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EXPLORATORY WORKSHOP**

**Charcoal to Black carbon:
defining common issues of quantification and
interpretation in archaeological, palaeoenvironmental
and carbon cycle research**



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Convened by:
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List of abstracts for oral presentations

Arranged alphabetically by first author

Fate of black carbon in arable soil environment

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Mollisols are known to contain stable, black humus components which originate from charred or coal-derived particles. As such black carbon (BC) significantly affects soil fertility and interferes with models on soil organic matter dynamics, an accurate prediction of BC input into soils and an elucidation of the mechanisms of BC turnover is essential. Our main aims were (i) to identify, localize and quantify BC in different native and arable Mollisols of the world, (ii) to reconstruct BC origin, and (iii) to elucidate the mechanisms affecting BC decay. After fractionation of soil from adjacent native and cultivated sites into particle-size and aggregate-density pools BC was characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX). Benzenepolycarboxylic acids (BPCA, revised method) served as specific molecular BC markers, the sources of which having been characterized using compound-specific natural ^{13}C and ^{14}C abundance measurements. For the assessment of the stability of BC, a long-term incubation experiment was performed.

The SEM/EDX analysis identified BC as particles of low O/C ratio. Its morphology was not specific for a given soil fraction but indicated different BC sources that were variably distributed among the soil C pools. Determination of benzenepolycarboxylic acids confirmed that especially the Chernozems were rich in BC, which partly contributed up to 20 % of total C, most of which being allocated in the mineral fractions. Arable cropping did not reduce the BC contents of the surface soil, though promoted the enrichment of BC in the silt fractions. Compound-specific radiocarbon measurements showed that for East German sites a significant part of black carbon (about 60% in the surface soil of Halle) was of fossil origin; with major fossil C inputs originating from the last 30 years. This fossil BC, however, was not stable but incorporated into soil humus. Incubation experiments revealed that initial BC decay was rapid and promoted by additional C substrates, however, that BC could not be assigned to one single, stable C pool. Instead there is increasing evidence that surface oxidations of BC promote chemical interactions of BC with the mineral phase; a significant fraction being even embedded of into micro-aggregates. Both chemical interactions and physical entrapment contribute, therefore, to a stabilization of the various soil BC forms in the long-term run.

The stability of charcoal in natural environments

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This paper will discuss accumulating evidence from different projects suggesting that charcoal can undergo significant alteration/degradation in at least some surficial environments on comparatively short timescales;

(i) preservation of charcoal in savanna soil

The Matopos fire trial, conducted in a fire-prone savanna region in Zimbabwe, provides an opportunity to examine variations in the abundance of oxidation-resistant elemental carbon (OREC) in a coarse-textured savanna soil. Separate plots at this site have been subjected to burning with one, three and five year return intervals or protected from burning over the last 50 years. The total 0–5 cm OREC inventory of the soil protected from fire is estimated to be $2.0 \pm 0.5 \text{ mg/cm}^2$, which is approximately half the “natural” OREC inventory at the study site of $3.8 \pm 0.5 \text{ mg/cm}^2$ (the mean for plots burnt every 1–5 years). The associated half-life for natural OREC loss from the 0–5 cm interval of the protected plots is calculated to be <100 years, with the half-life for large carbonized particles (>2000 μm) in the soil being considerably less than 50 years. Abundance and carbon-isotope data suggest that OREC in coarse particles is progressively degraded into finer particle sizes, with an increase in resistance to oxidative degradation of OREC in the finer particle sizes due to the progressive loss of more readily degraded material.

(ii) preservation of charcoal at the Nauwalabila I archaeological site

A detailed study of charcoal from this archaeological site in the Northern Territory, Australia, suggests that macroscopic charcoal below 110cm in the sandy sedimentary sequence has undergone a variable, but in places, severe degree of alteration. This alteration is thought to have occurred during a period of elevated groundwater table at the site during the early Holocene. Evidence for degradation is found in the morphological characteristics of the charcoal as well as in aberrant CN ratios, radiocarbon activities and stable carbon isotope composition.

(iii) behaviour of charcoal during pretreatment for radiocarbon dating

Over the last five years several hundred samples of archaeological charcoal have been radiocarbon dated using a new analytical protocol called ABOX-SC (acid-base-oxidation stepped combustion). The resistance of charcoal to dissolution/oxidation during this procedure is highly variable. Part of this difference may relate to the nature of the original charcoal but currently ‘anecdotal’ evidence suggests, for example, that charcoal from alkaline cave environments is particularly susceptible to dissolution/oxidation. This in turn suggests that it is the environmental conditions and not the intrinsic characteristics of the charcoal that has determined the chemical stability of the charcoal.

Radiocarbon dating of black carbon

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Radiocarbon, with a half life of 5,730 years, is an important tool in black carbon research. It can be used for dating, to determine rates of processes and to identify and quantify sources of carbon. Since a main objective of the workshop focuses on bringing together the different black carbon research areas, this presentation covers applications of radiocarbon across the often disparate black carbon research areas and discusses issues of sample preparation and standards for radiocarbon analysis common to many of the applications. A simple two-component mixing model is applied to radiocarbon data from soil-derived PAHs and used to distinguish and estimate PAHs from fossil-fuel (^{14}C free) and biomass burning (contemporary atmospheric ^{14}C) sources. Development of internationally accepted sample preparation techniques and reference materials for carbon isotopic measurements has been recognised as an essential facet in advancing black carbon research. Radiocarbon contributes to refining carbon cycle research, by enabling determination of carbon turnover rates eg in soils and quantifying the transfer of carbon from the terrestrial to freshwater, estuarine and marine environments. Problems being addressed include the stability of black carbon in the environment and apparent losses and/or underestimates in the black carbon budget between the different systems. Preparing black carbon samples for ^{14}C analysis to provide chronologies for palaeoenvironmental reconstruction (eg for lake sediment cores, volcanic eruptions) present some challenges. For example, optimising pre-treatments or determining suitability of material for analysis are not currently straightforward but are likely to evolve as understanding the characteristics of black carbon and its formation and transport improves. Radiocarbon analysis can contribute to this research via a wide variety of applications. Co-evolving technique development in the preparation and analysis of samples by ^{14}C AMS, particularly for small samples, will also be important.

