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Aromaticity and degree of aromatic condensation of char

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ABSTRACT

The aromatic carbon structure is a defining property of chars and is often expressed with the help of two concepts: (i) aromaticity and (ii) degree of aromatic condensation. The varying extent of these two features is assumed to largely determine the relatively high persistence of charred material in the environment and is thus of interest for, e.g., biochar characterization or carbon cycle studies. Consequently, a variety of methods has been used to assess the aromatic structure of chars, which has led to interesting insights but has complicated the comparison of data acquired with different methods. We therefore used a suite of seven methods (elemental analysis, MIR spectroscopy, NEXAFS spectroscopy, ^{13}C NMR spectroscopy, BPCA analysis, lipid analysis and helium pycnometry) and compared 13 measurements from them using a diverse sample set of 38 laboratory chars. Our results demonstrate that most of the measurements could be categorized either into those which assess aromaticity or those which assess the degree of aromatic condensation. A variety of measurements, including relatively inexpensive and simple ones, reproducibly captured the two aromatic features in question, and data from different methods could therefore be compared. Moreover, general patterns between the two aromatic features and the pyrolysis conditions were revealed, supporting reconstruction of the highest heat treatment temperature (HTT) of char.

1. Introduction

Natural and anthropogenic chars have recently received much attention (Manyà, 2012; Knicker, 2011; Glaser and Birk, 2012). Their role as important environmental constituents is increasingly being recognized; chars persist in soils and sediments, which has important implications for the global C budget (Schmidt and Noack, 2000) and they can exert beneficial properties on soils, improving fertility (Biederman and Harpole, 2013) and immobilizing hazardous compounds (Beesley et al., 2011). Moreover, anthropogenic chars (biochars) involve additional economic advantages; prudent biochar production can provide green energy, providing an interesting alternative to management of organic waste (Meyer et al., 2011).

With increasing interest in the use of charred material, there is a growing need to characterize and classify the material accurately in order to improve understanding of its properties and behavior in the environment. A defining property of chars and of pyrogenic organic matter in general (Preston and Schmidt, 2006) is their aromatic C structure (Lehmann and Joseph, 2009), which is believed to consist of at least two different aromatic C phases: (i) an amorphous phase comprising randomly organized aromatic rings and (ii) a crystalline phase, comprising condensed polyaromatic sheets that are turbostratically aligned (Franklin, 1951; Cohen-Ofri et al., 2006; Keiluweit et al., 2010). The concepts of aromaticity (the total proportion of aromatic C including both phases; McNaught and Wilkinson, 1997) and that of the degree of aromatic condensation (the proportion of the condensed aromatic C only; McBeath et al., 2011) relate to this two phase model. The varying extent of the two phases is believed to largely determine stability of the charred material against degradation in the environment (Lehmann et al., 2009; Singh et al., 2012). Consequently, aromaticity and the degree

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of aromatic condensation of a char likely influence its sequestration potential as well as the duration during which it can provide benefit to the soil (Nguyen et al., 2010).

The two features are themselves influenced by the feedstock, and the pyrolysis conditions. The type of feedstock contributes to the aromaticity and the degree of aromatic condensation by providing different chemical structures as starting material. For example, a high amount of aromatic structures in a feedstock (e.g. lignin in wood) can promote the resulting char aromaticity (Antal and Grønli, 2003). Similarly, different precursor materials attain a high degree of aromatic condensation at different temperatures (Setton et al., 2002). The pyrolysis conditions, in particular the highest heat treatment temperature (HTT), but also residence time, O_2 availability and pressure, influence the C properties of the resulting char (Shafizadeh, 1982; Lua et al., 2004). Aromaticity has been reported to increase with HTT from 200 °C to ca. 500 °C, where maximum aromaticity values are reached. The degree of aromatic condensation showed, on the other hand, a more gradual increase with HTT from 400 °C, reaching maximum values at > 1000 °C (McBeath et al., 2011; Schneider et al., 2011).

Considering the importance of the aromatic C structure in char and its dependence on many influencing factors, it is not surprising that various attempts have been made to measure these archetypal properties of char. A wide variety of chemical and physical methods has been used, including elemental analysis, molecular markers, solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, Raman spectroscopy, pyrolysis–gas chromatography-mass spectrometry (Py–GC–MS), X-ray diffraction, near edge X-ray absorption fine-structure spectroscopy (NEXAFS), X-ray photoelectron spectroscopy, measurement of surface area, He based solid density, electrical resistivity or high resolution transmission electron microscopy (HRTEM) (Derenne et al., 2005; McBeath et al., 2011; Charon et al., 2014).

