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Comparative analysis of black carbon in soils

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Abstract. Black carbon (BC), produced by incomplete combustion of fossil fuels and vegetation, occurs ubiquitously in soils and sediments. BC exists as a continuum from partly charred material to highly graphitized soot particles, with no general agreement on clear-cut boundaries of definition or analysis. In a comparative analysis, we measured BC forms in eight soil samples by six established methods. All methods involved removal of the non-BC components from the sample by thermal or chemical means or a combination of both. The remaining carbon, operationally defined as BC, was quantified via mass balance, elemental composition or by exploiting benzenecarboxylic acids as molecular markers or applying ¹³C MAS NMR (magic angle spinning nuclear magnetic resonance) spectroscopy. BC concentrations measured for individual samples vary over 2 orders of magnitude (up to a factor of 571). One possible explanation for this wide range of results is that the individual BC methods rely on operational definitions with clear-cut but different boundaries and developed for specific scientific questions, whereas BC represents a continuum of materials with widely contrasting physicochemical properties. Thus the methods are inherently designed to analytically determine different parts of the continuum, and it is crucial to know how measurements made by different techniques relate to each other. It is clear from this preliminary comparative analysis that a collection of BC reference materials should be established as soon as possible 1) to ensure long-term intralaboratory and interlaboratory data quality and 2) to facilitate comparative analyses between different analytical techniques and scientific approaches

1. Introduction

Black carbon (BC), produced by incomplete combustion of fossil fuels and vegetation fires, is relatively resistant to degradation and occurs ubiquitously in natural environments, including soils, sediments, seawater, and the atmosphere [Goldberg, 1985]. BC exists as a continuum from partly charred plant material through char and charcoal to soot and graphite particles with no general agreement on clear-cut boundaries [Seiler and Crutzen, 1980]. BC can form in two fundamentally different ways. The solid residues of plant tissues form char BC, whereas volatiles formed within (and recondensed from) flames comprise highly graphitized soot BC. In recent years, increasing attention has been given to geochemical and biological studies of different forms of BC owing to their potential importance in a wide range of biogeochemical processes. As examples, BC may represent a significant sink in the global carbon cycle [Kuhlbusch, 1998a], affect the Earth's radiative heat balance [Crutzen and

Andreae, 1990], compose a useful tracer for the Earth's fire history [Bird and Cali, 1998], be a significant fraction of carbon buried in soils [Glaser *et al.*, 2000; Schmidt *et al.*, 1999; Skjemstad *et al.*, 1996] and marine sediments [Masiello and Druffel, 1998], and be an important carrier of organic pollutants [Gustafsson and Gschwend, 1997]. BC is presently studied in a variety of widely separated scientific fields, with the result that essentially no generally accepted analytical protocols, terminologies and conceptual approaches exist [Schmidt and Noack, 2000].

There is a need to obtain accurate and comparable analysis of BC in different matrices to study the environmental impacts of BC. In response to this need a symposium was held August 1999 during the Ninth International V. M. Goldschmidt Conference at Harvard University. The symposium was attended by ~50 scientists from diverse backgrounds in biogeochemistry, biology, and paleoenvironmental and the health sciences. As an attempt to stimulate analytical discussion, some laboratories took part before the symposium in a preliminary comparative analysis of BC in soils on a small suite of soil samples distributed by J. O. Skjemstad. The major goal of the comparative exercise presented here was to identify trends among several techniques for measuring different forms of BC in soils as a guideline for further development of analytical methods and reference materials.