Modern and Fossil Charcoal: Aspects of Structure and Diagenesis

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The structures and compositions of modern and fossil charcoal samples were compared in order to evaluate charcoal degradation processes in archaeological sites. Modern charcoal samples produced in camp fires contain two major phases: graphite-like microcrystallites and a non-organized phase. These phases create a mosaic-like structure with differing relative proportions depending on the taxonomic source of the wood used. Fossil charcoal samples (Tel Dor, Israel: 3000 years BP and Kebara cave, Israel: around 50 to 40,000 years BP) also contain the graphite-like microcrystallites and the non-organized phases, but are clearly altered compared to modern charcoal. The graphite-like phase of the fossil charcoal has greatly reduced electrical conductivity, and its ESR properties show that it has markedly altered surface electronic states. Infrared spectra show the presence of additional carboxylate groups. Oxidation has therefore altered the structure. A “self-humification” process has appeared to alter the graphitic component, and probably the non-organized phase as well.

Why are there no black soils in the boreal region?

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Boreal forests are frequently impacted by lightning-induced fires. Although most fires today are human-caused and occur in tropical savannas, the biomass burnt in boreal and temperate ecosystems accounts for about 4% of global burnt biomass in normal fire years and 12% in extreme years.

The frequencies of fires in many parts of the boreal region are expected to rise. Temperatures in the northern continental regions are increasing faster than in other regions of the globe. Air temperatures during winter and spring have increased by 0.2 to 0.3°C over the last 4 to 5 decades. This temperature rise is drying vegetation and soils, creating fuel, and increasing the turbulence of the atmosphere and thus lightning storm frequency. There are also indications that fire frequencies will increase at the southern border of the boreal forest as the region warms and the grassland and agriculture belt shifts northwards.

Despite frequent fires, black carbon (BC) is not a significant component of soil organic matter in boreal soils, but in Mollisols, some Andisols, and a type of human-altered Ultisols called Terra Preta de Indio. In soils where BC storage is occurring, it can be up to 35% of soil organic carbon (depending on measurement technique). The absence of BC in boreal soils is a major clue to the mechanisms controlling BC storage in soils.

We present a conceptual model of BC storage in soils, based on the idea that the accumulation of BC in soils requires that both input and protection be maximized. Soil chemistry and BC chemical structure further control the function and movement of various BC types in soils.

In the case of boreal forests, the production rates of BC are low, because the fuel (bryophytes) mainly consist of non-aromatic precursors (carbohydrates) and fire temperatures are often low (smoldering combustion). And, it seems that the removal rates of BC are high, with the dominant process being combustion by fire due to very low rates of (bio-)turbation.

Radiocarbon dating of charcoal at Theopetra Archaeological site

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The cave of Theopetra is located on the NE side of a limestone rock formation, 3 km south of Kalambaka (21° 40' 46'' E, 39° 40' 51'' N), in Thessaly, central Greece. It is a unique prehistoric site for Greece, as the Middle and Upper Palaeolithic, Mesolithic and Neolithic periods are present here, bridging the Pleistocene with the Holocene (Y. Facorellis *et al.* 2001).

During the eighteen years of excavation, evidence of human activity, such as charcoal samples from hearths and bones from the two human skeletons, suitable for ¹⁴C dating was collected. The samples were dated in the Laboratory of Archaeometry of NCSR "Demokritos". The removal of any carbon compounds of non-archaeological origin was performed using the ABA conventional chemical pre-treatment (Longin 1971, Olsson 1979, Mook and Streurman 1983, Brown *et al.* 1988, Hedges and Law 1989, Arslanov and Svezhentsev 1993, Facorellis 1996).

After the chemical pre-treatment the samples were converted to CO₂ using the de Vries continuous combustion technique (de Vries and Barendsen 1953, Facorellis 1996). Then the produced CO₂ undergone several purification steps and finally it was measured inside cylindrical gas proportional counters (Facorellis *et al.* 1997). The laboratory possesses 8 such counters, four with a capacity of 4 lit and four with 2.5 lit. The smaller amount of ¹⁴C that is possible to be detected by these counters corresponds to an age of about 50,000 yrs BP (Facorellis and Maniatis 1999). This fact is particularly important, as it allowed the dating of samples originating from all the layers of the Theopetra cave, which cover all the age ranges of the radiocarbon dating method.

The sixty radiocarbon-dated samples, originating from 19 pits and from depths ranging from 0.10 m to 4.20 m, which were dated, gave an absolute time framework for the use of the cave. According to the ¹⁴C results, the earliest limit of human presence probably exceeds 48,000 years BP and the latest reaches the 2nd World War. Within these limits the ¹⁴C dating of samples from consecutive layers, in combination with the archaeological data, permitted the resolution of successive anthropogenic and environmental events such as alternations of the climate during the Pleistocene (Karkanis 2001).

However, ten burnt flint specimens unearthed in the II4 layer, corresponding to the lower part of the Middle Palaeolithic sequence of Theopetra cave, which have been dated by the TL method gave ages ranging between ca. 110 and 135 ky ago (Valladas *et al.*). This result is in disagreement with the technotypology of lithics (Panagopoulou, 2000) and the ¹⁴C dates, which support a much later date for the middle Palaeolithic layers.

In order to clarify the situation further ^{14}C dating of hand-picked charcoal fragments using the ABOX pretreatment and analytical protocol has been scheduled in collaboration with the Oxford Radiocarbon Accelerator Unit.

Pyrolysis GC/MS applications in black carbon research

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Pyrolysis is defined as the breaking apart of large molecules into smaller ones using only thermal energy. The combination of a pyrolysis with separation and detection techniques of the degradation products is known as analytical pyrolysis that enable qualitative investigations of the molecular building blocks of organic matter (OM) and relative quantitative assessments of their proportions and thermal stability in samples of similar origin.

Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) is used routinely to analyze complex substances such as tyre rubber, textiles, paint, glue, paper coatings, petrochemical sources, plant materials, coal, bacteria, and the whole range of synthetic polymers (Wampler, 1999). At our lab, this and other pyrolytic techniques have been used for many years to study the structural features of OM in a number of matrices. Part of our investigation has been focused to the study of stabilized forms of OM in soils and sediments, namely humic acids, humins and kerogens (González-Vila et al., 2001b,c; Martín et al., 2001) and more recently to Black Carbon (BC) forms present in soils, sediments and formed “de novo” during forest fires (González-Pérez et al., 2002, 2004; González-Vila and Almendros, 2003; González-Vila et al., 2001a, 2002; Kénéa et al., 2005; Knicker et al., 2005).

Black carbon is understood as a continuum from partly charred plant material through char and charcoal to graphite and soot particles condensed from the gas phase (Hedges et al., 2000; Masiello 2004). As biomass is charred aryl and O-aryl structures (aromaticity) increases with a concomitant loss in carbohydrate and lignin structures (Baldock and Smernik, 2002). The micromorphological and chemical features of this refractory material are described in Schmidt and Noack (2000), Poirier et al. (2000, 2002), Kénéa et al. (2005). It behaves as a highly aromatic material and, in the case of that formed by vegetation fires, often consists of randomly oriented stacks of few graphitic layers. In any case, the final BC produced is not necessarily graphitic, and this black material, even when completely amorphous, contains a substantial alkyl domain and a considerable oxygen content (endocyclic or lactone-like) (Poirier et al., 2002; Almendros et al., 2003; Kénéa et al., 2005).

