$  correlation coefficients and ANOVA F-values were calculated between the factor scores and the environmental variables.

## Results

Pyrolysis compounds included a range of alkenes (n:1) and alkanes (n); pristene (Pr); fatty acids (Fn); methylketones (Kn); an alcohol (Al); a terpene (T); aromatic compounds (A) containing benzene and indene related structures, toluene and styrene; four polyaromatic compounds (Pa); (poly)saccharide-derived

pyrolysis products (Ps) including furans, furaldehydes and monomeric sugars; lignin compounds derived from plant lignins of the guaiacol (G) and the syringol (S) types; nine phenol products (Ph) with various substituents; and twelve nitrogen-containing compounds (N, Figure 1). The first two factors explain 37.7% and 17.6% of the observed variation. Factor loadings of the variables (i.e. the pyrolysis compounds) and scores of the cases (i.e. the samples) are shown in Figure 1. F1 is significantly correlated with tree species, litter layer characteristics, soil properties and HWC (Table 1). Pine stands on dry, sandy soils with considerable litter accumulation in the litter layer and mor-type humus are correlated with negative values on F1. These stands have low soil pH, low soil N content and low HWC content. Broadleaved stands with mull-humus types on rich soils with high microbial contribution (HWC) are positively correlated with F1. F2 is negatively correlated with the mass of the litter layer alone.



**Figure 1. Factor analysis: factor loadings of the pyrolysis compounds (left) and factor scores of the samples (right) on the first two ordination axes. F1 opposes aromatics and short and mid-chain aliphatics (relatively recalcitrant) to lignin (especially syringols) and N-compounds. A gradient in dominant tree species can be observed along F1.**

## Discussion

### *Interpretation of pyrolysis-compounds*

Short and mid-chain aliphatic compounds in pyrograms of soils mainly originate from aliphatic biopolyesters, derived from plant lipid precursors or microbial lipids. Aromatic pyrolysis products originate from SOM compounds derived from proteins (toluene), tannins and other (poly)-phenols including black carbon. As for the short and mid-chain aliphatics, aromatics are considered relatively recalcitrant to (further) microbial decay. Polysaccharide-derived pyrolysis-products relate to SOM molecules with both vegetal and microbial precursors. Ps9, Ps11 and Ps15-22 (and particularly the levosugars, Figure 1) are commonly related to biopolymers with cellulose-type precursors, referring to relatively weakly-decomposed, plant-derived SOM. Smaller polysaccharide pyrolysis products are mostly associated with microbial material (Ps1, Ps2, Ps4-6). Syringols and guaiacols are lignin-derived compounds. SOM found under coniferous vegetation typically shows a clear dominance of lignin compounds related to guaiacol, while broadleaved forests have SOM with both guaiacol and syringol compounds. Phenols in pyrolysis can have a variety of origins including lignins, carbohydrates, proteins or polyphenols. N-containing compounds in SOM may originate from vegetal or microbial precursors, or may be formed by chemical interactions. Abundance of N-compounds in SOM in non-fertilized soils is linked to high microbial influence (Vancampenhout *et al.* 2009 and references therein).

### *Interpretation of the factor analysis*

Samples with strongly negative scores on the first factor F1 contain (i) a relative accumulation of aromatics and short and mid-chain aliphatics, which are fairly recalcitrant and indicative of degraded plant material; (ii) a relative absence of lignin (especially syringols) and (iii) a relative absence of N compounds. Strongly positive loadings on this axis on the other hand denote (i) the abundance of N-compounds, most likely linked to high microbial influence, and (ii) abundance of lignins and most of the polysaccharide compounds. Strongly negative loadings on F2 in combination with negative loadings on F1 indicate a relative abundance of possible markers of charring (benzofurans, benzonitrille, polyaromatics), while the lower right quadrant of the F1-F2 space represents a high abundance of lignin fragments, partly in combination with N-compounds.

