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Determining the degree of peat decomposition - A comparison of different methods

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Peat humification or decomposition is a frequently used proxy to extract past time changes in hydrology and climate from peat bogs. During the past century several methods to determine changes in peat decomposition have been introduced. Most of these methods are operationally defined only and the chemical changes underlying the decomposition process are often poorly understood and lack validation. Due to the chemically undefined nature of many humification analyses the comparison of results obtained by different methods is difficult if not misleading. In this study we compared changes in peat decomposition in cores of two peat bogs (Königsmoor (KK), Kleines Rotes Bruch (KRB)) from the Harz Mountains (Germany) using C/N ratios, Fourier Transform Infrared spectra absorption (FTIR) intensities, Rock Eval$^{®}$ oxygen- and hydrogen indices, δ13C and δ15N isotopic signatures and UV-absorption of NaOH peat extracts. In addition, one of the cores was analysed for changes in the peat's molecular composition using pyrolysis gas chromatography mass spectrometry (pyrolysis-GC-MS). Records of decomposition proxies show similar historical development at both sites, indicating external forcing such as climate as controlling process. Moreover, all decomposition proxies except UV-ABS and δ15N isotopes show similar patterns in their records and thus reflect in different extents signals of decomposition. Pyrolysis-GC-MS analyses of the KK core reveal that changes in peat molecular chemistry are mainly attributed to decomposition processes and to a lesser extend to changes in vegetation. Changes in the abundance of molecular compounds indicate that peat decomposition in the KK bog is mainly characterized by preferential decomposition of phenols and polysaccharides and relative enrichment of aliphatics during drier periods. Enrichment of lignin and other aromatics during decomposition was also observed but showed less variation, and presumably reflects changes in vegetation associated to changes in hydrology of the bogs. Significant correlations with polysaccharide and aliphatic pyrolysis products were found for C/N ratios, FTIR-band intensities and for hydrogen index values, supporting that these decomposition indices provide reasonable information despite their bulk nature. Correlation with oxygen index values and δ13C was lower assumingly indicating carboxylation of the peat during drier periods and enrichment of isotopically lighter peat components during decomposition, respectively. FTIR, C/N ratio, Pyrolysis-GC-MS analyses and Rock Eval hydrogen indices appear to reflect mass loss and related changes in the molecular peat composition during mineralization best. Different to the other investigated proxies, Pyrolysis-GC-MS and FTIR analyses allow disentangling decomposition processes and vegetation changes. UV-ABS measurements of alkaline peat extracts show only weak correlation with other decomposition proxies as they mainly reflect the formation of humic acids through humifcation and to a lesser extend mass loss during mineralization.