BC take part in a variety and relevant environmental processes; BC affects earth climate through its light-absorbing effect, it is part of the “missing carbon” in the global carbon balance (Gustafsson and Gschwend, 1998 and references therein) and is also a carrier-phase of

pollutants playing a key role in the sorption of contaminants including PAHs (Cornelissen et al., 2005).

Among BC components are polycyclic aromatic hydrocarbons (PAHs). There are three sources of PAHs: combustion of organic matter (pyrogenic), petroleum (petrogenic), and natural sources. While local areas can be impacted by petrogenic PAHs, combustion of organic matter is the largest source of PAHs to the environment with natural sources of PAHs limited to only a few compounds (retene and perylene). We may consider that Pyrolytic PAHs include all parent compounds other than retene and perylene, having MW>178. Alkylated homologue compounds are derived from fossil sources (fossil PAHs) (Brassell and Eglinton, 1980; Soclo et al., 2000; Killops and Killops, 2005). We may also consider that PAHs found in the BC matrix may have a constituent origin or being sorption or inherited products.

Although with limitations inherent to the technique, analytical pyrolysis is a valuable tool to identify a wide range of thermolabile components directly from BC containing matrices i.e. alkylic and aromatic hydrocarbons including PAHs (Fig. 1). Relevant molecules containing heteroatoms are also amenable by pyrolysis (Fig. 2).

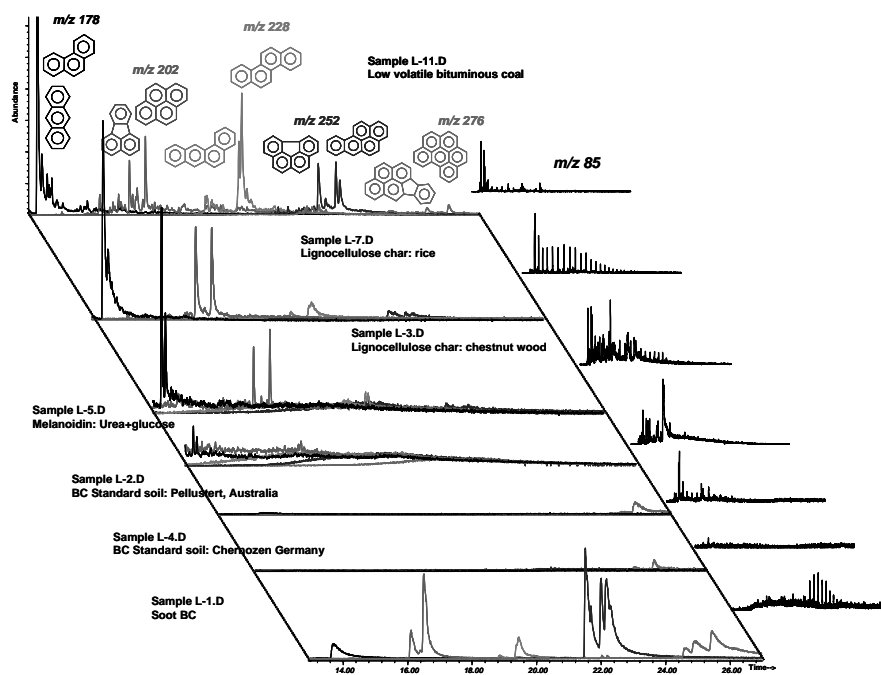


Fig. 1. Pyrograms of BC Ring Trial selected reference materials: SIM traces for pyrogenic PAHs (m/z 178, 202, 228, 252, 276) and alkylic compounds (n -alkenes).

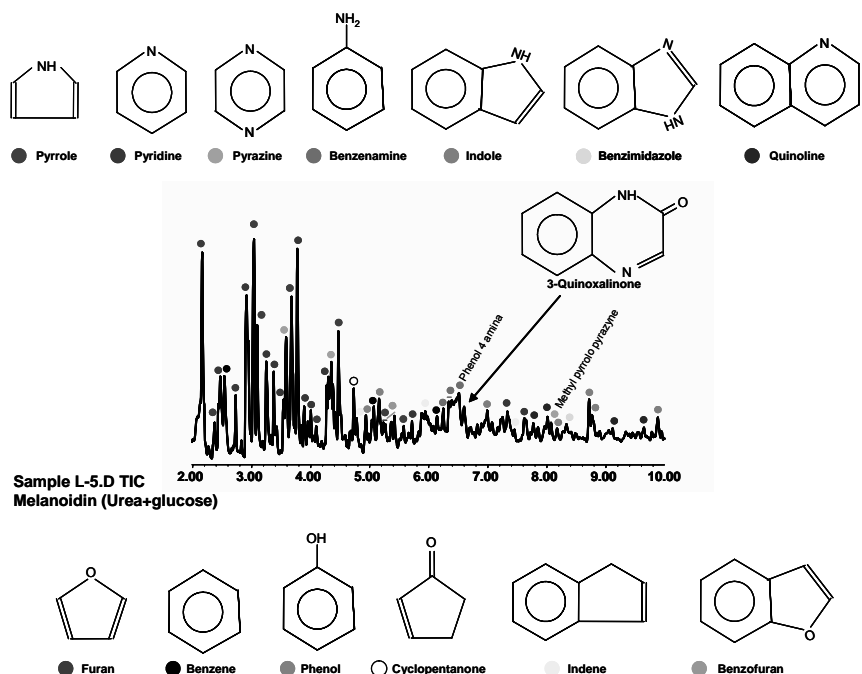


Fig. 2. Total Ion Pyrogram of BC Ring Triol Pseudomelanoidin (Urea+Glucose) reference material.

In general Py-GC/MS results provide valuable and complementary information to other analytical techniques like ^{13}C and ^{15}N NMR and when used in combination is allows the detection of molecular markers and the elucidation of relevant structural features in such materials (Fig. 3).

