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Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials

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Abstract

A wide selection of thermal, chemical and optical methods have been proposed for the quantification of black carbon (BC) in environmental matrices, and the results to date differ markedly depending upon the method used. A new approach is hydro-pyrolysis (hypy), where pyrolysis assisted by high hydrogen pressures (150 bar) facilitates the complete reductive removal of labile organic matter, so isolating a highly stable portion of the BC continuum (defined as BC_{hypy}). Here, the potential of hypy for the isolation and quantification of BC is evaluated using the 12 reference materials from the International BC Ring Trial, comprising BC-rich samples, BC-containing environmental matrices and BC-free potentially interfering materials. By varying the hypy operating conditions, it is demonstrated that lignocellulosic, humic and other labile organic carbon material (defined as non-BC_{hypy}) is fully removed by 550 °C, with hydrogasification of the remaining BC_{hypy} not commencing until over 575 °C. The resulting plateau in sample mass and carbon loss is apparent in all of the environmental samples, facilitating BC quantification in a wide range of materials. The BC_{hypy} contents for all 12 ring trial samples fall within the range reported in the BC inter-comparison study, and systematic differences with other methods are rationalised.

All methods for BC isolation, including hypy are limited by the fact that BC cannot be distinguished from extremely thermally mature organic matter; for example in high rank coals. However, the data reported here indicates that BC_{hypy} has an atomic H/C ratio of less than 0.5 and therefore comprises a chemically well-defined polyaromatic structure in terms of the average size of peri-condensed aromatic clusters of >7 rings (24 carbon atoms), that is consistent across different sample matrices. This, together with the sound underlying rationale for the reductive removal of labile organic matter, makes hypy an ideal approach for matrix independent BC quantification. The hypy results are extremely reproducible, with BC_{hypy} determinations from triplicate analyses typically within ±2% across all samples, limited mainly by the precision of the elemental analyser.

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1. INTRODUCTION

Black carbon (BC), also known as pyrogenic carbon, is defined as the carbon-rich (>60%) residue from incomplete combustion of fossil fuels and biomass (Goldberg, 1985),

Table 1
Summary of methods used in the BC ring trial (full details in Hammes et al., 2007).

Method (abbreviation)	Analytical rationale ^a	BC quantification	Reference ^a
Chemo-thermal oxidation (CTO-375)	Oxidation at 375 °C in air following acid pretreatment	Elemental analysis	Gustafsson et al. (1997)
Benzene polycarboxylic acid formation (BPCA)	Oxidation in nitric acid following acid pretreatment	GC/FID	Glaser et al. (1998)
Acid dichromate oxidation (K ₂ Cr ₂ O ₇)	Acid dichromate oxidation following acid pretreatment	Elemental analysis	Wolbach and Anders (1989)
Thermal/optical transmittance and reflectance (TOT/R)	Stepwise heating to 900 °C in He/O ₂	Laser reflectance or transmittance plus FID	Chow et al. (1993)
Thermogravimetry–differential scanning calorimetry (TG–DSC)	Heating to 990 °C in He/O ₂	Mass difference during heating	Lopez-Capel et al. (2005)
Sodium hypochlorite oxidation (NaClO)	Oxidation with NaClO following acid pretreatment	¹³ C NMR and elemental analysis	Simpson and Hatcher (2004a)
UV photo-oxidation (UV)	Photo-oxidation in oxygenated water after acid pretreatment	¹³ C NMR and elemental analysis	Skjemstad et al. (1996)
Multi-element scanning thermal analysis (MESTA) ^b	Heating to 800 °C in He/O ₂ with products combusted at 1100 °C	BC determined at 550 °C	Hsieh and Bugna (2008)

^a Methodologies summarised very briefly, see Hammes et al. (2007) and references therein for details.

^b Method not published at the time of the ring trial but assessed with many of the same samples.

that has both high aromaticity and high resistance to oxidative degradation (Bird and Gröcke, 1997; Schmidt and Noack, 2000; Preston and Schmidt, 2006). This definition of BC encompasses a broad continuum, from combustion residues (e.g. charred biomass and charcoal) to combustion condensates (e.g. soot), reflecting different precursors and formation processes (Schmidt and Noack, 2000; Schmidt et al., 2001; Masiello, 2004; Preston and Schmidt, 2006). Estimated global BC production rates are 50–270 Tg year⁻¹ (Kuhlbusch and Crutzen, 1995), and BC plays a key role in global processes, including atmospheric chemistry, radiative heat balance (e.g. Crutzen and Andreae, 1990), the global carbon cycle (e.g. Masiello, 2004), the transport and bioavailability of organic pollutants (Bucheli and Gustafsson, 2000) and as a tracer of fire history (Bird and Cali, 1998). It is therefore imperative that accurate and comparable analyses of BC are possible across a variety of matrices (Schmidt et al., 2001). However, due to the different definitions of BC, a large number of quantification methodologies are applied, depending upon the particular physical and chemical characteristics of BC that are of interest, and the purpose of the study (Hammes et al., 2007). For example, as aerosol BC (often termed elemental carbon, EC) is the main atmospheric absorber of visible light, this material is frequently isolated according to its light absorbing properties (Watson et al., 2005). In contrast, BC in soils and sediments is understood to form a long-term carbon sink, due to estimated BC half lives of 5–7 ky (Preston and Schmidt, 2006). Consequently, BC in these matrices is frequently isolated on the basis of its chemical recalcitrance.

The various methods for the quantification of BC have been summarised and reviewed elsewhere (e.g. Schmidt et al., 2001; Watson et al., 2005; Hammes et al., 2007), and can be broadly classified as thermal, optical, chemical, combined thermo-optical or thermo-chemical, spectroscopic, microscopic and molecular marker methods (Masiello, 2004). Chemical and thermal methods typically

quantify BC by elemental analysis of the sample residue after removal of the non-BC sample fraction, while other methodologies directly measure BC in the whole sample. As BC is typically isolated via operational, rather than chemical parameters, individual methodologies only identify BC from a specific portion of the BC continuum, with no one method being able to isolate or quantify BC across the whole range (Schmidt et al., 2001; Currie et al., 2002; de la Rosa et al., 2011). The methodological dependence of BC quantification has been highlighted in multiple method intercomparison studies (e.g. Horvath, 1993; ten Brink et al., 2004; Watson et al., 2005; Hitzemberger et al., 2006; Hammes et al., 2007; Bae et al., 2007; Reisinger et al., 2008). For example, Schmidt et al. (2001) found variation over one order of magnitude between BC contents of urban aerosol samples using nine different quantification methodologies, and of over two orders of magnitude for BC content of soil samples using six different methodologies. Likewise, Currie et al. (2002) found BC values of an “urban dust” standard (NIST SRM 1649a) ranged between 6.8% and 52% using 13 different quantification methods.

This variation in BC quantifications partly reflects differences in the operational definition of BC between methods, and partly a variety of positive and negative methodological biases in BC isolation (e.g. Nguyen et al., 2004; Hammes et al., 2008). These problems were highlighted in a comprehensive and systematic intercomparison study by Hammes et al. (2007), where the BC content of 12 reference materials was determined by the seven different methods summarised in Table 1. While concentrating on methods used for BC determination in soil and sediment samples, this study also included BC-rich soot and chars, together with a number of potentially interfering materials such as coals, a type I kerogen and a melanoidin negative control. The 12 samples from this study, known as the International BC Ring Trial (referred to hereafter as the “ring trial”) are summarised in Table 2, with full details available in Hammes et al. (2007)

Table 2
Samples from the BC ring trial as used in this study (full details in Hammes et al., 2007).