**Table 1. Spearman  $\rho$  correlation coefficients (r) and ANOVA F-values (F) relating site variables to the results of the factor analysis in Figure 1. Correlations are significant at 0.01(\*\*) or 0.05 (\*) level.**

	Factor 1		Factor 2	
	F	r	F	r
Forest management				
Dominant tree species	16.56**		1.67	
Basal area		-0.08		-0.23
Stem number		-0.34		0.24
Cover herb layer		0.25		0.15
Forest age class	2.50		0.20	
Litter layer				
Humus index <sup>A</sup>		-0.69**		-0.08
Dry mass of litter layer		-0.69**		-0.50*
Soil properties				
Moisture class		0.55*		-0.13
Clay percentage		0.65**		0.02
Silt percentage		0.69**		0.00
Sand percentage		-0.73**		-0.04
pH (H <sub>2</sub> O)		0.59*		0.44
N (%)		0.67**		0.04
N (Mg/ha)		0.55*		-0.02
Soil carbon				
C (%)		0.47		-0.07
C (Mg/ha)		0.36		-0.08
C/N ratio		-0.41		-0.35
Microbial activity				
CO <sub>2</sub> respiration		0.35		0.15
Hot Water Carbon <sup>B</sup>		0.77**		0.24

<sup>A</sup>Ponge and Chevalier (2006), <sup>B</sup>Ghani *et al.* 2003

The top centre of the F1-F2 space in Figure 4.3 represents compounds both indicative for relatively fresh (Ph8, alkanes 28-31 and possibly Ps22 and N12) and microbial (Ps3, alkane 15 and possibly Ps22 and N12) material, suggesting an admixture of both. Factor scores in Figure 1 emphasize a strong effect of dominant tree species on extractable-SOM chemistry (F1). Former heathland stands are still clearly distinguishable. The second factor F2 stresses the deviating composition of sample QuFD compared to samples taken under oak on light textured soils and under beech. This site has a complex site history, which could explain its unusual composition.

#### *Influence of environmental factors*

Despite the high inter-correlation between the environmental factors, the influence of dominant tree species on F1 is striking (Figure 1). Moreover, species are arranged along F1 according to their litter quality (Cornelissen 1996), indicating that input quality is an important determinant of the extractable-SOM composition in maritime temperate forests. An important accumulation of degraded, fairly recalcitrant mid-chain alkenes/alkanes and aromatics is observed in the extractable SOM under pine and former heathland forests. This accumulation coincides with a strong degradation of lignin- and cellulose-derived compounds (Figure 1) and associated to ecosystems with poor litter quality, moder type humus with thick and heavy litter layers, having low soil pH, low soil N content and low HWC content (table 1). This accumulation of recalcitrants (aromatics and short and mid-chain aliphatics) appears a common feature in soils where not all conditions for efficient decay are met (due to substrate limitations, occlusion, acidity, toxic ions, complexation, sorption, low fertility or oxygen deprivation; e.g. Burman and Roscoe 2009; Ferreira *et al.* 2009). Soils under forested heathland and pine moreover have very low relative amounts of N-compounds (Figure 1). Oppositely, no accumulation of recalcitrants is present in the extractable SOM under poplar, which coincides with high abundance of N compounds, polysaccharides and syringols, generally linked to broadleaved forests with high microbial influence.

This is further evidenced by the high positive correlation of F1 to microbial proxies (HWC) and to ecosystems with high litter quality, mull-type humus and thin litter layers (table 1). Remarkably, the soil's nutrient status shows stronger correlation to the decomposition of recalcitrants than oxygen deprivation. No general relation of extractable-SOM chemistry with time under forest was found, yet forested heathland and

the younger pine forests (forested since 1940 or longer) clearly have more negative scores on F1, as compared to PiC(W) and PiCD (permanently forested at least since 1775 and 1850, respectively). This indicates that the former heathland vegetation still has a detectable influence on the extractable-SOM chemistry under pine forests established for 60 years or more. Under poplar, beech and oak however, the period under forest does not appear to have much effect on extractable-SOM chemistry.

## Conclusion

The results of this study indicate that vegetation is a major factor determining the extractable-SOM composition in maritime temperate forests. Aliphatics and aromatics accumulate in the extractable SOM of ecosystems with poor soils and low litter quality. Their decomposition seems hampered in such conditions, whereas all carbon sources seem effectively used if conditions for decomposition are favorable (i.e. eutrophic ecosystems with high litter quality, which show no accumulation of recalcitrants yet high amounts of N-compounds). Correlations between extractable-SOM chemistry, litter layer properties and Hot-Water-Carbon content further support this hypothesis. The long lasting influence of former heathland on the accumulation of recalcitrants in the extractable-SOM composition of pine forests indicates that chemical recalcitrance is relevant in certain ecosystems for several decades.

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