Biogeosciences, 9, 1935–1955, 2012
www.biogeosciences.net/9/1935/2012/
doi:10.5194/bg-9-1935-2012
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Biogeosciences

A molecular perspective on the ageing of marine dissolved organic matter

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Received: 27 October 2011 – Published in Biogeosciences Discuss.: 29 November 2011
Revised: 3 April 2012 – Accepted: 5 April 2012 – Published: 1 June 2012

Abstract. Dissolved organic matter (DOM) was extracted by 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). $\Delta^{14}C$ 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 $\Delta^{14}C$ values. Decreasing SPE-DOM $\Delta^{14}C$ 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 $\Delta^{14}C$ distribution for all 137 samples. Based on single mass peaks, a degradation index (I_{DEG}) was developed to compare the degradation state of marine SPE-DOM samples analyzed with FT-ICR MS. A correlation between $\Delta^{14}C$, I_{DEG}, DOC values and amino sugar yield supports that SPE-DOM analyzed with FT-ICR MS reflects trends of bulk DOM. DOM weighted normalized mass peak magnitudes were used to compare aged and recent SPE-DOM on a semi-quantitative molecular basis. The magnitude comparison showed a continuum of different degradation rates for the detected compounds. A high proportion of the compounds should persist, possibly modified by partial degradation, in the course of thermohaline circulation. Prokaryotic (bacterial) production, transformation and accumulation of this very stable DOM occur primarily in the upper ocean. This DOM is an important contribution to very old DOM, showing that production and degradation are dynamic processes.

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_2 (Hedges, 1992; Hansell et al., 2009; Tans, 2010). Since the average age of bulk DOC below the thermocline is about 4000 yr in the Sargasso Sea and about 6000 yr in the central North Pacific, marine DOM plays an important role in long-term carbon storage and sequestration of atmospheric CO_2 (Williams and Druffel, 1987; Bauer, 2002). This older DOM pool represents a refractory background with concentrations of

35–45 µmol kg^{-1} (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 and 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 refractory DOM in surface waters. Hereby, microbes produce the very stable DOM, which persists over very long time scales in the world oceans. 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 and 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 samples have been compared with this technique, preventing a systematic comparison of FT-ICR MS data and additional analytical parameters.

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 and 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 (Williams and Druffel, 1987; Druffel et al., 1992), 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 Δ^{14}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 BP) 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 is 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 environmental parameters, DOC, amino sugars and bacterial activity, each determined independently. Our ultimate goal was to elucidate molecular trends that are characteristic for the entire Atlantic Ocean.

2 Materials and methods

2.1 Sampling

Water samples were collected along a transect from 50.2° N to 31.4° S in the eastern Atlantic Ocean in November 2008 during the cruise ANT-XXV/1 of R/V *Polarstern*. Surface water was sampled three 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 seven selected stations from surface to bottom (Fig. 1). 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

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, 1g, Varian, Mega Bond Elut) according to 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 passed 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 into pre-combusted glass ampoules and stored at −20 °C.

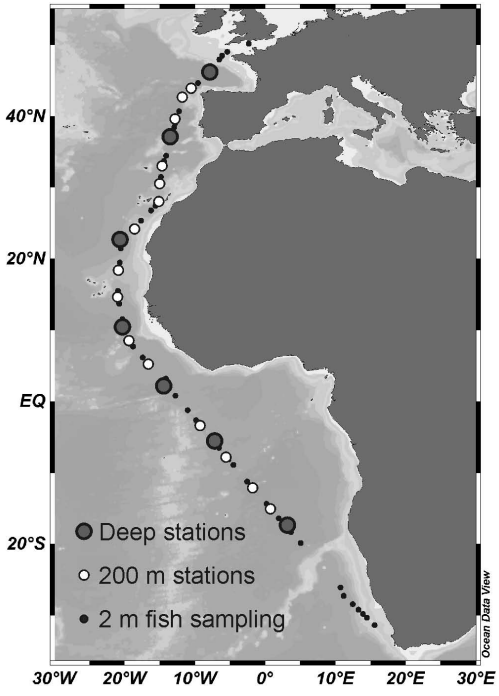

Fig. 1. Map of the sampling locations on the cruise ANT-XXV/1 of RV Polarstern.

