

**A molecular  
perspective on the  
ageing**

R. Flerus et al.

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# A molecular perspective on the ageing of marine dissolved organic matter

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## Abstract

Dissolved organic matter (DOM) was extracted with solid phase extraction (SPE) from 137 water samples from different climate zones and different depths along an Eastern Atlantic Ocean transect. The extracts were analyzed with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with electrospray ionization (ESI).  $\Delta^{14}\text{C}$  analyses were performed on subsamples of the SPE-DOM. In addition, the amount of dissolved organic carbon was determined for all water and SPE-DOM samples as well as the yield of amino sugars for selected samples. Linear correlations were observed between the magnitudes of 43% of the FT-ICR mass peaks and the extract  $\Delta^{14}\text{C}$  values. Decreasing SPE-DOM  $\Delta^{14}\text{C}$  values went along with a shift in the molecular composition to higher average masses ( $m/z$ ) and lower hydrogen/carbon (H/C) ratios. The correlation was used to model the SPE-DOM  $\Delta^{14}\text{C}$  distribution for all 137 samples. Based on single mass peaks a degradation index was developed to compare the degradation state of marine SPE-DOM samples analyzed with FT-ICR MS. A correlation between  $\Delta^{14}\text{C}$ , degradation index, DOC values and amino sugar yield supports that SPE-DOM analyzed with FT-ICR MS reflects trends of bulk DOM. A relative mass peak magnitude ratio was used to compare aged SPE-DOM and fresh SPE-DOM regarding single mass peaks. The magnitude ratios show a continuum of different reactivities for the single compounds. Only few of the compounds present in the FT-ICR mass spectra are expected to be highly degraded in the oldest water masses of the Pacific Ocean. All other compounds should persist partly thermohaline circulation. Prokaryotic (bacterial) production, transformation and accumulation of this very stable DOM occurs probably primarily in the upper ocean. This DOM is an important contribution to very old DOM, showing that production and degradation are dynamic processes.

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## 1 Introduction

Marine dissolved organic matter (DOM) is one of the major active reservoirs of the global carbon cycle. The amount of marine dissolved organic carbon (DOC) is estimated to be 662 Gt, which is comparable to the amount of carbon in atmospheric CO<sub>2</sub> (Hedges, 1992; Hansell et al., 2009; Tans, 2010). Since the average age of bulk DOC below the thermocline is about 4000 years in the Sargasso Sea and about 6000 years in the central North Pacific, marine DOM plays an important role in long-term carbon storage and sequestration of atmospheric CO<sub>2</sub> (Williams and Druffel, 1987; Bauer, 2002). This older DOM pool represents a refractory background with concentrations of 35–45 μmol kg<sup>-1</sup> (Hansell and Carlson, 1998; Ogawa et al., 1999) upon which labile and semi-labile pools of DOM are superimposed in the upper ocean. Numerous studies have examined the fluxes, remineralization or temporal variability of accumulated DOC (e.g. Goldberg et al., 2009; Hansell et al., 2009; Carlson et al., 2010). Jiao et al. (2010) proposed the concept of the microbial carbon pump as a potential process for the production of “modern” refractory DOM in surface waters. However, the mechanisms of production, diagenesis and preservation of highly stable DOM are still unknown. The molecular analysis is particularly challenging as only a minor fraction of the DOM can be analyzed molecularly and identified as carbohydrates, lipids, amino acids or amino sugars (Benner, 2002).

Ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with electrospray ionization (ESI) was successfully applied to distinguish thousands of compounds of different elemental compositions in ultra-filtered and solid-phase extracted marine DOM (SPE-DOM) (Koch et al., 2005; Hertkorn et al., 2006; Kujawinski et al., 2009). Ultrahigh resolution allows elemental formulas to be assigned for individual mass peaks (Stenson et al., 2003). Water samples of different spatial origin can be distinguished based on the molecular information from FT-ICR MS analysis. However, to date only a few numbers of samples have been compared with this technique preventing a systematic comparison of FT-ICR MS data and additional analytical parameters.

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Radiocarbon age and amino sugars are critical diagnostic parameters to assess the production of refractory DOM. The analysis of amino sugars in seawater provides very valuable information on the early diagenesis of DOM (Benner and Kaiser, 2003; Davis et al., 2009; Kaiser and Benner, 2009). Radiocarbon age provides a timeline from carbon fixation in the upper ocean and its subsequent turnover and flux to the deep ocean for bulk DOC and individual components or compound classes (Druffel et al., 1992; Aluwihare et al., 1997; Loh et al., 2004; Repeta and Aluwihare, 2006). Due to the analytical challenge of radiocarbon analysis of bulk DOC, the radiocarbon age has only been determined for a few samples at some locations including the Central North Pacific (Druffel et al., 1992; Williams and Druffel, 1987), the Southern Ocean (Druffel and Bauer, 2000) and the Sargasso Sea (Bauer et al., 1992; Druffel et al., 1992). A handful of additional studies have been performed on  $\Delta^{14}\text{C}$  of marine DOM fractions of differing size or chemical components such as humic isolates, lipid extracts, carbohydrate-like DOM and protein-like DOM. The high molecular weight ( $>10$  kD) DOM is of recent age suggesting greater lability and faster turnover, whereas the low molecular weight ( $<1$  kD) DOM is apparently older (Santschi et al., 1995; Loh et al., 2004). Humic substances isolated with XAD-resins are similar to bulk C pools with radiocarbon ages only slightly older (Druffel et al., 1989). The oldest age (up to 17 000 yr) was determined in lipid extracts (Loh et al., 2004). However, each DOM fraction still consists of multiple compounds with a continuum of ages, and consequently the bulk age of DOM represents an average of all the individual compounds. To date a direct linkage between radiocarbon age and DOM on a molecular level has not been reported.

The aim of this study was to investigate the ageing, processes and associated molecular changes of DOM along an Eastern Atlantic Ocean transect. Our combination of FT-ICR MS with radiocarbon age analysis of SPE-DOM from different depths and biogeochemical regions provided a unique opportunity to investigate the age-composition and related molecular signatures of a large ocean system. To discuss the data in a broader ecological and biogeochemical context, FT-ICR MS data were combined for the first time with the environmental parameters, DOC, amino sugars and bacterial

activity, each determined independently. Our ultimate goal was to elucidate trends that are characteristic for the entire Atlantic Ocean.

## 2 Materials and methods

### 2.1 Sampling

5 Water samples were collected along a transect from 50.2° N to 31.4° S in the East Atlantic Ocean in November 2008 during the cruise ANT-XXV/1 of R/V *Polarstern*. Surface water was sampled 3 times per day with a fish sampler, which was fixed alongside the ship providing a continuous flow of surface water (~2 m water depth). Water from 200 m and the fluorescence maximum was sampled daily with a rosette sampler connected to a CTD, as well as water from 7 selected stations from surface to bottom (see details in Koch and Kattner, 2011). Samples for the analysis of DOC and amino sugars were filtered through GF/F filters (Whatman, pre-combusted for 4 h, 450 °C) and stored in pre-combusted glass ampoules at -20 °C.

### 2.2 DOM extraction

15 FT-ICR MS measurement requires the concentration and desalting of marine DOM. Therefore DOM was extracted on board using solid phase extraction (SPE) for which the term SPE-DOM will be used in the following. Filtered samples were acidified with HCl (hydrochloric acid, p.a. grade, Merck) to pH 2. The DOM was extracted using SPE cartridges (PPL, 1 g, Varian, Mega Bond Elut; Dittmar et al., 2008). The cartridges were rinsed with methanol (LiChrosolv; Merck), followed by acidified ultra-pure water (Milli-Q, pH 2, HCl) and then 5 L of seawater was gravity filtered through each cartridge. Subsequently remaining salt was removed with acidified ultra-pure water. After drying with nitrogen gas, DOM was eluted with 5 mL methanol and stored in pre-combusted glass ampoules at -20 °C.

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## 2.3 Analyses

The DOC concentration was determined by high temperature catalytic oxidation with a Shimadzu TOC-VCPN analyzer. Water samples were acidified in the auto-sampler and analyzed directly. The DOC content of the SPE-DOM was determined by evaporation of 50  $\mu\text{L}$  methanol extract re-dissolved in ultra-pure water.

Bacterioplankton production was estimated by  $^3\text{H}$ -leucine uptake (Smith and Azam, 1992). Triplicate subsamples (1.5 mL) and one trichloroacetic acid-killed control were amended with 5 nM  $^3\text{H}$ -leucine (Amersham, specific activity  $160\text{ Ci mmol}^{-1}$ ) and incubated at in situ temperature ( $\pm 2^\circ\text{C}$ ) in the dark. Incubation time varied depending on depth:  $\sim 2$  h for upper waters (up to 200 m) and up to 12 h (below 200 m). Samples were processed according to Smith and Azam (1992) and radioassayed with a Wallac scintillation counter after addition of 1 mL of Ultima Gold AB scintillation cocktail. The disintegrations per minute (DPM) of the killed control were subtracted from the mean DPM of the corresponding duplicate samples and converted to leucine incorporation rates. A conversion factor of  $3.1\text{ kg C mol}^{-1}$  was applied (Kirchman, 1993).

Concentrations of galactosamine (GalN), mannosamine (ManN) and glucosamine (GlcN) were determined by high-performance anion-exchange chromatography coupled to a pulsed amperometric detector (Kaiser and Benner, 2000). After hydrolysis in 3M HCl (5 h,  $100^\circ\text{C}$ ) samples were neutralized with a self-absorbed ion retardation resin (AG11 A8, Biorad) and stored frozen until analysis. Samples were desalted by solid-phase extraction using Biorad's AG50 X8 resin in the  $\text{Na}^+$ -form before chromatographic separation. Subsequently, GalN, ManN and GlcN were separated isotropically on a Dionex PA20 anion-exchange column with 2 mM NaOH at a flow rate of  $1\text{ mL min}^{-1}$ .