Group	Sample	Details	TC ^a (%)
Environmental matrices	Vertisol	Sandy clay soil; Urrbrae, South Australia (37% clay)	3.1
	Chernozem	Light sandy clay soil; Hildesheim, Germany (19% clay)	2.0
	Marine sediment	Baltimore harbour, Chesapeake Bay, Maryland, USA (NIST SRM 1941b, 2004)	3.0
	Aerosol	Urban dust, Washington DC, USA (NIST SRM 1649b, 2009)	18.0
	Dissolved organic matter (DOM)	Suwannee River natural organic matter, Georgia, USA (IHSS)	47.1
Laboratory produced BC-rich materials	Grass char	Grass (<i>Oryza sativa</i>) char (450 °C for 5 h under nitrogen)	57.4
	Wood char	Chestnut (<i>Castanea sativa</i>) char (450 °C for 5 h under nitrogen)	71.9
	<i>n</i> -Hexane soot	Soot collected from an open <i>n</i> -hexane flame	92.9
Potentially interfering materials	Melanoidin	Negative control, nitrogen rich biopolymer	54.3
	Green River shale	Green River Formation (Mahogany zone) Utah, USA (USGS SGR-1)	27.2
	Lignite coal	Beulah-Zap lignite, North Dakota, USA (Argonne National Laboratory)	58.5
	Bituminous coal	Pocahontas #3, Virginia, USA (Argonne National Laboratory)	85.9

^a Data from this study, values show minor variations to the averages reported by Hammes et al. (2007).

and at <http://www.geo.uzh.ch/en/units/physical-geography-soilbio/services/black-carbon-reference-materials/>.

Potential underestimation of sample BC content was identified in some of the popular methods, due to the aggressive removal of labile carbon. In the chemo-thermal oxidation (CTO) approach (Gustafsson et al., 1997; Elmquist et al., 2004) only the most condensed BC forms are quantified (Hammes et al., 2007), while during acid dichromate oxidation ($K_2Cr_2O_7$); (Wolbach and Anders, 1989; Bird and Gröcke, 1997) inadvertent oxidation of the sample BC fraction is possible (Knicker et al., 2007). In addition, negative biases in the benzene polycarboxylic acid formation method (BPCA) have been attributed to incomplete conversion of all BC to BPCAs (Nguyen et al., 2004). Overestimation of sample BC is possible due to artificial quantification of non-BC material as BC, which occurs if the CTO temperature is maintained below 375 °C (Elmquist et al., 2004). Positive biases can also result from in situ charring of non-BC material (Simpson and Hatcher, 2004b), incomplete $K_2Cr_2O_7$ oxidation of hydrophobic materials (Knicker et al., 2007), or the presence of BPCAs derived from non-BC sources (Brodowski et al., 2005). To mitigate such biases, various pretreatment steps and modifications have been adopted (e.g. Gelinas et al., 2001), but a risk with some modifications is handling and transfer losses which themselves can lead to underestimation of BC (Elmquist et al., 2004). Adaptations of thermal/optical transmittance and reflectance methods (TOT/R) have been applied in measurement of atmospheric BC (e.g. Chow et al., 1993; Watson et al., 2005), and of BC in soils and sediments (Han et al., 2007). However, despite this, it would appear that there is inadequate discrimination between BC and non-BC organic matter in terrestrial and marine environments by these methods (Hammes et al., 2007).

Other methods described in the ring trial, such as thermogravimetry–differential scanning calorimetry (TG–DSC), oxidation with sodium hypochlorite (NaClO)

followed by BC determination by ^{13}C NMR and photo-oxidation with UV, together with the multi-element scanning thermal analysis (MESTA) method of Hsieh and Bugna (2008) (not included in the ring trial) have been applied less widely, as they require more specialised equipment. While each of these methods have been shown to detect BC across much of the BC continuum, biases may arise, with TG–DSC susceptible to interference from mineral impurities such as clays (e.g. Plante et al., 2005), and UV-oxidation procedures may overestimate the BC content of soils and sediments (Simpson and Hatcher, 2004b). In addition, while NaClO oxidation was tested with seven of the 12 ring trial samples (Hammes et al., 2007), the study of MESTA used only six, which did not include the potentially interfering materials (Hsieh and Bugna, 2008), and so their efficacy for BC quantification still needs to be tested across a wider range of samples.

It is clear that currently no one method has gained wide acceptance as providing accurate and robust BC determinations across a wide range of sample types. In this study, the 12 reference materials employed in the ring trial are used for the systematic assessment of the efficacy of a new method, hydrolysis (hypy), which has recently been proposed as a means of isolating and quantifying BC in soils and chars (Ascough et al., 2009, 2010). Hypy refers to pyrolysis assisted by high hydrogen pressures (150 bar) with a dispersed sulphided molybdenum (Mo) catalyst. The underlying principle for BC determination is that thermally labile macromolecular organic matter is reductively liberated, primarily being converted into dichloromethane-soluble oil, leaving behind a refractory fraction of thermally stable, highly aromatic carbonaceous material defined as BC_{hypy}. Thus, it has been found that at a pressure of 150 bar, hypy conversions of labile carbon (defined as non-BC_{hypy}) close to 100% are achieved for immature type I and II kerogens (Roberts et al., 1995; Love et al., 1997; Murray et al., 1998) and biomass (Rocha et al., 1999; Beramendi-Orosco

et al., 2006). For highly volatile bituminous coals, the conversions equate to the vitrinite plus liptinite (reactive maceral) contents, with the residue being derived from inertinite (Li et al., 1996). Further, it has been shown that the hydrocarbon products of hypy are released in higher yields with minimal structural rearrangement in comparison with traditional analytical pyrolysis methods such as pyrolysis–gas chromatography–mass spectrometry (Love et al., 1997), with the advantage that it should be possible to identify and characterise the non-BC_{hypy} fraction of charcoal samples at a molecular level (Ascough et al., 2010). In contrast with normal pyrolysis conditions, the combination of high-pressure hydrogen and the Mo catalyst suppresses both BC formation and, for BC that is present, aromatic ring growth. Further, the relatively high sweep gas velocity used in fixed-bed reactors and the small particle size of material analysed, means that conversion is not limited by mass transfer effects.

In the present study the results of hypy BC isolation were compared with those obtained in the ring trial. Additionally, BC values were obtained for the ring trial samples using dichromate oxidation, one of the most widespread methods in use for BC quantification to date, for direct comparison with values obtained by hypy. The results of dichromate oxidation presented in Hammes et al. (2007) exhibit considerable variation, reflecting the susceptibility of acidified dichromate oxidations to laboratory-specific variations in methodology (De Leenheer and Van Hove, 1958; De Vos et al., 2007). Consequently, to enable a more accurate comparison of the two methods we also exposed the 12 reference materials to a single standardized dichromate oxidation procedure, thereby minimizing the variation in the dataset.

2. METHODS

2.1. Reference materials

Detailed descriptions have been previously published for the 12 reference materials used in this study as listed in Table 2 (Hammes et al., 2007). Briefly they comprise five BC-containing environmental matrices, three laboratory-produced BC-rich materials, and four BC-free potentially interfering materials. The samples were obtained as fine powders from the sources recommended by the Black Carbon Ring Trial Steering Committee (2011), with no further mechanical processing required. Although sieved to a smaller grain size, the urban aerosol sample used here (1649b) is composed of the same material (SRM 1649a) as used in the ring trial (National Institute of Standards and Technology, 2007, 2009). In addition to BC quantification, the only further analysis of the samples required was the characterisation of the maceral composition of the lignite, in order to identify the presence of ancient pyrogenic BC in the form of inertinite (Vorres, 1990).

2.2. Hydropyrolysis

Hydropyrolysis (hypy) tests were performed using the procedure described by Ascough et al. (2009). The samples

were first loaded with the Mo catalyst using an aqueous/methanol solution of ammonium dioxodithiomolybdate $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$, and placed within shortened borosilicate pipette ends (20 mm long) plugged at each end with pre-cleaned quartz wool (Fig. 1). The samples were pyrolysed with resistive heating from 50 to 250 °C at 300 °C min⁻¹, and then from 250 °C to the final temperature at 8 °C min⁻¹ (25 °C increments from 450 to 575 °C and then to a final temperature of 595 °C), then held for 2 min, under a hydrogen pressure of 150 bar. A hydrogen sweep gas flow of 5 L min⁻¹, measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor for subsequent trapping on dry ice cooled silica (Meredith et al., 2004). Three replicate tests with a final temperature of 550 °C were performed on all samples to assess the reproducibility of the hypy technique for BC isolation.

