



Photo-lability of deep ocean dissolved black carbon

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Abstract. Dissolved black carbon (DBC), defined here as condensed aromatics isolated from seawater via PPL solid phase extraction and quantified as benzenepolycarboxylic acid (BPCA) oxidation products, is a significant component of the oceanic dissolved organic carbon (DOC) pool. These condensed aromatics are widely distributed in the open ocean and appear to be tens of thousands of years old. As such DBC is regarded as highly refractory. In the current study, the photo-lability of DBC, DOC and coloured dissolved organic matter (CDOM; ultraviolet-visible absorbance) were determined over the course of a 28 day irradiation of North Atlantic Deep Water under a solar simulator. During the irradiation DBC fell from 1044 ± 164 nM-C to 55 ± 15 nM-C, a 20-fold decrease in concentration. Dissolved black carbon photo-degradation was more rapid and more extensive than for bulk CDOM and DOC. The concentration of DBC correlated with CDOM absorbance and the quality of DBC indicated by the ratios of different BPCAs correlated with CDOM absorbance spectral slope, suggesting the optical properties of CDOM may provide a proxy for both DBC concentrations and quality in natural waters. Further, the photo-lability of components of the DBC pool increased with their degree of aromatic condensation. These trends indicate that a continuum of compounds of varying photo-lability exists within the marine DOC pool. In this continuum, photo-lability scales with aromatic character, specifically the degree of condensation. Scaling the rapid photo-degradation of DBC to rates of DOC photo-mineralisation for the global ocean leads to an estimated photo-chemical half-life for oceanic DBC of less than 800 years. This is more than an order of magnitude shorter than the apparent age of DBC in the ocean. Consequently, photo-degradation

is posited as the primary sink for oceanic DBC and the apparent survival of DBC molecules in the oceans for millennia appears to be facilitated not by their inherent inertness but by the rate at which they are cycled through the surface ocean's photic zone.

1 Introduction

Dissolved organic matter (DOM) plays a major role in key biogeochemical processes: providing sustenance at the base of microbial foodwebs; transporting carbon (C), nutrients and trace elements from the land to the oceans; and mediating fluxes of C from vegetation and soils, to rivers, the oceans, and eventually, the atmospheric CO₂ pool. The DOM pool in the oceans represents one of the largest global C pools (~700 Pg-C; Hansell, 2002), storing approximately the same amount of C as is found in all living organisms on Earth. Due to its great size, even minor changes in the dynamics of the DOM pool or its components can impact the global ecosystem, particularly ocean C-storage and atmospheric CO₂.

The DOM pool is of further interest as an information rich set of tracers, diverse in source, reactivity and history. These molecules carry the signatures of their source and subsequent journey through the environment to their point of analysis. The great potential of mining this information led Hedges (2002) to state that “the future of oceanographic research belongs in large part to those who can learn to read these molecular messages”. This paper focuses upon one component signature within the DOM pool: dissolved black carbon.

In the context of this study, dissolved black carbon (DBC) refers specifically to dissolved polycyclic aromatics. As far as is known, DBC can only be formed thermogenically, making it a specific tracer for thermally altered DOM (Dittmar, 2008). Heating of organic matter results in a number of reactions, including condensation reactions which yield polycyclic aromatics (alternatively referred to as polycyclic aromatic hydrocarbons and condensed aromatics in the literature). The benzenepolycarboxylic acid (BPCA) oxidation products of these condensed aromatics are identified and quantified as DBC (Dittmar, 2008). The parent molecules from which these BPCAs are derived are assumed to have molecular weights ranging from approximately 430 to 530 Daltons based upon the fraction detected by high resolution mass spectrometry (Dittmar and Koch, 2006).

Dissolved black carbon was recently found to occur throughout a number of major ocean water masses at concentrations between 600 and 810 nanomols of carbon per L (nM-C) or $\sim 2\%$ of total dissolved organic carbon (DOC) (Dittmar and Paeng, 2009). This makes DBC one of the most prevalent of organic molecular classes quantified in the global ocean. By comparison lignin derived phenols, the oxidation products of aromatic compounds from terrestrial plants, occur at $<0.1\%$ of total DOC (Opsahl and Benner, 1997; Hernes and Benner, 2006), total hydrolysable amino acids at $\leq 1.9\%$, total hydrolysable neutral sugars at $\leq 4.5\%$ and total hydrolysable amino sugars at $\leq 0.6\%$ (Kaiser and Benner, 2009).

Dissolved black carbon has been observed in the abyssal ocean, leading to suggestions of a deep ocean source, possibly associated with heating at hydrothermal vents (Dittmar and Koch, 2006). Strong land-ocean concentration gradients (Mannino and Harvey, 2004; Dittmar 2008) also indicate that a terrestrial source for marine DBC exists and polycyclic aromatics have been identified in the high resolution mass spectra of Congo (Stubbins et al., 2010) and Amazon (Kim et al., 2004) river water. Jurado et al. (2008) report deposition of black carbon to the global ocean, though they do not quantify the condensed aromatics comprising the DBC pool specifically. The molecular signatures of DBC were also found to be elevated in glacier DOM derived from aerosol deposition (Stubbins et al., 2012). Therefore, deposition of combustion derived aerosols likely provides an additional source of DBC to the surface ocean. As a significant fraction of aerosols are formed through the burning of fossil fuels (Jurado et al., 2008), it is also likely that any DBC deposited to the ocean surface is radiocarbon depleted.

