

Black carbon in marine sediments

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Abstract

Concentrations of black carbon were determined for a number of marine sediments. A comparison of black carbon based on thermal oxidation and hot concentrated nitric acid pretreatments revealed that the latter significantly overestimates combustion derived carbon phases. Black carbon accounts for about 15 to 30% of total organic carbon and therefore reduces the fraction of unidentified sedimentary organic carbon. Examination of a relict oxidation front in a Madeira Abyssal Plain turbidite provided the first evidence for significant black-carbon degradation (about 64%) in marine sediments given time (10–20 kyr) and oxygen exposure. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: black carbon; soot carbon; organic carbon; sediments; degradation; Black Sea; turbidite; North Sea; Scheldt Estuary; Eastern Mediterranean

1. Introduction

Black carbon is usually defined as the highly condensed carbonaceous residue from incomplete combustion processes. It has been found omnipresent in the atmosphere, ice, soils and sediments due to its widespread production and its supposed chemical and microbiological inertness in the environment (Goldberg, 1985). Its distribution in the atmosphere has been investigated in detail because of its strong absorbance of solar radiation, its catalytic effects on chemical reactions and its importance to the global carbon cycle (Seiler and Crutzen, 1980; Kulbusch and Crutzen, 1995). Black carbon could represent a significant sink for carbon dioxide because vegetation fires and wood fuel combustion transfer carbon

from the relatively fast biological-atmosphere carbon cycle to the long-term geological carbon cycle.

Estimates of global black carbon formation (0.05–0.270 Gt yr⁻¹; Kulbusch and Crutzen, 1995) are of the same order as those of riverine input of particulate organic carbon to the ocean (0.17 Gt yr⁻¹; Ludwig et al., 1996) and burial of organic carbon in marine sediments (0.13–0.6 Gt yr⁻¹; Berner, 1982; Middelburg et al., 1997). If these flux estimates are correct, black carbon should contribute considerably to the organic matter being buried in marine sediments.

The sedimentary record of black carbon has been used as a record of forest fires and fossil fuel emissions (Smith et al., 1973; Bird and Cali, 1998), and past atmospheric oxygen content, because the presence of charcoals provides a lower limit to atmospheric oxygen levels (Cope and Chaloner, 1980). Verardo and Ruddiman (1996) proposed that the

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black carbon record may improve estimates of marine organic carbon burial and may contain paleoenvironmental information. The distribution of black carbon in surface sediments may significantly affect the distribution, speciation and bioavailability of polycyclic aromatic hydrocarbons (Gustafsson et al., 1997; Gustafsson and Gschwend, 1998).

Here we compare two recently developed techniques for black carbon determinations in sediments (Gustafsson et al., 1997; Verardo, 1997) and apply them to surface sediments from the North Atlantic Ocean, the North Sea, the Eastern Mediterranean, the Black Sea, and an intertidal flat in the Scheldt estuary (The Netherlands). The contribution of black carbon to total organic carbon will be discussed. We will also present results from the oxidised and reduced sediment zones from a relict turbidite in the Madeira abyssal Plain which indicate that black carbon was degraded significantly within 10–20 kyr.

2. Materials and methods

There is no unique definition of black carbon (Goldberg, 1985; Kulbusch, 1995) and many terms are in use (e.g. soot, black carbon, elemental carbon and charcoal). The definition chosen usually reflects the operational technique applied or the processes studied. The former three terms are usually applied to the combustion products formed at higher temperatures than charcoal (Lim and Cachier, 1996). Following a review of the literature we selected two methods: (1) a thermal oxidation method for soot carbon (Gustafsson et al., 1997) and (2) the HNO_3 method for charcoal (Verardo, 1997). Both methods have specifically been developed for determination of low quantities of black carbon in complex sedimentary matrices containing refractory macromolecular organic matter and large amounts of carbonate minerals. They both rely on in situ acidification to remove inorganic carbonate and carbon analysis of the residue by an elemental analyser, but they differ in the pretreatment procedure to remove non-black-carbon organic matter.