Subsamples of SPE-DOM were quantitatively transferred to combusted ( $500^\circ\text{C}$ ) quartz tubes (6 mm diameter), evaporated under a stream of  $\text{N}_2$ , sealed under vacuum and combusted at  $900^\circ\text{C}$  to  $\text{CO}_2$  using a CuO/Ag metal catalyst (Sofer, 1980). The  $\text{CO}_2$  from break-seals was subsequently reduced to graphite in an atmosphere

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of H<sub>2</sub> over a cobalt catalyst (Vogel et al., 1987). Graphite targets were analyzed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory.  $\Delta^{14}\text{C}$  is defined as the (per mil) deviation of a sample from the <sup>14</sup>C activity of a 1950 standard, corrected for fractionation according to Stuvier and Polach (1977).

5 Total measurement uncertainties for  $\Delta^{14}\text{C}$  analyses of these samples were typically  $\pm 4\text{‰}$ .

FT-ICR MS analyses of 137 SPE-DOM samples was performed with an Apex Qe mass spectrometer (Bruker Daltonics) equipped with a 12 T superconducting magnet (Bruker Biospin) and an Apollo II Dual electrospray source (Bruker). Prior to analysis, SPE-DOM was adjusted to similar DOC concentrations by dilution with methanol (factor 3.1–9.7). The diluted extracts were analysed with ESI in negative ion mode (capillary voltage  $-4.2\text{ kV}$ , infusion flow rate  $2\ \mu\text{L min}^{-1}$ ). Spectra were calibrated internally with compounds, which were repeatedly identified in marine DOM samples (339.10854, 369.11911, 411.12967, 469.13515, 541.15628 *m/z*; Flerus et al., 2011). 512 scans were added to acquire one spectrum. All ions were singly charged and the mass accuracy was below  $\pm 0.2\text{ ppm}$  for the ions used for the internal calibration.

## 2.4 FT-ICR MS data evaluation

The mass spectra were evaluated in the range *m/z* 200–500 to guarantee a sufficient mass accuracy for the correct elemental formula assignment. For each peak with a signal to noise ratio of  $S/N \geq 3$ , elemental formulas were calculated in the range of  $\pm 0.5\text{ ppm}$  as described elsewhere (Koch et al., 2005, 2007). The isotopes included for the formula calculation were as follows: <sup>12</sup>C (0– $\infty$ ), <sup>13</sup>C (0–1), <sup>1</sup>H (0– $\infty$ ), <sup>16</sup>O (0– $\infty$ ), <sup>14</sup>N (0–2), <sup>32</sup>S (0–1). The average mass accuracy for all assigned peaks was  $< \pm 0.2\text{ ppm}$ . For unambiguous elemental formula assignment the “nitrogen-rule” was applied and the following thresholds were defined:  $O/C \leq 1.2$  and  $H/C \leq 2C+2+N$  (Koch et al., 2005). All formulas with <sup>13</sup>C isotopes were removed from the data set as they represent duplicates of the <sup>12</sup>C parent molecules. In addition, all formulas which were present in less than 6 mass spectra were also excluded to avoid false formula

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assignments. Prior to mass spectra comparison, the mass peak magnitudes of each spectrum were normalized to the sum of all identified mass peak magnitudes of the respective spectrum and a signal intensity threshold of 100 ppm was applied. Based on the 100 ppm cutoff on a presence-absence basis, 42 % of the detected molecular formulas were detected in all 137 samples, 76 % were present in at least 100 samples showing the typical magnitude pattern of marine SPE-DOM (Fig. 1). Most mass peaks, which were not present in all samples, showed magnitudes close to the cutoff limit of 100 ppm. Due to the molecular similarities of the samples, our data evaluation was based on normalized peak magnitudes instead of the presence/absence-based approach as it was applied for biomarker approaches for DOM in glacial or riverine environments (Bhatia et al., 2010; Sleighter and Hatcher, 2008).

### 3 Results and discussion

The  $\Delta^{14}\text{C}$  values ranged from  $-279\%$  in surface water (2 m) to  $-446\%$  in deep water extracts ( $>2500$  m, Fig. 2). The highest surface water  $\Delta^{14}\text{C}$  values were comparable with the  $\Delta^{14}\text{C}$  values determined by Druffel and Bauer (1992) in the Sargasso Sea. In comparison to the results from the Sargasso Sea, our  $\Delta^{14}\text{C}$  values in deeper water layers ( $>1000$  m) were more negative and closer to XAD isolates. 43 % of the FT-ICR mass peaks showed either a significantly linear positive (POS) or linear negative (NEG) correlation ( $p < 0.01$ ) with the  $\Delta^{14}\text{C}$  values (peaks with a correlation factor  $> 0.8$  and elemental formulas are presented in Table A1 and A2 in Appendix A). To reduce the data set, the magnitudes of all highly significantly POS and NEG correlating mass peaks were summed up separately. The summed magnitudes of these mass peaks account for  $66 \pm 1.4\%$  of the summed magnitudes of all peaks in each spectrum. The linear relationship between the  $\Delta^{14}\text{C}$  values and the summed magnitudes (Fig. 3a, b) were used to calculate two  $\Delta^{14}\text{C}$  values for each of the 137 SPE-DOM samples. The  $\Delta^{14}\text{C}$  values calculated with the POS summed magnitudes linearly correlated with values calculated with the NEG summed magnitudes with a slope of approximately 1.

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Hence, the arithmetic average of the two calculated  $\Delta^{14}\text{C}$  values was used as the final  $\Delta^{14}\text{C}$  value ( $\Delta^{14}\text{C}_{\text{Cal}}$ ) for each sample. The  $\Delta^{14}\text{C}_{\text{Cal}}$  values are presented for the upper 200 m in Fig. 4, and as single values for the deep water in Table 1a.

We calculated average relative magnitude ratios for single (identical) formulas in aged ( $\Delta^{14}\text{C}_{\text{Cal}}$ :  $< -450\text{‰}$ , water depths  $>800\text{ m}$ ) and young ( $\Delta^{14}\text{C}_{\text{Cal}}$ :  $> -280\text{‰}$ , water-depths  $<100\text{ m}$ ) samples. Subsequently, masses were considered which were present in at least 123 (90%) of all samples. With this approach, 73% of all mass peaks (covering  $97\% \pm 1.4$  of the summed magnitudes per sample) were included in the calculation. The remaining mass peaks showed low magnitudes close to the cut-off of 100 ppm. A few mass peaks were present in selected sample groups such as surfactant-derived sulphur compounds which were detected in the anthropogenically impacted areas such as the English Channel. However, these mass peaks were characteristic for spatially narrow areas and did not reflect trends for the bulk samples. Because the bulk concentrations and the age of SPE-DOC decreased with depth we assume that the masses with the highest relative magnitude ratios  $>1$  (aged vs. fresh) were not or less degraded compared to compounds represented by mass peaks with low ratios  $<1$ .

### 3.1 Molecular characteristics of DOM diagenesis

We observed clear differences in the molecular characteristics between significantly correlated POS and NEG mass peaks. The peak magnitudes of the POS masses were generally much lower than those of the NEG mass peaks and the average  $m/z$  was inversely correlated with  $\Delta^{14}\text{C}$  values (Fig. 5). The magnitude averaged  $m/z$  increased from  $392.1 \pm 1.3$  for young ( $\Delta^{14}\text{C}_{\text{Cal}}$ :  $> -280\text{‰}$ ) to  $401.7 \pm 0.5$  for aged SPE-DOM ( $\Delta^{14}\text{C}_{\text{Cal}}$ :  $< -450\text{‰}$ ). Previous studies showed an increasing extent of diagenetic processing (Kaiser and Benner, 2009) and a decreasing bioreactivity (Amon and Benner, 1996) with decreasing molecular size from high molecular weight DOM ( $>1\text{ kDa}$ ) to low molecular weight DOM ( $<1\text{ kDa}$ ). Further, Dittmar and Kattner (2003) suggested a

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comparatively higher refractory character for small DOM molecules. However, these previous results were obtained with gel permeation chromatography or ultrafiltered DOM (UDOM) and include or represent high molecular weight DOM (>1 kDa). In contrast, our study focused on SPE-DOM (extraction efficiency  $42.5 \pm 3.9\%$  C of bulk DOC) analyzed in the lower FT-ICR MS  $m/z$  range between 200–500 Da. This highly detailed analysis offers to identify additional trends within this SPE fraction. Hertkorn et al. (2011) obtained results using nuclear magnetic resonance spectroscopy (NMR), which allows indirect conclusions for a similar trend of SPE-DOM with depth.

The van Krevelen diagram (Kim et al., 2003) showed differences in the elemental composition of the POS and NEG masses (Fig. 6). The majority of CHO compounds of the POS formulas were in the high H/C range (1.4–1.7), whereas all CHO compounds of the NEG masses were in the medium to low H/C range (0.9–1.4, Fig. 6a, b). Within a similar region of the van Krevelen diagram  $m/z$  differed significantly between POS and NEG formulas: in the region of  $H/C \leq 1.4$ , the average mass for NEG formulas is  $427.9 \pm 48.1$  and for the few POS formulas  $298.1 \pm 32.6$ . CHON compounds of the POS masses had low to medium H/C ratios (1.15–1.50) and medium O/C ratios (0.33–0.63). CHON compounds of NEG formulas occurred only in the low H/C (0.95–1.35) and medium O/C range (0.35–0.65, Fig. 6c, d). This is probably due to low magnitudes in the high H/C range, which fell below the cutoff of 100 ppm. The H/C ratio shift also affected the weighted average DBE, which was in the range from 4–9 for the POS masses and in the range from 7–13 for the NEG masses.