Black carbon is commonly described as refractory (e.g. Preston and Schmidt, 2006), an impression formed through observations of particulate black carbon's bio-resistance and accumulation in soils and marine sediments (Druffel, 2004). Black carbon comprises a continuum of thermo-altered molecules from slightly altered biopolymers through highly condensed polycyclic aromatic compounds to graphitic carbon. Temperature plays a role in determining

black carbon's chemistry, with chars produced at low temperature being less condensed and richer in polar functional groups than those produced at higher temperatures (Kuo et al., 2008; Keiluweit et al., 2010; Schneider et al., 2010). These variations in black carbon's molecular structure influence its reactivity and fate in the environment.

In the oceans, the high molecular weight fraction (>1000 Da) of DBC (condensed aromatics) was recently reported to have an apparent radiocarbon age of $18\,000 \pm 3\,000$ years before present (Ziolkowski and Druffel, 2010) making DBC the most ^{14}C depleted class of dissolved organic molecules identified as distributed throughout the oceans. The discovery that DBC is present at similar concentrations throughout the deep ocean (Dittmar and Paeng, 2009) also implies that it is highly recalcitrant. In contrast to this impression, all dissolved polycyclic aromatics identified in the Fourier transform ion cyclotron resonance mass spectra of Congo River water were lost after 57 days of irradiation under simulated sunlight (Stubbins et al., 2010). This result, as well as observations of depleted concentrations of DBC in ocean surface waters (Dittmar and Paeng, 2009) and the well documented photo-reactivity of other dissolved aromatic compounds (Vähätalo et al., 1999; Opsahl and Benner, 1998; Stubbins et al., 2008; Spencer et al., 2009) indicate that photo-degradation may be a significant sink for DBC in natural waters. Therefore, the presented work sought to determine the photo-labile fraction of DBC in deep seawater.

2 Methods

2.1 Sample collection

Bermuda Atlantic Time Series (BATS) cruise 252 on board the RV Atlantic Explorer (6th to 10th November 2009) was joined to collect North Atlantic Deep Water (NADW), one of the major global deep ocean water masses. The NADW sample was collected by CTD on 09/11/2009 from 3000 m at the BATS site ($31^{\circ}40' \text{N}; 64^{\circ}10' \text{W}$). Three Niskin bottles were fired at 3000 m. As soon as the CTD was on deck and secure, large surface area $0.2\ \mu\text{m}$ capsule filters were attached (Polycap TC, Whatman) directly to the Niskin bottles' nipples and sample was gravity filtered into a 20 L fluorinated high density polyethylene carboy (Nalgene). The filters and carboy were precleaned by soaking for at least 24 h in acidified ultrapure (MilliQ) water (pH2 with hydrochloric acid; p.a.), soaking in basic ultrapure water for a further 24 h ($0.1\ \text{M}$ sodium hydroxide; p.a.), and rinsing with copious volumes of ultrapure water (filters flushed with $>20\ \text{L}$; carboy quintuple rinsed). The sample was then stored frozen in the dark at -20°C onboard RV Atlantic Explorer until she docked in Norfolk, Virginia, USA (19/12/2009). At this point the carboy was collected and taken to Old Dominion University, approximately 10 minutes drive from the dock, and returned to a -20°C freezer. From there, the sample

was later transported the nine hours to Skidaway Institute of Oceanography (SKIO), Georgia, USA in a large cooler with other frozen samples and placed back in a -20°C freezer upon arrival. Thus, the sample remained frozen from shortly after collection until defrosting for the irradiation study.

2.2 Irradiations

On the 20th of September 2010 the thawed sample was transferred to six 2 L precombusted spherical quartz irradiation flasks. A further 4 L aliquot was divided between two 2 L combusted borosilicate flasks, which were then wrapped in aluminium foil. All samples were then placed under a solar simulator fitted with 12 UVA-340 bulbs (integrated irradiance $\sim 25\text{ Wm}^{-2}$; Q-Panel), which provide a spectral shape and flux closely approximating natural sunlight from 295 to 365 nm (Stubbins et al., 2008), the main wavelength range for environmental photochemical reactions involving coloured dissolved organic matter (CDOM). The temperature in the solar simulator was kept at approximately 20°C using a side mounted fan. Sample water temperatures were likely higher as measured temperatures for test samples have been between 25°C and 30°C . Duplicate 2 L flasks were taken from the light table after 2, 6 and 28 days. One day of irradiation using this solar simulator design is approximate to 1.27 times daily solar irradiance during the winter at 36.89°N or 0.67 times the daily (12 h) irradiance at the equator (Helms et al., 2008; Spencer et al., 2009).

