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Using BPCA and pyrolysis-GC/MS patterns as a measure of charring intensity

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Many questions remain on the molecular properties of Black C (organic fire residues such as charcoal and soot). Here we compare parameters from two methods that have recently shown to be related to the degree of thermal modification ("charring intensity") of charcoal-Black C: i) the proportion of mellitic acid (B6CA) among benzenepolycarboxylic acids in the BPCA method [1,2,3] and ii) the relative proportions and degree of alkylation of pyrolysis products from Black C in pyrolysis-GC/MS [4]. For that purpose we used laboratory chars from rice straw (grass) and chestnut wood (wood) produced at 200–1000 ºC under N2 flow. The chars obtained at 450 ºC are reference materials of the Black Carbon Ring Trial [5].

Positive correlations between the charring temperature and BPCA and pyrolysis patterns confirm that these methods can be used to study the degree of thermal impact of charred remains. Pyrolysis-GC/MS allowed us to track the thermal degradation of the major biocomponents lignin, polysaccharides, tannin, aliphatic chain lipids, triterpenoids, chlorophyll and proteins, mostly between 250 and 450 ºC. The proportions of the pyrolysis products of Black C (benzene, toluene, benzonitrile, PAHs, etc.) and also the ratios that reflect the abundance of aliphatic cross-linkages between aromatic moieties (benzene/toluene, naphthalene/alkylnaphthalenes, benzofuran/alkylbenzofurans), increase with charring intensity. Nonetheless, chars obtained at T > 600 ºC (especially for wood) gave low quality pyrograms and poor reproducibility because of high thermal stability.

The relative contributions of B6CA, one of the molecular markers used for the BPCA method, are indicative for the degree of condensation of the chars. The BPCA approach showed a clear increase in the relative contribution of B6CA from ca. 5 % at 200 ºC to ca. 95 % at 1000 ºC, confirming the ability of this parameter to assess charring intensity. The relative contribution of B6CA remains almost constant at ca. 30 % between 250 and 450 ºC.

Thus, with regard to estimating the charring intensity of Black C, the BPCA method is more suitable for high T chars (> 450 ºC) while pyrolysis-GC/MS seems more appropriate in the lower T range (< 500 ºC). This is not surprising as larger clusters of polyaromatic domains (high T) can be assessed by the BPCA method but are resistant against pyrolysis. On the other hand, smaller clusters and non-polycondensed portions of Black C (low T) are amenable to pyrolysis-GC/MS but escape the analytical window of the BPCA method. The two methods may therefore be considered complementary, with BPCA giving reliable quantitative data on Black C content and charring degree of high T chars while pyrolysis-GC/MS is quantitatively weak but provides highly detailed information on the molecular properties of especially lower T chars.

References

[1] Brodowski, S., Rodionov, A., Haumeier L., Glaser, B., Amelung, W. (2005) Org. Geochem. 36, 1299-1310.
[2] Glaser, B., Haumeier, L., Guggenberger, G., Zech, W. (1998) Org. Geochem. 29, 811-819.
[3] Schneider, M.P.W., Hilf, M., Vogt, U.F., Schmidt, M.W.I., Org. Geochem. (submitted)
[4] Kaal, J., Rumpel, C. (2009) Org. Geochem. 40, 1179-1187.
[5] Hammes, K., Schmidt, M.W.I., Smernik, R.J. et al. (2007) Global Biogeochemical Cycles 21, 1-18.