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Heat impact caused molecular level changes in solid and dissolved soil organic matter

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The ubiquitous abundance of pyrolysed, highly aromatic organic matter, called "Black Carbon" (BC), in all environmental compartments became increasingly important in different fields of research beyond intensive investigated atmospheric aerosol due to climatic relevance.
Its predominant high resistance to abiotic and biotic degradation resulted in turnover times from less than a century to several millennia. This recalcitrance led to the enrichment of BC in soils, accounting for 1–6% (European forest soils) to 60% (Chernozems) of total soil organic matter (SOM). Hence, soil BC acts an important sink in the global carbon cycle. In contrast, consequences for the nitrogen cycle up to date are rather inconsistently discussed.
Soil related dissolved organic matter (DOM) is a major controlling factor in soil formation, an important pathway of organic matter transport and one of the largest active carbon reservoirs on earth, if considering oceans and other bodies of water.
The aim of this study was to evaluate the effects of artificially simulated wildfire by thermal treatment on the molecular composition of water extractable soil organic matter (DOM).
Soils from two outdoor lysimeters with different management history were investigated. Soil samples, non-heated and heated up to 350°C were analyzed for elemental composition (carbon, nitrogen and sulfur) and for bulk molecular composition by Pyrolysis-Field Ionization Mass Spectrometry (Py-FIMS) and synchrotron-based X-ray Absorption Near-Edge Spectroscopy (XANES) at the C- and N K-edges.

DOM-samples obtained by hot water extraction, desalting and concentration by solid phase extraction were subsequently analyzed by flow injection analysis in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR-MS), equipped with an ESI source and a 7 T supra-conducting magnet (LTQ-FT Ultra, ThermoFisher Scientific). This technique is the key technique for the analysis of complex samples due to its outstanding mass resolution (used 400.000 at m/z 400 Da) and mass accuracy ($\leq$ 1 ppm), simultaneously providing molecular level details of thousands of compounds. The characteristics and differences of the FTICR-MS spectra with as many as ten or more peaks at each nominal mass are discussed: heated samples showed considerable higher intensities of even numbered peaks. An in-house developed, automated post processing was used for further exploitation of the data with the aim of an unambiguous assignment of as many peaks as possible. Obtained mass lists were transformed for sorting and preparation/ interpretation of graphics like Kendrick and van Krevelen plots.
The heat-treated solid samples show decreasing C/N ratios and the formation cyclic and N-heterocyclic compounds in good agreement among the various methods (Py-FIMS and C- and N-XANES). Detailed insight into the hot-water extracts by FTICR-MS showed clear qualitative as well as quantitative changes in the number and the intensity of nitrogen and nitrogen + sulfur containing compounds, respectively, which generally became enriched under soil heating. This demonstrates for the first time, that not only the bulk SOM is affected in structure by heat impact but also the more mobile DOM.
We assume, that heat impact volatilizes and oxidizes parts of the organic substances is as expected but another part of the substances incorporates (further) nitrogen atom(s) similar to the generation of new compounds under the conditions of plasma etching in nitrogen atmosphere. This would explain to some extent, why soils are e.g. after fire clearing of vegetation are highly fertile for a short period (better plant acceptable compounds) but become more infertile in the long run, especially under tropical conditions with frequently heavy rain that would lead to an increased leaching of compounds with higher polarity.