Apart from the direct pyrolysis, it is also possible to perform this technique in the presence of alkilant salts like tetramethylammonium hydroxide (TMAH) providing detailed structural information on building blocks of natural macromolecules without the application of any extraction procedures. The TMAH-thermochemolysis technique hydrolyzes and methylates ester and ether linkages, and assists in the depolymerization and methylation of lignin (Fillee et al., 1999). TMAH-thermochemolysis overcomes the limitations of conventional pyrolysis products because it assists in converting polar products to less polar derivatives that are more amenable to chromatographic separation. Moreover, this procedure avoids decarboxylation and produces the methyl esters of carboxylic acids and methyl ethers of hydroxyl groups, rendering many of the polar products volatile enough for GC analysis (Chefetz et al. 2002, and references therein) (Fig. 4).

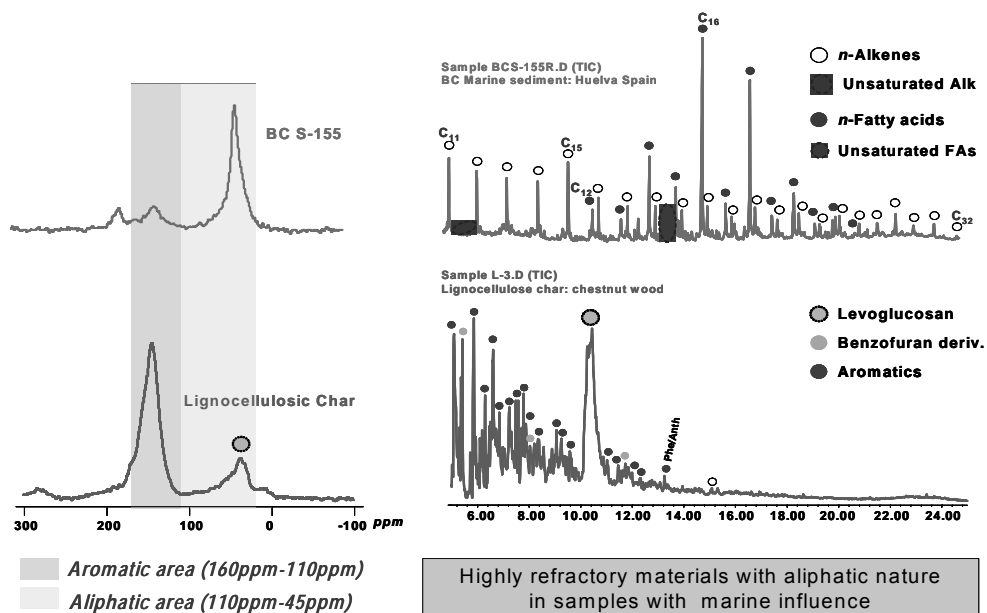


Fig. 3. Solid State ^{13}C NMR spectra and Py-GC/MS pyrograms of a BC sample isolated from a marine sediment (Huelva, Spain) and a BC containing reference material (BC Ring Trial charred chestnut wood).

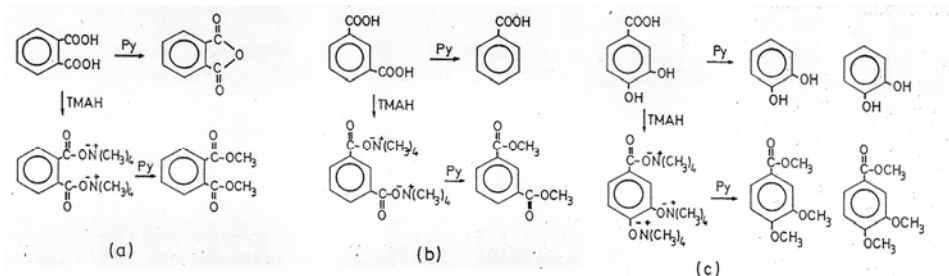


Fig. 4. Mechanism of benzenecarboxylic acids pyrolysis in the absence and the presence of TMAH.

This technique has been used to characterize resilient organic matter (Martín et al., 1995, 2001; Fabbri et al., 1996; Hatcher and Clifford, 1994; González-Vila et al., 2001b), cuticular resilient plant materials (del Río and Hatcher, 1998; McKinney et al., 1996), and more recently as a complementary tool to analyze biomarkers in kerogens (Almendros et al., 1998; González-Vila et al., 2001c), fossil remains (Almendros et al., 1999) and BC containing sediments (Simpson et al., 2005) (Fig.5).