2.3 Ultraviolet-visible absorption spectra

Following irradiation, 20 mL aliquots were transferred from the flasks to combusted glass vials, which were then capped with Teflon septa and placed in the dark for approximately 8 h in order to return to room temperature. Subsequently this aliquot was drawn through a 10 cm flow through quartz absorbance cell situated in the light path of an Agilent 8453 ultraviolet-visible spectrophotometer and sample CDOM absorbance spectra were recorded. An aliquot of ultrapure water (MilliQ) was run immediately before and after the sample and these two ultrapure water spectra were averaged to provide a blank. Blank corrected absorbance spectra were then corrected for offsets due to scattering and instrument drift by subtraction of the average absorbance between 700 and 800 nm (Stubbins et al., 2011). Data output from the spectrophotometer were in the form of dimensionless absorbance or optical density (OD) and were subsequently converted to the Napierian absorption coefficient, a (m^{-1} ; Hu et al., 2002). Spectral slope (S , nm^{-1}) in the ranges 275 to 295 nm and 350 to 400 nm, together with the ratio of these slopes (slope ratio) were calculated following Helms et al. (2008).

2.4 Dissolved organic carbon

The total amount of DOM in a sample was defined in terms of the major building block of dissolved organics, DOC. In

order to analyse DOC, the rest of the sample was acidified to pH 2 by addition of hydrochloric acid (p.a.) to the irradiation flasks. A subsample was then taken and analyzed for non-purgable organic carbon using a Shimadzu TOC-VCPH analyzer fitted with a Shimadzu ASI-V autosampler following the methodology recommended by the manufacturer. Standards were prepared by the volumetric dilution of a stock solution containing $500\text{ }\mu\text{m-DOC}$ (potassium hydrogen phthalate, p.a.) to produce the following series of standards: 0, 2, 5, 8, 10, 25, 50, 75, $100\text{ }\mu\text{m-DOC}$. In addition to standards, aliquots of deep seawater reference material, Batch 10, Lot# 05–10, from the Consensus Reference Material Project (CRM) were analyzed to check the precision and accuracy of the DOC analyses. Analyses of the CRM deviated by less than 5 % from the reported value for these standards (41 to $44\text{ }\mu\text{m-DOC}$; <http://yyy.rsma.miami.edu/groups/biogeochem/Table1.htm>). Standard and sample volumes analyzed were 20 to 40 mL. Routine minimum detection limits in the investigators, laboratory using the above configuration are $2.8 \pm 0.3\text{ }\mu\text{m-C}$ and standard errors are typically $1.7 \pm 0.5\%$ of the DOC concentration (Stubbins and Dittmar, 2012).

2.5 Solid phase extraction

The remaining volume (1507 to 1975 mL) of acidified seawater was then solid phase extracted following the method of Dittmar et al. (2008). In brief, samples were loaded onto 1 g Varian Bond Elut PPL solid phase extraction columns at a flow rate of approximately 2 mL per minute. The columns were then rinsed with 20 mL of pH 2 ultrapure water to wash off residual salts and dried with zero grade air (Air-Gas) before being eluted with 6 mL of HPLC grade methanol (Fisher). The DOC extraction efficiency was determined for each sample by evaporating an aliquot of the methanol extract to dryness, redissolving it into a known volume of ultrapure water and determining the DOC concentration in this solution. The DOC in the aliquot of dried methanol (mg-C) was calculated as the concentration in the aqueous solution multiplied by the aqueous solution's volume. The total DOC yield (mg-C) in the 6 mL of methanol eluate was then calculated by multiplying the dried aliquot's DOC yield by 6 mL and dividing by the volume of methanol aliquot that was dried. The percentage yield was then determined by dividing the total DOC yield by the amount of DOC originally passed through the columns (i.e. the concentration of DOC in the irradiated NADW aliquots multiplied by the volume of each aliquot loaded onto the PPL columns).

2.6 Dissolved black carbon quantification

Dissolved black carbon was determined at the molecular level via a modified version of the benzenepolycarboxylic acid (BPCA) method after Dittmar (2008). In brief, 140 to $600\text{ }\mu\text{L}$ of the PPL methanol extracts, corresponding to