2.3 Analyses

The DOC concentration was determined by high temperature catalytic oxidation with a Shimadzu TOC-VCPN analyzer. Before analysis water samples were acidified in the auto-sampler and purged with O_2 for 5 min. The DOC content of the SPE-DOM was determined by evaporation of 50 µl methanol extract re-dissolved in 6.5 ml ultra-pure water.

Bacterioplankton production was estimated by ^{3}H-leucine uptake (Smith and Azam, 1992). Triplicate subsamples (1.5 ml) and one trichloroacetic acid-killed control were amended with 5 nM ^{3}H-leucine (Amersham, specific activity 160 Ci mmol^{-1}) and incubated at in situ temperature (±2 °C) in the dark. Incubation time varied depending on depth: ∼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 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 3 M HCl (5 h, 100 °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 Na^+-form before chromatographic separation. Subsequently, GalN, ManN and GlcN were separated isocratically on a Dionex PA20 anion-exchange column with 2 mM NaOH at a flow rate of 1 ml min^{-1}.

Subsamples of SPE-DOM (0.2–1 mg C) were quantitatively transferred to combusted (500 °C) quartz tubes (6 mm diameter), evaporated under a stream of N_2, sealed under vacuum and combusted at 900 °C to CO_2 using a CuO/Ag metal catalyst (Sofer, 1980). The CO_2 from break seals was subsequently reduced to graphite in an atmosphere of H_2 over a cobalt catalyst (Vogel et al., 1987). Graphite targets were analyzed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. Δ^{14}C is defined as the (per mil) deviation of a sample from the ^{14}C activity of a 1950 standard, corrected for fractionation according to Stuvier and Polach (1977). Total measurement uncertainties for Δ^{14}C analyses of these samples were typically ±4 ‰. A blank analysis of a SPE cartridge was determined before and no measurable amount of CO_2 was found (<1 µg).

FT-ICR MS analysis 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 kV, infusion flow rate 2 µl min^{-1}). Spectra were calibrated internally with compounds, which were repeatedly identified in marine DOM samples (*m/z* 339.10854, 369.11911, 411.12967, 469.13515, 541.15628; Schmidt et al., 2009; Flerus et al., 2011). 512 scans were added to acquire one spectrum. All ions were singly charged and the mass accuracy was below 0.2 ppm > mass accuracy > −0.2 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* 200–600. For each identified peak in the spectra (signal to noise > 3; Data analysis 3.4; Bruker Daltonics), elemental formulas were calculated in the mass accuracy range of ±0.5 ppm (e.g. Koch et al., 2005, 2007). The isotopes included for the formula calculation were as follows: ^{12}C (0–∞), ^{13}C (0–1), ^{1}H (0–∞), ^{16}O (0–∞), ^{14}N (0–2), ^{32}S (0–1). The average mass accuracy for all assigned peaks was < ±0.2 ppm. For unambiguous elemental formula assignment, the "nitrogen-rule" and following thresholds were applied: O/C ≤ 1.2 and H/C ≤ 2C + 2 + N (Koch et al., 2005). All formulas with ^{13}C isotopes were removed from the data set as they represent duplicates of the ^{12}C parent molecules.

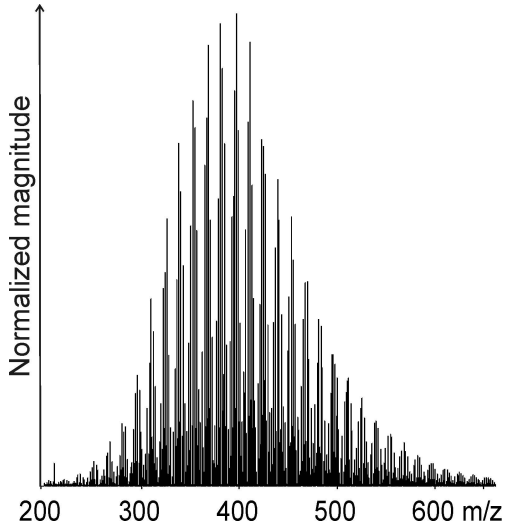

Fig. 2. Negative ESI FT-ICR mass spectrum of a representative marine SPE-DOM sample from the eastern Atlantic Ocean.

