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Solid-state NMR and IRMS characterization of smouldered peat from ombrotrophic cores

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Smouldering fires are slow, low temperature, flameless and the most persistent form of combustion of organic matter (OM) in porous form.

Although smouldering fires of peatlands represent a large perturbation of the atmospheric chemistry, to date, most studies on smouldering focused on ignition, carbon (C) losses or emissions, whereas the literature still lacks understanding of the OM evolution following these events.

The potential to track OM changes able to serve as new proxies for the identification of past fire events along peat cores is extremely important, especially considering that bogs are often used as natural archives of paleoenvironmental changes.

In the present work we show preliminary results about solid-state Nuclear Magnetic Resonance (NMR) and Isotope-Ratio Mass Spectroscopy (IRMS) characterization of peat OM along three Sphagnum peat columns (26 cm deep) having different initial moisture contents (MC): 50% MC, 100% MC, and 200% MC.

The ^{15}N spectrum of fresh peat (FP) used as control shows, as expected, only an amide signal, which is in agreement with the ^{13}C NMR spectrum where mainly signals of carbohydrates and alkyl C can be observed. Further signals can be observed in the aromatic region, most probably due to lignin derivatives. Following the smouldering event, selected peat samples from both the 50% and 100% MC series show, as expected, signals supporting the occurrence of fire. In detail, the ^{15}N-signals between -200 and -250 ppm are typical for pyrrole or indole type N. This is in accordance with the ^{13}C NMR spectra showing considerable intensity in the aromatic region, most likely from char residues.

Isotopic signatures (i.e., δ^{13}C and δ^{15}N) show a very interesting behaviour. In detail, δ^{13}C seems to be slightly affected by smouldering, although the information about vegetational changes are preserved, whereas the δ^{15}N shows a trend positively correlated with the relative N enrichment observed in smouldered peat samples, as also supported by ^{15}N NMR.

While further research is in progress to find reliable proxies allowing reconstruction of ancient smouldering events along peat profiles, our data provide an additional important insight towards assessing palaeoenvironmental conditions and highlighting that smouldering fires may have been overlooked as the cause of molecular and chemical variations observed in peat cores.

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