~2 μmol DOC, were transferred into pre-combusted (400 °C, 4 h) 1 mL glass ampoules, dried over night at 50 °C in an oven, and then redissolved in 500 μL of nitric acid (65 %, p.a.). The ampoules were then sealed and heated to 170 °C in a stainless steel pressure bomb inside a furnace for 9 h. After the ampoules had cooled, aliquots of 450 μL were transferred into 1 mL maximum recovery vials (Waters). The nitric acid was evaporated in a centrifugal evaporator (RVC 2–18, Christ, Germany) and the samples were redissolved in 100 μL of phosphate buffer solution (Na_2HPO_4 and NaH_2PO_4 each 5 mM in ultrapure water, buffered pH 7.2). BPCAs were quantified on a Waters ACQUITY UPLC (Ultra Performance Liquid Chromatography) system composed of a binary solvent manager, a sample manager, a column manager and a photodiode array light absorbance detector (PDA e λ). BPCAs were separated on a Waters ACQUITY UPLC BEH C18 Column (2.1 \times 150 mm, 1.7 μm) with an aqueous phase / methanol gradient modified after Dittmar (2008). The aqueous phase consisted of a tetrabutylammonium bromide solution (4 mM, ACS quality) in phosphate buffer (Na_2HPO_4 and NaH_2PO_4 each 5 mM in ultrapure water, pH 7.2). The injection volume was 10 μL . BPCAs were identified according to retention time and absorbance spectra (220 to 380 nm). Quantification was performed using the adsorption signal at 240 nm and external calibration. B3CAs and to some degree B4CAs are decomposed during the nitric acid oxidation procedure which negatively impacts the reproducibility and precision of the method (Dittmar, 2008). Furthermore, 1,2,4,5-B4CA is the only B4CA that is commercially available as a standard. Therefore, only the three robustly quantifiable BPCAs: 1,2,4,5-B4CA, B5CA and B6CA are reported. An extensive BPCA data set collected for the Southern Ocean (Dittmar and Paeng, 2009), the Gulf of Mexico (Dittmar et al., 2012) and other regions (unpublished) was used to develop a power-function relationship ($R^2 = 0.998$; $n = 352$) to predict the concentration of DBC from the sum of the quantitatively dominant and robustly quantified B5CA and B6CA. This extrapolation reduced the analytical error range of replicate analysis for the calculation of total DBC within the model dataset to below 2 % and provided a method to compare the data reported here with the total DBC concentrations reported elsewhere (Dittmar, 2008; Dittmar and Paeng, 2009). The concentrations of the individual BPCAs quantified are reported in Table 1 to enable comparison to other data on a BPCA by BPCA basis. The individual BPCA and total DBC concentrations reported here should be regarded as conservative estimates as either their extraction from the water column using PPL or their recovery during oxidation may not have been 100 % efficient.

3 Results and discussion

3.1 Dissolved organic carbon and coloured dissolved organic matter photo-degradation

Concentrations of DOC decreased $76 \pm 8 \%$ during the irradiation of NADW, falling from an initial $50.8 \pm 0.4 \mu\text{M}$ to $12.3 \pm 4.2 \mu\text{M}$ over 28 days (Table 1). Previous long-term irradiation studies report that photo-labile DOC constitutes between zero and 90 % of bulk DOC, with the highest percentage DOC photo-mineralisation reported for wetland plant leachates (Vähätalo and Wetzel, 2004). Two terrestrially dominated, high CDOM natural waters contained ~45 % photo-labile DOC (Obernosterer and Benner, 2004; Spencer et al., 2009), whereas photo-labile DOC made up less than 10 % of total DOC in a phytoplankton dominated lake and the waters of a phytoplankton culture (Obernosterer and Benner, 2004).

The previous irradiations noted above were conducted under various light sources, in irradiation vessels of varying pathlength and include samples with varying absorption coefficients. As such, the quantity and quality of light received by CDOM chromophores varied between those studies and the work presented here. Nevertheless, it is apparent that in terms of its photo-lability, NADW DOC has more in common with the terrestrially influenced samples than those freshly derived from phytoplankton. Lignin in solid phase extracts and the $\delta^{13}\text{C}$ of high molecular weight DOM, both signatures of DOM source, indicate that terrestrial DOM is exported to NADW from the Arctic Ocean (Hernes and Benner, 2006). However, Hernes and Benner (2006) also suggest that such terrestrial inputs constitute only 1.6 % of deep water DOC at BATS. It is therefore unlikely that the elevated photo-lability of NADW DOC stems principally from terrestrial inputs. Deep water DOM in the North Atlantic, as in other basins, has an apparent age of approximately 4000 years before present based upon $\Delta^{14}\text{C}$ -DOC (Bauer, 2002). Four thousand years is longer than the turnover time of the ocean and suggests a pool of highly recalcitrant DOM persists in the dark of the deep ocean. Furthermore, microbes and animal heterotrophs produce CDOM when utilizing bio-labile forms of organic matter (e.g. Ortega-Retuerta et al., 2009) and it has been suggested that the refractory DOM is not just conserved in the deep ocean, but that the microbes of the deep ocean rework DOM and sinking particles producing more recalcitrant (Jiao et al., 2010), more coloured DOM (Yamashita and Tanoue, 2008; Nelson et al., 2010), much in the same way as microbes produce coloured humic materials in soils. Therefore the high photo-lability of NADW DOC may result from inputs of terrestrial DOM and/or the reworking of autochthonous marine DOM and sinking particles into more coloured, photo-labile forms.

CDOM light absorption at 300 nm decreased $95 \pm 5 \%$ from $0.35 \pm 0.02 \text{ m}^{-1}$ to $0.02 \pm 0.02 \text{ m}^{-1}$ during the irradiation (Table 1). That close to 100 % of CDOM absorbance

Table 1. Summary of results of North Atlantic Deep Water photodegradation over 28 days. Parameters included: dissolved organic carbon (DOC), coloured dissolved organic matter Naperian absorption coefficient at 300 nm (CDOM α_{300}), spectral slope in the range 275–295 nm ($S_{275-295}$), the slope ratio ($S_{275-295} : S_{350-400}$), percentage of total DOC extractable using PPL, the concentration of dissolved black carbon (DBC), DBC as a percentage of total DOC, and the concentrations and ratios of the individual DBC derived benzenepolycarboxylic acids.