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. These relative peak magnitudes are presented in per mill (‰) and a magnitude cutoff of 0.05 ‰ was applied. All mass peaks present in less than five mass spectra were excluded from the final data set, in favor of identifying bulk trends. Since masses with low signal to noise ratios tend to show less mass accuracy, this procedure allowed an improved formula assignment. Ambiguously identified mass peaks were checked according to the "chemical building block" approach (Koch et al., 2007). Each oxygen atom in a molecular formula could be replaced with a CH_4-fragment, forming a pseudo-homologous series with a mass difference, $\Delta m = 36.4$ mDa. Therefore, the number of oxygen atoms in a molecular formula must exceed the number of "CH_4-O" pseudo-homologous series members; otherwise it is considered as falsely assigned.

Finally, an evaluation data set was obtained showing 2850 mass peaks with only few doubly-assigned molecular formulas (average: 2 ± 1 double assignments per sample). On a presence-absence basis and the 0.05 ‰ cutoff, 54 % of the detected molecular formulas were present in more than 135 samples, while 74 % were present in at least 100 samples showing the typical peak magnitude distribution of marine SPE-DOM (Fig. 2). Most mass peaks, which were not present in all samples, showed normalized magnitudes close to the cutoff limit. Due to the high degree of similarity between all samples, our data evaluation was based on normalized peak magnitudes instead of a presence/absence-based approach as previously applied for biomarker approaches in glacial or riverine DOM (Bhatia et al., 2010; Sleighter and Hatcher, 2008).

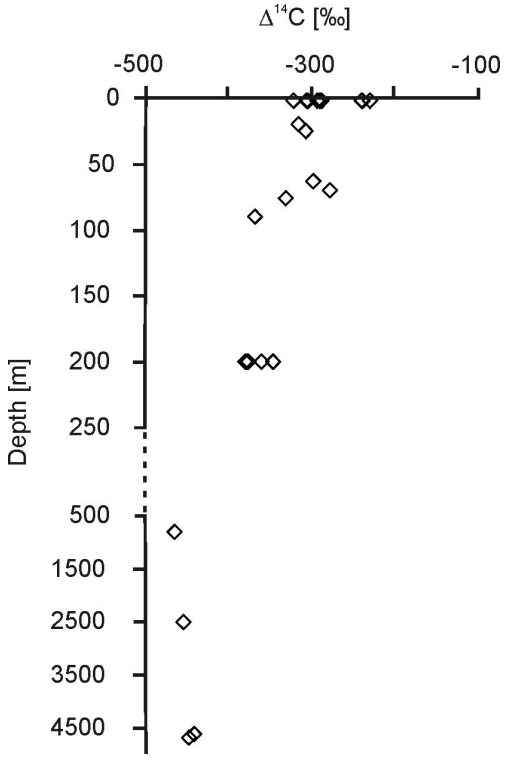

Fig. 3. $\Delta^{14}C$ values of marine SPE-DOM from the eastern Atlantic Ocean.

2.5 Statistical analysis

For statistical analysis we performed a non-parametric two-sided Mann-Whitney U-test for the comparison of weighted average parameters of SPE-DOM samples and two groups of peaks. The null hypothesis was that two groups differ by a location shift of "0" and the significance level α is 0.01.

3 Results and discussion

$\Delta^{14}C$ values ranged from a maximum of -229 ‰ in surface water extracts (2 m) to -464 ‰ in deep water extracts (>2500 m, Fig. 3). The highest surface $\Delta^{14}C$ values were comparable with the surface (3 m) $\Delta^{14}C$ value determined by Druffel and Bauer (1992) in the Sargasso Sea (-238 ‰). In comparison to the reported values from the Sargasso Sea, our $\Delta^{14}C$ values in deeper water (>2 m) were slightly more negative, ranging between that of bulk DOC and XAD isolates (Bauer et al., 1992), pointing to an almost representative extraction. However, from polarity-driven reversed-phase chromatography and the lower extraction efficiency for organic nitrogen compared to organic carbon, we know that the method discriminates against highly polar (and presumably small) compounds.