The very similar FT-ICR MS spectra patterns of marine DOM as well as the presence of the most important mass peaks in each spectrum are clear indicators for a large portion of compounds representing the molecular background of marine DOM (Koch et al., 2005; Hertkorn et al., 2006; Gonsior et al., 2011). Further, elemental composition trends were determined also for the bulk of mass peaks. The magnitude averaged H/C ratios decreased from  $1.27 \pm 0.01$  in young ( $\Delta^{14}C_{\text{Cal}}: > -280\text{‰}$ ) to  $1.25 \pm 0.00$  in aged SPE-DOM ( $\Delta^{14}C_{\text{Cal}}: < -450\text{‰}$ ). These bulk trends can be visualized by the relative magnitude ratios of the single mass peaks in young and aged SPE-DOM (Fig. 7). This

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broader picture shows a continuous transition from mass peaks with the lowest ratios to mass peaks with the highest ratios, covering a continuum of different reactivity rates. The magnitude averaged DBE increased from  $7.76 \pm 0.05$  in young to  $8.10 \pm 0.03$  in aged SPE-DOM. Surprisingly no clear trend was found in the magnitude averaged O/C ratios, and we are currently examining potential reasons for this disparity.

Hertkorn et al. (2006) analysed surface and deep UDOM from the Pacific Ocean using NMR and FT-ICR MS. They identified carboxyl-rich alicyclic molecules (CRAM) as a major constituent in surface and deep UDOM which was suggested to resist biodegradation. The area occupied by CRAM in the van Krevelen diagram corresponds well with the area of our highest SPE-DOM magnitude ratios (aged vs. fresh). Hence, CRAM is obviously also a significant contributor to SPE-DOM. The trends are similar for CHO, CHON and CHOS compounds.

### 3.2 East Atlantic Ocean DOM degradation state and degradation index

The linear correlation between single mass peaks and SPE-DOM  $\Delta^{14}\text{C}$  provides the possibility to compare SPE-DOM samples in terms of their degradation state. To calculate a degradation index we selected 5 positively (POS) correlating and 5 negatively (NEG) correlating mass peaks (Table 2) which were present in all mass spectra with sufficient magnitude and which also occurred in previous ~400 samples from other locations and environments. The index  $I_{\text{DEG}}$  is calculated using the molecular formulas given in Table 2:

$$I_{\text{DEG}} = \frac{\sum \text{magnitude}_{\text{NEG}} / \sum \text{magnitude}_{(\text{NEG}+\text{POS})}}{(\sum \text{magnitude}_{\text{POS}} / \sum \text{magnitude}_{(\text{NEG}+\text{POS})} \times 100) + 1} \times 1000$$

$I_{\text{DEG}}$  increases with the degradation state of the sample. We observed from our database that  $I_{\text{DEG}}$  also depends on the instrument, extraction technique and environment. For example, samples from soils and sediments generally revealed lower values for  $I_{\text{DEG}}$  than for ocean water (data not shown). However, if similar sample extracts are measured with the same instrument in series the  $I_{\text{DEG}}$  trends are comparable.

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$I_{\text{DEG}}$  for our East Atlantic Ocean samples was in the range of 14.6–29.1 for the surface samples (Fig. 8a) and 30.1–40.1 for deep water >200 m.  $I_{\text{DEG}}$  showed a strong correlation with the  $\Delta^{14}\text{C}$  values and the DOC values. In particular, in the upper 200 m changes in DOC concentrations were reflected in the  $I_{\text{DEG}}$ . The lowest  $I_{\text{DEG}}$  was found in the area with the youngest SPE-DOM in the upper 25 m between 2–12° N along with the highest DOC concentrations. This was the most stratified region with thermocline depths of 25–30 m. The accumulation of freshly produced DOC in highly stratified water was also reported by Carlson et al. (1994) and Goldberg et al. (2009). At 200 m depth the lowest  $I_{\text{DEG}}$  and the youngest SPE-DOM were north of 40° N. The highest  $I_{\text{DEG}}$  as well as the oldest SPE-DOM and lowest bulk DOC concentrations matched with the tropical divergences around 15° N and 10° S which are upwelling areas.

To support the differentiation in fresh and old DOM, amino sugars were determined directly in water samples as an independent measurement. Amino sugars are bioreactive compounds and the DOC-normalized yield of amino sugars is an indicator for the degradation state of DOM (Benner and Kaiser, 2003; Kaiser and Benner, 2009). The significant correlation between  $\Delta^{14}\text{C}_{\text{Cal}}$  and the yield of amino sugars is consistent with previous observations indicating they are more reactive than bulk DOC and indicates that our mass peak magnitude based  $\Delta^{14}\text{C}$  calculation is reasonable (Fig. 9). The exponential relation between the amino sugar yield and  $\Delta^{14}\text{C}_{\text{Cal}}$  also suggests that a fraction of the youngest and most bioavailable compounds was not recovered by SPE or was not detected by FT-ICR MS analysis.

Finally, also the bacterial activity correlated with  $I_{\text{DEG}}$ ,  $\Delta^{14}\text{C}_{\text{Cal}}$  and amino sugar yields in the upper 200 m of the water column (Fig. 8b). The highest bacterial activity was determined in the same area, where also the youngest and least degraded SPE-DOM with the highest DOC values occurred. This is an indicator for bacterial reworking processes of DOM in the upper ocean.

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### 3.3 Degradation continuum

Several studies present strategies to explain mechanisms of redistribution of DOM in the water column. These studies are based on two or three component models (Williams and Druffel, 1987; Beaupre and Druffel, 2009; Hansell et al., 2009; Beaupre and Aluwihare, 2010). The models suggest a refractory DOM background fraction and labile or semi labile fractions of DOM with distinct isotopic compositions. Beaupre and Druffel (2009) used 2-component Keeling plots to estimate the radiocarbon age of the background and the fresh DOM fractions. Applying the Keeling plot to the SPE-DOM samples from the seven deep stations results in similar values for the fresh SPE-DOM fraction at every station (Table 3). This provides further evidence that the radiocarbon age of SPE-DOM is representative of that for the bulk DOC. Beaupre and Druffel (2009) calculated  $\Delta^{14}\text{C}$  for the background DOM, but since  $\Delta^{14}\text{C}$  was too low for the oldest water sample they considered a multiple component system. Our results indeed show a wide spectrum of DOM reactivity represented by varying relative magnitude ratios of young and aged samples, supporting the hypothesis of a continuum of DOM reactivity and age.

As mentioned above, we assume that the compounds in the FT-ICR mass spectra are degraded over time, but to varying extents. To elucidate at which point during the thermohaline circulation a single compound would be completely degraded, we performed a rough estimate using the following assumptions: (i) each mass peak either represents one compound or several compounds with similar degradation rates. A recent study by Witt et al. (2009) shows that the structural variability of a single elemental formula in the FT-ICR mass spectra is probably not as high as expected for natural organic matter; (ii) a compound is regarded as highly degraded, when the relative magnitude falls below 100 ppm. Using the linear equation resulting from the correlation between the mass peak magnitudes and  $\Delta^{14}\text{C}_{\text{Cal}}$ , a theoretical  $\Delta^{14}\text{C}$  limit ( $\Delta^{14}\text{C}_{\text{Lim}}$ ) can be calculated for each mass peak at which the smallest relative magnitude (100 ppm) is reached. The calculated  $\Delta^{14}\text{C}_{\text{Lim}}$  values for highly degraded compounds ranged from

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–427‰ to <–1000‰ for mass peaks with a relative magnitude ratio of aged vs. young samples of 0.8 or less and from –590‰ to <–1000‰ for the mass peaks with relative magnitude ratios 0.8–1. The oldest samples in this study are from the deep Atlantic Ocean. More aged extracts would be expected in the Pacific Ocean where the lowest  $\Delta^{14}\text{C}$  value of bulk DOC is –546‰ (Druffel et al., 1992). Since the  $\Delta^{14}\text{C}_{\text{Cal}}$  of SPE-DOM was also correlated with the DOC concentration (Fig. 9b) it can be estimated that the SPE-DOM  $\Delta^{14}\text{C}$  would be about –556‰ at the Pacific’s oldest water mass, where DOC values of  $34\ \mu\text{mol kg}^{-1}$  were determined (Hansell et al., 2009). All compounds of masses with  $\Delta^{14}\text{C}_{\text{Lim}} < -556\text{‰}$  are expected to be highly degraded in the oldest water masses. This applies for only 2.5 % of all mass peaks. Since the extraction efficiency was similar for all samples, and the extracts were diluted to similar concentrations before FT-ICR MS measurements, a loss of additional mass peaks due to lower bulk DOC concentrations is not expected.