The catalyst loading for the soils and marine sediment was 5% by weight, for all other samples except the DOM it was at 10% by weight. The water solubility of the DOM precluded conventional catalyst loading; instead for each temperature an aliquot (15 mg) was dissolved in methanol, adsorbed to 100 mg of the catalyst and dried in a vacuum oven at 60 °C for 1 h. Placing each sample in a borosilicate glass reactor insert secured at the top and bottom with quartz wool allowed for the accurate weight loss during pyrolysis of each sample to be determined. For the sample of Green River shale, inorganic carbonate (3.2%, Gladney and Roelandts, 1988), was removed prior to catalyst loading by exposing 50 mg aliquots to 1.5 mL 1 M HCl overnight (Hedges and Stern, 1984).

2.3. Dichromate oxidation

Acidified dichromate oxidations were performed after Bird and Gröcke (1997), using 50 mL polypropylene centrifuge tubes. Aliquots of the reference materials (100 mg for soils and sediments and 30–50 mg for all other samples), decarbonated as above, were mixed with 20 mL of acidified dichromate solution (0.1 M potassium dichromate, 2 M sulphuric acid) and maintained at 60 °C in an orbital incubator shaker (KS4000i, IKA, Staufen, Germany) for 1, 2, 3 or 7 days. For incubation at 60 °C, these exposure times correspond with the dichromate oxidation degree-hours used in the four laboratories participating in the ring trial (Hammes et al., 2007). Tubes were wrapped in aluminium foil to reduce the effects of static electricity during open handling operations with dry samples. To minimize the number of washing steps, and hence sample loss, the samples were not pre-treated before oxidation. No significant decolourization (i.e. transition from orange to green) of the oxidizing solution occurred during incubations so no replacement of exhausted oxidizing solution was required. On termination of incubation the tubes were cooled to room temperature and 10 mL methanol (HPLC grade) added before sample recovery by centrifugation 1600g, 10 min (Grossman and Ghosh, 2009). Methanol was used to promote sample sedimentation by reducing both the density and the polarity of the acidified dichromate solution. After removal of the supernatant the samples were washed twice by

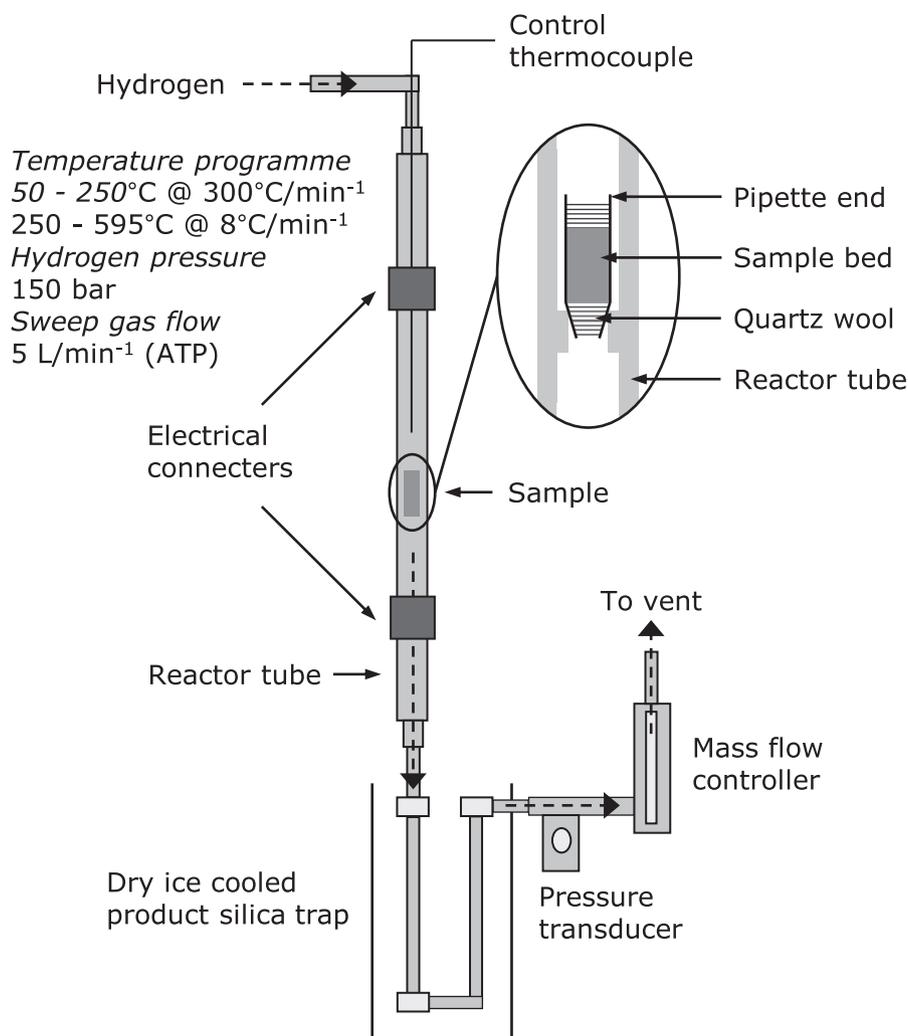


Fig. 1. Schematic representation of the hydrolysis apparatus.

centrifugation as described above. The samples were then re-suspended in 5 mL deionized water and stored at -20°C prior to freeze-drying and subsequent elemental analysis.

2.4. Black carbon quantification

The BC_{hypy} content of each sample was derived by comparing the organic carbon (OC) content of the catalyst loaded samples prior to hypy with those of their hypy residues (Eq. (1)). Elemental analyses were performed in duplicate on a Thermo Scientific 1112 Flash EA.

$$\text{BC}_{\text{hypy}}(\text{BC}/\text{OC}\%) = \frac{\text{Residual OC (mg C in hypy residue including spent catalyst)}}{\text{Initial OC (mg C in sample including catalyst)}} \times 100$$

(1)

For the dichromate residues, the total organic carbon (TOC) contents were determined by dry combustion of decarbonated sub-samples (Nelson and Sommers, 1996) using a Costech elemental analyser (EA) (Milan, Italy) fitted with a zero-blank auto-sampler, and the BC content of each reference material was calculated by mass balance.

2.5. Maceral analysis

Since the inertinite content of the Beulah Zap lignite was not available, an aliquot of this coal was set into thermoplastic resin using a STRUERS Labopress-3 mounting press. The resultant mount was polished using STRUERS Rotopol-Pedemat equipment, and analysed with a LEITZ Ortholux II-Pol BK reflected light microscope. A $50\times$ oil immersion lens was used together with a $10\times$ binocular eyepiece ($500\times$ overall magnification). The macerals present at 500 points were recorded using a SWIFT automatic point counter, and converted to a percentage of the total sample.

3. RESULTS AND DISCUSSION

3.1. Environmental matrices

3.1.1. Soils (*Vertisol* and *Chernozem*)

The two soils were selected for the ring trial to assess the BC detection efficacy of different methods in soils with high (*Vertisol*) and low (*Chernozem*) clay contents (Hammes et al., 2007). The carbon loss for both soils over the

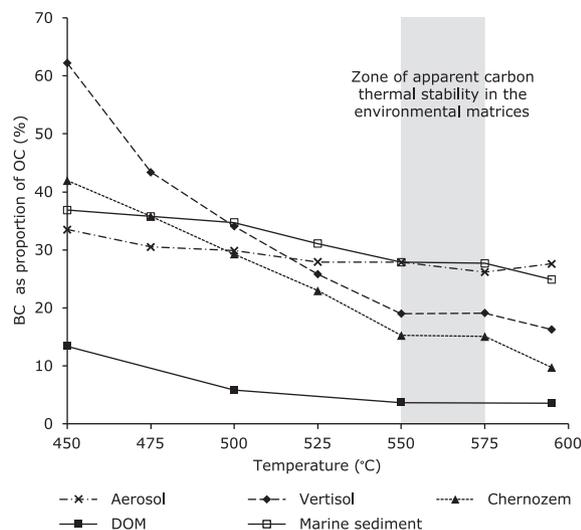


Fig. 2. Black carbon (BC) as proportion of organic carbon (OC) as measured for the residues of the environmental matrices after hypy at different temperatures.