2. Material and Methods

2.1. Soils

The eight Australian soils investigated for BC contents (Table 1) originated from the surface horizons of Vertisols, Mollisols, Alfisols, and Oxisols [Soil Survey Staff, 1994]. Total organic

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Table 1. Characteristics of the Investigated Australian Soils and Results of the BC Measurements^a

Soil	Location	Depth, cm	Soil Classification ^b	pH, H ₂ O	Clay Mass %	Inorganic Carbon, g kg soil ⁻¹	Organic Carbon, g kg soil ⁻¹	C/N, mass ratio	Var _{max} Between Methods ^c	Black Carbon Determined by Method 1-4 ^d					
										1-1	1-2	2-1	2-2	3	4
SS6	Tallagalla QLD	0-5	Hapludoll	6.6	47	0.2	70.5	11.6	38	52.8 ±27.6	1.46	5.8 ±0.3	9.2 ±0.4	37.2	1.4
Qld	Chinchilla QLD	0-10	Chromustert	5.7	52	<0.01	38.4	11.6	14	-	-	36.3 ±0.1	9.5 ±0.5	131.1	39.5
Buck	Kimba SA	0-10	Natrixeraif	7.7	22	1.0	15.8	9.9	220	47.0 ±0.5	1.08	29.3 ±3.2	13.8 ±1.4	44.8	101.1
SS7	Toowoomba QLD	0-5	Kandiustox	5.9	13	<0.01	143.0	19.9	220	41.8 ±2.2	0.69	16.7 ±1.3	7.1 ±0.2	89.7	151.6
URB-P	Adelaide SA	0-10	Rhodoxeraif	5.5	13	<0.01	26.7	9.9	16	-	-	23.4 ±0.3	13.7 ±1.1	64.6	212.7
B211	Toowoomba QLD	0-5	Chromustert	6.8	77	<0.01	34.3	10.7	38	-	-	6.3 ±0.8	7.0 ±0.9	109.0	239.8
Acu1	Gumeracha SA	0-10	Agrixeroll	5.1	18	<0.01	25.6	11.1	36	58.7 ±5.2	7.15	39.5 ±3.9	23.4 ±2.9	76.4	258.1
SS8	Toowoomba QLD	0-10	Pellustert	8.0	70	1.0	27.3	17.1	571	57.9 ±5.6	0.57	17.9 ±3.3	15.5 ±2.8	96.8	325.5

^a From *Sjogren et al.* [1999]; Abbreviations are as follows: QLD: Queensland, SA: South Australia. Dashes indicate data not determined. Standard deviation is indicated by ±

^b From Soil Survey Staff [1994].

^c Maximum variation between methods calculated as Var_{max} = largest value/smallest value determined for a sample.

^d See Table 2 for brief descriptions of methods 1-4. Values are given in g black carbon kg⁻¹ total organic carbon.

Table 2. Brief Outline of the Methods Applied ^a

Method	Methodological Approach	Pretreatment	Oxidation	BC Determination
1-1	Thermal oxidation no extraction ^b	sieved < 2 mm air dried	thermal oxidation 375°C, 24 hours	C,N-elemental analysis, mass difference
1-2	with extraction / hydrolysis ^c	identical	extraction/oxidation 1 x HCl (1N), 30 min, 20°C 2 x 10% HF + 1N HCl 12 h, 20°C 2 x TFA (2N), 3 hours, 100°C, 1 x TFA (4N), 18 hours, 100°C, 1 x TFA (6N), 18 hours, 100°C 1 x HCl (6N) 24 hours, 110°C, wash H ₂ O, dried thermal oxidation identical	identical
2-1	Chemical / thermal oxidation no HF ^d	sieved < 2 mm dried and ground 105° C dried and ground	extraction/oxidation 2 x NaOH, 1 x HNO ₃ (65%), 5 x NaOH, 1 x HCl, 2 x H ₂ O thermal oxidation 340° C, 2 hours in pure oxygen flow	C,H-elemental analysis, mass difference
2-2	with HF ^e	identical	extraction / oxidation identical, except: HNO ₃ (70%), 4 x NaOH, 1 x HF, 2 x H ₂ O	identical
3	chemical oxidation molecular marker BCA ^f	air dried, sieved < 2mm, ground extraction HCl (32%), 170° C, 4 hours pressure; filtered, wash H ₂ O, 40° C dried	chemical oxidation HNO ₃ (65%), 170° C, 8 hours pressure; filtered, washed with H ₂ O cation exchange; freeze dried	BCA as molecular markers via GC/FID
4	chemical oxidation UV - ¹³ C NMR ^g	air dried, wet sieved < 53 µm	chemical oxidation high energy UV-treatment demineralization HF (2%)	elemental analysis, mass difference, ¹³ C MAS NMR

