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Improved assessment of pyrogenic carbon quantity and quality in soils by liquid chromatography

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Fire-derived (pyrogenic) carbon (PyC) is produced by the incomplete combustion of biomass, for example during wildfires. It can persist in the environment for a long time due to its relative resistance against biological and chemical breakdown. Its accurate quantification in soils, sediments and other environmental media is of great interest because the slow turn-over of PyC has implications for the global carbon cycle. It is thus relevant for climate scenarios and mitigation. Moreover, PyC in pedological and sedimentological records can be used to reconstruct wildfire history, which is closely linked to climate history. PyC assessment is also a valuable tool for characterizing biochars and other pyrogenic products.

A whole suite of PyC quantification methods exists because PyC is not a defined chemical structure but rather a continuum of thermally altered biomass. The benzene polycarboxylic acids (BPCA) analysis is a molecular marker method that was shown to yield conservative estimates of PyC quantity in soils and environmental samples. In addition, it yields unique qualitative information about the degree of aromaticity and condensation of PyC, which is indicative for the pyrolysis temperature of PyC and its resistance against degradation. The commonly used BPCA method consists in digesting samples with nitric acid that breaks down the PyC into a suite of BPCAs, which are cleaned, derivatized and finally analyzed by gas chromatography-flame ionization detection (GC-FID).

Here, we present a modified BPCA quantification method for soils, sediments and other environmental samples that uses a high performance liquid chromatography system coupled to diode array detection (HPLC-DAD). We demonstrate that this method greatly enhances the reproducibility of PyC measurements while significantly reducing analysis time. Moreover, much less sample material is needed for precise PyC assessment and we show that the HPLC-DAD method yields more consistent PyC measurements than the GC-FID method. Additionally, the new method also facilitates δ13C and 14C measurements of the PyC fraction in these complex matrix samples. The isotopic information of PyC further supports the assessment of carbon budgets in soils, sediments or (bio-)chars and the reconstruction of past burning and climate events, as will be shown with examples.