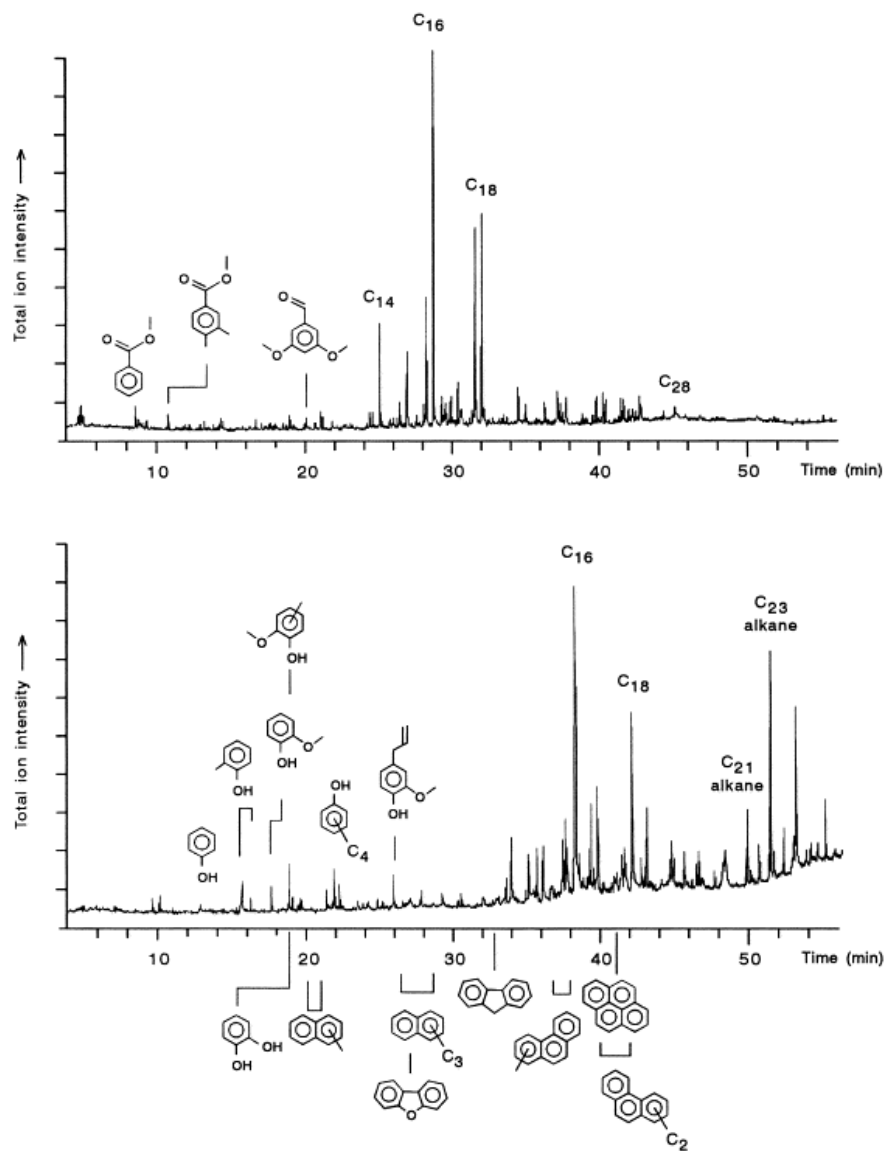


Fig. 5. Total ion chromatograms of the pyrolysis products from Miocene remains of *Glyptostrobus europaeus*; thermochemolysis with TMAH (top) and conventional Curie Point pyrolysis (bottom). (From Almendros et al., 1999).

These and other examples about the use of analytical pyrolytic techniques to BC structural features and dynamics will be discussed during the meeting.

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Further testing and application of the chemothermal oxidation approach to the study of BC in marine sediments

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Black Carbon (BC) is a relatively inert and ubiquitous form of condensed organic matter produced by incomplete combustion of a variety of fossil fuel and biomass materials. Despite the myriad of important roles played by BC, ambiguity persists as to the level of BC in complex matrices, such as aquatic sediments, as parallel comparison of different methods yields highly variable results. Method artifacts that obviously would return inaccurate results include organic matter charring (overestimation) and losses of hydrophobic soot-BC during solution handling or combustion (underestimation). It is also possible that different methods simply probe different forms of BC as BC particles exist as a continuum from partly charred plant material through char and charcoal to soot and graphitic-like particles, with expected differences in recalcitrancy.

Laboratory tests of the different analytical approaches have provided significant insights and are one central tenet in moving the field ahead. A complementary approach is to assess real BC field data within the auxiliary geochemical framework of the studied regime. Estimates of the BC concentration in real environmental samples based on the chemothermal oxidation (at 375°C) CTO-375 method (Gustafsson et al., 1997, 2001) were scrutinized for consistency with additional geochemical and environmental data collected simultaneously.

The field tests assessing geochemical consistency of obtained BC results include:

- (i) Comparison of BC analyses in chronologically-constrained sedimentary archives with knowledge of society's varying energy budgets in the source area
- (ii) Correlation analysis of the spatial distribution patterns of molecular combustion markers (e.g., PAHs, PCDD/Fs) and analyses of BC (compared with TOC)
- (iii) Ability of BC analyses to quantitatively explain the solid-water and solid-air distribution of PAHs given knowledge of BC sorption coefficients
- (iv) Natural abundance ^{14}C data of BC isolates compared with ^{14}C data of TOC and ^{14}C data of the molecular combustion markers such as pyrogenic PAHs

Problems with radiocarbon dating charcoal from archaeological sites

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Charcoal is one of the more common material types dated in archaeology. In Oxford, however, the vast majority of archaeological AMS determinations are of bone (65%+) or other proteinaceous materials (eg horn, keratin, hair, skin, leather, parchment). Charcoal is rather less commonly dated (between 15-20% of all samples) because in general bone dates archaeological events more accurately, since in many cases it is the actual event (eg the human body or the cut-marked bone).

Three factors contribute to the reliable AMS dating of charcoal/black carbon. First, the composition of the charcoal and whether it will accurately date the archaeological event. If the charcoal is of a long-lived species of wood there is a reasonable chance it will produce a date that is offset to the archaeological event by a non-systematic, but always older, amount. The analysis of wood species is crucial, but rarely undertaken in many contexts. Its importance is reduced as the sample to be dated becomes older. Second, contamination. Since charcoals have a large surface area, extensive environmental contamination is possible in some circumstances. Most radiocarbon laboratories implement a routine acid-base-acid (A-B-A) pretreatment designed to remove carbonate and humic/fulvic contaminants. This is assumed to remove the majority of contaminants, but will not in all cases. Novel pretreatment methods developed recently attest to the fact that for samples >5 half-lives, this assumption is often unwarranted. Finally, there is the question of the taphonomy and post-depositional characteristics of the site or context. This crucially depends upon the archaeological interpretation of the site and can never really be known. This will only be touched on briefly here.

A range of techniques appears to offer promise for screening potentially unreliable charcoal/black carbon samples for AMS dating. These include the type of analytical data already routinely collected in radiocarbon facilities including ORAU such as %C, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C-N ratios. Data concerned with this will be presented in the paper and case studies used to illustrate various points.

Humification and Stability of Charcoal in Soil

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Wildfires result in considerable portions of severely or partly charred necromass which are incorporated into the soil. Due to the refractory nature of such thermally-condensed products, they are assumed to increase the passive soil organic carbon pool. However, measurements of black carbon (BC) production and loss processes are not balanced. In situ degradation, erosion but also translocation within the soil profile may be responsible for the obvious BC loss.

To study the impact of forest fires on soil organic matter (SOM) quantity and quality, burnt and control soils from various forest ecosystems in Spain and Southern Portugal were analyzed by organic elemental analysis and solid-state nuclear magnetic resonance (NMR) spectroscopy. Soils were probed one to twenty years after the fires. Also sites affected by two fires within two years were included.

For an Arenosol derived from the coastal area in Southern Portugal, already one year after the fire, a considerable amount of charred residues was incorporated into the Ah horizon, whereas the litter layer predominantly consisted of fresh plant litter lost from the decaying trees. Its sandy texture offers only few reaction sites for organic matter adsorption which could contribute to stabilization of charred residues. This explains why most of the charred residues were recovered with the particulate organic matter (POM) and dissolved organic matter (DOM) fractions. After rainfall, these fractions can easily be translocated with the infiltrating water and thus can contribute to a relative enrichment of aromatic structures from charred residues in deeper horizons. Oxidation of those compounds prior to transportation increases the solubility and the formation of colloids which facilitates this process.

Although the fire enhanced the aromatic C content in all studied soils, there was no common pattern with respect to fire-induced changes of the size of the SOM pool. Comparing single and double-burnt sites, no additional char input was observed for the double-burnt site, possibly because of complete combustion of young shrubs and char remains during the second fire. The high O-alkyl C portion found for the additional C accumulated after the fire (C_{add}) of the double-burnt soil is best explained by reduced litter degradation.