The FT-ICR MS analyzed SPE-DOM represents a fraction of the marine DOM for which most of the compounds are expected to persist one or more cycles through the global ocean circulation (~1000 yr). At the same time the compounds are expected to degrade very slowly with a continuum of different decomposition rates (Fig. 10). Our results support the hypothesis of old carbon recycling (Ogawa and Tanoue, 2003) as well as a broad and continuous distribution of  $\Delta^{14}\text{C}$  ages as proposed by Bauer et al. (1992) and are also consistent with the reactivity continuum proposed by Amon and Benner (2002). Compounds, which are degraded within decades and expected to be detected on a presence – absence analysis, are probably underrepresented in the FT-ICR mass spectra. The presence of an absolute refractory fraction, that is hidden in a mixture with degrading compounds, cannot be excluded. However, our results lend support to the theory of a continuum of reactivity. Since the  $\Delta^{14}\text{C}$  trends in SPE-DOM reflect  $\Delta^{14}\text{C}$  trends of bulk DOM we propose to apply the degradation continuum of the SPE-DOM also for bulk DOM. Terms as “labile”, “semi-labile”, “refractory (recalcitrant)”, “background” or “excess” DOM as used in different studies (Williams and Druffel, 1987; Beaupre and Druffel, 2009; Hansell et al., 2009; Beaupre and Aluwihare, 2010, Jiao

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et al. 2010) are generally useful to distinguish among the reactivities of different DOM fractions, but the complexity of DOM reactivity is better described as a continuum.

### 3.4 The microbial carbon pump

The microbial carbon pump provides a conceptual framework for understanding the role of microbial processes in recalcitrant DOM generation and relevant carbon storage in the ocean (Ogawa et al., 2001; Jiao et al., 2010). It is hypothesized that the transformation of labile and semi-labile DOM through microbial processes leads to the accumulation of recalcitrant DOM in the ocean. Indeed, the highest bacterial activity as well as the maximum abundance of the reactive parameters, DOC, amino sugars and  $\Delta^{14}\text{C}_{\text{Cal}}$ , was determined in surface waters of the highly stratified region between 0–15° N.

The majority of the FT-ICR mass peaks were present in samples with young SPE-DOM as well as with old SPE-DOM. Of all mass peaks, the estimated fraction of the least reactive masses is 69 %, accounting for >90 % of the summed magnitudes per sample. We hypothesize that this low reactivity fraction is produced and accumulates in the upper ocean. Fresh and highly reactive DOM is rapidly consumed by prokaryotes (Carlson and Ducklow, 1996) and partially converted to low reactivity DOM (Ogawa et al., 2001). The recently produced younger compounds mix with older compounds of similar reactivity in the upper ocean, and this mixture is then further degraded by bacterial activity (Ogawa and Tanoue, 2003) and thereby aged during the thermohaline circulation.  $\Delta^{14}\text{C}$  values of deep ocean DOC depend on the amount of low reactivity DOM produced by prokaryotes in the upper ocean and on the speed of degradation of this DOM during thermohaline circulation. Production and degradation appear to be in a steady state, since no apparent changes were detected in time-series studies of  $\Delta^{14}\text{C}$  of DOC concentrations (Goldberg 2009; Beaupre and Aluwihare 2010).

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## 4 Conclusions

In this study FT-ICR MS measurements and the radiocarbon age of marine SPE-DOM were directly compared with other compositional characteristics of DOM and the ocean circulation for the first time. The results show that trends in bulk DOC radiocarbon ages are reflected in the radiocarbon age determined from a correlation between selected FT-ICR mass peaks and SPE-DOM  $\Delta^{14}\text{C}$  values. With this knowledge the degradation state of other marine DOM samples can be estimated by comparing FT-ICR mass peaks. Since this method was only applied for the Atlantic Ocean it is important to continue these studies in other oceanic regions for verification of this approach. For this, the degradation index  $I_{\text{DEG}}$  was suggested as a simple tool to evaluate relative degradation states in a set of similarly treated samples. So far  $I_{\text{DEG}}$  is only applied for SPE-DOM samples (PPL extracts) from the Atlantic Ocean and thus has to be verified for other regions.

We propose a degradation continuum of the compounds represented in the FT-ICR mass spectra, but only some of them are expected to be completely degraded during thermohaline circulation. Prokaryotic (bacterial) production, transformation and accumulation of this very stable DOM occurs probably primarily in the upper ocean (Benner and Herndl, 2011). This DOM is an important contribution to very old DOM, showing that production and degradation are dynamic processes. To elucidate these complex processes it is important to further investigate sources, transformations and fates of DOM in the ocean. The FT-ICR MS data provide novel insights into the molecular composition of highly degraded DOM. Microbial degradation experiments and studies of aggregation processes combined with FT-ICR MS will help to gain a better understanding of DOM cycling in the ocean.

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**Table 1.** Calculated SPE-DOM  $\Delta^{14}\text{C}$  values [‰] and DOC [ $\mu\text{mol L}^{-1}$ ] in the deep water layers.

Depth [m]	Parameter	46° N 8° W	37° N 14° W	23° N 20° W	11° N 20° W	2° S 14° W	5° N 7° W	17° S 3° W	24° S 9° W
400–500	$\Delta^{14}\text{C}$ [‰]		–406						
800–900	$\Delta^{14}\text{C}$ [‰]				–465	–461	–442	–443	
1100–1800	$\Delta^{14}\text{C}$ [‰]		–451	–476				–442	
2500	$\Delta^{14}\text{C}$ [‰]			–481					
4000–5000	$\Delta^{14}\text{C}$ [‰]	–449	–481	–473	–455	–445	–453		
400–500	DOC [ $\mu\text{mol L}^{-1}$ ]	56	58						
800–900	DOC [ $\mu\text{mol L}^{-1}$ ]				45	47	46	49	
1100–1800	DOC [ $\mu\text{mol L}^{-1}$ ]		48			52	54	47	
2500	DOC [ $\mu\text{mol L}^{-1}$ ]	48		45					
4000–5000	DOC [ $\mu\text{mol L}^{-1}$ ]	48	45		47		41	47	45

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**Table 2.** Sum formulas of compounds represented by mass peaks which are provided to compare marine SPE-DOM regarding the degradation state.

NEG correlating compounds	POS correlating compounds
$C_{17}H_{20}O_8$	$C_{13}H_{18}O_7$
$C_{17}H_{20}O_9$	$C_{14}H_{20}O_8$
$C_{19}H_{22}O_{10}$	$C_{15}H_{22}O_7$
$C_{20}H_{22}O_{10}$	$C_{15}H_{22}O_8$
$C_{20}H_{24}O_{11}$	$C_{16}H_{24}O_8$

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**Table 3.** Calculated  $\Delta^{14}\text{C}$  values of excess SPE-DOM and corresponding Keeling slope values for the 7 deep stations of the East Atlantic Ocean.

Station	$\Delta^{14}\text{C}$ of excess SPE-DOM	Keeling slope
46° N, 8° W	-121	-6880
37° N, 14° W	108	-11 394
23° N, 20° W	17	-10 050
11° N, 20° W	50	-9938
2° N, 14° W	68	-10 203
5° S, 7° W	76	-10 550
17° S, 3° W	44	-10 239

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**Table A1.** POS molecular formulas: Complete list of mass peaks and assigned molecular formulas which showed a highly significant positive correlation ( $p < 0.01$ ) with SPE-DOM  $\Delta^{14}\text{C}$ .