Time (days)	DOC (μM)	CDOM α_{300} (m^{-1})	$S_{275-295}$ (nm^{-1})	Slope* ratio	% DOC extracted	DBC (nM)	% DBC	B4 [#] (nM)	B5 (nM)	B6 (nM)	B5/B4	B6/B4	B6/B5
0	50.8 ± 0.4	0.35 ± 0.02	−0.021	1.6	74 ± 2	1044 ± 164	2.1	3.2 ± 0.4	16.3 ± 2.6	5.2 ± 0.9	5.1	1.6	0.32
2	49.9 ± 1.8	0.28 ± 0.04	−0.039	2.6	70 ± 4	872 ± 38	1.7	2.9 ± 0.2	13.9 ± 0.7	3.9 ± 0.1	4.8	1.4	0.28
6	47.4 ± 2.6	0.22 ± 0.03	−0.046	4.0	70 ± 5	741 ± 15	1.6	2.7 ± 0.1	11.8 ± 0.2	3.2 ± 0.1	4.4	1.2	0.27
28	12.3 ± 4.2	0.02 ± 0.02	−0.089	–	67 ± 5	55 ± 15	0.2	0.2 ± 0.1	0.9 ± 0.3	0.2 ± 0.0	3.9	0.9	0.23

*No slope ratio is presented for 28 days as the slope from 350 to 400 nm was not measurable using a 10 cm path length cuvette.

[#]B4 in this study refers solely to 1,2,4,5-Benzenetetracarboxylic acid.

was photo-labile is consistent with results from long-term irradiation studies of freshwaters (Vähätalo and Wetzel, 2004; Spencer et al., 2009). In further agreement with previous work studying the photo-degradation of DOM from freshwaters (Obernosterer and Benner, 2004; Spencer et al., 2009), estuaries (Moran et al., 2000), plant leachates (Vähätalo and Wetzel, 2004) and a phytoplankton culture (Obernosterer and Benner, 2004), CDOM was found to bleach more efficiently than bulk DOC (Table 1). The spectral slope between 275 and 295 nm ($S_{275-295}$) became steeper and the slope ratio ($S_{275-295} : S_{350-400}$; (Helms et al., 2008) became greater as the irradiation proceeded (Table 1). Such trends in these two parameters are indicative of a decrease in molecular weight and are generally observed during CDOM photo-bleaching (Helms et al., 2008).

3.2 PPL solid phase recovery of dissolved organic carbon

The percentage of DOC that was recovered using PPL solid phase extraction decreased slightly from 74 ± 2 % for the initial sample to 67 ± 5 % after 28 days of irradiation (Table 1) suggesting the preferential photo-degradation of stickier, hydrophobic molecules. The modest decrease in extraction efficiencies (7 ± 7 %) occurred alongside major gross removal of DOC (>75 %) and shifts in the quality of DOM as indicated by the shifts in carbon normalised light absorption and spectral slope parameters (Table 1).

3.3 Quantitative dissolved black carbon photo-degradation

Dissolved black carbon occurred at a concentration of 1044 ± 164 nM-C in NADW prior to irradiation. This is slightly higher than in the deep waters of the Southern Ocean (Dittmar and Paeng, 2009). During the irradiation, each of the analysed BPCAs decreased significantly and continuously, resulting in a decrease in total DBC from 1044 ± 164 nM-C to 55 ± 15 nM-C (Fig. 1a; Table 1). This equates to a 95 % decrease over the 28 day irradiation and corroborates earlier work in which all DBC compounds identified

in Fourier transform ion cyclotron (FT-ICR) mass spectra of Congo River water were absent after 57 days of irradiation under the same solar simulator used here (Stubbins et al., 2010) and other FT-ICR MS studies which noted a reduction in condensed compounds in DOM extracts following irradiation (Kujawinski et al., 2004; Gonsior et al., 2009). The magnitude of these losses demonstrates that photo-degradation could be an important process for DBC removal from natural waters, and may explain the low concentrations of DBC observed in Southern Ocean surface waters (Dittmar and Paeng, 2009).

The percentage of total DOC constituted by DBC decreased from 2.1 % at the start to 0.2 % at the end of the irradiation (Fig. 1b; Table 1). The decrease in the carbon-normalised DBC shows that DBC, like CDOM and aromatic compounds such as lignin (Opsahl and Benner, 1998; Vähätalo et al., 1999; Spencer et al., 2009), is preferentially photo-degraded relative to bulk DOC. DBC concentrations fell hand-in-hand with CDOM α_{300} (Fig. 2) indicating tight coupling between the photo-degradation of condensed aromatics (DBC) and the loss of bulk aromatic carbon as typified by CDOM. Previous work with ¹⁴C-labelled compounds demonstrated that the core aromatic structures of synthetic lignin are photo-mineralised to carbon dioxide (Vähätalo et al., 1999). Though the current study does not resolve the mechanism of DBC photo-degradation, the concomitant loss of ~76 % of DOC during the irradiation suggests that much of the DBC is also mineralised to carbon dioxide and carbon monoxide, the main inorganic photo-products of DOC photo-degradation (Miller and Zepp, 1995; Mopper and Kieber, 2002).