Samples were thoroughly ground in an agate mortar mill and very well homogenised to reduce variability between replicates and to reduce any potential charring during thermal treatments. Organic carbon

(OC) was determined according to Nieuwenhuize et al. (1994) and involves the determination of total carbon using an automatic elemental analyser (Carlo Erba type NA-1500) following the partitioning of inorganic and organic carbon phases by acidification with 25% HCl in situ within precleaned silver cups (12 mm \times 5 mm; Van Loenen Instruments, D2010). The soot carbon method of Gustafsson et al. (1997) follows that for organic carbon, except that there is a pretreatment in which the samples are thermally oxidised at 375°C for 14 h in the presence of oxygen at atmospheric partial pressure. The carbon remaining after thermal oxidation and HCl acidification is considered to be soot (SC1). Gustafsson et al. (1997) have extensively tested their method with synthetic samples and observed no interference but for corn pollen which were partly recovered as soot. The average blank value for OC and SC1 is 4.1 $\mu\text{g C}$, which mainly originates from the Ag containers used.

The charcoal method of Verardo (1997) is also similar to the organic carbon method, except that aluminium containers are used, instead of HCl, 10 times 30 μl of concentrated nitric acid (50°C) is added, and that the chromatographic column was kept at 35°C instead of 80°C to better separate the nitrogen (derived from nitric acid) and carbon dioxide peaks. Recovery and interference tests indicated that refractory carbon in coal, humic acids and *Lycopodium* spore tablets were removed by the hot nitric acid treatment and that natural charcoal and elemental carbon were quantitatively recovered as charcoal (Verardo, 1997). For reasons given below, we will refer to this fraction as nitric acid resistant carbon (NARC) and not charcoal. Samples were also subjected to hot nitric acid treatment after thermal oxidation (SC2). The average blank value for NARC and SC2 is 5.1 $\mu\text{g C}$, which mainly originates from the nitric acid. Reproducibility of carbon measurements is better than 5% at concentrations above 0.1 wt.%, but is on the order of 20% at concentrations less than 0.05 wt.%.

Sediment samples were obtained from various locations covering a range of environments (Table 1). Sediments from the Molenplaat (MOL1–5), an intertidal flat in the Scheldt estuary, are sandy and dynamic. Sediments from the Iberian Margin (OMEX1–5) are carbonate-rich and cover a range of water depths and grain sizes. Black Sea sediments

Table 1
Sample characteristics, organic carbon and black carbon

Sample	Depth in sediments (cm)	Water depth (m)	Latitude (N)	Longitude (E/W)	Median grain size (μm)	OC (wt.%)	SC1 (wt.%)	SC2 (wt.%)	NARC (wt.%)	SC/OC (%)
Molenplaat, Schelde estuary, The Netherlands										
MOL1	4–5	intertidal	51.26	03.57E	153	0.309	0.043	0.063	0.173	17
MOL2	4–5	intertidal	51.26	03.57E	109	0.372	0.056	0.077	0.280	18
MOL3	4–5	intertidal	51.26	03.57E	147	0.158	0.038	0.029	0.128	21
MOL4	4–5	intertidal	51.26	03.57E	153	0.093	0.041	0.037	0.160	42
MOL5	4–5	intertidal	51.26	03.57E	173	0.108	0.043	0.046	0.178	41
Iberian Margin, Atlantic Ocean										
OMEX	7–8	175	43.44	08.33W	83	0.470	0.095	0.085	0.445	19
OMEX	7–8	766	43.47	08.54W	127	0.240	0.075	0.065	0.201	29
OMEX	7–8	1522	43.41	09.27W	152	0.220	0.047	0.024	0.117	16
OMEX	7–8	2200	43.46	09.33W	12	0.630	0.163	0.152	0.528	25
OMEX	7–8	4909	44.01	09.54W	7	0.510	0.126	0.148	0.422	27
Northwestern Black Sea										
BS5	4–5	24	44.45	29.35E	13	1.262	0.220	0.242	1.206	18
BS6	4–5	54	43.45	28.48E	6	0.783	0.197	0.180	0.641	24
BS9	4–5	57	44.34	29.46E	11	1.638	0.233	0.254	1.388	15
BS10	4–5	72	44.18	30.05E	18	2.147	0.299	0.334	1.975	15
BS13	4–5	13	46.03	30.29E	19	1.111	0.274	0.260	1.034	24
BS15	4–5	13	46.33	31.25E	18	2.997	0.379	0.380	2.256	13
BS21	4–5	1997	43.22	32.10E	13	4.459	0.793	0.797	3.268	18
BS22	4–5	1494	43.18	30.02E	13	5.260	0.815	0.956	2.944	17
BS24	4–5	137	44.00	30.29E	24	2.288	0.337	0.383	1.913	16
North Sea										
GB	4–5	20	54.05	8.09E	38	2.093	0.457	0.441	1.443	21
SK	4–5	270	58.05	10.15E	12	2.424	0.367	0.417	1.834	16
FF	4–5	39	53.42	4.30E	77	0.559	0.090	0.119	0.458	19
BF	4–5	28	53.00	3.52E	233	0.078	0.032	0.041	0.101	47
BGA	4–5	4.9	51.45	3.48E	143	0.219	0.093	0.093	0.183	42
BGB	4–5	2.7	51.46	3.46E	285	0.055	0.028	0.039	0.084	61
Madeira Abyssal Plain										
			30.44	25.22W	< 10					
MAPox1	756–766	5400				0.182	0.102	0.045	0.205	40
MAPox2	767–777	5400				0.228	0.069	0.111	0.187	39
MAPox4	795–802	5400				0.361	0.123	0.122	0.283	34
MAPred1	807–817	5400				1.139	0.215	0.266	0.858	21
MAPred4	927–940	5400				1.137	0.277	0.292	0.917	25
Eastern Mediterranean										
			34.52	21.07E	< 10					
MED1	0–0.5	2539				0.417	0.142	0.154	0.314	35
MED2	9–11	2539				0.222	0.112	0.060	0.169	39
MED3	24.5–25	2539				2.598	0.729	0.596	2.396	25