Elemental formula	M	Elemental formula	M	Elemental formula	M
C <sub>12</sub> H <sub>16</sub> O <sub>6</sub>	256.0946882	C <sub>14</sub> H <sub>20</sub> O <sub>8</sub>	316.1158176	C <sub>16</sub> H <sub>24</sub> O <sub>8</sub>	344.1471177
C <sub>12</sub> H <sub>16</sub> O <sub>7</sub>	272.0896029	C <sub>14</sub> H <sub>20</sub> O <sub>8</sub> S <sub>1</sub>	348.0878883	C <sub>16</sub> H <sub>24</sub> O <sub>8</sub> S <sub>1</sub>	376.1191884
C <sub>12</sub> H <sub>16</sub> O <sub>8</sub>	288.0845175	C <sub>14</sub> H <sub>20</sub> O <sub>9</sub> S <sub>1</sub>	364.0828029	C <sub>16</sub> H <sub>24</sub> O <sub>9</sub>	360.1420323
C <sub>13</sub> H <sub>14</sub> O <sub>6</sub>	266.0790382	C <sub>14</sub> H <sub>22</sub> O <sub>5</sub>	270.1467238	C <sub>16</sub> H <sub>26</sub> O <sub>7</sub>	330.1678532
C <sub>13</sub> H <sub>14</sub> O <sub>7</sub>	282.0739528	C <sub>14</sub> H <sub>22</sub> O <sub>6</sub>	286.1416384	C <sub>16</sub> H <sub>26</sub> O <sub>8</sub>	346.1627678
C <sub>13</sub> H <sub>14</sub> O <sub>8</sub>	298.0688674	C <sub>14</sub> H <sub>22</sub> O <sub>7</sub>	302.136553	C <sub>17</sub> H <sub>25</sub> O <sub>9</sub> N <sub>1</sub>	387.1529314
C <sub>13</sub> H <sub>16</sub> O <sub>5</sub>	252.0997736	C <sub>14</sub> H <sub>22</sub> O <sub>8</sub>	318.1314677	C <sub>17</sub> H <sub>26</sub> O <sub>10</sub>	390.152597
C <sub>13</sub> H <sub>16</sub> O <sub>6</sub>	268.0946882	C <sub>14</sub> H <sub>22</sub> O <sub>9</sub>	334.1263823	C <sub>17</sub> H <sub>26</sub> O <sub>11</sub>	406.1475117
C <sub>13</sub> H <sub>16</sub> O <sub>7</sub>	284.0896029	C <sub>15</sub> H <sub>22</sub> O <sub>10</sub>	362.1212969	C <sub>17</sub> H <sub>26</sub> O <sub>6</sub>	326.1729386
C <sub>13</sub> H <sub>16</sub> O <sub>8</sub>	300.0845175	C <sub>15</sub> H <sub>22</sub> O <sub>6</sub>	298.1416384	C <sub>17</sub> H <sub>26</sub> O <sub>7</sub>	342.1678532
C <sub>13</sub> H <sub>17</sub> O <sub>6</sub> N <sub>1</sub>	283.1055873	C <sub>15</sub> H <sub>22</sub> O <sub>7</sub>	314.136553	C <sub>17</sub> H <sub>26</sub> O <sub>8</sub>	358.1627678
C <sub>13</sub> H <sub>17</sub> O <sub>7</sub> N <sub>1</sub>	299.1005019	C <sub>15</sub> H <sub>22</sub> O <sub>7</sub> S <sub>1</sub>	346.1086237	C <sub>17</sub> H <sub>26</sub> O <sub>9</sub>	374.1576824
C <sub>13</sub> H <sub>18</sub> O <sub>5</sub>	254.1154237	C <sub>15</sub> H <sub>22</sub> O <sub>8</sub>	330.1314677	C <sub>18</sub> H <sub>28</sub> O <sub>10</sub>	404.1682471
C <sub>13</sub> H <sub>18</sub> O <sub>6</sub>	270.1103383	C <sub>15</sub> H <sub>22</sub> O <sub>9</sub>	346.1263823	C <sub>18</sub> H <sub>28</sub> O <sub>7</sub>	356.1835032
C <sub>13</sub> H <sub>18</sub> O <sub>7</sub>	286.1052529	C <sub>15</sub> H <sub>22</sub> O <sub>9</sub> S <sub>1</sub>	378.098453	C <sub>18</sub> H <sub>28</sub> O <sub>9</sub>	388.1733325
C <sub>13</sub> H <sub>18</sub> O <sub>8</sub>	302.1001675	C <sub>15</sub> H <sub>24</sub> O <sub>6</sub>	300.1572885	C <sub>19</sub> H <sub>28</sub> O <sub>11</sub>	432.1631617
C <sub>13</sub> H <sub>20</sub> O <sub>6</sub>	272.1259884	C <sub>15</sub> H <sub>24</sub> O <sub>7</sub>	316.1522031	C <sub>19</sub> H <sub>28</sub> O <sub>12</sub>	448.1580763
C <sub>13</sub> H <sub>20</sub> O <sub>7</sub>	288.120903	C <sub>15</sub> H <sub>24</sub> O <sub>8</sub>	332.1471177	C <sub>19</sub> H <sub>30</sub> O <sub>10</sub>	418.1838972
C <sub>13</sub> H <sub>20</sub> O <sub>8</sub>	304.1158176	C <sub>15</sub> H <sub>24</sub> O <sub>9</sub>	348.1420323	C <sub>19</sub> H <sub>30</sub> O <sub>9</sub>	402.1889825
C <sub>14</sub> H <sub>18</sub> O <sub>7</sub>	298.1052529	C <sub>16</sub> H <sub>23</sub> O <sub>9</sub> N <sub>1</sub>	373.1372813	C <sub>20</sub> H <sub>30</sub> O <sub>11</sub>	446.1788118
C <sub>14</sub> H <sub>19</sub> O <sub>6</sub> N <sub>1</sub>	297.1212373	C <sub>16</sub> H <sub>24</sub> O <sub>10</sub>	376.136947	C <sub>20</sub> H <sub>30</sub> O <sub>12</sub>	462.1737264
C <sub>14</sub> H <sub>20</sub> O <sub>4</sub>	252.1361591	C <sub>16</sub> H <sub>24</sub> O <sub>11</sub>	392.1318616	C <sub>20</sub> H <sub>32</sub> O <sub>8</sub>	400.209718
C <sub>14</sub> H <sub>20</sub> O <sub>5</sub>	268.1310737	C <sub>16</sub> H <sub>24</sub> O <sub>5</sub>	296.1623739	C <sub>20</sub> H <sub>32</sub> O <sub>9</sub>	416.2046326
C <sub>14</sub> H <sub>20</sub> O <sub>6</sub>	284.1259884	C <sub>16</sub> H <sub>24</sub> O <sub>6</sub>	312.1572885	C <sub>21</sub> H <sub>32</sub> O <sub>10</sub>	444.1995472
C <sub>14</sub> H <sub>20</sub> O <sub>7</sub>	300.120903	C <sub>16</sub> H <sub>24</sub> O <sub>7</sub>	328.1522031	C <sub>21</sub> H <sub>32</sub> O <sub>11</sub>	460.1944618

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**Table A2.** NEG molecular formulas: Complete list of mass peaks and assigned molecular formulas which showed a highly significant negative correlation ( $p < 0.01$ ) with SPE-DOM  $\Delta^{14}\text{C}$ .