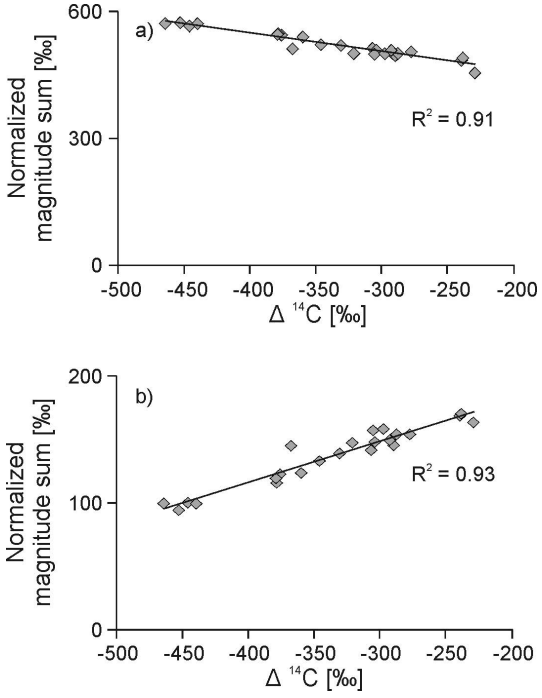

Fig. 4. Normalized magnitude sum [‰] of **(a)** negatively and **(b)** positively correlated FT-ICR mass peaks of eastern Atlantic Ocean SPE-DOM versus Δ^{14}C values of the SPE-DOM. The sums ($\sum$NEG, $\sum$POS) were built by adding the normalized magnitudes of the single with Δ^{14}C highly negatively or positively correlating mass peaks for each sample.

43 % of the normalized FT-ICR mass peak magnitudes showed either a significantly linear positive (POS) or negative (NEG) correlation with Δ^{14}C ($R > 0.5$, $p < 0.01$) (peaks and elemental formulas are presented in Tables A1 and A2 in Appendix A). The magnitudes of all significantly POS and NEG correlating mass peaks were summed up separately ($\sum$POS, $\sum$NEG), resulting in two average calibration functions (Fig. 4a, b). The $\sum$POS and $\sum$NEG mass peaks account for 61 ± 1 % of the summed magnitudes of all peaks in each spectrum, therefore representing a large and consistent fraction of peaks for the complete sample set. The two individual calibration functions were then used to calculate two different Δ^{14}C values for any of the 137 SPE-DOM samples, both resulting in almost identical Δ^{14}C values. Hence, the arithmetic mean of the two calculated Δ^{14}C values was used as the final Δ^{14}C value ($\Delta^{14}C_{Cal}$) for each sample. $\Delta^{14}C_{Cal}$ values for the upper 200 m are presented as depth-section (Fig. 5), and for the few deep water samples as individual values (Table 1).

This approach enabled us to apply calculated $\Delta^{14}C_{Cal}$ values for the whole sample set, allowing to define the groups of "recent" ($\Delta^{14}C_{Cal}$: > -280 ‰, $n = 29$) and "aged" samples ($\Delta^{14}C_{Cal}$: < -450, $n = 10$). Within both groups, the peak magnitude distributions were similar. To obtain a semi-quantitative approach of the reactivity of individual

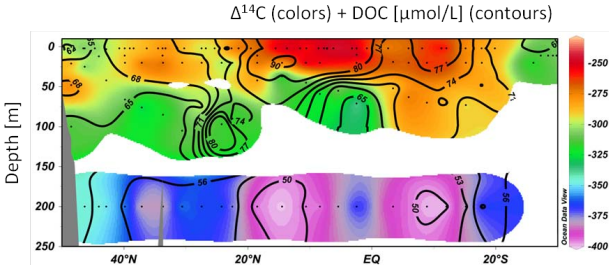

Fig. 5. Calculated SPE-DOM Δ^{14}C values (colors) and measured bulk DOC concentrations (contours) in the upper 250 m of the water column in the eastern Atlantic Ocean. The $\Delta^{14}C_{Cal}$ values and the DOC concentrations are significantly positively correlated.