450–550 °C range corresponds to the loss of labile (i.e. non- BC_{hypy}) carbon from the soil organic matter (Fig. 2). This is consistent with observed conversions of lignocellulosic material and humic acids to volatile products between 450 and 550 °C (Rocha et al., 1999; Ascough et al., 2010). The subsequent plateau in remaining carbon content between 550 and 575 °C represents a zone of apparent thermal stability when non- BC_{hypy} organic matter (e.g. lignocellulosic material, humic acids, proteins and lipids), together with relatively labile pyrogenic carbon has been removed, and the residual carbon represents the sample BC_{hypy} content, that is the portion of the BC continuum which is stable under hypy conditions. At 595 °C, following the

plateau phase, significant further loss of carbon occurs, via hydrogasification to yield predominately methane (Li et al., 1996; Ascough et al., 2009).

The BC_{hypy} (at 550 °C) content of these samples (BC/OC) is 19.0% ($\pm 0.3\%$; mean $\pm 1\sigma$) for the Vertisol and 15.2% ($\pm 0.5\%$) for the Chernozem. These values are within the range of BC contents reported by Hammes et al. (2007) (Fig. 3), although they are greater than those from both other thermal methods (e.g. CTO-375; METSA), and the results of our 7-day dichromate oxidations, Vertisol 3.6% ($\pm 0.4\%$) and Chernozem 7.0% ($\pm 0.3\%$). The dichromate oxidation results from this study are consistent with those of the ring trial (Vertisol 3.5–19.4%; Chernozem 3.8–11.7%), in which the large variation was attributed to different oxidation times employed across participating laboratories (Hammes et al., 2007). The BC_{hypy} values are lower than those obtained by TOT/R and TG–DSC, methods that Hammes et al. (2007) suggested may overestimate the BC content in soils due to the inefficient removal of interfering matrices such as carbonates (Currie et al., 2002) and clays (Plante et al., 2005). The very close concordance in the trend of residual OC content with increasing temperature apparent for the two soils with contrasting clay and TOC contents, suggests that hypy is able to isolate a constant BC_{hypy} fraction from soils exhibiting a range of textures.

3.1.2. Marine sediment

This sample from Baltimore Harbour is thought to represent BC present dominantly as soot in a fine sedimentary matrix (Hammes et al., 2007). Much of the organic matter in the sample is found to be very labile, with 36.9% of the OC remaining at 450 °C. With an increase in temperature there is minor continued degradation, before a plateau in the residual OC content is reached between 550 and

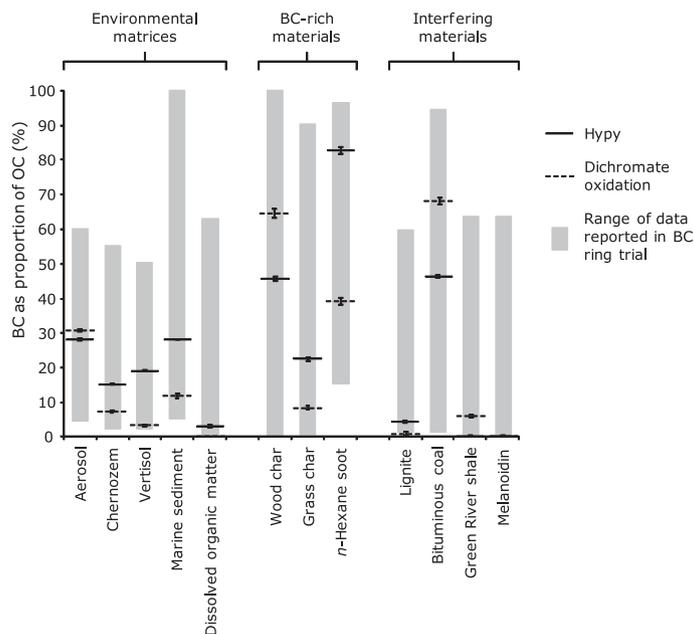


Fig. 3. Comparison between BC determination by hypy and dichromate oxidation superimposed on the range of BC values reported in the BC ring trial (data from Fig. 2 in Hammes et al., 2007). Error bars represent 1 standard deviation from triplicate analysis (see Section 3.4).

575 °C, which is again followed by a further decrease to 595 °C (Fig. 2). The BC_{hypy} content of this sample at 550 °C ($27.9\% \pm 0.1\%$) is in the centre of the ring trial range (Fig. 3). This value is similar to that of our dichromate oxidation ($31.0\% \pm 1.2\%$), although lower than the ring trial dichromate results, and the TG–DSC (100%) and UV (49.4%). These methods have previously been suggested to overestimate BC in the marine sediment due to interfering matrix effects, although these higher values may also reveal the presence of BC with less condensed structures (Hammes et al., 2007). In common with CTO-375, the BC_{hypy} value for the marine sediment is significantly greater than that found for the two soils, probably due to a greater abundance of highly condensed soot-derived material in the sediment (Hammes et al., 2007).

3.1.3. Aerosol

The OC content of BC soot in an aerosol matrix (SRM 1649b) is dominated by a very labile phase, with approximately 70% of the initial OC removed by hypy at temperatures below 450 °C. The remaining ~30% carbon (predominantly BC) appeared to be largely very stable, with only minimal further degradation below 595 °C. The high stability of this fraction may be due to a high proportion of condensed soot-like BC material present in this sample, as identified in previous studies (Currie et al., 2002; Hammes et al., 2007). At 550 °C, BC_{hypy} was $27.9\% (\pm 0.6\%)$, in the centre of the range reported by Hammes et al. (2007) (Fig. 3), and the intercomparison study of Currie et al. (2002), which reported a range of BC contents for this sample from 6.9% to 52.0%. The BC_{hypy} value is higher than methods CTO-375 and BPCA, and again much lower than for TG–DSC. The hypy results are more comparable with those reported for methods TOT/R and UV (and MESTA, Hsieh and Bugna, 2008), which suggests that in common with these methods hypy is able to detect a relatively wide range of aromatic structures as BC (when compared to CTO-375), while being less susceptible to the methodological matrix artifacts identified by Currie et al. (2002). The dichromate oxidation result from this study ($11.8\% \pm 0.9\%$) is significantly lower than those reported during the ring trial (Hammes et al., 2007), and may be due to losses encountered due to sample handling.

The hypy results suggest that marine sediments and urban aerosols from highly industrialised environments exhibit relatively high BC_{hypy} contents, thought to be dominated by very refractory soot-BC derived from fossil fuel burning. The soils from agricultural environments have much lower BC_{hypy} contents, where a higher relative abundance of less condensed, more labile BC (ring size <7), derived from comparatively low temperature vegetation burning, may be under-detected by this method.

3.1.4. Dissolved organic matter

This sample of riverine DOM was included in the ring trial due to the possibility that it may contain a small amount of soluble condensed aromatic structures (Hammes et al., 2007). Due to its soluble nature this sample had to be mixed with the catalyst by a different method than the other reference materials, and in addition hypy was performed in

50 °C increments rather than 25 °C. As expected, the DOM sample is extremely labile under hypy conditions, with 87% of the carbon converted to volatile products by 450 °C. With increasing temperature, while most of the remaining carbon becomes labile there is small but significant portion which is stable at 550 °C, and so is defined here as BC_{hypy} (3.7%). This carbonaceous fraction does not undergo any significant degradation between 550 and 595 °C (3.6% remaining), indicating that it is very stable.