OC: organic carbon concentration; SC1: carbon after thermal oxidation/HCl treatment; SC2: carbon after thermal oxidation/hot nitric acid treatment; NARC: hot nitric acid resistant carbon; SC/OC: contribution of soot carbon (average of SC1 and SC2) to organic carbon.

are from the north western shelf area including the mouths of the Danube (BS5), Dniestr (BS13) and Dniepr (BS15) and a transect from the Danube delta to the anaerobic, sulphide-containing deep basin

(BS9, BS10, BS24, BS22, BS21). The samples from the North Sea, a continental shelf, have been investigated in detail for their biochemical composition and cover a range of degradation states and grain sizes

(Dauwe and Middelburg, 1998). Samples from the Madeira abyssal plain *f* turbidite (MAPox-red) have been studied in detail by Cowie et al. (1995) and Prahl et al. (1997) and will be used to estimate the extent of post-depositional oxidation of black carbon. Sediments from the Eastern Mediterranean comprise hemipelagic (MED1–2) muds and an organic-carbon rich sapropel (MED3; De Lange et al., 1994).

3. Results and discussion

3.1. Soot, charcoal and organic carbon contents

Soot concentrations determined with the thermal oxidation/HCl method (SC1) and thermal oxidation/HNO₃ method (SC2) are very well correlated ($r^2 = 0.96$; $n = 33$) with a slope (1.02 ± 0.04) and intercept (0.00 ± 0.04) not significantly different from 1 and 0, respectively (Fig. 1). This indicates that the fraction of carbon resistant to thermal oxidation (soot) is not removed by hot nitric acid. Although some pollen may survive thermal oxidation (Gustafsson et al., 1997), they are most likely degraded during acidification with hot concentrated nitric acid (Verardo, 1997).