3.4 Qualitative dissolved black carbon photo-degradation

The molecular DBC method as applied here quantifies three broad classes of DBC oxidation products, each with a different number of carboxylic groups (Dittmar, 2008). These are the: benzeneTETRAcarboxylic acids (B4; only the 1,2,4,5-B4CA isomer was quantified here);

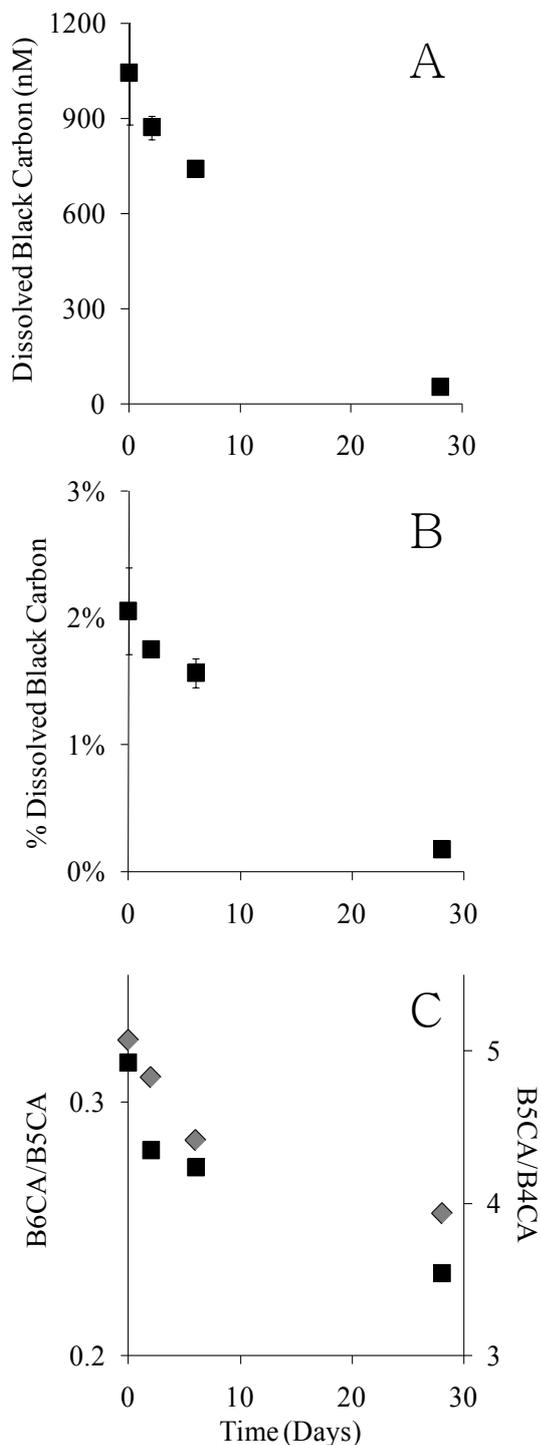


Fig. 1. Photodegradation of dissolved black carbon (DBC) in North Atlantic Deep Water over the course of a 28 day irradiation. Panel A: DBC concentration. Panel B: DBC as a percentage of total dissolved organic carbon. Panel C: ratios of DBC derived benzenecarboxylic acids. Ratios decrease as DBC becomes less condensed. Black squares are B6CA/B5CA. Grey diamonds are B5CA/B4CA.