While most of the ring trial methods reported zero BC for this sample (as is inevitable for those methods which define BC as being insoluble e.g. dichromate and UV oxidation) the occurrence of a small amount of BC within DOM is certainly possible, with recent studies identifying BC-like highly condensed aromatic ring structures (CARS) in soil and riverine DOM (Kim et al., 2004; Hockaday et al., 2006). Such CARS found within DOM have been shown to be derived from pyrogenic sources (Hockaday et al., 2007; Hilscher and Knicker, 2011), and so dissolved BC may be an important transport mechanism for BC from rivers to marine sediments (Sleighter and Hatcher, 2008; Stubbins et al., 2010). The BC-like CARS are thought to be solubilised due to the presence of multiple carboxyl groups providing polarity sufficient to overcome the hydrophobicity of aromatic domains (Hockaday et al., 2006). Under hypy conditions it would be expected that such functionalised CARS would be hydrogenated and reduced to their corresponding hydrocarbons (Sephton et al., 2005; Meredith et al., 2006), with those of relatively small size (e.g. 7 peri-condensed rings or fewer, with up to 24 carbon atoms) volatilised to form part of the hypy product (Ascough et al., 2010), and the larger ring clusters remaining in the hypy residue forming the minor residual BC_{hypy} apparent for this sample.

The only ring trial method to report a positive BC value for this sample was BPCA, which gave a very similar value (4.5%, Hammes et al., 2007) to that found by hypy. BPCA is well suited to identifying BC components in solution, and has recently been used to report significant BC components in riverine and marine DOM (Dittmar, 2008; Ziolkowski and Druffel, 2010), and to demonstrate the solubilisation of aged pyrogenic chars (Abiven et al., 2011).

3.2. Laboratory produced BC-rich materials

3.2.1. Chars (*grass and wood*)

The wood and grass chars, produced at 450 °C in an inert nitrogen atmosphere (Hammes et al., 2006) were included in the ring trial to assess the effect of starting material upon BC detected by the various methods (Hammes et al., 2007). The chars have been characterised in detail by Hammes et al. (2006), and while the atomic H/C and O/C ratios of the two chars are almost identical, the wood char has a higher TOC (71.9%) and lower nitrogen content (1.6%) than the grass char (57.4% and 12.4% respectively), and also a much lower ash content (wood char 0.5%; grass char 19.2%, Hammes et al., 2006).

The wood char is significantly more stable during hypy with a greater residual OC content than the grass char at all temperatures (Fig. 4). Increasing degradation is

apparent for both samples at each incremental temperature up to 595 °C, and so unlike the environmental samples, a distinct plateau region is not reached, although the carbon loss between 575 and 595 °C is relatively small. This may be due to the BC present in the environmental samples having been subject to degradation in the natural environment which will have removed the smaller, more labile aromatic structures, as observed by Hockaday et al. (2006) for a fire-impacted forest soil. In contrast, the modern charcoals are likely to contain a continuum of bound polycyclic aromatic hydrocarbons (PAH), with those of up to *ca.* 7 peri-condensed rings (24 carbon atoms) likely to be progressively stripped off with increasing temperature, with coronene previously shown to be the largest PAH cleaved from charcoals under hypy conditions (Ascough et al., 2010). In addition, the plateau may not be observed because the BC_{hypy} contents are higher than for the environmental samples, and the proportion of labile organic matter lower. Clearly, an important issue is what point to select for measuring the BC_{hypy} content. If a temperature of 550 °C were used for BC determination on the basis of results for the environmental samples (Section 3.1), the BC_{hypy} content of the wood char would be 46.6% ($\pm 1.4\%$), and the grass char 22.5% ($\pm 0.9\%$). The lack of a zone of thermal stability between 550 and 575 °C across which to measure the BC content introduces a degree of uncertainty that was not apparent for the environmental samples. Therefore, rather than defining the proportion of the OC remaining in the hypy residue at 550 °C, it may be more appropriate to quote the range in BC/OC values as measured from 550 to 575 °C, which for the wood char is 39.1–46.6%, and for the grass char 19.8–22.5%. The extent of carbon loss decreases for both the wood and the grass chars above 575 °C and this could represent the onset of hydrogasification to methane.

The greater BC_{hypy} content of wood char, over that derived from grass is consistent with the previously observed greater degree of aromatic condensation in this sample (based on ¹³C NMR analysis cross polarisation observabil-

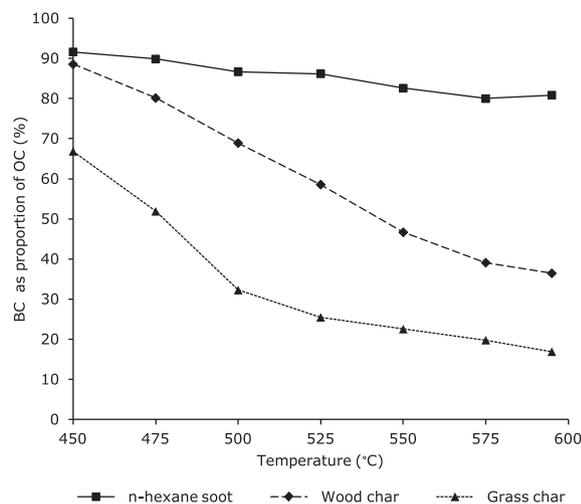


Fig. 4. Black carbon (BC) as proportion of organic carbon (OC) as measured for the residues of the laboratory produced BC-rich materials after hypy at different temperatures.

ity; Hammes et al., 2008). All ring trial methods also reported greater BC content for the wood than the grass char, except CTO-375 and NaClO which both reported zero BC in the wood char and low BC contents (<11%) for the grass char, which was thought to reflect carbon trapped within silica phytoliths in the grass char (e.g. Krull et al., 2003), that was protected under the aggressive regimes of these methods (Hammes et al., 2007).

The relatively low BC_{hypy} contents of the wood and grass chars (when determined at 550–575 °C) are to be expected given that the temperature of formation for these samples was only 450 °C, which may have allowed for products of the incomplete thermal degradation of cellulose and lignin to be preserved in the initial char (Hammes et al., 2007). In terms of the aromatic ring size distribution that is preserved in the BC-residue under hypy conditions, Ascough et al. (2010) showed the 7 peri-condensed ring compound coronene, with 24 carbon atoms to be the largest PAH present in the non-BC_{hypy} fraction cleaved from a variety of charcoals. This is larger than the average cluster size of 3 rings found by Sun et al. (2012) for chars generated at 450 °C, and the same as the maximum size of condensed aromatic domains found by McBeath et al. (2011) in biochars produced at 500 °C. Therefore, it can be assumed that char-BC generated at a temperature of 450 °C will have an aromatic structure that is not sufficiently condensed to be entirely captured in the analytical window of hypy.

However, while somewhat limited to the more condensed and refractory portion of the BC continuum, hypy, unlike some other more aggressive methods (e.g. CTO-375 and NaClO), does appear able to preserve a considerable portion of the BC present in these samples, especially for the wood char, which were formed at a temperature (450 °C), that is broadly representative of natural fires (e.g. Turney et al., 2006). It would be expected that chars formed at higher temperatures, such as encountered in scrubland fires (e.g. 700–1000 °C, Schmidt and Noack, 2000) would be more resistant to degradation under hypy conditions, with McBeath et al. (2011) finding aromatic structures larger than 19 rings abundant in charcoals produced at over 700 °C. This would result in greater measured BC_{hypy} values, as observed by Nguyen et al. (2004) for the determination of BC in high temperature chars (1000 °C) by CTO-375, and Schneider et al. (2010) for a thermosequence of biochars produced between 200 and 700 °C with BPCA analysis.

The remaining ring trial methods (K₂Cr₂O₇, TOT/R, TG–DSC, UV) all reported high, but variable BC contents for both chars (Hammes et al., 2007), as found with dichromate oxidation in this study for the wood char (64.9% \pm 2.8%), although the result for the grass char was anomalously low (8.9% \pm 1.2%).