Analyses were performed in the following laboratories: 1-1 and 1-2. School of Oceanography, Seattle; 2-1, Max-Planck-Institut für Biogeochemie Jena; 2-2, U. S. Environmental Protection Agency, Athens; 3, Soil Science and Soil Geography, Bayreuth; 4, CSIRO Land and Water Adelaide.

Abbreviations are as follows HF, hydrofluoric acid; UV, high energy ultraviolet oxidation; HCl, hydrochloric acid; HNO₃, nitric acid; BCA, benzenecarboxylic acids; NaOH, sodium hydroxide; H₂O, deionized water; TFA, trifluoroacetic acid; CP, cross polarization.

^a Numbers 1 to 4 correspond to those in text, Table 1 and Figure 1 GC/FID, gas chromatography/flame ionization detector; MAS, magic angle spinning; NMR, nuclear magnetic resonance.

^bFrom *Gustafsson et al.* [1997] modified.

^cFrom *Gustafsson et al.* [1997] modified with an extensive pretreatment by extraction/hydrolysis.

^dFrom *Kuhlbusch* [1995].

^eFrom *Kuhlbusch* [1995] modified.

^fFrom *Glaser et al.* [1998].

^gFrom *Skjemstad et al.* [1996, 1999].

carbon contents ranged between 15.8 and 143.0 g carbon per kg soil, with mass ratios of carbon-to-nitrogen varying between 9.9 and 19.9 and clay contents between 13 and 77%. Carbonate concentrations were low to undetectable.

2.2. Methods to Measure Black Carbon in Soils and Sediments

The principal geochemical approaches used to quantify BC in soils and sediments and a summary of the methods involved in this study, are presented below and in Table 2. A more detailed review of the various analytical approaches is given by *Schmidt*

and *Noack* [2000] and *Kuhlbusch* [1998b]. Analytical details of the methods involved here are available in the cited literature.

Analytical techniques for BC in sediments and soils basically attempt to differentiate between three forms of carbon, i. e., inorganic carbonates, thermally unaltered organic carbon (such as humic substances or plant material), and BC. The BC component itself can be separated into char BC and soot BC, the latter of which is characterized by the presence of highly condensed aromatic structures which are particularly resistant to oxidation. Methods for BC identification can be divided into 1) optical, 2) thermal, and 3) chemical categories and rely on the assumption that the three carbon classes can be distinguished by their optical

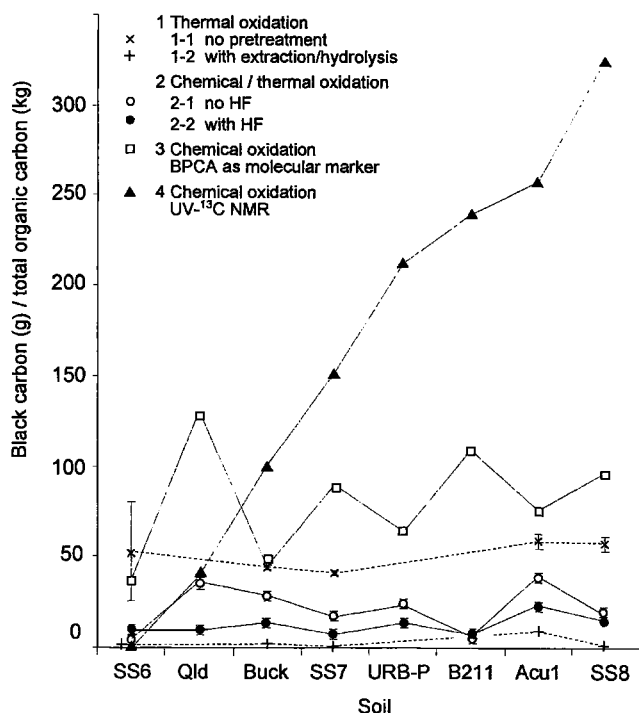


Figure 1. Measurement of black carbon (BC) by six methods and five laboratories. BC is expressed as a mass proportion of the total soils organic carbon. For clarity, samples have been ordered according to BC concentrations obtained by method 4, and data points have been connected by lines.