In the single burnt soils sampled one to two years after the fire, the lowest fire intensity resulted in the highest aromatic enrichment factor, $EF_{(aromatic\ C)}$ indicating the highest local accumulation

of char. The respective additional carbon (C_{add}) disclosed an $EF_{(aromatic\ C)}$ -to- $EF_{(alkyl\ C)}$ ratio (B_{char}) of ~ 1 supporting a low charring degree. Extensive combustion and volatilization at higher fire intensities yielded in a decrease of $EF_{(aromatic\ C)}$ and an increase of B_{char} . These trends are in good agreement with fire intensity and forest fuel combustibility in the various sites and therefore, these indices could be used to elucidate quality and quantity of char input occurring during and after forest fires.

Considering that none of the topsoils after single burning showed an $EF_1 > 1$ for the O-alkyl C content, one can assume minor or no accumulation of fresh or only slightly charred necromass within one to two years after the fire event. This finding is in contrast to results obtained for a sample set, collected five years after an intense fire. Here, a considerable part of C_{add} was attributable to fire-unaffected organic sources. It seems that the long recovery time of five years has been long enough to allow the recovery of a new vegetation of shrubs and herbs resulting in biomass and litter production which was high enough to explain the doubling of the C-concentration in the fire-affected topsoil. Also, a decreased microbial activity may have contributed to the accumulation of organic material in the soil.

Although indications were found that, irrespective of the fire type, oxidation of char occurred already during the early post-fire period, the difference in aromaticity, but also the efficiency of the recovery of the vegetation cover after the fire, is expected to affect recalcitrance and degradability of the charred residues. Consequently, after incorporation into the soil, the long-term impact of the pyrogenic necromass on the chemical composition and stability of SOM is also expected to vary with respect to type and intensity of the forest fire. Because char in soil is commonly considered as an efficient C-sink, potential variation in its recalcitrance may be an important consideration if the role of BC in C-sequestration in soils is elucidated.

Mediterranean fire histories from micro-charcoal analysis: analytical methods and preliminary results for the LGIT

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Microscopic charcoal analysis has been used to reconstruct past fire activity over a range of spatial and temporal scales in Europe, the Americas and Australasia. By contrast, and despite the importance of fire in modern landscape ecology, few systematic attempts have been made in the circum-Mediterranean region to reconstruct long-term fire histories using micro-charcoals or other methods of analysis. Additionally, no method of microscopic charcoal analysis has been adopted world-wide. This paper presents the results, firstly, of a systematic experimental investigation into different charcoal extraction and quantification techniques and, secondly, the application of one methodology (contiguous core sampling + sieving + heavy liquid separation + total abundance count) to two core sequences from central Turkey that span the last glacial-interglacial climatic transition (LGIT). Techniques evaluated to extract charcoal from lake sediments included standard pollen preparation (without HF), the Oregon Sieving Technique and heavy liquid separation, the last of these extracting the highest number of fine (<180µm) charcoal particles from the sediments. The experimental results imply that fine charcoal particles are potentially vulnerable to both fragmentation and chemical dissolution during processing. At Eski Acıgöl (Roberts *et al. Holocene*, 2001, 11, 719-734), then a deepwater crater lake, overall micro-charcoal concentrations in sediments are low and were dominated by influx from regional- rather than local-scale fire events. This record therefore provides a good proxy for overall fire frequency/intensity across the central Anatolia plateau, whose (hypothetical) modern "natural" vegetation is predominantly open oak savanna parkland. The lake sediment sequence from Akgöl also spans the LGIT, but records much higher overall micro-charcoal abundance. This extensive shallow lake was subject to periodic local-scale burning of the marsh surface at times of lowered water table, and thus received episodic local charcoal influx superimposed on background regional airborne sources. These results suggest that site type / catchment area and sampling / analytic methodology can critically influence reconstructed fire histories. The roles of climate, vegetation and humans in determining fire histories during the LGIT in the East Mediterranean region are discussed.

Biomass burning and black carbon production

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Vegetation fires are a significant source for atmospheric aerosol particles. Estimates indicate that about 7 % of the global aerosol emissions are due to biomass burning and these emissions account for about one third of the global radiative forcing due to anthropogenic aerosol emissions. The Intergovernmental Panel on Climate Change (IPCC, 2001) has identified radiative forcing by aerosols as one of the major uncertainties in the global radiation budget largely due to the uncertainties in light absorption by aerosols. Since, black carbon (BC) is the globally most significant light absorbing aerosol component, the exact quantification of the BC fraction of combustion particles and biomass burning aerosols in particular is one of the most important topics of current atmospheric research.

Despite its significance, the BC content of atmospheric aerosols is relatively poorly characterized in part due to a lack of accurate measurement techniques. The most frequently used techniques can be distinguished in optical and thermal-desorption methods. The former (e.g. Aethalometer, PSAP, Caruso, photoacoustic spectrometer) utilize the light absorption properties of BC and the latter determine the amount of BC (or elemental carbon) from the evolved gaseous CO₂ under oxidizing conditions. Both methodological approaches suffer from uncertainties and measurement artefacts, which are not well-characterized for the highly variable atmospheric aerosols.

Here we discuss the strengths and weaknesses of optical and thermal-desorption BC methods including the Aethalometer, Caruso and photoacoustic spectrometer as well as thermal-desorption methods utilizing solvent extraction and various temperature profiles (e.g. NIOSH, IMPROVE). We also present data from an extensive laboratory measurement campaign investigating particle emissions from the combustion of various types of biofuel. These measurements indicate that the emission factor of BC, i.e. the mass of emitted BC per mass of burnt fuel, is relatively constant at about 0.45 ± 0.1 g/kg independent of fuel type and burning conditions (smouldering, flaming).

The Determination of Black Carbon in Soils

Michael W. I. Schmidt (1), including results from The Black Carbon Steering Committee (1-6), and The Black Carbon Ring Trial Team (7)

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Black carbon (BC) is a collective term used to describe recalcitrant organic, produced by incomplete combustion of fossil fuels and vegetation. It 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 (Hedges et al. 2000). The individual analytical BC methods rely on operational definitions with clear-cut but different boundaries and are developed for specific scientific questions whereas BC represents a continuum of materials with widely contrasting physicochemical properties. Thus, different methods may be 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. The inherent difference can be illustrated by the results of a first comparative analysis on eight

soil samples by six established methods (Schmidt et al., 2001). 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 benzene carboxylic acids as molecular markers or applying ^{13}C MAS NMR spectroscopy. BC concentrations measured for individual samples vary over two orders of magnitude.