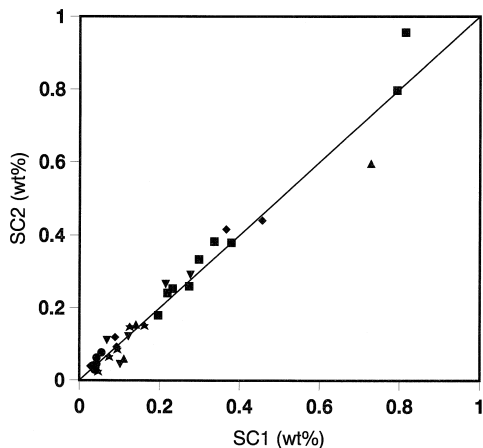


Fig. 1. Agreement between soot carbon results based on thermal oxidation/HCl treatment (SC1) and those based on thermal oxidation/hot nitric acid treatment (SC2). The solid line represents the best fit ($r^2 = 0.96$, $n = 33$): $SC2 = (1.02 \pm 0.04)SC1 + (0.00 \pm 0.04)$. Sample identification: dots: Molenplaat; stars: Iberian Margin; squares: Black Sea; rhombi: North Sea; inverted triangle: Madeira Abyssal Plain turbidite; triangle: Mediterranean.

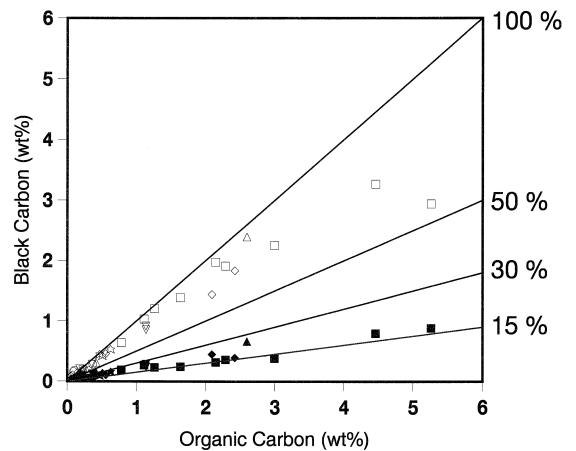


Fig. 2. Relation between organic carbon (OC), soot carbon (solid symbols, average of SC1 and SC2) and charcoal (NARC, open symbols). Lines representing 15, 30, 50 and 100% black carbon contributions to organic carbon are shown as well. Sample identification as in Fig. 1.

Soot contents range from 0.03 to 0.9 wt.% C (Table 1) and correlate with organic carbon contents (Fig. 2). Soot carbon contributes about 15 to 30% to total organic carbon with a tendency for deep-sea samples and other organic-carbon poor samples to contain a larger proportion of soot carbon (Fig. 3), perhaps an artefact of accumulated errors. Literature

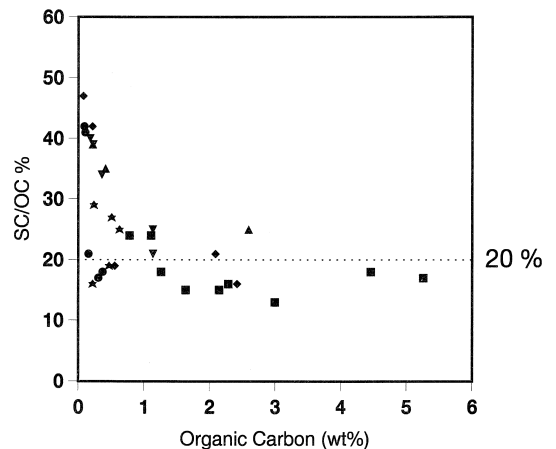


Fig. 3. Relation between organic carbon (OC) and the contribution of soot carbon (average of SC1 and SC2) to organic carbon (SC/OC). A line representing 20% black carbon contributions to organic carbon is shown as well. Sample identification as in Fig. 1.

data for the soot-to-organic carbon contribution range from 5 to 38% in Western Mediterranean sediments (Lim and Cachier, 1996) and 3 to 13% in North American shelf sediments (Gustafsson and Gschwend, 1998). The correlation between soot and organic carbon is probably due to their common dependence on grain size and hydrodynamic sorting during deposition.

