



## Direct evidence from hydroxyprolysis for the retention of long alkyl moieties in black carbon fractions isolated by acidified dichromate oxidation

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### ABSTRACT

Chemical oxidation with acidified potassium dichromate is one of the more commonly used of a range of available methods for the quantification of black carbon (BC) in soils and sediments. There are potential uncertainties with this method however, with indications that not all non-BC material is susceptible to oxidation. An emerging approach to BC quantification is hydroxyprolysis (hyppy), in which pyrolysis assisted by high hydrogen pressure facilitates the reductive removal of labile organic matter, so isolating a highly stable portion of the BC continuum that is predominantly composed of >7 ring aromatic domains.

Here, results from the hyppy of the BC fraction isolated by dichromate oxidation (BC<sub>dox</sub>) from a BC-rich soil are presented, which demonstrated that 88% of the total carbon initially defined as BC was stable under hyppy conditions (defined as BC<sub>hyppy</sub>). More notably, hyppy allowed the non-BC<sub>hyppy</sub> fraction to be characterised. In addition to a number of PAHs, the non-BC<sub>hyppy</sub> fraction was also found to contain a significant abundance of *n*-alkanes, with a marked predominance of even-numbered homologues. These compounds are probably derived from lipids, hydrogenated during hyppy, which survived dichromate oxidation due to their hydrophobic nature. Hyppy of the dichromate oxidation residue from a sample of Green River shale, known to contain no BC of pyrogenic origin revealed that the significant apparent BC<sub>dox</sub> content (BC/OC = 5.7%) was also largely due to the presence of *n*-alkanes within the oxidation residues. The distribution of these compounds, biased towards longer chain homologues with no significant even/odd preference, indicated that they were largely derived from long *n*-alkyl chains within this highly aliphatic matrix.

Hyppy therefore provides compelling direct evidence for the incomplete removal of non-BC material by dichromate oxidation from both a BC-rich soil and a BC-free oil shale, with the molecular characterisation of the non-BC<sub>hyppy</sub> fraction allowing the potential sources of this material to be deduced.

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### 1. Introduction

Black carbon (BC), also known as pyrogenic carbon is the carbon-rich, recalcitrant product of the incomplete combustion of biomass and fossil fuels [1], that has both high aromaticity and high resistance to oxidative degradation [2,3]. An accurate and reproducible method for the quantification of BC is desirable if we are to assess its occurrence and stability in a range of environments. Currently a variety of thermal, chemical, spectroscopic, molecular marker and optical methods are used, which inevitably give a wide range of

results, as previously described in a number of BC inter-comparison studies [4–6]. As BC is typically isolated via operational, rather than chemical parameters, individual methodologies can only identify BC from a specific portion of the BC continuum, with no one method able to isolate or quantify BC across the whole range [5–7].

Chemical oxidation by acidified potassium dichromate is currently one of the most widespread methods employed for BC determination [2,8], as it requires little specialist equipment, with the BC content of the sample isolated due to its chemical recalcitrance relative to the more labile non-BC material [4]. However, the strong chemical oxidation procedures used to remove the non-BC material have been reported to attack BC, with the concomitant potential to underestimate BC [9]. While in contrast, there are also reports of oxidation residues containing non-BC, paraffinic structures, which would imply an overestimation of the true BC content [9].

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The chemical structure of BC residues (and potentially associated non-BC material) isolated by chemical oxidation with acidified potassium dichromate, chromic acid or sodium hypochlorite has been probed by a variety of analytical methods including  $^{13}\text{C}$  NMR spectroscopy [9,10], and pyrolysis-gas chromatography–mass spectrometry (Py-GCMS), either directly [11], or following thermochemolysis with tetramethyl ammonium hydroxide (TMAH) [12]. These studies have identified possible refractory alkyl moieties within the BC oxidation residues isolated from peat humic acids [12], soils [10], charcoals [9] and marine sediments [13]. Py-GCMS has also been employed to study the structure and degree of thermal alteration of range of pure BC materials such as charcoal, soot and biochar [14,15], although the technique has the known potential to promote the alteration of products cleaved from macromolecular structures [16].

An emerging pyrolytic approach for isolating and quantifying BC in soils and chars is hydroxyprolysis (hypy), in which pyrolysis assisted by high hydrogen pressure (150 bar) facilitates the reductive removal of thermally labile organic matter, with this primarily being converted into dichloromethane-soluble oil, leaving behind any refractory carbon as the residue [17]. The refractory fraction of thermally stable, highly aromatic carbonaceous material with an atomic H/C ratio of  $<0.5$ , is thought to be composed of peri-condensed aromatic clusters with  $>7$  rings (24 carbon atoms), and can be defined as the portion of the BC continuum which is stable under hypy conditions ( $\text{BC}_{\text{hypy}}$ ) [18]. The high hydrogen pressure and slow heating rate employed, together with the presence of a sulphided molybdenum catalyst, prevent the generation of secondary char [19] that is encountered with other chemical or thermal oxidative methods. It has been found that at a pressure of 150 bar, hypy conversions of labile carbon (defined as non- $\text{BC}_{\text{hypy}}$ ) close to 100% are achieved for immature type I and II kerogens [20], and biomass [21]. Tests on a selection of standard reference materials have found that a final hypy temperature of  $550^\circ\text{C}$  was best able to distinguish  $\text{BC}_{\text{hypy}}$  from potentially interfering materials, although, in common with other BC isolation methods not from a high rank bituminous coal which contained large aromatic ring clusters that are chemically indistinguishable from BC [18]. It was also observed that hypy differentiated between relatively labile biochars reporting low  $\text{BC}_{\text{hypy}}$  values from more refractory, high  $\text{BC}_{\text{hypy}}$  soot, in both pure samples, and when dispersed in environmental matrices, implying that it discriminated against the portion of the BC continuum that is composed of aromatic structures with a relatively low degree of condensation (average cluster size of  $<7$  aromatic rings) [18].