The need for intercomparison of BC methods is obvious. To address this need, a committee was formed during the 1999 Geochemical Society Meeting Goldschmidt Conference to develop representative and accessible BC reference materials for the entire environmental sciences community. It was clear from the preliminary comparative analysis that a collection of BC reference materials should be established as soon as possible i) to ensure long-term intra- and inter-laboratory data quality, and ii) to facilitate comparative analyses between different analytical techniques and scientific approaches. The final recommendations of the steering committee for Black Carbon Reference Materials included (i) five matrices containing BC (soot, charcoal, aerosol, soil, and sediment); and (ii) five materials potentially creating BC during analysis (shale, melanoidin, natural organic matter, and coal), for use in detecting methodological artifacts Schmidt et al. (2003). Further details can be found at the Web site: <http://www.geo.unizh.ch/phys/bc>.

Early 2003/4, these reference materials were produced and distributed and analyzed in a comparative analysis project using these reference materials to gauge how different methods can be used to interpret BC components in aerosol, soils, and sediments. The intention of the study is not to advocate a single technique; rather, such a comparative analysis will help immensely to better understand what is actually being determined by the different methods and how these results relate to one another. Reference materials were requested by 24 research groups of many disciplines, including atmospheric, environmental, marine and soil sciences. Participating research groups analyzed the materials and made available all results and details of their methodology in August 2005 for discussion and eventual group publication. Summarizing, the aim of this contribution will be to present results of the comparative analysis of reference materials for organic geochemical analysis of black carbon and to stimulate discussion.

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The role of fire in seasonally-dry eastern Africa: evidence from sedimentary charcoal

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Recently published output from Dynamic Global Vegetation Models (e.g., Bond *et al.* 2005) indicates an important role for fire in determining the distributions of forest and grassland biomes. This role is often overlooked when considering the potential future impacts of future increases in atmospheric CO₂ content and climate change. This paper discusses sedimentary evidence, including charcoal, of the influence of fire as one of a complex of factors affecting both the distribution and composition of vegetation in seasonally-dry parts of eastern Africa.

Biomass burning records from charcoal and black carbon in natural archives

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This review focuses on the commonly analytical methods and definitions used to characterize sedimentary combustion-derived products. New optical and chemical methods are used for the reconstruction of past biomass burning activity and its impact on the global Black Carbon (BC) cycle. The dark particles $>0.2 \mu\text{m}$ remaining after the partial digestion of organic matter are optically counted by automated-image analysis and defined as charcoal. The elemental carbon remaining after a thermal and a chemical oxidative treatments is quantified as BC (quantification limit is $7.8\mu\text{g}$ and recovery is 83%). Charcoal and BC records from late-Pleistocene equatorial Pacific Ocean and late-Holocene African lacustrine sediment cores, are interpreted regarding transport mechanisms and biomass burning activities. Results show that dark carbon-rich particles burial in the open-ocean area is partially controlled by low-latitude atmospheric circulation patterns (i.e. summer monsoon dynamics), while surface runoff/erosion from forest soils is an important sources of particles for the tropical lake. However, in the oceanic sedimentary record from the west equatorial Pacific recovering the last 360 ky, charcoal and BC sediment fluxes increase by three fold between 53-43 and 12-10 ky, suggesting that human colonization and changes in practices in the Indo/Pacific region have induced shifts in fire regimes. In the crater lake record from Tanzania recovering the last 4 ky, charcoal and BC sediment fluxes increase by three fold between 1.6 and 0.9 ky, synchronously with the extend of Late Iron Age and agricultural innovations in the east African Rift. These results demonstrate that fire regimes have changed throughout Late Pleistocene and during the Holocene, due to changes in climate, vegetation, and human practices. The emissions of dark carbon-rich particles in the environment have probably tripled under anthropogenic influence, such as appearance, land-use innovations, and social changes (settlement, agriculture, metallurgy).

Key words: Sediments, biomass burning, carbon cycle, charcoal, black carbon, human impact

Archaeological perspectives on charcoal taphonomy: Tropical archaeobotany: an elusive search for charred plant macroremains

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Wood and charcoal have long provided a chronological framework for archaeological deposits through dendrochronology and radiocarbon dating. More recently though, charcoal and other macroscopic plant remains from archaeological sites have been used both as proxy palaeoenvironmental indicators, and to investigate how past human populations exploited a range of plant products. These interpretations have been drawn mainly from the taxonomic composition of assemblages, with the remains of seeds and cereals generally identified through low power microscopy, and wood charcoal identified through the microscopic anatomical structures which are often excellently preserved and visible at magnifications of x100-500. Inferences about regional vegetation change are regarded as strongest where large datasets pool results from a number of archaeological sites and span securely dated stratigraphy, though ecological signatures are sometimes apparent from an individual site. Spatial and chronological analyses of charcoals from archaeological deposits also tell us about how people formerly used and disposed of wood and wood products. On-going work in Pompeii, southern Italy, will be used here as an example of how ecological and cultural signatures are blended within archaeological charcoal assemblages, and the challenges of dissociating these two strands of information.

Two new directions for archaeological anthracology will be mentioned. One is the chemical analysis of wood and fuel residues and strontium isotope studies of timber to study fuel supplies, trade, and resource depletion. The second is the recording of biological features of wood growth which are linked with woodland management practices such as coppicing. Both approaches are currently being explored by staff and students at the University of Bradford investigating the fuel supply to the blast-furnace at Rievaulx in North Yorkshire.

This broad range of interpretations about human use of wood resources in the past depends, of course, upon understanding and controlling for the taphonomy of the assemblages. Experimental approaches are aiding our understanding of how wood burns in open fires and in deliberate charcoal manufacture.

Key words: Archaeobotany, fuel supplies, Pompeii, Rievaulx, charcoal taphonomy

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Analysis of microcharcoal for palaeoenvironmental reconstruction

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Analysis of the microfossil charcoal particles (<100 μ) contained in lake sediments are routinely used in palaeoenvironmental reconstruction to infer past episodes of climate change and/or human activity. The range of climate and human induced conditions thought to invoke burning, are however, wide-ranging and in many cases contradictory. In response to climate change for example, increased burning has been linked to intervals of increased aridity (drier vegetation = more burning) and conversely increased humidity (more moisture = greater availability of biomass for burning). Likewise studies that have attempted to link burning to human activities have demonstrated both increased and decreased burning frequencies associated with human impact. From the published literature therefore, there appears to be a confusing array of hypotheses as to what an increased presence of microfossil charcoal particles in lake sedimentary sequences actually demonstrates. One of the main problems appears to be that most, if not all, of the attempts to link the microfossil charcoal record to palaeoenvironmental reconstruction are qualitative – thus if the peak in charcoal concentration coincides with a known interval of human activity or climate change – usually measured ‘by eye’ - then a causal link is inferred. Interestingly, however, the same reasoning rarely applies if the opposite is found – thus if there is no peak associated with a known interval of climate/human activity, this negative correlation is usually ignored. In order to try and make interpretation of the analysis of microfossil charcoal in sedimentary sequences more quantitative we therefore set about testing statistically the relationship between microfossil charcoal and known intervals of climate change and/or human activity. We analysed the records from eight sedimentary sequences in order to determine which of the various hypothesis relating to increased microfossil charcoal in sedimentary sequences are statistically robust. Preliminary results from this study will be presented and indicate that the current trend in palaeoclimatic reconstruction to use microfossil charcoal records from sedimentary sequences in order to infer long-term climatic change, needs far greater scrutiny.

