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Chemical recalcitrance of biochar and wildfire charcoal: how similar are they?

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The enhanced chemical resistance to biological degradation of pyrogenic materials, either produced during wildfires (charcoal) or by man (biochar), makes them long-term carbon sinks once incorporated in soils. In spite of their fundamental similarities, studies comparing the chemical recalcitrance of biochar and wildfire charcoal are scarce because analogous materials for accurate comparison are not easily available.

Using solid-state 13C cross polarization–magic angle spinning nuclear magnetic resonance spectroscopy we characterized the chemical recalcitrance of pyrogenic materials generated from the same unburnt feedstooks (litter and dead wood from Pinus banksiana): (a) charcoal from a high-intensity wildfire and (b) biochar obtained by slow pyrolysis [3 treatments: 2 h at 350, 500 and 650°C]. For quantification, the spectra were divided into four regions representing different chemical environments of the 13C nucleus: alkyl C (0–45 ppm), O-alkyl C (45–110 ppm), olefinic and aromatic C(110–160 ppm), and carbonyl C (160–210 ppm). As an indicator of chemical recalcitrance, the degree of aromaticity (%) was calculated as follow: aromatic-C $*$ 100 / (alkyl C+ O alkyl-C + aromatic-C).

The pyrogenic materials derived from wood show higher degrees of aromaticity (68 to 88%) than pyrogenic material derived from litter (40 to 88%). When comparing biochar and wildfire charcoal, biochars produced at 500 and 650°C always have higher degrees of aromaticity than wildfire charcoals, irrespective of the original feedstock. Wildfire charcoals always show a more heterogeneous chemical composition, with alkyl and O-alkyl compounds present even in charcoal generated at very high temperatures (temperatures up to 950 °C were recorded on the litter surface during the wildfire). However, biochars produced at 500 and 650 °C are mostly aromatic, and only the biochars produced at 350 °C show partial contribution of alkyl-C compounds. Our results suggest that biochar-type pyrogenic materials have in general a higher chemical recalcitrance than wildfire charcoal and, thus, we advice caution when transfer knowledge between the biochar and the wildfire charcoal research communities.