DOM compounds in our Atlantic Ocean sample set, the normalized mass peak magnitudes were weighted by the respective bulk seawater DOC concentration. The relative changes in the magnitudes were calculated using a linear regression model (ordinary least squares, all 137 samples), resulting in predicted decreases of 22 to 167 %. A rate of 100 % or more is here defined as compounds with magnitudes falling below the 0.05 ‰ threshold. Since 100–167 % was a result of the definition and these compounds were still visible as very small mass peaks in the spectra, we will use the term "highly degraded" for this group. The compounds with estimated decreases >100 % were yet observed to be highly degraded in the oldest SPE-DOM in the Atlantic Ocean. This applied for only 4 % (number %) of the compounds. The magnitude weighting resulted in the disappearance of the negative correlations of magnitudes with Δ^{14}C. In fact, the NEG peaks now exhibited a positive correlation with Δ^{14}C as well, suggesting that both, POS and (formerly) NEG correlating compounds detected by FT-ICR MS decrease with age.

3.1 Molecular characteristics of DOM diagenesis

We observed clear differences in the molecular characteristics between POS and NEG compounds. The peak magnitudes of the POS compounds were generally much lower than those of the NEG compounds and the average *m/z* was inversely correlated with Δ^{14}C values (Fig. 6). Comparing recent and aged samples revealed a highly significant difference (Mann-Whitney U-test; $p < 0.01$) in the weighted average *m/z* values of 11.1 Da. The magnitude average *m/z* therefore slightly increased from 407.8 ± 2.1 for recent to 417.9 ± 0.8 for aged SPE-DOM. Previous studies showed a decrease in molecular size from high molecular weight DOM (>1 kDa) to low molecular weight DOM (<1 kDa) as a result of increased diagenetic processing (Kaiser and Benner, 2009) and a decreasing bioreactivity (Amon and Benner, 1996). Dittmar and Kattner (2003) also suggested a comparatively higher refractory character for small DOM molecules. However, these previous results were

Table 1. Calculated SPE-DOM $\Delta^{14}C_{Cal}$ values [‰] and bulk DOC values [$\mu mol\,L^{-1}$] in the deep water layers of the eastern Atlantic Ocean.

Depth (m)	Parameter	46° N 8° W	37° N 14° W	23° N 20° W	11° N 20° W	2° S 14° W	5° S 7° W	17° S 3° W	24° S 9° W
400–500	$\Delta^{14}C$ (‰)		−402						
800–900	$\Delta^{14}C$ (‰)				−456	−465	−448	−451	
1100–1800	$\Delta^{14}C$ (‰)		−436	−459				−449	
2500	$\Delta^{14}C$ (‰)			−462					
4000–5000	$\Delta^{14}C$ (‰)	−443	−463	−456	−450	−451	−454		
400–500	DOC ($\mu mol\,L^{-1}$)	56	58						
800–900	DOC ($\mu mol\,L^{-1}$)				45	47	46	49	
1100–1800	DOC ($\mu mol\,L^{-1}$)	50	48			52	54	47	
2500	DOC ($\mu mol\,L^{-1}$)	48		45					
4000–5000	DOC ($\mu mol\,L^{-1}$)	48	45		47		41	47	45

obtained using size-related separations such as ultrafiltration and gel permeation chromatography. In contrast, we used absorbent enriched samples (SPE-DOM), preventing a direct comparison with the previous studies. Based on SPE-DOM samples Hertkorn et al. (2012) obtained results that also suggested a similar trend of decreasing SPE-DOM molecular size with depth.

The van Krevelen diagram (Kim et al., 2003) showed differences in the elemental composition of the POS and NEG formulas (Fig. 7). The majority of CHO compounds of the POS formulas showed high H/C ratios (1.53 ± 0.2), whereas the NEG CHO formulas showed medium to low H/C ratios (1.15 ± 0.2, Fig. 7a, b). Within the region of H/C ≤ 1.4 of the van Krevelen diagram, the average mass for NEG and POS formulas was *m/z* 441 and *m/z* 300, respectively. Most of the POS formulas containing nitrogen (CHON) showed higher H/C ratios (1.43 ± 0.2). CHON compounds of NEG formulas occurred only in the low H/C region, similarly to the CHO compounds (1.16 ± 0.2, Fig. 7c, d). The H/C ratio shift also affected the DBE, ranging between 2 and 11 for the POS formulas and between 7 and 14 for the NEG formulas.

