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Characterization and quantification of biomarkers from biomass burning at a recent wildfire site in Northern Alberta, Canada

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Abstract

The composition of organic matter (OM) in pine vegetation and soil samples from a pine forest which was charred by a wildfire was analyzed using solid-state nuclear magnetic resonance (^{13}C NMR) and gas chromatography–mass spectrometry (GC–MS) of solvent extracts to study the effects of thermal alteration on soil organic matter (SOM). The NMR data revealed the presence of unaltered biomolecules (cellulose, proteins) and low contents of aromatic C (15%) in the charred pine wood and cones while the charred soil samples exhibited higher contents of aromatic C (39–56%). The solvent extraction of charred and uncharred plant and soil samples yielded diterpenoids, triterpenoids, steroids, a series of aliphatic lipids, phenols and carbohydrates indicating the predominant input of higher plant OM and minor contributions from microorganisms and/or fauna. The lower yield of solvent extractable aliphatic lipids in the charred samples versus the uncharred samples suggests that these compounds are thermally degraded during a wildfire. Molecular markers for the burning of cellulose (levoglucosan, mannosan, galactosan) were detected in all charred samples. The comparison of charred and uncharred samples allowed the identification of unaltered pine derived biomolecules and their thermal alteration products in the charred samples. Terpenoid and steroid biomolecules were in part altered during incomplete combustion to aromatic, unsaturated and polar derivatives ("pyromolecules") that still retained the characteristic skeleton of their precursors. Since some of the polar degradation products found in the charred soils can be generated either from thermal or microbial degradation, the aromatic and unsaturated hydrocarbon products are preferred as molecular markers for SOM burning. Ratios of biological precursors to aromatic (diterpenoids) or unsaturated products (steroids) indicate that the cyclic lipids in the pine wood and the soil surface horizon were highly altered. In conclusion, the solvent extractable lipids and carbohydrates in charred SOM are valuable, source-specific molecular markers for the burning of plant biomass and for tracing the biogeochemistry of charred residues in soils.

1. Introduction

The burning of soils in wildfires or prescribed field and clear-cut fires releases CO_2 and organic compounds into the atmosphere and affects the composition of the soil organic matter (SOM)

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(Almendros et al., 1988; Simoneit, 1999; Oros et al., 2002; González-Pérez et al., 2004). Since the combustion of organic matter (OM) in forests and soils is often incomplete due to limited O_2 availability, the plant biomass is not completely converted to CO_2 and H_2O, but thermally altered to low and medium molecular weight degradation products and highly condensed macromolecular charring products such as charcoal and soot, collectively referred to as black carbon (BC). Part of the thermal degradation products are released with smoke particles to the atmosphere while another portion remains in the charred soils. Due to the structural changes of biomolecules, the thermally oxidized SOM exhibits a higher resistance against (bio)degradation and becomes part of the refractory C pool (González-Pérez et al., 2004).

The contents of BC and molecular markers such as levoglucosan have been used as indicators for the degree of thermal degradation of SOM (Glaser et al., 1998; Schmidt et al., 2001; Simoneit et al., 1999; Simoneit, 2002). The characterization and quantification of BC in soils through common hydrolytic methods is difficult due to its highly refractory and complex structure (Kögel-Knabner, 2000). Benzenecarboxylic acids generated from the chemical oxidation of BC were proposed as molecular markers to quantify BC in soils (Glaser et al., 1998). In addition, solid-state ^{13}C nuclear magnetic resonance (NMR) techniques have also been applied to quantify BC in soils (Skjemstad et al., 1999; Simpson and Hatcher, 2004). However, due to the heterogeneity of soil samples, solid-state ^{13}C NMR spectroscopy provides “bulk” BC properties and does not provide source specific information nor the degree of thermal alteration of specific molecules. Furthermore, NMR-based methods are considered to provide BC “estimates” due to concerns with quantitation and interference from non-BC components (Simpson and Hatcher, 2004). Therefore, complementing NMR analyses with compound specific biomarker methods is advantageous because biomarker methods provide molecule specific source information, accurate quantities, and the degree of molecular alteration.

The monosaccharide levoglucosan is generated during the incomplete combustion of cellulose and was suggested as a molecular marker for plant biomass burning (Simoneit et al., 1999). Levoglucosan is easily identified and quantified using gas chromatography–mass spectrometry (GC–MS) and was detected in aerosol particles (smoke), post-fire soils and in sediments (Simoneit et al., 1999; Elias et al., 2001; Oros et al., 2002; Simoneit, 2002; Abas et al., 2004). Low molecular weight compounds such as lipids were also used as molecular markers to investigate the influence of burning on SOM. Post-fire soils were reported to have higher yields of free lipids, shorter-chain length of homologous aliphatic lipid series (alkanes, fatty acids) and a different composition of resin terpenoids than the soils before burning (Almendros et al., 1988). The lipid biomarkers found in charred plant OM or in smoke resulting from the burning of vegetation can yield information about the biological sources and the degradation processes induced by high temperatures during the incomplete combustion of the plant biomass (Simoneit, 2002). Characteristic lipid compounds are generated during the burning of higher plant materials which can be used as molecular markers (biomarkers) to determine the biological source of the biomass (Oros and Simoneit, 2001a,b; Simoneit, 2002). Different species of trees were reported to yield characteristic biomarkers (terpenoids, steroids, lignin monomers) found in the smoke generated from the burning of the wood (Oros and Simoneit, 2001a,b). Similar biomarkers that reflected the original vegetation were also detected in soils that were charred in fires (Oros et al., 2002) and in volcanic ashes obtained after the eruption of Mount St. Helens, USA (Pereira and Rostad, 1983). During incomplete combustion (smoldering), the biomolecules are in part altered to a series of thermal degradation products (“pyromolecules”) through oxidative processes such as decarboxylation, demethylation, dehydration and oxidation (Simoneit, 2002). Despite these degradation processes, the characteristic skeleton of the biomolecules often remains intact and the generated degradation products can still be assigned to their parental biomarker classes. The degree of thermal alteration of the plant OM depends on the temperature and duration of the charring processes (Shafizadeh, 1984). Under flaming conditions ($T > 300$ °C) pyrolytic processes are predominant and polycyclic aromatic hydrocarbons (PAHs) and soot are generated. In contrast, depolymerization, water elimination, oxidation, volatilization of unaltered biomolecules and the formation of charcoal occur at smoldering temperatures (<300 °C).

In this study, solvent extractable biomarkers in pine forest soil and vegetation samples which were charred during a wildfire were analyzed to investigate the alteration of SOM during incomplete burning