Elemental formula	M	Elemental formula	M	Elemental formula	M
C <sub>17</sub> H <sub>18</sub> O <sub>10</sub>	382.0899968	C <sub>20</sub> H <sub>22</sub> O <sub>9</sub> N <sub>2</sub>	434.1325303	C <sub>22</sub> H <sub>25</sub> O <sub>10</sub> N <sub>1</sub>	463.147846
C <sub>17</sub> H <sub>18</sub> O <sub>8</sub>	350.1001675	C <sub>20</sub> H <sub>23</sub> O <sub>10</sub> N <sub>1</sub>	437.1321959	C <sub>22</sub> H <sub>25</sub> O <sub>11</sub> N <sub>1</sub>	479.1427606
C <sub>17</sub> H <sub>18</sub> O <sub>9</sub>	366.0950822	C <sub>20</sub> H <sub>23</sub> O <sub>11</sub> N <sub>1</sub>	453.1271106	C <sub>22</sub> H <sub>26</sub> O <sub>10</sub>	450.152597
C <sub>17</sub> H <sub>20</sub> O <sub>8</sub>	352.1158176	C <sub>20</sub> H <sub>23</sub> O <sub>9</sub> N <sub>1</sub>	421.1372813	C <sub>22</sub> H <sub>26</sub> O <sub>11</sub>	466.1475117
C <sub>17</sub> H <sub>20</sub> O <sub>9</sub>	368.1107322	C <sub>20</sub> H <sub>24</sub> O <sub>10</sub>	424.136947	C <sub>22</sub> H <sub>26</sub> O <sub>12</sub>	482.1424263
C <sub>18</sub> H <sub>18</sub> O <sub>8</sub>	362.1001675	C <sub>20</sub> H <sub>24</sub> O <sub>10</sub> N <sub>2</sub>	452.143095	C <sub>22</sub> H <sub>26</sub> O <sub>13</sub>	498.1373409
C <sub>18</sub> H <sub>18</sub> O <sub>9</sub>	378.0950822	C <sub>20</sub> H <sub>24</sub> O <sub>11</sub>	440.1318616	C <sub>22</sub> H <sub>26</sub> O <sub>9</sub>	434.1576824
C <sub>18</sub> H <sub>20</sub> O <sub>10</sub>	396.1056468	C <sub>20</sub> H <sub>24</sub> O <sub>12</sub>	456.1267762	C <sub>22</sub> H <sub>27</sub> O <sub>10</sub> N <sub>1</sub>	465.1634961
C <sub>18</sub> H <sub>20</sub> O <sub>11</sub>	412.1005615	C <sub>20</sub> H <sub>24</sub> O <sub>9</sub> N <sub>2</sub>	436.1481804	C <sub>22</sub> H <sub>27</sub> O <sub>9</sub> N <sub>1</sub>	449.1685815
C <sub>18</sub> H <sub>20</sub> O <sub>6</sub>	332.1259884	C <sub>20</sub> H <sub>25</sub> O <sub>10</sub> N <sub>1</sub>	439.147846	C <sub>22</sub> H <sub>28</sub> O <sub>11</sub>	468.1631617
C <sub>18</sub> H <sub>20</sub> O <sub>7</sub>	348.120903	C <sub>20</sub> H <sub>25</sub> O <sub>11</sub> N <sub>1</sub>	455.1427606	C <sub>22</sub> H <sub>28</sub> O <sub>12</sub>	484.1580763
C <sub>18</sub> H <sub>20</sub> O <sub>8</sub>	364.1158176	C <sub>20</sub> H <sub>26</sub> O <sub>11</sub>	442.1475117	C <sub>22</sub> H <sub>30</sub> O <sub>12</sub>	486.1737264
C <sub>18</sub> H <sub>20</sub> O <sub>9</sub>	380.1107322	C <sub>20</sub> H <sub>26</sub> O <sub>12</sub>	458.1424263	C <sub>23</sub> H <sub>24</sub> O <sub>10</sub>	460.136947
C <sub>18</sub> H <sub>21</sub> O <sub>10</sub> N <sub>1</sub>	411.1165459	C <sub>21</sub> H <sub>20</sub> O <sub>10</sub>	432.1056468	C <sub>23</sub> H <sub>24</sub> O <sub>11</sub>	476.1318616
C <sub>18</sub> H <sub>21</sub> O <sub>7</sub> N <sub>1</sub>	363.131802	C <sub>21</sub> H <sub>20</sub> O <sub>9</sub>	416.1107322	C <sub>23</sub> H <sub>24</sub> O <sub>12</sub>	492.1267762
C <sub>18</sub> H <sub>22</sub> O <sub>11</sub>	414.1162115	C <sub>21</sub> H <sub>21</sub> O <sub>12</sub> N <sub>1</sub>	479.1063751	C <sub>23</sub> H <sub>26</sub> O <sub>10</sub>	462.152597
C <sub>18</sub> H <sub>22</sub> O <sub>7</sub>	350.136553	C <sub>21</sub> H <sub>22</sub> O <sub>10</sub>	434.1212969	C <sub>23</sub> H <sub>26</sub> O <sub>11</sub>	478.1475117
C <sub>18</sub> H <sub>22</sub> O <sub>9</sub> N <sub>2</sub>	410.1325303	C <sub>21</sub> H <sub>22</sub> O <sub>11</sub>	450.1162115	C <sub>23</sub> H <sub>26</sub> O <sub>12</sub>	494.1424263
C <sub>18</sub> H <sub>23</sub> O <sub>10</sub> N <sub>1</sub>	413.1321959	C <sub>21</sub> H <sub>22</sub> O <sub>12</sub>	466.1111261	C <sub>23</sub> H <sub>27</sub> O <sub>11</sub> N <sub>1</sub>	493.1584107
C <sub>19</sub> H <sub>19</sub> O <sub>9</sub> N <sub>1</sub>	405.1059812	C <sub>21</sub> H <sub>22</sub> O <sub>9</sub>	418.1263823	C <sub>23</sub> H <sub>28</sub> O <sub>10</sub>	464.1682471
C <sub>19</sub> H <sub>20</sub> O <sub>11</sub>	424.1005615	C <sub>21</sub> H <sub>23</sub> O <sub>10</sub> N <sub>1</sub>	449.1321959	C <sub>23</sub> H <sub>28</sub> O <sub>11</sub>	480.1631617
C <sub>19</sub> H <sub>20</sub> O <sub>7</sub>	360.120903	C <sub>21</sub> H <sub>24</sub> O <sub>10</sub>	436.136947	C <sub>23</sub> H <sub>28</sub> O <sub>12</sub>	496.1580763
C <sub>19</sub> H <sub>21</sub> O <sub>10</sub> N <sub>1</sub>	423.1165459	C <sub>21</sub> H <sub>24</sub> O <sub>10</sub> N <sub>2</sub>	464.143095	C <sub>23</sub> H <sub>29</sub> O <sub>11</sub> N <sub>1</sub>	495.1740608
C <sub>19</sub> H <sub>21</sub> O <sub>9</sub> N <sub>1</sub>	407.1216313	C <sub>21</sub> H <sub>24</sub> O <sub>11</sub>	452.1318616	C <sub>23</sub> H <sub>30</sub> O <sub>10</sub>	466.1838972
C <sub>19</sub> H <sub>22</sub> O <sub>10</sub>	410.1212969	C <sub>21</sub> H <sub>24</sub> O <sub>12</sub>	462.1420323	C <sub>23</sub> H <sub>30</sub> O <sub>11</sub>	482.1788118
C <sub>19</sub> H <sub>22</sub> O <sub>10</sub> N <sub>2</sub>	438.1274449	C <sub>21</sub> H <sub>25</sub> O <sub>10</sub> N <sub>1</sub>	451.147846	C <sub>23</sub> H <sub>30</sub> O <sub>12</sub>	498.1737264
C <sub>19</sub> H <sub>22</sub> O <sub>11</sub>	426.1162115	C <sub>21</sub> H <sub>26</sub> O <sub>11</sub>	454.1475117	C <sub>24</sub> H <sub>26</sub> O <sub>10</sub>	474.152597
C <sub>19</sub> H <sub>22</sub> O <sub>12</sub>	442.1111261	C <sub>21</sub> H <sub>26</sub> O <sub>12</sub>	470.1424263	C <sub>24</sub> H <sub>26</sub> O <sub>11</sub>	490.1475117
C <sub>19</sub> H <sub>22</sub> O <sub>9</sub> N <sub>2</sub>	422.1325303	C <sub>21</sub> H <sub>26</sub> O <sub>9</sub> N <sub>2</sub>	450.1638304	C <sub>24</sub> H <sub>28</sub> O <sub>10</sub>	476.1682471
C <sub>19</sub> H <sub>23</sub> O <sub>10</sub> N <sub>1</sub>	425.1321959	C <sub>21</sub> H <sub>27</sub> O <sub>10</sub> N <sub>1</sub>	453.1634961	C <sub>24</sub> H <sub>28</sub> O <sub>11</sub>	492.1631617
C <sub>19</sub> H <sub>24</sub> O <sub>10</sub> N <sub>2</sub>	440.143095	C <sub>21</sub> H <sub>27</sub> O <sub>11</sub> N <sub>1</sub>	469.1584107	C <sub>24</sub> H <sub>28</sub> O <sub>9</sub>	460.1733325
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C <sub>20</sub> H <sub>20</sub> O <sub>10</sub>	420.1056468	C <sub>21</sub> H <sub>28</sub> O <sub>12</sub>	472.1580763	C <sub>24</sub> H <sub>30</sub> O <sub>11</sub>	494.1788118
C <sub>20</sub> H <sub>20</sub> O <sub>11</sub>	436.1005615	C <sub>22</sub> H <sub>22</sub> O <sub>10</sub>	446.1212969	C <sub>24</sub> H <sub>32</sub> O <sub>11</sub>	496.1944618
C <sub>20</sub> H <sub>22</sub> O <sub>10</sub>	422.1212969	C <sub>22</sub> H <sub>22</sub> O <sub>11</sub>	462.1162115	C <sub>25</sub> H <sub>28</sub> O <sub>10</sub>	488.1682471
C <sub>20</sub> H <sub>22</sub> O <sub>10</sub> N <sub>2</sub>	450.1274449	C <sub>22</sub> H <sub>22</sub> O <sub>9</sub>	430.1263823	C <sub>25</sub> H <sub>30</sub> O <sub>10</sub>	490.1838972
C <sub>20</sub> H <sub>22</sub> O <sub>11</sub>	438.1162115	C <sub>22</sub> H <sub>23</sub> O <sub>12</sub> N <sub>1</sub>	493.1220252	C <sub>25</sub> H <sub>32</sub> O <sub>10</sub>	492.1995472
C <sub>20</sub> H <sub>22</sub> O <sub>12</sub>	454.1111261	C <sub>22</sub> H <sub>24</sub> O <sub>10</sub>	448.136947	C <sub>25</sub> H <sub>34</sub> O <sub>10</sub>	494.2151973
C <sub>20</sub> H <sub>22</sub> O <sub>9</sub>	406.1263823	C <sub>22</sub> H <sub>24</sub> O <sub>11</sub>	464.1318616	C <sub>26</sub> H <sub>32</sub> O <sub>9</sub>	488.2046326

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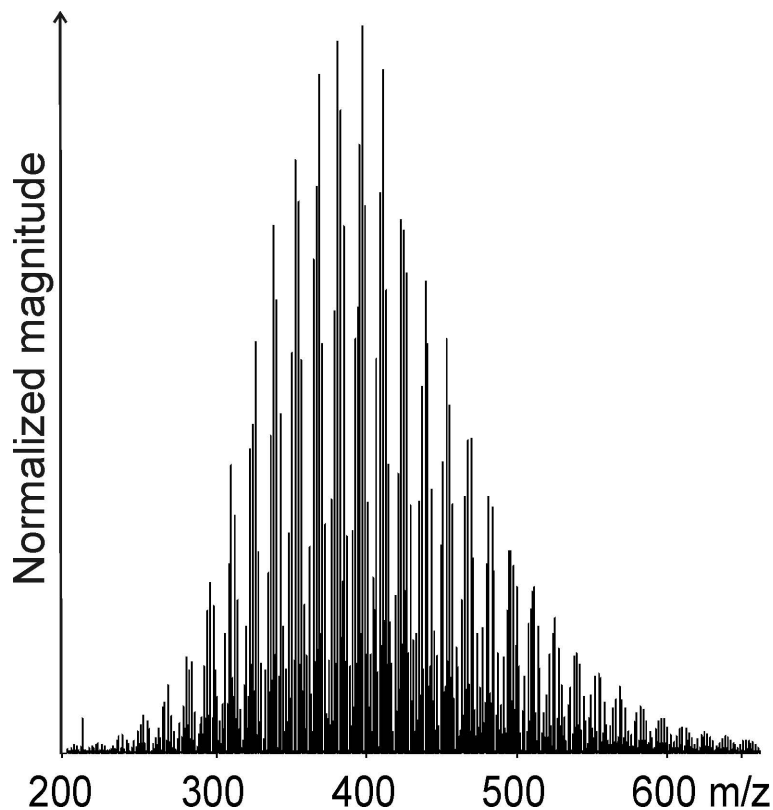
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**Fig. 1.** Negative ESI FT-ICR mass spectrum of a representative marine SPE-DOM sample from the Eastern Atlantic Ocean.