Although it is well known that the efficiency of microbial degradation is often related to the polarity of the substrate, we did not observe a shift in the O/C ratios with increasing age of the samples. For both NEG and POS groups, CHO and CHON compounds showed average O/C values of 0.48 ± 0.3 and 0.49 ± 0.2, respectively, showing no significant differences. With the exception of two mass peaks, CHOS compounds only occurred in the POS formulas having similar H/C values as the POS CHO and CHON compounds (Fig. 7e, f) with slightly higher O/C ratios (0.6 ± 0.2). However, only little is known about the role of CHOS compounds in DOM and a considerable contribution of anthropogenic input to these compounds cannot be excluded.

The strong molecular similarity, as detected in this and other studies using FT-ICR MS, is considered to represent the refractory molecular background of marine DOM (Koch

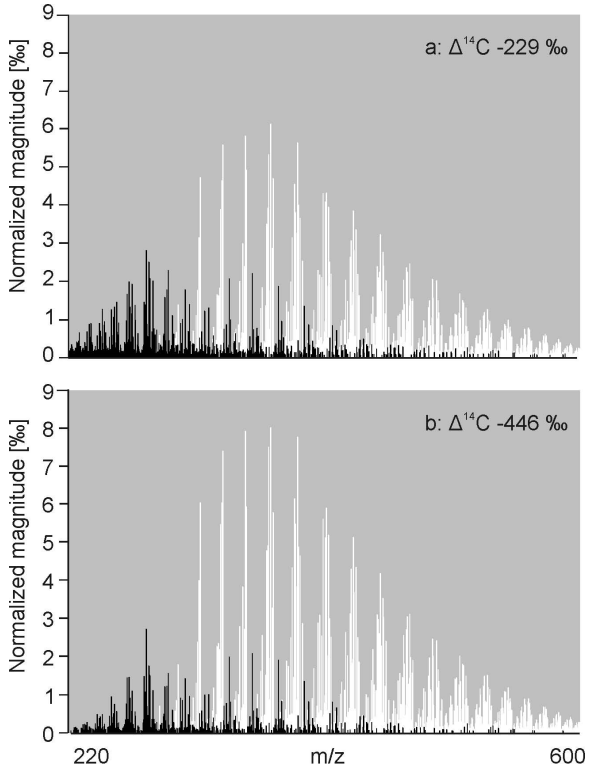

Fig. 6. Selected normalized FT-ICR mass peaks of eastern Atlantic Ocean SPE-DOM. The mass peaks show a significant linear correlation with $\Delta^{14}C$. **(a)** Surface sample extract with $\Delta^{14}C = -229$ ‰ and **(b)** deep sea sample extract with $\Delta^{14}C = -446$ ‰. The black colored masses are positively correlated with $\Delta^{14}C$ and are present in a higher proportion in the more recent SPE-DOM, whereas the white colored masses are negatively correlated with $\Delta^{14}C$ and present in a higher proportion in the aged SPE-DOM. The difference in the *m/z* between black and white masses is also reflected in the weighted average *m/z* of the whole SPE-DOM spectra and shifts from 407 (surface sample, $\Delta^{14}C = -229$) to 413 (deep sea sample, $\Delta^{14}C = -446$).