Charcoal concentrations (NARC) based on the hot nitric acid digestion technique range from 0.08 to 3.2 wt.% and always account for more than 50% of the organic carbon (Fig. 2). Based on the same technique, Verardo and Ruddiman (1996) have reported that NARC was the dominant (> 50%) component of the organic carbon preserved in tropical Atlantic deep-sea sediments. If the NARC fraction indeed corresponds to charcoal, a product of terrestrial biomass burning, this would imply that the majority of organic carbon in marine sediments is terrestrial (charcoal and non-charcoal terrestrial carbon). This is clearly at odds with isotopic, elemental, NMR and molecular compositional constraints (Hedges and Oades, 1997; Bird and Cali, 1998). For instance, North Sea sediments contain at least 70% NARC and have $\delta^{13}\text{C}$ values ranging from -21.5 to -22.2‰ (Dauwe and Middelburg, 1998). If all NARC would be charcoal with a $\delta^{13}\text{C}$ of -27 to -26‰ , this would imply that the marine organic carbon end-member should have $\delta^{13}\text{C}$ values heavier than -11‰ . It is therefore more likely that hot nitric acid resistant carbon comprises not only charcoal (and soot), but also non-hydrolysable macromolecules from marine sources (De Leeuw and Largeau, 1993; Bird and Cali, 1998).

3.2. Black carbon and the unidentified fraction of sedimentary organic carbon

Despite significant improvements in analytical techniques and considerable efforts to characterise sedimentary organic carbon, a large fraction of it remains biochemically uncharacterised (Hedges and Oades, 1997). This unidentified fraction varies from about 40% in coastal sediments to more than 80% in deep-sea sediments. (e.g., Cowie et al., 1995; Wakeham et al., 1997; Dauwe and Middelburg, 1998). The major groups identified are amino acids, carbohydrates, lipids, and hexosamines (Cowie et al., 1995; Hedges and Oades, 1997). For a number of our

samples there is additional information on the biochemical composition and the contributions of various biochemicals and soot carbon to total organic matter are shown in Fig. 4. The relative contributions of biochemical groups are remarkably similar: carbohydrates (8–19%), amino acids (8–19%) and hexosamines (< 2.2%). The total contribution of these hydrolysable fractions (17–41%) is similar to that of soot (16–42%), but smaller than the non-soot fraction (39–66%) that remains after hot nitric acid treatment ($[\text{NARC} - \text{SC}]/\text{OC}$). It therefore appears

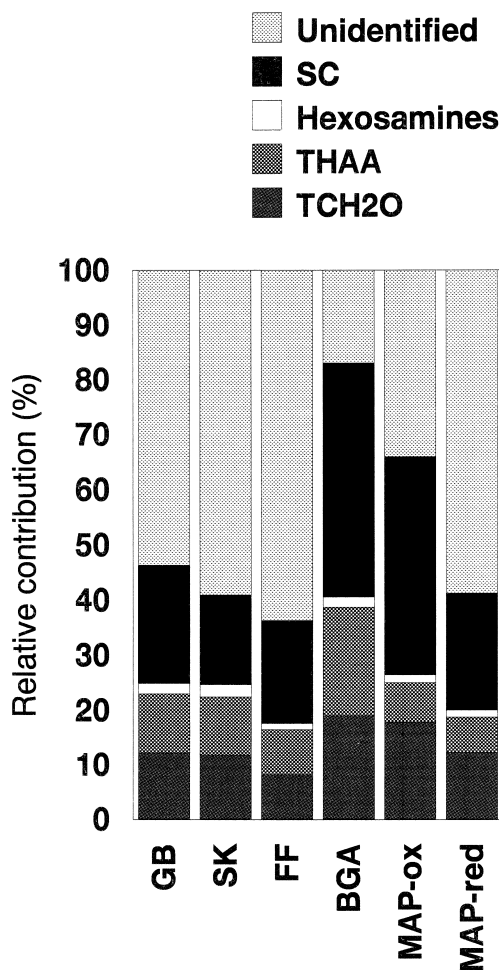


Fig. 4. Cumulative contribution of carbohydrates, total hydrolysable amino acids, hexosamines and soot carbon (SC) to total organic carbon. TCH₂O, THAA and hexosamine results for GB, SK, FF and BGA from Dauwe and Middelburg (1998) and for MAPox and MAPred from Cowie et al. (1995) and our own unpublished data.

that inclusion of black carbon in comprehensive analyses of sedimentary organic matter will significantly reduce the unidentified fraction.

