

MOBILE ORGANIC COMPOUNDS IN BIOCHAR. RELATIONSHIPS WITH CARBONISATION DEGREE AND BIO-OIL COMPOSITION

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During biochar production, pyrolysis vapors released from biomass can interact with the porous aromatic biochar structure. Given the complex chemical composition of pyrolysis vapors, a wide range of organic compounds with different polarities and molecular mass can be retained in biochar with the potential to be released into the environment. The presence of these species will ultimately influence biochar quality and safety for soil applications. While our knowledge on the production, occurrence and fate of priority contaminants, such as polycyclic aromatic hydrocarbons, is increasing and led to the definition of threshold values, the relevance of non-regulated organic compounds has been less investigated. In particular, volatile organic compounds (VOCs) and water-soluble organic compounds (WSOCs) are worth of consideration because of their mobility into air and aqueous phase.

The present study was aimed at investigating the chemical nature of VOCs and WSOCs in biochar in relation with their formation in biomass carbonization. To this purpose methods based on solid-phase microextraction (SPME) were applied to sample VOCs and WSOCs released by biochar in the headspace and water extracts, respectively. Compounds sorbed in the SPME fiber were analyzed by GC-MS. Biochar samples with different carbonization degree were produced from corn stalk pyrolyzed at increasing temperatures from 350 to 650 °C under reproducible conditions. Bio-oil was collected during pyrolysis and the chemical composition compared to that of VOCs and WSOCs occurring in the corresponding biochar samples. Further elucidations on the structure of WSOCs in biochar and bio-oil were gathered by negative electrospray ionization coupled with ultra-high resolution mass spectrometry (Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FT-ICR-MS) as well as fluorescence spectroscopy with Parallel Factor Analysis (PARAFAC). The SPME methods were also applied to biochar samples from different origins.

Semi-volatile VOCs and WSOCs of poorly carbonized biochars comprised a variety of chemical species (figure); their number and quantity decreased with increasing carbonization extent (decreasing H/C and volatile matter). Biochar WSOCs were featured by aliphatic and aromatic carboxylic acids, while bio-oil WSOCs were dominated by lignin phenols and their distribution did not change markedly with increasing pyrolysis temperature. The pattern of higher molecular weight species in poorly carbonized biochar was comparable to that of the corresponding bio-oils, but increasing carbonization reduced the homologues with higher degree of aromaticity. Moreover, fluorescent aromatic components of biochar WSOCs resembled those of soil organic matter (fulvic acids), while lignin-like moieties were distinctive of bio-oil. The observed differences in the bio-oil/biochar molecular patterns suggested a fractionation of the sorbed pyrolysis products, enhanced in more carbonized biochar, attributed to porosity, hydrophobic effect and π - π interactions that concurred to block preferentially phenol derivatives. Apparently this segregation reduced the potential toxicity of bio-oil contamination or even promote plant growth as emerged in seed germination experiments.

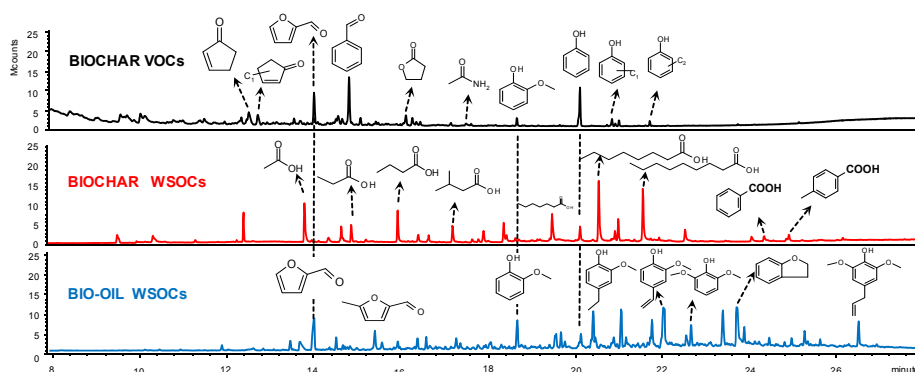


Figure. SPME and GC-MS analysis of VOCs and WSOCs in biochar and bio-oil produced from slow pyrolysis of cornstalk at 350 °C. GC-column DBFFAP.