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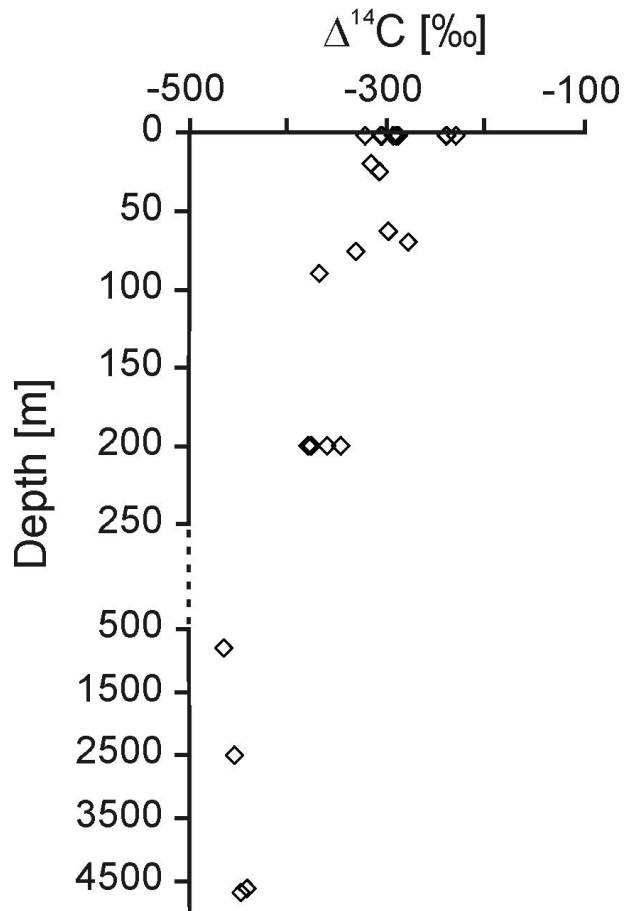
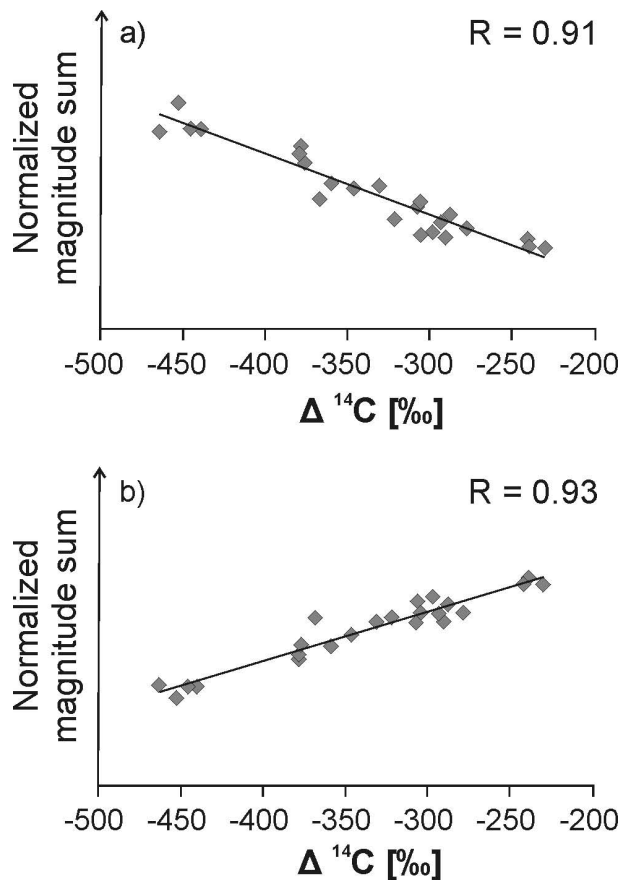


Fig. 2.  $\Delta^{14}\text{C}$  values of marine SPE-DOM from the Eastern Atlantic Ocean.



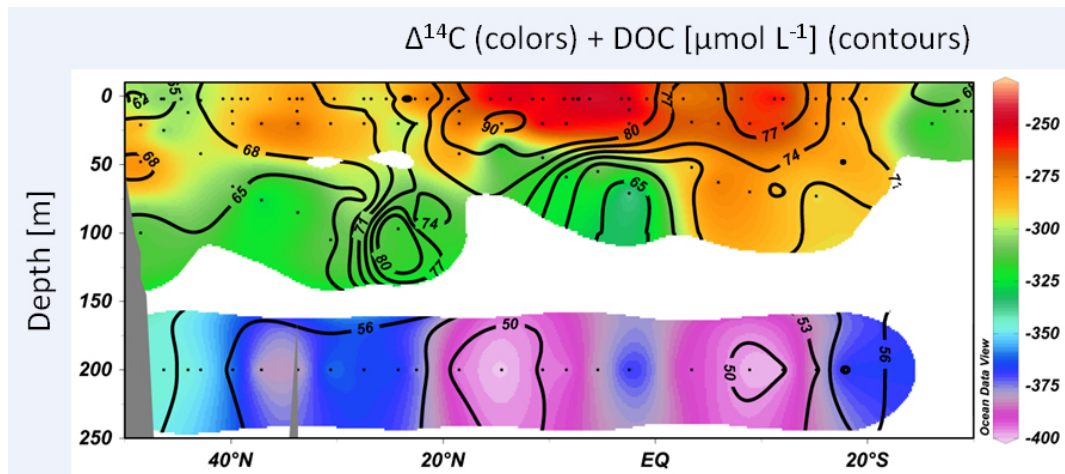
**Fig. 3.** Linear correlation between the  $\Delta^{14}\text{C}$  values and the FT-ICR mass peaks of East Atlantic Ocean SPE-DOM. The sum of the normalized magnitudes of the mass peaks with a highly significant correlation of (a) negatively correlated and (b) positively correlated masses are plotted versus  $\Delta^{14}\text{C}$  values.

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**Fig. 4.** Calculated SPE-DOM  $\Delta^{14}\text{C}$  values (colors) and measured water sample DOC concentrations (contours) in the upper 250 m of the water column in the East Atlantic Ocean. The  $\Delta^{14}\text{C}$  values and the DOC concentrations are significantly positively correlated.

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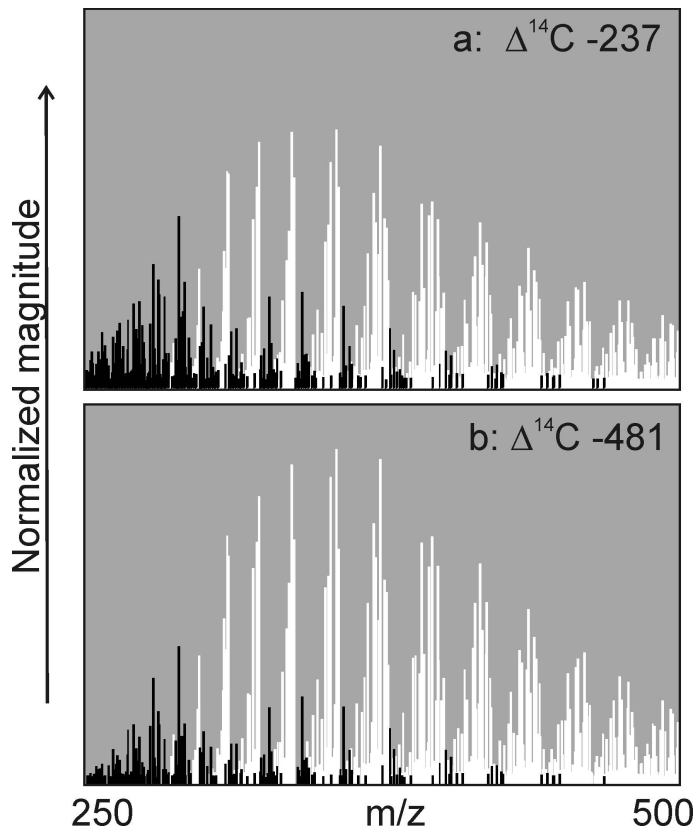
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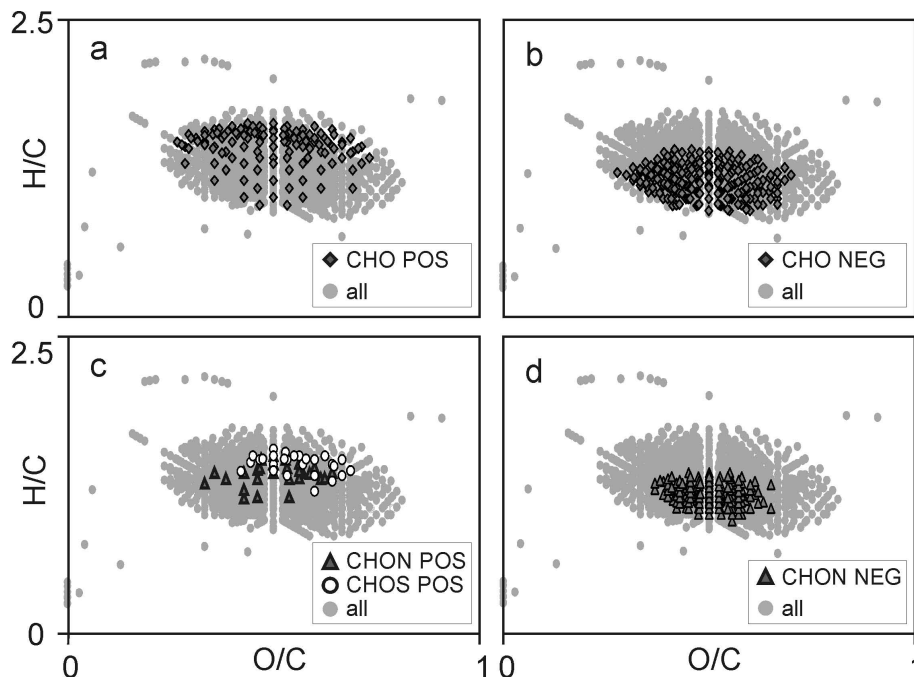




**Fig. 5.** Selected normalized FT-ICR mass peaks of Eastern Atlantic Ocean SPE-DOM. The mass peaks show a significant linear correlation with  $\Delta^{14}\text{C}$ . **(a)** Surface sample extract with  $\Delta^{14}\text{C} = -237$  and **(b)** deep sea sample extract with  $\Delta^{14}\text{C} = -481$ . The black colored masses are positively correlated with  $\Delta^{14}\text{C}$  and the white colored masses negatively.

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**Fig. 6.** Van Krevelen diagrams of compounds in Eastern Atlantic Ocean SPE-DOM that are correlated with  $\Delta^{14}\text{C}$  ( $R > 0.9$ ,  $p < 0.01$ ): **(a)** positively with CHO compounds; **(b)** negatively with CHO compounds; **(c)** positively with CHON and CHOS compounds; **(d)** negatively with CHON compounds. The grey dots in the background show all compounds found in all Atlantic Ocean water extracts.