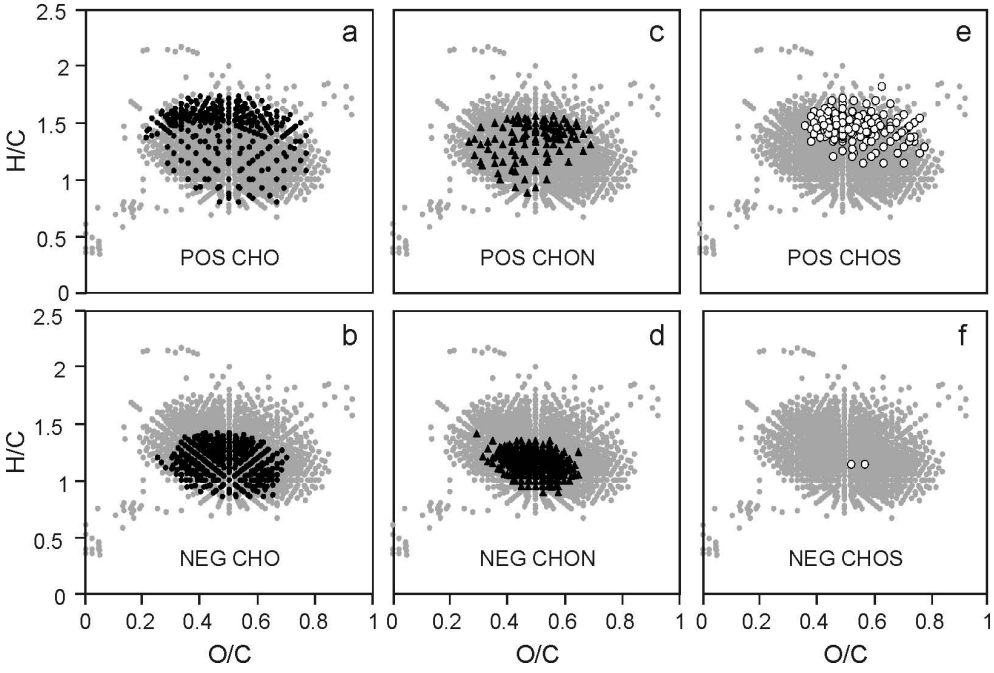

Fig. 7. Van Krevelen diagrams of compounds in eastern Atlantic Ocean SPE-DOM that are significantly correlated with $\Delta^{14}C$ ($p < 0.01$): **(a)** positively with CHO compounds; **(b)** negatively with CHO compounds; **(c)** positively with CHON compounds; **(d)** negatively with CHON compounds; **(e)** positively with CHOS compounds; **(f)** negatively with CHOS compounds. The grey dots in the background show all compounds found in the majority of Atlantic Ocean water extracts.

et al., 2005; Hertkorn et al., 2006; Gonsior et al., 2011). In our study, we observed depth and age-related trends in the total average elemental composition of the spectra. These trends were similar to the trends observed for the POS and NEG formulas. We found a highly significant difference in the weighted average H/C ratios between recent and aged samples (Mann-Whitney U-test, $p < 0.01$). The magnitude-averaged H/C ratios decreased from 1.268 ± 0.006 in recent to 1.245 ± 0.003 in aged SPE-DOM. Accordingly, the magnitude-averaged DBE increased from 8.03 ± 0.06 in recent to 8.43 ± 0.03 in aged SPE-DOM. Again, 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 region occupied by CRAM in the van Krevelen diagram corresponds well with the region of our NEG mass peaks, which are assumed to be compounds resistant to degradation. Hence, CRAM could also be a significant contributor to SPE-DOM. However, it has to be pointed out that the elemental composition can represent a large variety of possible structural isomers (Hertkorn et al., 2007). Nevertheless, a recent study by Witt et al. (2009) demonstrated that the structural variability represented by a single elemental formula in the FT-ICR mass spectra is probably not as high as expected for natural organic matter.

3.2 East Atlantic Ocean DOM degradation state

The linear correlation between single mass peaks and SPE-DOM $\Delta^{14}C$ allows to compare SPE-DOM samples in terms of their degradation state. Since FT-ICR MS is increasingly used for marine DOM studies, we present a degradation index that can be easily used to estimate and compare the degradation state of marine SPE-DOM. To calculate the degradation index, we selected 5 POS (POS_{Ideg}) and 5 NEG (NEG_{Ideg}) formulas (Table 2) with a particularly high correlation with the radiocarbon age. The 10 selected masses were also present in ∼400 previously analyzed samples from other locations and environments and therefore suitable to be implemented in a versatile index describing the relative degradation state of an individual sample within a given set of samples. The index I_{DEG} was calculated using the molecular formulas given in Table 2 and can be directly applied to the raw peak magnitudes:

$$I_{DEG} = \Sigma(\text{magnitudes}\, NEG_{Ideg}) / \Sigma(\text{magnitudes}\, (NEG_{Ideg} + POS_{Ideg})) \quad (1)$$

