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Soot/black carbon *vs*. chars in environmental media: Potential discrimination between these combustion by-products through elemental, molecular, and bulk isotopic analyses.

P. Louchouarn (1,2) and S. Houel (2,3)

(1) Department of Earth and Environmental Sciences, Columbia University, (2) Lamont Doherty Earth Observatory and Earth Institute, New York, USA, pl2065@columbia.edu, (3) Now at GEOTOP - University of Québec at Montréal, Canada, stephane_houel @yahoo.fr

This study tested a recently improvement to the chemothermal oxidation method (CTO) for quantification of soot/graphitic black carbon (GBC) on a series of certified standard materials and "group defined" standards. The application of the "Gelinas" method, which involves prior demineralization and organic matter hydrolysis, confirmed 1) the reproducibility of GBC results as compared to results from other labs, 2) the lack of GBC in chars and coals, and most importantly 3) the potential for artifacts from the CTO methods such as overestimated GBC levels in samples rich in labile organic matter (i.e. wetlands and upwelling marine sediments). Additionally, the absolute and relative abundance of a suite of molecular markers, including Benzenepolycarboxylic acids (BPCA) and levoglucosan, appear as promising proxies for charcoal abundance in complex environmental media. Our results from standard charcoals in oligohaline wetland sediments of the Hudson Estuary confirm independent measurements of microfossil charcoals, which point to discrete incidences of marsh burning in these systems. Our analyses also document important external anthropogenic inputs of charred materials in modern periods. Experimental combustion of several of the marsh horizons shows that residual charred marsh materials can be depleted by as much as $\sim$3-5‰ in δ^{13}C signature with respect to the unburned material. This shift, similar to that existing between lignin and cellulose macromolecules, suggests that selective enrichment of charred lignin in charcoal horizons preserved in organic-rich environmental matrices may induce biases in isotopic bulk proxies during reconstruction of

C4 *vs*. C3 plant inputs.