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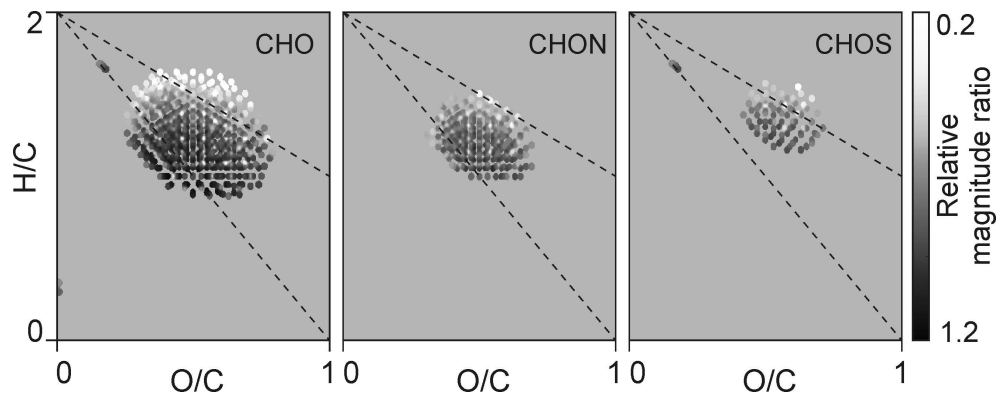
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**Fig. 7.** Van Krevelen diagrams of CHO, CHON and CHOS compounds in Eastern Atlantic Ocean SPE-DOM. Shown are the relative magnitude ratios of the compounds from old deep water DOM to young surface water DOM. Lowest ratios are represented by white color, highest ratios by black color. The upper dotted line refers to any fully saturated open chain aliphatic carboxylic acids; the lower dotted line connects the virtual end members  $\text{CH}_2$  and CO and bisects nearly the compositional space of CRAM (from Hertkorn et al. 2006).

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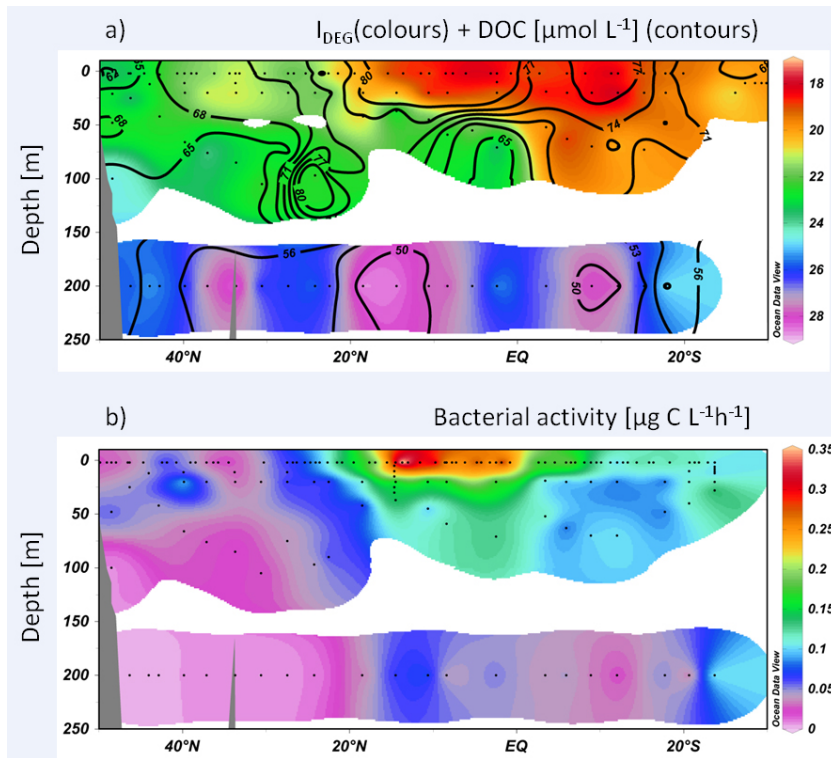
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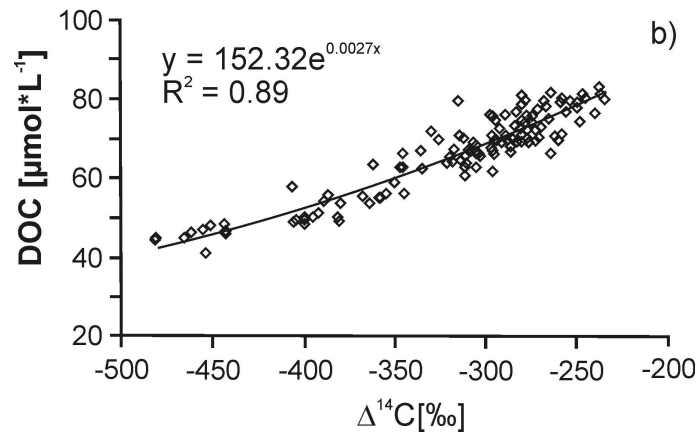
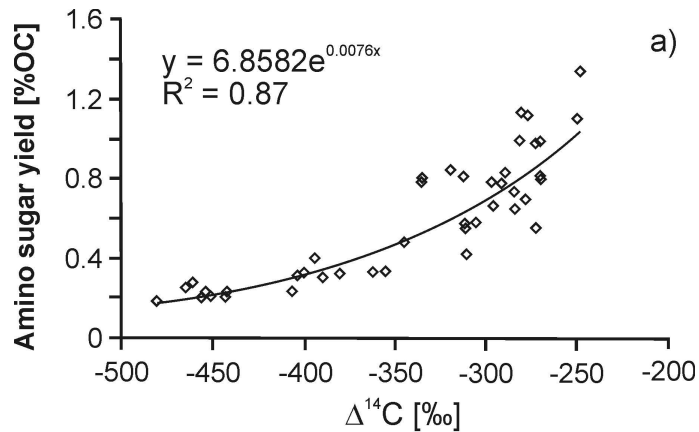
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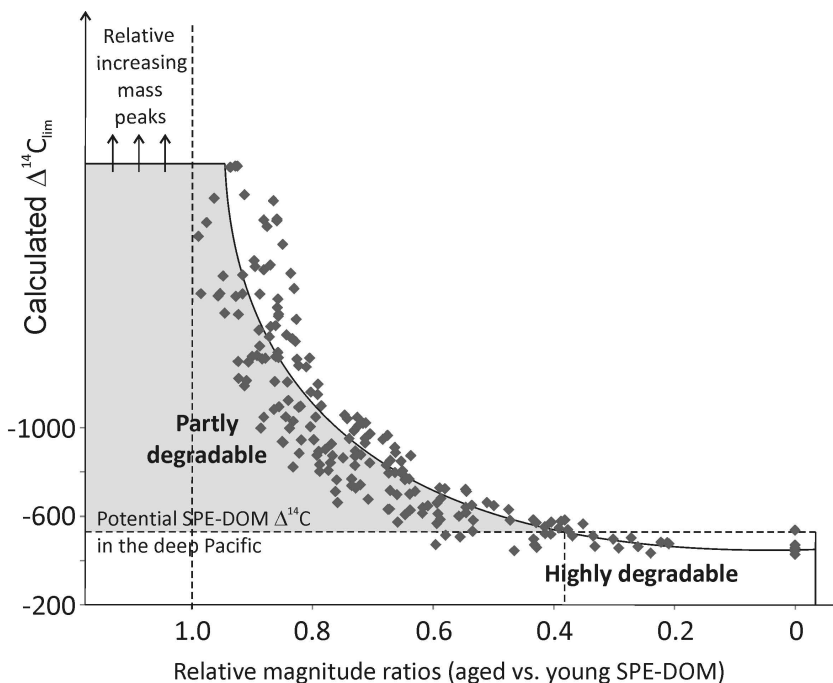




**Fig. 8.** (a)  $I_{\text{DEG}}$  (colors) and measured water sample DOC concentrations (contours); (b) the bacterial activity determined as utilized  $\mu\text{g CL}^{-1}\text{h}^{-1}$  in the upper 250 m of the water column in the East Atlantic Ocean.  $I_{\text{DEG}}$  and the DOC concentrations are significantly negatively correlated. The bacterial activity maximum coincides with the lowest  $I_{\text{DEG}}$ , the DOC maximum and the youngest SPE-DOM (Fig. 4).



**Fig. 9.** Correlation and equations of **(a)** amino sugar yields and **(b)** DOC concentrations of Atlantic Ocean water and calculated  $\Delta^{14}\text{C}$  values of the corresponding SPE-DOM.



**Fig. 10.** Calculated limit of  $\Delta^{14}\text{C}$  ( $\Delta^{14}\text{C}_{\text{Lim}}$ ) for Atlantic Ocean SPE-DOM compounds represented by FT-ICR mass peaks.  $\Delta^{14}\text{C}_{\text{Lim}}$  is a theoretical SPE-DOM  $\Delta^{14}\text{C}$  value at which a compound is regarded to be highly degraded.  $\Delta^{14}\text{C}_{\text{Lim}}$  is plotted versus the relative magnitude ratios obtained by comparing old deep water SPE-DOM vs. young surface water SPE-DOM. All compounds with a  $\Delta^{14}\text{C}_{\text{Lim}} > -556$  (SPE-DOM  $\Delta^{14}\text{C}$  value expected in the oldest Pacific water mass) are expected to be highly degraded. All other compounds should persist partly thermohaline circulation. The various different ratios demonstrate the degradation continuum of SPE-DOM. Compounds, which are most stable against degradation, have a relative magnitude ratio  $>1$  due to magnitude normalization. A calculation of a  $\Delta^{14}\text{C}_{\text{Lim}}$  value is not possible.

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