3.3. Black carbon degradation

Black carbon is usually assumed to be chemically and biologically inert in the marine environment because (1) it has been identified in sediments of 65 Ma (Herring, 1985), (2) there is no down-core trend in size distribution of black carbon particles (Herring, 1985) and (3) it reacts very slowly towards chemical oxidation (Wolbach and Anders, 1989). Although microbiological breakdown during laboratory experiments has been reported (Potter, 1908; Shneour, 1966), there is as yet no information on degradation in marine sediments. The natural oxidation experiments provided by the Madeira Abyssal Plain *f* turbidite (Middelburg and De Lange, 1988; Prahl et al., 1989, 1997; Keil et al., 1994; Cowie et al., 1995) can be used to test the assumption of black carbon inertness. This distal turbidite originates from the northwestern African margin and was introduced to the Madeira Abyssal Plain about 140 kyr ago as a 4–4.5 m thick ungraded, uniform mud deposit (Middelburg and De Lange, 1988). The emplacement of this turbidite caused the exposure of labile and reduced components to oxic pelagic conditions. The post-depositional exposure to oxygen (and nitrate) under pelagic conditions during 10–20 kyr resulted in carbon removal in the uppermost section due to a downward progressing oxidation front (Wilson et al., 1985). A comparison between the organic matter concentrations and composition of the oxidised upper and reduced, unreacted lowermost section provides a unique opportunity to establish the extent of black carbon degradation.

Post-depositional oxidation of the upper section resulted in a decrease in total organic carbon from 1.14 to 0.25 wt.% and soot carbon from 0.27 to 0.10 wt.% (Fig. 5). Post-depositional oxidation removed about 77% of the organic carbon, but only about 64% of the soot carbon. Selective preservation of soot carbon increased its contribution to organic carbon from about 23 to 40% (Fig. 5) and is consistent with the preferential removal of marine organic matter and the selective preservation of terrestrial organic matter in these sediments (Prahl et al., 1997).

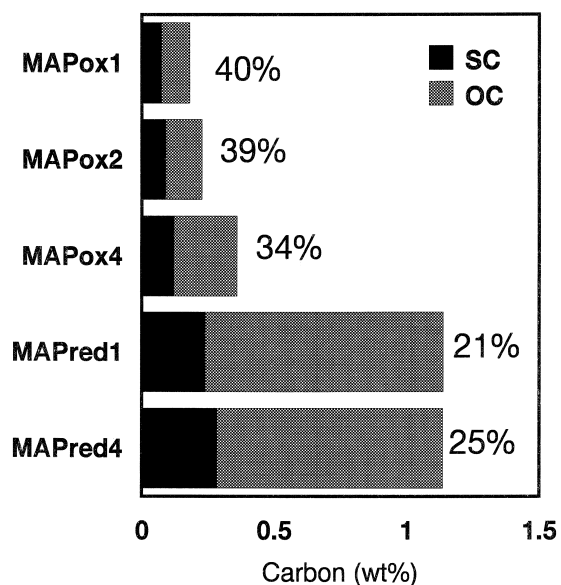


Fig. 5. Organic carbon (OC) and soot carbon (average of SC1 and SC2) in oxidised and reduced sections from the MAP *f* turbidite. MAPox1,2,4 have been subjected to extensive post-depositional oxidation, whereas MAPred1,4 have experienced little alteration since deposition. The relative contribution of soot carbon to organic carbon is also indicated.

These data definitely indicate that black carbon is degraded in marine sediments when exposed to oxygen (and nitrate), although the microbiological or chemical mechanisms involved remain unknown and require further study. Degradation of black carbon in marine sediments complicates the use of its sedimentary record to trace biomass burning (Herring, 1985; Verardo and Ruddiman, 1996; Bird and Cali, 1998) and to constrain past atmospheric oxygen levels (Cope and Chaloner, 1980). Our data also provide support for the oxygen exposure time impact on carbon preservation (Hartnett et al., 1998). It has been proposed that black carbon formation may represent a significant sink of atmospheric carbon dioxide and a minor source of oxygen (Kulbusch and Crutzen, 1995). This is based on the premise that black carbon is not degraded in the bio- and geosphere after formation. The observed degradation of black carbon in marine sediments during prolonged exposure to oxygen provides a small negative feedback between oxygen in the atmosphere (and ocean) and black carbon burial.

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