3.2.2. *n*-Hexane soot

This sample, which represents BC produced in the gas phase from an inefficiently combusted open hexane flame, has a very high carbon content (92.9%), surface area (73.9 m² g⁻¹, Hammes et al., 2007), and has been characterised in detail elsewhere (e.g. Akhter et al., 1985; Smith and Chughtai, 1995). Under hypy conditions the *n*-hexane soot is very stable with only ~10% labile carbon removal below

450 °C (Fig. 4), a BC_{hypy} content defined between 550 and 575 °C of 80.0–82.6%, and no further carbon loss observed at 595 °C (80.8%). All ring trial methods reported a BC content of >50% for this sample except CTO-375 and BPCA (Hammes et al., 2007). In common with hypy, methods TOT/R, TG–DSC and UV reported a BC content of >80%, with such high values thought to reflect the high thermal and chemical resistance of this sample (Hammes et al., 2007). The MESTA method also reported >80% BC, with the small proportion of non-BC material detected in this sample ascribed to partially oxidised carbon (Hsieh and Bugna, 2008). Significant apparent oxidation of this sample occurred during $K_2Cr_2O_7$ oxidation (BC/OC = 39.2%), with relatively large errors ($\pm 1.8\%$), which was attributed to sample handling problems associated with the hydrophobic nature of the sample (Elmqvist et al., 2004).

The much greater BC_{hypy} content for the *n*-hexane soot compared with the wood and grass chars shows that hypy discriminates against labile char-BC relative to more refractory soot-BC, as suggested by the results from the environmental matrices. The greater stability of the soot under hypy conditions is probably related to its more condensed structure as reflected by its lower H/C and O/C atomic ratios (Hammes et al., 2008), which will also result in the soot having a lesser hydrogasification reactivity as shown by the absence of significant carbon loss between 575 and 595 °C. The lower stability of char-BC relative to soot-BC as determined by CTO-375 has been ascribed to the greater density of heteroatoms, lower aromaticity, and the greater internal microporosity, due to the lower formation temperature of char-BC (Elmqvist et al., 2006).

3.3. Potentially interfering materials

3.3.1. Melanoidin

The melanoidin (residue formed from the reaction of urea with glucose) was included in the study to act as a negative control, i.e. as a sample that contains no material produced by combustion (Hammes et al., 2007). All ring trial methods except TOT/R reported a near zero BC content for the melanoidin, although in CTO-375 charring of the melanoidin during heating was thought to result in a positive BC determination bias of 2.4% (BC/OC) (Hammes et al., 2007). Under hypy conditions the weight loss of melanoidin has been shown to be 100% at 525 °C (Ascough et al., 2010), although the presence of the spent catalyst allows for the detection of any melanoidin derived carbon in the hypy residues. At 450 °C the residue contained 5.3% of the starting melanoidin carbon, while this was reduced to just a trace, <0.3%, at temperatures of 550 °C and above (Fig. 5). The standard deviation of the duplicate analysis of all samples on the elemental analyser averaged at 0.5, and so to reflect this uncertainty it would be appropriate to quote the BC content of this sample as <1%.

3.3.2. Green River shale

This carbon-rich shale is thought to contain chemically resistant non-pyrogenic carbon (Hammes et al., 2007). Due to its low thermal maturity (Bishop et al., 1998), the

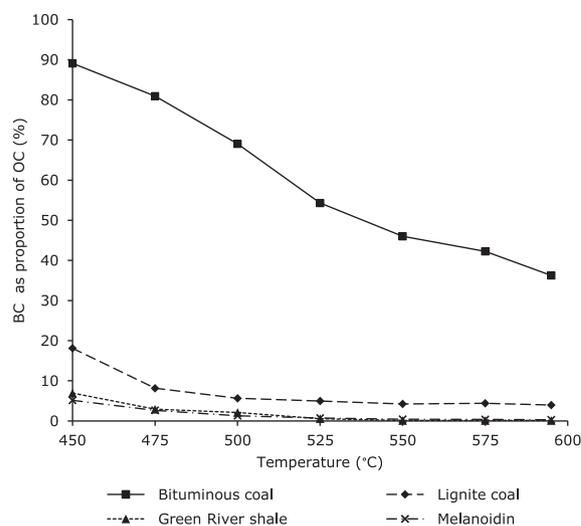


Fig. 5. Black carbon (BC) as proportion of organic carbon (OC) as measured for the residues of the potentially interfering materials after hypy at different temperatures.

carbon present in this sample is predominantly very labile during hypy, with only 6.9% of the initial OC remaining at 450 °C. As shown in Fig. 5 this small amount of residual carbon rapidly degraded with increasing temperature, with near complete conversion apparent by 550 °C, resulting in a trace BC_{hypy} value (BC/OC = 0.3%) determined at this temperature.

A number of the ring trial methods such as TG–DSC and $K_2Cr_2O_7$ oxidation were observed to significantly over-estimate the BC content of this sample (Hammes et al., 2007), by quantifying chemically recalcitrant carbon, such as the fused aromatic structures known to be present in the sample (Trehwella et al., 1986) as BC. Ineffective removal of non-BC material from this sample was apparent in our $K_2Cr_2O_7$ oxidation analysis, which gave a BC content of 5.7% ($\pm 1.4\%$), in which the positive bias is partly ascribed to methodological issues arising from the hydrophobicity of the sample.

3.3.3. Beulah Zap lignite

This immature, relatively low carbon lignite was selected in the ring trial to differentiate coal from pyrogenic BC (Hammes et al., 2007). Previous studies using hypy on the behaviour of immature kerogens such as oil shales have shown conversions approaching 100% for thermally labile material (Roberts et al., 1995; Love et al., 1995). Under hypy conditions this lignite was thermally very labile, with only 18.1% of the initial OC remaining at 450 °C, and as shown in Fig. 5 rapid further degradation occurred thereafter with increasing temperature. However carbon conversion was not total, resulting in a BC_{hypy} content determined at 550 °C of 4.2% ($\pm 0.6\%$). This residual carbon appeared to be very stable with no significant further degradation between 550 and 595 °C. A likely source of this BC is inertinite from ancient fire occurrences incorporated during deposition (Scott, 2000; Dickens et al., 2004). The inertinite content was determined to be 16.8% (Table 3), which is

Table 3
Vitrinite reflectance (VR_r) and maceral analysis data of the coal samples.

Coal	VR_r (%)	Maceral (vol.%)			
		Vitrinite	Liptinite	Inertinite	
				Semi-fusinite	Fusinite
Lignite ^a	0.25 ^c	80.4	2.0	11.2	5.6
Bituminous ^b	1.68 ^c	89	1	10	

^a Data from this study, remaining 0.8% as pyrite.

^b Data from Hower et al. (1995).

^c Data from Busch et al. (2003).

consistent with previous reports (Hower et al., 1995). However, of this total inertinite, 11.2% was found to be semi-fusinite, while only 5.6% was characterised as fusinite. Therefore, it appears the BC_{hypy} content correlates extremely closely with the fusinite content. It is widely accepted that many classes of inertinite, especially fusinites and semi-fusinites, have a pyrogenic origin (e.g. Scott, 1989), with fusinites defined as having a reflectance $>2\%$ and a temperature of formation of $>400\text{ }^\circ\text{C}$ (Scott, 2000). The higher temperature of formation of fusinite relative to semi-fusinite, and a consequent more condensed aromatic structure (Guo and Bustin, 1998) leads to greater stability under hypy conditions, and the apparent correlation between BC_{hypy} and fusinite content in this sample.

As with the Green River shale, the BC_{hypy} content for this sample as determined by hypy was very much towards the lower end of those from the BC ring trial, in which the NaClO -based method was in very close agreement (5% BC), and the more aggressive CTO-375 method reported 1% BC. The greater BC contents measured by the other ring trial methods suggested that they over-estimated the BC content of this sample (Hammes et al., 2007).

3.3.4. Bituminous coal

This high rank, low-volatile bituminous coal while composed predominantly of vitrinite (89%), (Table 3) has an inertinite content of 10% (Vorres, 1990; Hower et al., 1995). The carbon content of this coal was very recalcitrant, with a significant amount remaining after hypy at $550\text{ }^\circ\text{C}$ (Fig. 5). Therefore, this was the only potentially interfering sample that gave a significant positive BC_{hypy} content ($46.0\% \pm 0.9\%$), meaning there is a significant contribution from the pyrolysed vitrinite. A high BC content for this sample was reported for all methods in the ring trial with the exception of CTO-375 and BPCA, with many methods reporting that most of carbon in this sample was found to be BC (Hammes et al., 2007). This sample was also very resistant to $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation, with $68.2\% (\pm 2.0\%)$ of the initial OC remaining after 7 days of treatment.