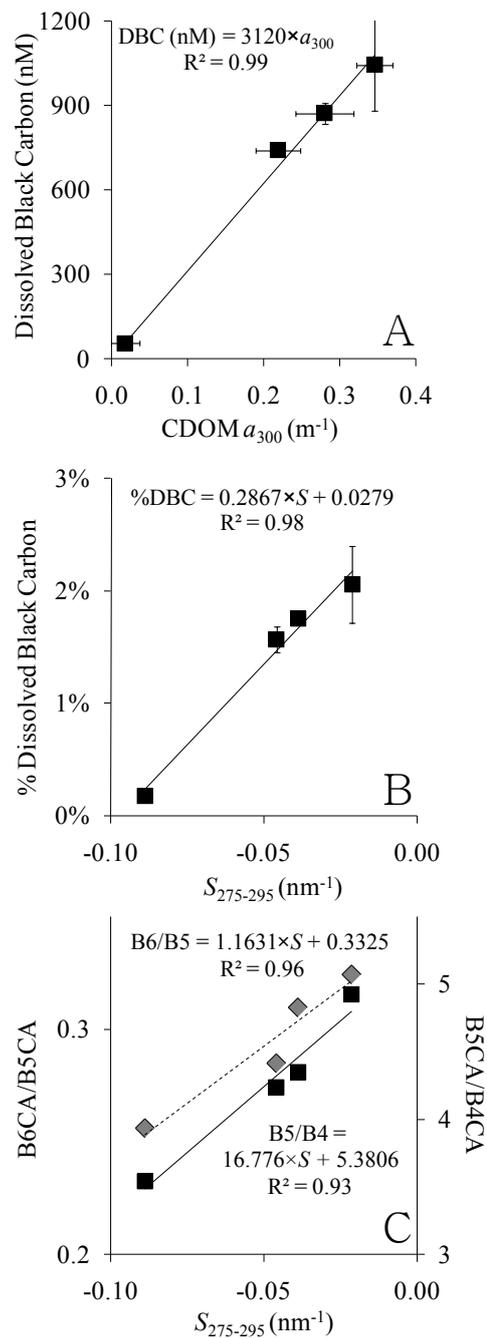


Fig. 2. Correlations between the optical properties of coloured dissolved organic matter (CDOM) and dissolved black carbon (DBC) quantity and quality over the course of a 28 day irradiation. Panel A: DBC concentration versus the CDOM Napierian absorption coefficient at 300 nm ($\text{CDOM } a_{300}$). Panel B: DBC as a percentage of total dissolved organic carbon versus the CDOM spectral slope between 275 and 295 nm ($S_{275-295}$). Panel C: ratios of DBC derived benzenecarboxylic acids versus $S_{275-295}$. Black squares and solid regression line are for B6CA/B5CA. Grey diamonds and broken regression line are for B5CA/B4CA.

benzenePENTAcid (B5); and, benzeneHEXAcid (B6). Each of these BPCAs provides structural information about DBC. B6 is indicative of highly condensed aromatics, whereas the benzene products with lower numbers of carboxylic substitutes are indicative of molecules with smaller numbers of condensed rings at their core (Schneider et al., 2010). North Atlantic Deep Water DBC had a B6/B5 of 0.32 (Table 1; Fig. 1c) consistent with the seawater samples analyzed by Dittmar (2008) and the relatively small size and low levels of condensation of polyaromatics identified in the oceans by FT-ICR MS (Dittmar and Koch, 2006).

In addition to reducing the amount of DBC, photo-degradation of DOM also altered the ratio of the different classes of BPCA discussed above. Figure 1c presents the trends in B6/B5 and B5/B4, which decreased as DBC became less condensed during the photo-degradation (note: B5/B4 is calculated as the ratio of B5CA to 1,2,4,5-B4CA and is therefore an overestimate of the ratio of B5CA to all possible B4CA isomers). This shift towards less condensed DBC components during irradiation is seen for all the ratios of BPCAs (Table 1). The steepening of spectral slope ($S_{275-295}$) during the irradiation was correlated with % DBC and with the values for B6/B5 and B5/B4 (Fig. 2b and c; Table 1) verifying that $S_{275-295}$ is a valuable proxy for the aromatic quality of DOM and that $S_{275-295}$ may also provide a proxy for the tracking of DBC quality (B6:B5:B4) in natural waters.

The changes in DBC as a percentage of bulk DOC and the ratios of the various BPCAs to one another (Table 1) indicate a continuum of photo-labile DOM. In this continuum, lability follows the trend B6>B5>B4>bulk DOC, i.e. the more condensed a compound, the more photo-labile it will be. A result in agreement with Fourier transform ion cyclotron mass spectrometry data from an irradiation study of Congo River water (Stubbins et al., 2010). Presumably the less condensed aromatics that yield B3CA oxidation products and were not quantified here would be less photo-reactive than their more condensed analogues. Photo-degradation may be responsible for the shift from highly condensed aromatics seen in terrestrial waters to less condensed DBC structures identified in the open ocean (compare values for different environments in Dittmar and Paeng, 2009; Dittmar, 2008; Ziolkowski and Druffel, 2010). Ratios between BPCAs will likely provide useful proxies for the photo-degradation state of DBC, much the same as acid:aldehyde ratios are indicative of lignin diagenesis (Hedges et al., 1988; Opsahl and Benner, 1995; Spencer et al., 2009). By extension, DBC:DOC and BPCA ratios should also offer insight into the irradiation history of the bulk DOM pool within a water body. Critical to the use of these ratios as indicators of photo-degradation history will be an understanding of other factors that may also alter BPCA ratios. Factors of potential relevance include, but are not limited to, differences in source material (Guggenberger et al., 2008; Haumaier, 2010), aging in soil (Abiven et al., 2011)

or the water column, and sorption, the latter having a significant influence upon the ratios of various lignin-derived phenols (Hernes et al., 2007).