List of abstracts for poster presentations

Arranged alphabetically by first author

The chemothermal oxidation BC method: evaluation of ex situ pretreatments, matrix-catalyzed effects, standard addition approaches, and thermal stability of various black carbons

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The highly condensed products and residues of incomplete combustion of biomass and fossil fuel termed black carbon (BC) partake in a multitude of important geochemical processes. However, ambiguity persists since different quantification methods give highly variable results, leaving it unclear whether this reflects method difficulties or that different methods simply mirror different parts of the BC spectrum. The wet chemical pre-treatment – wet chemical oxidation (wet-wet) methods (e.g., Wolbach & Anders 1989; Verardo 1997; Masiello *et al.*, 2002; Song *et al.*, 2002) have the advantage over thermal oxidation methods that there is a lower risk of charring. However, the extensive handling of samples in liquid solutions may lead to losses of BC particles, which, due to their hydrophobic character, tend to adsorb to inner surfaces of test tubes and to the water-air interface (e.g. Gélinas *et al.*, 2001; Elmquist *et al.*, 2004). Underestimation of total BC can also occur when the thermal energy applied during the combustion step is higher than the stability of some BC constituents.

Here we further evaluate and develop the chemothermal oxidation (CTO) approach (Gustafsson *et al.*, 1997; 2001; Elmquist *et al.*, 2004), which is perhaps the most commonly applied method for quantification of BC in sediments. The CTO-375 method involves 18 h thermal oxidation at 375°C of small and well-ground samples in active airflow to oxidize organic matter, and micro-acidification *in situ* in Ag capsules to remove carbonates followed by quantification of the residual carbon as BC using elemental analysis. Standard additions of incremental amounts of pure diesel soot (NIST standard reference material 2975) to four different sediments resulted in 14% to 52% lower estimates of sedimentary BC concentrations compared with the ordinary CTO-375 method (Elmquist *et al.*, 2004). The linear standard addition slopes suggested that 38%, 51%, 78% and 101% of added SRM-2975 BC was accounted for. Separate experiments supported the notion that the somewhat lower recovery of the BC in the matrix-associated additions, compared to when run as pure standards, could be caused by either a smearing effect or a mineral-oxide catalyzed oxidation of the BC (Elmquist *et al.*, 2004). Lowering of the combustion temperature may prove useful to compensate for these effects.

The stability of different BC types (diesel soot SRM-2975, n-Hexane soot, Wood char and Grass char) was tested in a thermogram study where laboratory produced BC materials (from BC ring

trial) were combusted at various temperatures. A model-deduced estimation of the temperature when 50% carbon remained in the residue ($T_{50\%}$) reflects the thermal stability of the material. $T_{50\%}$ of the tested BC materials was as follows: 392° (SRM-2975), 369° (n-Hexane), 314° (Wood char) and 241° (Grass char). These further laboratory-based test of the CTO-375 method combines with field-based evaluations to suggest that the CTO-375 method appears generally applicable to the quantification of soot-BC in sediments. For quantitative estimates of also the more labile char-BC components, complementary approaches are required. ~~.g., Cornelissen et al., 2004; Quenea et al., this symposium).~~

Defining and evaluating reference materials for black carbon quantification by colour, BET surface area, elemental composition, $\delta^{13}\text{C}$ and ^{13}C NMR

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Quantification of BC has recently gained significance, since it could explain much of the carbon not accounted for in global carbon budgets. BC has a very heterogeneous nature, and the term BC is used collectively for a whole spectrum of combusted carbonaceous compounds that can be found in every kind of environment. Apart from the matrix heterogeneity, a wide variety of methods exist with which to measure BC. The highly variable results produced from these different methods, even on the same samples, must somehow be made comparable. This would aid the understanding of the contribution of BC to the global C cycle. In this paper we describe standard set of reference materials, which are easily obtainable, well-characterised and representative of different environments, for intercomparative analysis of BC. Our main results include: (i) presentation of well-defined reference materials using several techniques – including elemental analyses, $\delta^{13}\text{C}$, ^{13}C NMR, colour and surface area measurements, (ii) representativeness of the reference materials and (iii) a discussion on the implications of reference material characteristics on various methods, showing potential pitfalls such as artefact formation.

Analysis of Black Carbon in Reference Materials using TG-cDTA

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Black Carbon is an important component of natural organic matter that may play a significant role in global climate change. However, due to the complexity of natural organic matter and BC, it is difficult to delineate the proportion of BC in soil and sedimentary C budgets (Simpson & Hatcher, 2004).

Black Carbon content in recommended BC standards (BC Ring Trial) was estimated by Thermogravimetry and calculated differential thermal analysis (TG-cDTA). This technique was used to obtain continuous and simultaneous measurement of weight loss (TG) and energy change (c-DTA) during the thermal decomposition of BC standards. Samples were heated from 20 to 990 °C, at 20 °C min⁻¹, under an helium flow (20% oxygen) of 50 mL min⁻¹.

TG is a direct and relatively rapid technique for comparing the abundance of more and less stable components in soils, sediments, and plant materials. (Lopez-Capel *et al.*, 2005). There is no loss of sample due to handling or treatment, and the proportions of individual phases can be calculated from observed weight losses.

Initial weight loss is dominated by the exothermic decomposition of labile aliphatic and carboxyl groups (approx. 300-350°C) whilst exothermic loss of more refractory aromatic C occurs at higher temperatures (approx. 450-500°C), and very refractory organic matter at 500-650 °C, or even higher for bituminous coals (650-800 °C). If calcium carbonate minerals are present they decompose at higher temperatures (700-750 °C) and can be quantified, except when overlapping with BC at such temperature.

The BC content estimated by TG-cDTA is within range with estimations obtained by other thermic methods. However, quantification may have been overestimated in composite samples where BC could not be clearly differentiate from ROM. This works demonstrates the potential of TG-cDTA in the investigation of BC materials.

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