and chemical properties, volatility, and oxidizability. Violations of this assumption, however, vary in degree with sample composition and method and thus result in operational definitions. In our study on BC in soils, only thermal and chemical methods were included.

2.2.1. Thermal techniques. Thermal techniques typically rely on heating of a sample in air or oxygen. Thus organic carbon (OC) is volatilized or oxidized leaving BC in the sample. The remaining carbon can then be measured by a variety of sensitive methods. Quantification of the BC relies on the assumption that temperature conditions can be chosen to volatilize/oxidize other organic carbon while BC remains nonvolatile. Thermal methods, developed for atmospheric BC particles, are not always directly applicable to the complex matrices found in soils and sediments, which characteristically contain lower BC concentrations and may include closely associated organic matter that is not easy to volatilize or thermally degrade. In this study, we included a thermal technique (method 1-1 in Table 2 and Figure 1), where BC is defined as the fraction of the dried, sieved sample which survives exposure to HCl vapor and a subsequent thermal pretreatment at 375°C in air for 24 hours [Gustafsson *et al.*, 1997].

2.2.2. Chemical techniques. These techniques often involve removal of carbonates and silicates as a pretreatment step. To remove organic material, such as kerogen and humic substances, chemical oxidants (e. g., acid dichromate, nitric acid, hydrogen peroxide, and UV-activated oxygen species) are used, often in combination, and at different temperatures. The resistant carbon fraction can then be characterized by different methods. In this

study, we included combined chemical/thermal approaches (method 1-2, newly modified from method 1-1, and method 2-1, 2-2), a molecular tracer technique (method 3), and a UV-induced oxidation followed by spectroscopic analysis (method 4). Method 1-2 combines chemical extractions/hydrolysis and thermal oxidation, i. e., sequential removal of carbonates (1N HCl), silicates (HF), carbohydrates (trifluoroacetic acid), and residual protein material (6N HCl). Method 2 also relies on a combined chemical/thermal oxidation. Mass, carbon, and hydrogen contents are determined after several treatments, i. e., NaOH and HNO₃ extraction, removal of carbonates by HCl and silicates with HF, followed by a thermal (340°C) treatment for 2 hours [Kuhlbusch, 1995]. We called this method 2-2, whereas the identical method without the HF treatment is referred to as method 2-1. Method 3 exploits benzenecarboxylic acids (BCA) as molecular markers for the presence of BC, assuming a constant BCA/BC mass ratio [Glaser *et al.*, 1998]. The production of these compounds by high temperature and high pressure oxidation with HNO₃ is quantified after derivatization and gas chromatographic analysis. Method 4 relies on a high-energy UV photo-oxidation of soil particles suspended in oxygen-saturated water [Skjemstad *et al.*, 1999] to oxidize non-BC components prior to analysis of the fraction of non-lignin aromatic carbon by cross-polarization magic-angle-spinning (CP/MAS) ¹³C NMR spectroscopy.

3. Results and Discussion

The BC concentrations measured by six different techniques are summarized in Figure 1 and Table 1. There we report BC concentrations as a mass percentage of the total organic carbon.