It has been shown that hydrocarbon products of the hypy of kerogens and sedimentary organic matter, especially those of relatively high molecular weight ( $>\text{C}_{10}$ ) are released in higher yields and with minimal structural rearrangement in comparison to traditional analytical pyrolysis methods such as Py-GCMS [19,22]. Therefore, as well as isolating a  $\text{BC}_{\text{hypy}}$  fraction for quantification, hypy also allows, following analysis by GC–MS, for the characterisation of the non- $\text{BC}_{\text{hypy}}$  material at a molecular level [23]. While hypy cannot characterise the  $\text{BC}_{\text{hypy}}$  fraction itself, once isolated, the composition of this fraction can be studied by methods such as elemental analysis and  $^{13}\text{C}$  NMR spectroscopy [18,23].

Here, we present results evaluating the potential of hypy for the isolation, quantification and characterisation of the  $\text{BC}_{\text{hypy}}$  and non- $\text{BC}_{\text{hypy}}$  fractions from two “BC residues” isolated by acidified potassium dichromate oxidation, including one from the Green River shale that was used in the International BC Ring Trial described by Hammes et al. [4], and has a BC content determined by dichromate oxidation significantly greater than that determined by hypy [18].

## 2. Methods

### 2.1. Samples

The sample of soil SS has described in detail by Song et al. [24], and is a yellow/brown coloured sandy soil (TOC = 1.55%), from a paddy field near to Guangzhou City, PR China. Prior to analysis the sample was air dried with plant debris removed, and sieved to  $<1.0$  mm. Due to the location of the sampling site near to the urban area of Guangzhou city, with the associated extensive use of fossil fuels and resultant high atmospheric particulate matter concentrations, this sample was thought likely to contain large quantities of coal and BC, as reflected in the very high  $\text{BC}_{\text{dox}}$  content determined by dichromate oxidation ( $\text{BC}/\text{OC} = 35.9\%$ ) [24].

The sample of Green River shale, is from the Mahogany zone of the Green River Formation, Utah, USA, and was supplied by the United States Geological Survey (Geochemical Reference Materials SGR-1). It was included in the International BC Ring Trial [4] as one of the non-BC containing interfering materials because, while it contains chemically resistant carbon including fused aromatic structures [25], these are not from pyrogenic sources [4]. It is a relatively immature lacustrine oil source rock of Eocene age, 45–43 Ma [26], with a high carbon content (27.2% TOC [4]). It was supplied as a fine powder, with no further processing undertaken.

### 2.2. Dichromate oxidation

The  $\text{BC}_{\text{dox}}$  fraction from soil SS was recovered as described in detail by Song et al. [24]. Briefly the sample (70 g) was first digested in a hot mixture of HF and HCl to remove mineral matter, followed by Soxhlet extraction in a mixture of methanol, acetone and benzene to remove the extractable organic matter. The residues were then extracted in NaOH to remove the humic acids, before acidified dichromate oxidation (0.1 M potassium dichromate, 2 M sulphuric acid, at  $60^\circ\text{C}$  for 60 h) to isolate the BC.

Acidified dichromate oxidation of the Green River shale was performed following the method of Bird and Gröcke [2], as described in detail by Meredith et al. [18]. Briefly, 100 mg aliquots (in triplicate) were mixed with 20 ml of acidified dichromate solution (0.1 M  $\text{K}_2\text{Cr}_2\text{O}_7$ , 2 M  $\text{H}_2\text{SO}_4$ ) and maintained at  $60^\circ\text{C}$  in an orbital incubator shaker for 7 days. When cool, 10 ml of methanol (HPLC grade) was added to promote sample sedimentation before sample recovery by centrifugation  $1600 \times g$ , 10 min [27]. After removal of the supernatant the samples were washed twice by centrifugation as described above. The samples were then re-suspended in 5 ml deionized water and stored at  $-20^\circ\text{C}$  prior to freeze-drying and subsequent elemental analysis.

### 2.3. Hydroxyprolysis

Hydroxyprolysis (hypy) tests were performed using the procedure described previously by Ascough et al. [17]. The dichromate oxidation residues described above were first loaded with 5% by weight of 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), to allow for the accurate weight loss during pyrolysis of each sample to be determined [18]. The samples were pyrolysed with resistive heating from  $50^\circ\text{C}$  to  $250^\circ\text{C}$  at  $300^\circ\text{C min}^{-1}$ , and then from  $250^\circ\text{C}$  to  $550^\circ\text{C}$  at  $8^\circ\text{C min}^{-1}$ , before being held at the final temperature for 2 min, all under a hydrogen pressure of 15 MPa. A hydrogen sweep gas flow of  $5 \text{ L min}^{-1}$ , measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor, and subsequently trapped on dry ice cooled silica [28].

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