3.5 The oceanic photo-chemical sink of dissolved black carbon

Although further work is required to determine the photo-lability of DBC in other waters and to conduct more controlled apparent quantum yield experiments designed for the calculation of environmentally relevant DBC photo-degradation rates, the data presented here can be used to generate an initial, though poorly constrained estimate for the photo-chemical turnover of DBC in the global ocean. In the current irradiations, the photo-degradation of DBC and CDOM light absorption were well correlated (Fig. 2a), unfortunately there is no estimate of the global oceanic photo-chemical CDOM sink for use in scaling DBC photo-degradation to the global ocean. However, DBC to DOC photo-degradation ratios can be used and scaled to estimates of global DOC photo-mineralisation. Dissolved black carbon constituted 18 % of total DOC photo-mineralisation after two days. After 28 days DBC contributed only 3 % to the total DOC loss. The photo-degradation state of DOM in natural surface waters is hard to predict making it unclear which of these ratios more closely represents the ratio of DBC:DOC photo-degradation in the open ocean. Therefore, each of these ratios was scaled to total oceanic DOC photo-mineralisation, rates of which, not including the photo-production of bio-labile DOC, have been estimated to be between 705 and 2680 Tg-C yr⁻¹ (Mopper and Kieber, 2001; Stubbins et al., 2006). Scaling DBC photo-degradation to upper and lower limits for both DBC:DOC photo-degradation ratios and estimates of DOC loss resulted in global DBC photo-mineralisation rates of between 20 to 490 Tg-C yr⁻¹. Assuming that DBC constitutes about 2 % of the 700 Pg-C of DOC in the global ocean (Dittmar and Paeng, 2009), the 14 Pg-C standing stock of oceanic DBC could be completely photo-degraded within 28 to 773 years. This initial estimate is considerably shorter than the apparent age of DBC in the open ocean (Ziolkowski and Druffel, 2010), suggesting that photo-chemistry is the dominant sink for marine DBC. Therefore, the apparent persistence of DBC in the oceans for millennia is facilitated not by the inherent inertness of DBC molecules, but by the slow pace of ocean turnover which controls the supply of DBC to photic surface waters.

4 Conclusions

In surface and deep ocean waters the high molecular weight fraction of DBC has the greatest apparent age of any widespread, dissolved organic compound (radiocarbon age >15 000 years before present; Ziolkowski and Druffel, 2010) and in the deep ocean DBC concentrations show limited

variability (Dittmar and Paeng, 2009). Such results indicate that oceanic DBC is highly refractory. Although DBC in surface waters is apparently old, its concentrations vary, with higher concentrations associated with coastal inputs and lowest concentrations found in the open ocean (Dittmar and Paeng, 2009). This spatial trend is analogous to that for CDOM, which is elevated in coastal waters and depleted in the open ocean gyres, with the major global trends in surface waters driven by coastal inputs and removal through photo-degradation (Blough and Del Vecchio, 2002; Coble et al., 2002; Nelson and Siegel, 2002; Nelson et al., 2007; Del Vecchio et al., 2009). Though data is much scarcer for DBC, it appears that these same processes may also control DBC distribution in surface waters. The data presented here certainly indicate DBC to be highly photo-labile with ~95 % of DBC in the initial sample being lost within 28 days of irradiation (Fig. 1a; Table 1) and an estimate of the rate of DBC photo-degradation in the global ocean indicates that the entire stock of oceanic DBC could be photo-degraded in approximately 30 to 800 years.

Total DBC was correlated with CDOM light absorption throughout the experiment (Fig. 2a). Similarly, the % contribution of DBC to total DOC and the ratios of BPCAs to one another correlated with the CDOM spectral slope (Fig. 2a and b). These correlations suggest that the optical properties of the total oceanic CDOM pool are closely related to the amount and quality of DBC present. These correlations also suggest that CDOM optical properties may prove to be useful proxies for the concentration and the quality of DBC present in natural waters. The great power of these proxies is that they would allow DBC concentrations to be estimated from the thousands of existing CDOM data points in publications (e.g. Kitidis et al., 2006; Siegel and Michaels, 1996; Nelson et al., 1998; Rochelle-Newall et al., 1999; Siegel et al., 2005; Nelson and Siegel, 2002; Yamashita and Tanoue, 2004) and in open databases (e.g. www.ices.ucsb.edu/GlobalCDOM/; www.nodc.noaa.gov/; <http://bcodmo.org/>; www.bodc.ac.uk and www.pangaea.de/). Optical proxies would also enable the remote sensing of surface DBC based upon robust estimates of the CDOM absorbance in surface waters (e.g. Siegel et al., 2002). Further work is required to determine relationships between DBC and CDOM optical properties in natural waters.

New analytical techniques have delivered an understanding that DOM is an assortment of molecules and this understanding has led to the development or borrowing of new tools to look ever closer at dissolved organic molecules. On examination the chemistries and reactivities of the molecules differ widely from one another, such that two molecules from the same locations (soil, river, ocean) can have wildly different fates in the environment. It therefore makes sense to subdivide the DOM pool where possible, building up global budgets for quantifiable components of the DOM pool. In the case of DBC, a logical approach would be to build a budget for each BPCA, to relate this to total DBC, and finally,

where relevant and with careful assumptions, to relate this to the cycling of more inclusive components of the DOM pool, such as photo-labile or bio-refractory DOM, for which DBC seems to offer a promising tracer.

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