Thermal oxidation (method 1-1) resulted in BC concentrations exhibiting only small differences between samples compared to the other methods. Concentrations varied between 41.8 and 58.7 g BC kg⁻¹ soil C as measured for five of the eight samples. When combined with extraction/hydrolysis (method 1-2) as a pretreatment, measured concentrations of BC were lower by factors of 8–10. Chemical / thermal oxidation (method 2) produced small yields of BC (5.8–39.5 g BC kg⁻¹ soil C), with more variation in BC concentration than with thermal oxidation (methods 1-1 and 1-2). We ran this method similarly in two laboratories, except for a final demineralization step (HF) before thermal oxidation. This HF treatment produced a slight offset to lower concentrations, except for samples SS6 and B211. Method 3, using the detection of BCA as molecular tracers, often resulted in higher BC concentrations (37.2–109.0 g BC kg⁻¹ soil C) than the methods discussed previously, and also differences between the samples were larger. High-energy UV photo-oxidation (method 4), combined with elemental analysis and ¹³C NMR spectroscopy, showed the largest differences between samples and also measured the widest range of BC concentrations in this set of samples (1.4–325.5 g BC kg⁻¹ soil C).

Overall BC concentrations measured by the six methods varied (i. e., between factors of 14 and 571) between individual samples and did not reveal systematic offsets between methods. Thus correlating results between methods are very difficult. However, a trend for methods 1 and 2 is that measured BC concentrations generally decreased with increasing intensity of chemical attack prior to elemental analysis. That is, BC values are highest if the sample is only heated (375°C / 24 hours), intermediate when samples are extracted several times with acids and bases before heating (340°C / 2 h), smaller yet again when

samples were additionally demineralized (HF) before heating, and smallest when additional hydrolyses were carried out following demineralization.

Although the number of samples and methods compared is small, one possible explanation for these variable results is that the compared methods measure different fractions of the BC continuum. A contributing factor may be that the associated matrix interferes with the analysis of BC. For example, thermal treatment of untreated samples may generate a reducing atmosphere inside mineral-associated organic components, which then form BC artifactually to different extents, depending on mineralogy, particle composition, and geometry. Many methods for measuring BC in the presence of other organic materials rely on the resistance of the highly aromatized components of BC to extremely oxidizing conditions, produced either thermally or chemically. To gain specificity against other organic materials present in soils, many methods provide correspondingly conservative measures of BC, and therefore probably overlook much of the combustion products present. If UV photo-oxidation (method 4) is less severe than other types of oxidation, this could explain the larger BC concentrations typically determined by method 4.

4. Conclusions

The comparative analysis of black carbon (BC) in eight soil samples by six methods has clearly demonstrated the need for improved measurement and definition by the present community of scientists addressing the BC component in soils and probably also sediments. BC was determined by separate laboratories each using their method of expertise. Values measured had a range over 2 orders of magnitude. Differences varied by factors between 14 and 571, with no systematic methodological or interlaboratory offsets detectable unambiguously.

Basically, the problem leading to the observed differences in results obtained by the various methods is that BC exists as a continuum of thermally altered material, whereas many methods rely on operational definitions with clear-cut but different boundaries. Within the continuum, the analytical windows of individual methods strongly depend on the objectives of a particular study (e. g., quantification of BC for carbon cycling in soils, reconstruction of fire history), and vary with the associated matrix (soil type, sedimentary environment). At present, very little is known about the comparability of the chemical and physical properties of the BC components measured by the individual methods. Systematic comparative analysis on well-defined standard materials could help immensely to circumvent these problems and allow a better understanding of what is actually being determined by the different methods and how these results relate to each other, ultimately leading to more accurate measurements of BC in soils and sediments.

At present there are no reference BC samples widely available for interlaboratory comparison or instrument stability tests nor is there a consensus on how such samples might best be prepared and preserved. Overall, it is clear from this preliminary exercise that a collection of BC reference materials should be established as soon as possible to facilitate their comparative analysis by a range of commonly used techniques in a number of different laboratories. These efforts will provide a more thorough understanding of what is actually being determined by different BC methods and the impact of different matrices on these

methods. We would suggest that ultimately such an understanding would lead to improved methodological designs for BC analytical techniques.

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