Clearly, this sample demonstrates the difficulty of distinguishing modern “fire derived” BC from mature coals where the aromatic structure in terms of condensation overlaps with that of pyrogenic BC to a significant degree. This is highlighted by the fact those ring trial methods that did report a low value for this coal, CTO-375 and BPCA also reported relatively low values for the *n*-hexane soot, suggesting that these methods identify only a very limited

part of the BC continuum as BC. In contrast, hypy appears to identify a greater range of condensed aromatic structures as BC_{hypy} as is discussed further in Section 3.6.

3.4. Reproducibility of hypy BC data

In order to assess the reproducibility of the BC determination by hypy each sample was analysed in triplicate at $550\text{ }^\circ\text{C}$. The replicate data (Table 4) shows a reproducibility of $\pm 2\%$ (mean $\pm 1\sigma$) across all samples. Provided the sample is well homogenized prior to treatment, a consistently high degree of measurement precision can be achieved by using hypy to remove the same (non- BC_{hypy}) components from a wide range of sample types. As the temperature of hypy is so well constrained, typically $\pm 2\text{ }^\circ\text{C}$ at $550\text{ }^\circ\text{C}$, the variability in carbon degradation should be minor, therefore this error is most likely due to errors associated with the analytical balance and the reproducibility of the elemental analyser. As noted in Section 3.3.1 the standard deviation of the duplicate analysis of all samples on the elemental analyser averaged at 0.5. Therefore, for samples such as the melanoidin and Green River shale, which have near-zero BC contents, it is appropriate to quantify the BC/OC as $<1\%$.

The errors associated with the dichromate oxidation (Table 5) were greater than those for the hypy, largely due to sample handling problems that were especially apparent with samples of a hydrophobic nature.

As described in Section 3 the degradation of the carbon fraction in the three BC-rich materials and the bituminous coal between 550 and $575\text{ }^\circ\text{C}$ introduces a degree of uncertainty in the BC determination of these samples. This is illustrated in Table 6 and demonstrates that with the exception of these four carbon-rich samples the only other sample for which this uncertainty is greater than 0.5% is the urban aerosol (1.7%). While it would be possible to undertake hypy at both 550 and $575\text{ }^\circ\text{C}$ in order to quantify this degree of uncertainty, in practice we would envisage using only a single temperature of $550\text{ }^\circ\text{C}$.

3.5. Advantages and limitations of hypy for BC quantification

Hypy-derived BC values are generally lower than those from methods such as TOT/R and TG–DSC, which are known to be prone to overestimate BC due to matrix effects, especially among the environmental matrices (Schmidt et al., 2001; Lopez-Capel et al., 2005; Hammes

Table 4
Replicate analysis for BC_{hypy} determination (BC/OC%) by hypy at 550 °C.

Replicate	Aerosol	Chernozem	Vertisol	Marine sediment	DOM	Wood char	Grass char	<i>n</i> -Hexane soot	Lignite coal	Bituminous coal	Green River shale	Melanoidin
550 °C A	28.3	15.6	19.3	27.9	3.4	45.0	22.6	82.0	3.7	45.1	0.2	0.4
550 °C B	28.1	15.4	19.0	27.8	3.2	47.6	23.4	80.9	4.8	45.9	0.3	0.2
550 °C C	27.2	14.7	18.7	28.0	3.5	47.3	21.6	84.8	4.3	47.0	0.3	0.5
Average	27.9	15.2	19.0	27.9	3.7	46.6	22.5	82.6	4.2	46.0	0.3	0.4
±1σ	0.6	0.5	0.3	0.1	0.7	1.4	0.9	2.0	0.6	0.9	0.1	0.1

Table 5
Replicate analysis for BC determination (BC/OC%) by dichromate oxidation for 7 days.

Replicate	Aerosol	Chernozem	Vertisol	Marine sediment	DOM ^a	Wood char	Grass char	<i>n</i> -Hexane soot	Lignite coal	Bituminous coal	Green River shale	Melanoidin
7 day A	32.3	6.7	3.4	12.9	–	64.1	8.4	39.9	0.2	70.5	5.9	0.0
7 day B	30.0	8.0	4.1	11.1	–	62.6	8.1	37.1	2.4	67.5	4.7	0.0
7 day C	30.7	6.5	3.3	11.5	–	67.9	10.2	40.5	1.8	66.6	6.4	0.0
Average	31.0	7.1	3.6	11.8	–	64.9	8.9	39.2	1.5	68.2	5.7	0.0
±1σ	1.2	0.8	0.4	0.9	–	2.8	1.2	1.8	1.2	2.0	0.9	0.0

^a Not measured by dichromate oxidation as zero value inevitable due to sample solubility.

Table 6
Uncertainty in the BC_{hypy} determination (BC/OC%) between 550 and 575 °C due to ongoing carbon degradation.

Temperature	Aerosol	Chernozem	Vertisol	Marine sediment	DOM	Wood char	Grass char	<i>n</i> -Hexane soot	Lignite coal	Bituminous coal	Green River shale	Melanoidin
550 °C	27.9	15.2	19.0	27.9	3.7	46.6	22.5	82.6	4.2	46.0	0.3	0.4
575 °C	26.2	15.1	18.3	27.7	3.6 ^a	39.1	19.8	80.0	4.4	42.3	0.3	0.4
Range	1.7	0.2	0.7	0.2	0.1	7.6	2.8	2.6	0.2	3.8	0.0	0.0

^a Analysis at 600 °C.

et al., 2007). Hypy was able to detect BC in both of the laboratory produced chars in contrast to the more aggressively harsh oxidation methods CTO-375, NaClO and MESTA (Hammes et al., 2007; Hsieh and Bugna, 2008), although the BC_{hypy} values reported for the chars were much lower than for the *n*-hexane soot, suggesting hypy under-detects BC with a relatively low degree of aromatic condensation. The hypy values are however significantly higher than those reported by CTO-375 for all of the environmental matrices, suggesting that hypy isolates a wider, more representative portion of the BC continuum as a whole, rather than being limited to just the most condensed forms of BC (Hammes et al., 2007).

There is no evidence of significant charring causing an overestimation of BC by hypy with near-zero BC_{hypy} values reported for melanoidin and the Green River shale, while the positive values for the two coals reflect the inertinite (ancient BC) content of the lignite, and the chemical similarity between high maturity coals and BC for the bituminous coal. BC_{hypy} determinations appear to be largely matrix independent (although pre-treatment is required for carbonate-rich samples), and together with previous studies showing complete conversion of lignocellulosic material (Rocha et al., 1999; Ascough et al., 2010) gives confidence that the BC_{hypy} values reported for the environmental samples do not show significant positive bias. The BC_{hypy} results are very similar to those from the UV photo-oxidation method for those samples rich in refractory soot-like BC such as the aerosol and *n*-hexane soot, and in common with the CTO-375 method hypy is able to discriminate between these, and samples with more labile char-BC contents derived from vegetation burning such as the two agricultural soils (Hammes et al., 2007). In addition, the BC_{hypy} values are noticeably lower than those from UV photo-oxidation for the chars, soils, and the interfering materials. This is consistent with previous results that suggest the “gentler” oxidative regime of UV photo-oxidation may result in methodological artifacts so overestimating the amount of BC in comparison with other methods, such as K₂Cr₂O₇ and NaClO oxidation (Simpson and Hatcher, 2004b; Hammes et al., 2007).

As no sample pre-treatment, with the exception of catalyst loading and decarbonation is required prior to hypy, BC determinations are not subject to losses during wet solution handling as previously described for methods such as CTO-375 (e.g. Elmquist et al., 2004), and evident in the results of dichromate oxidation in this study for samples such as the aerosol and *n*-hexane soot.