While the wealth of methods for aromatic structure characterization of char is fascinating, with the methods continuing to grow in number and quality, it has become increasingly difficult to compare data using different methods and to relate the findings from them. Matters are complicated by the fact that terms such as aromaticity can have multiple technique-specific meanings (McBeath et al., 2011). Moreover, from a practical point of view, researchers and practitioners may have limited resources and instrumentations and would like to optimize both insightful data acquisition and reasonable analysis cost. Efforts to compare different methods and their measurements and to put them in a common framework are therefore required, thereby guiding the interpretation of differently acquired data and suggesting suitable methods for specific analysis problems.

Here, we have used an extensive suite of 7 different methods that provided 13 measurements (cf. Table 1) in a comparative study to evaluate their assessment of the aromatic structure in charred materials. A large sample set, consisting of 38 different laboratory char samples (cf. Table 2), was analyzed using each

Table 1
Methods considered comparatively for assessing aromaticity and/or degree of aromatic condensation of chars (names of derived indices in bold).

Measurement principle	Method	Index (M_{index})	Measurement	Reference
Elemental composition	Elemental analysis	**$O–C_{index}$** **$H–C_{index}$**	C, H and O content (%), H/C, O/C	Baldock and Smernik (2002), Hammes et al. (2006)
Functional groups	Mid-infrared spectroscopy (MIR)	**MIR_{index}**	Aromaticity ratio (%), (1420 + 821)/(1510 + 1320) cm^{-1}	Wood (1988), Guo and Bustin (1998), Moore and Owen (2001)
	Near-edge X-ray absorption fine structure spectroscopy (NEXAFS)	**$NEXAFS\text{-}aroma_{index}$**	Aromaticity ratio (%), 285 eV/286–288 eV	Francis and Hitchcock (1992), Agren et al. (1995), Kuznetsova et al. (2001), Brandes et al. (2008), Keiluweit et al. (2010)
		$NEXAFS\text{-}cond_{index}$	Degree of condensation ratio (%), 284 eV/285 eV	
	^{13}C Nuclear magnetic resonance spectroscopy (NMR)	**$NMR\text{-}aroma_{index}$**	Deconvolution on fitted spectrum with assigned aromatic peaks	McBeath and Smernik (2009), McBeath et al. (2011)
	– with sorbed ^{13}C label	**$NMR\text{-}cond_{index}$**	$-\Delta\delta$ (ppm), Shift of sorbed ^{13}C labelled benzene – shift of benzene	
Molecular markers	Benzene polycarboxylic acid (BPCA) analysis	**$BPCA\text{-}aroma_{index}$**	Total BPCA amount per organic carbon (g/kg): BPCA/C	Schneider et al. (2011), Wiedemeier et al. (2013)
		$BPCA\text{-}cond_{index}$	Ratio of B6CA per total BPCA amount (%), B6CA/BPCA	
	Lipid analysis	**TLE_{index}**	Total lipid extract yield (g), TLE	Wiesenberg et al. (2009, 2010), Wiedemeier et al. (2015)
	– *n*-alkanes	**ACL_{index}**	Average chain length, ACL	
	– Polycyclic aromatic hydrocarbons	**PAH_{index}**	Ratio of 4–6 ring to 2–3 ring polycyclic aromatic hydrocarbons (%)	
Density	He pycnometry	**$Pycno_{index}$**	Skeletal density (g/cm^3)	Brown et al. (2006), Brewer et al. (2009, 2014)

Table 2
Laboratory chars measured with each method.

Feedstock	Pyrolysis procedure	HTT	*n*	Thermosequence
Chestnut (Wood) (*Castanea sativa*)	A: 5 h HTT, N_2 flow	200–1000 °C	12	Wood-A
Rice (Grass) (*Oryza sativa*)		200–1000 °C	12	Grass-A
Pine (Wood) (*Pinus ponderosa*)	B: 1 h HTT, Closed chamber	100–700 °C	7	Wood-B
Fescue (Grass) (*Festuca arundinacea*)		100–700 °C	7	Grass-B