In addition to the isolation of a BC fraction, hypy also provides a means for the characterisation of the non-BC_{hypy} fraction of carbonaceous samples as described by Ascough et al. (2010). While the non-BC_{hypy} fraction from soils are likely to be dominated by the well documented products of decomposition of labile organic matter such as lignocellulosic material and humic acids, the analysis of products from samples such as biochars provide a means to characterise these materials with better preservation than typically encountered with more traditional pyrolytic methods.

The absence of a universally recognised structural definition of BC means that, hypy, in common with all other

Table 7
Elemental analysis of the chars, soot, bituminous coal and their hypy residues.

Sample	Fresh material ^a				550 °C Hypy residue					
	C (%)	H (%)	O (%)	Ash (%)	C (%)	H (%)	O (%)	Weight loss (%)	Ash (%)	Spent catalyst (%)
Wood char	68.2	4.0	27.1	0.5	80.2	3.0	1.5	62.6	1.2	17.4
Grass char	58.6	3.5	22.7	19.2	34.0	1.4	20.6	65.2	49.7	18.7
<i>n</i> -Hexane soot	89.8	1.4	8.5	3.5	84.6	1.1	2.5	21.9	4.0	8.3
Bituminous coal	91.0	4.4	2.0	4.7	73.6	2.8	5.1	50.8	8.7	13.2

^a Data for chars from Hammes et al. (2006); soot from Akhter et al. (1985) and coal from Vorres (1990).

available methods, cannot be claimed to isolate BC *per se*. Furthermore, as some carbonaceous material, especially high rank coals, contain large aromatic ring clusters that are chemically indistinguishable from highly condensed BC, it is clear that hypy, again in common with the other methodologies will not be able to isolate pyrogenic-derived BC from highly mature sedimentary organic matter. In addition, due to the requirement for mixing catalyst with the samples via solution it is clear that hypy is not ideal for analysing water soluble material, although high conversions were obtained for the DOM sample after methodological modification, other methods, especially BPCA appear to be more suitable for identifying BC components in solution (Hammes et al., 2007).

3.6. Composition and characteristics of the BC fraction isolated by hypy

In addition to quantifying the amount of BC in each sample by operationally defining BC_{hypy} to be that fraction which is stable under specific conditions (550 °C, 150 bar H₂), it is beneficial to characterise the isolated BC_{hypy} fraction to identify what part of the BC continuum is being defined as BC. Elemental analyses of the hypy residues from the BC-rich materials and the bituminous coal are listed in Table 7, with the atomic ratios of the starting materials and residues plotted on a Van Krevelen diagram (Fig. 6). As expected, hypy is shown to reduce the atomic H/C ratio of the residues, especially those of the wood and grass chars, to a maximum of 0.5. The *n*-hexane soot is less affected due to its inherent high aromaticity. This diagram also emphasises the chemical similarity of the bituminous coal to BC, and hence the difficulty in distinguishing modern “fire-derived” BC from highly aromatic high rank coals, with the H/C ratio of the coal hypy residue being identical to that of the wood char residue.

The aromaticity of the BC_{hypy} fraction inferred from an H/C ratio of <0.5 (i.e. >7 peri-condensed ring PAHs, with up to 24 carbon atoms) is consistent with the non-BC_{hypy} products composed of <7 ring PAHs, generated by hypy for 5 archaeological charcoals as described by Ascough et al. (2010). It would be assumed that the non-BC_{hypy} fraction of these samples will show a similar distribution of PAHs and be restricted in aromatic cluster size to 7 and fewer. The cleavage of small, pyrogenic PAHs from the macromolecular structure of BC by hypy will inevitably lead to the under-detection of BC from samples with a relatively low degree of aromatic condensation, such as low temperature chars. Pyrogenic PAHs with <7 rings however

have been found as the degradation products of BC in soils, rivers and marine systems (Dittmar and Koch, 2006; Hockaday et al., 2006, 2007). Therefore, the BC_{hypy} fraction, composed as it is of more highly condensed aromatic clusters is likely to be less susceptible to degradation, and so more recalcitrant in the environment than the total BC fraction of soils and sediments.

The O/C atomic ratios of the hypy residues are complicated by the oxygen content of the ash present in the samples. This is most apparent for the grass char, reported to contain 19.2% ash (Hammes et al., 2008), and the bituminous coal with 4.7% ash (Vorres, 1990). Assuming that the ash is unaffected by the hypy procedure, and allowing for the weight loss apparent at 550 °C (Table 7), the residues of these samples will contain approximately 50% and 10% ash, respectively. Most of the oxygen present in the residue is likely to be associated with the ash, especially the silica-containing phytoliths present in the grass char (Hammes et al., 2007), and alumino-silicate minerals in the bituminous coal (Vorres, 1990). By assuming that the carbon and hydrogen are associated with the non-ash

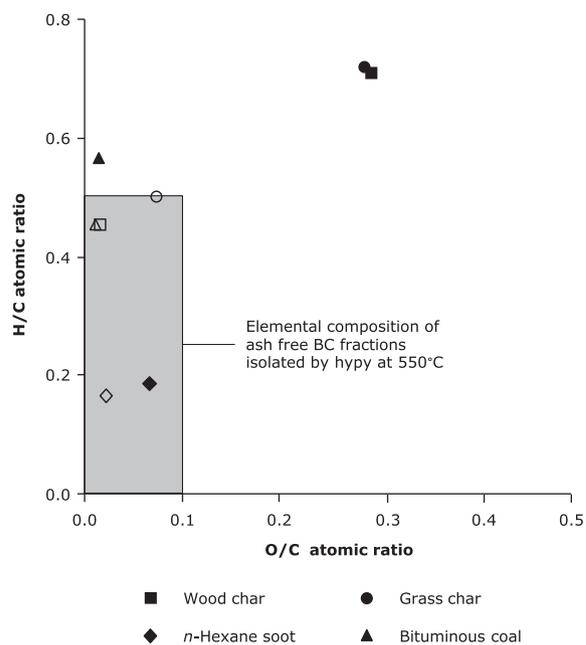


Fig. 6. Van Krevelen diagram showing the atomic ratios of the chars, soot, bituminous coal (closed symbols) and their hypy residues (open symbols). O/C values corrected for ash content of hypy residues.

fraction and then by calculating the O content of the hypy residues by difference on an ash, and spent catalyst free basis gives a maximum O content of 2% for the samples. Therefore, as shown on Fig. 6 we can assume that the true O/C ratios for the hypy BC samples are all <0.1. This is consistent with the archaeological charcoals reported by Ascough et al. (2010), who observed a reduction in the O/C ratio from between 0.09 to 0.37 for the fresh charcoals, to between 0.03 and 0.07 following hypy.

4. CONCLUSIONS

1. Reported BC_{hypy} values for all of the reference materials fall within the range of BC contents reported in the ring trial. Determinations are highly reproducible, with strong evidence that at temperatures above 550 °C non-BC organic matter is effectively removed from soils and sediments by hypy with minimal charring.
2. BC_{hypy} isolation appears to be largely independent of matrix effects, with the method providing good discrimination between potentially interfering materials, with the exception of the bituminous coal, as the high rank of this coal means the sample contains large aromatic ring clusters that are chemically indistinguishable from BC.
3. Hypy appears to discriminate between relatively labile biochars reporting low BC_{hypy} values, from more refractory, high BC_{hypy} soot in pure samples, and also between environmental samples from industrial sites with BC predominantly derived from the combustion of fossil fuels, and agricultural sites dominated by the burning of vegetation.
4. Previous studies (Ascough et al., 2010), have shown that the non- BC_{hypy} fraction of charcoals contains, in addition to non-BC organic matter, pyrogenic PAHs of <7 peri-condensed rings (of up to 24 carbon atoms), cleaved from the macromolecular char structure. Therefore hypy can be seen to discriminate against BC with a relatively low degree of aromatic condensation from lightly charred samples, such as biochars produced at relatively low temperatures.
5. Hypy does however appear able to isolate a relatively consistent portion of the BC continuum from a wide range of environments, which is comprised of poly-aromatic structures with >7 rings, and a H/C atomic ratio of <0.5. This highly condensed aromatic fraction will be very recalcitrant in the environment, and less susceptible to degradation as observed for smaller aromatic clusters.

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