The value of I_{DEG} ranges between 0–1 and increases with the degradation state of the sample, because the magnitude contribution of NEG formulas increases. We observed

Table 2. Formulas utilized for magnitude summation in order to calculate the degradation index I_{DEG}.

NEG correlating compounds	POS correlating compounds
$C_{21}\,H_{26}\,O_{11}$	$C_{13}\,H_{18}\,O_{7}$
$C_{17}\,H_{20}\,O_{9}$	$C_{14}\,H_{20}\,O_{7}$
$C_{19}\,H_{22}\,O_{10}$	$C_{15}\,H_{22}\,O_{7}$
$C_{20}\,H_{22}\,O_{10}$	$C_{15}\,H_{22}\,O_{8}$
$C_{20}\,H_{24}\,O_{11}$	$C_{16}\,H_{24}\,O_{8}$

however from our database that the absolute value of I_{DEG} is dependent on instrument, extraction technique and environment. For example, samples from soils and sediments had generally lower values for I_{DEG} than samples from ocean water (data not shown). If similar sample extracts are measured with the same instrument in series, the I_{DEG} trends are comparable. However, since no comparable data exist, $\Delta^{14}C$ values should only be calculated using I_{DEG} in combination with measured reference $\Delta^{14}C$ values. Also, C18 extracted samples did not reliably show the respective peaks for the I_{DEG} calculation.

For our eastern Atlantic Ocean samples, I_{DEG} was in the range from 0.628–0.756 for the surface samples (Fig. 8a) and 0.756–0.808 for deeper water >200 m (Table 3). I_{DEG} showed a strong correlation with the $\Delta^{14}C$ values and the bulk DOC concentrations. In particular, in the upper 200 m changes in DOC concentrations were reflected in the I_{DEG}. The lowest I_{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 surface water was also reported by Carlson et al. (1994) and Goldberg et al. (2009). At 200 m depth the lowest I_{DEG} and the youngest SPE-DOM were calculated north of 40° N. The highest I_{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. The location of the tropical divergences was obtained from CTD temperature profiles of the cruise. So far, the narrow range and small number of data points of $\Delta^{14}C$ values, DOC concentrations and FT-ICR MS spectra for deep (>500 m) and bottom water samples circumvent a detailed oceanographic discussion of abyssal water masses of terms of DOM degradation.

To support the differentiation in fresh and old DOM, amino sugars were determined directly in bulk water samples as an independent measurement. Amino sugars are bioactive 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

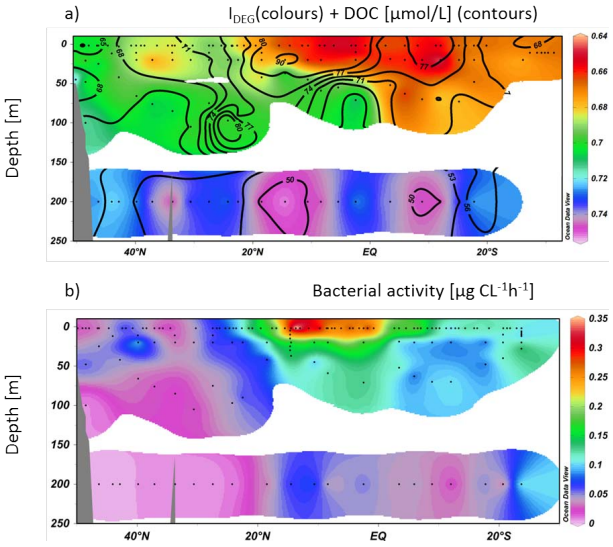

Fig. 8. **(a)** Values of the degradation index I_{DEG} for SPE-DOM samples from the eastern Atlantic Ocean (colors) and bulk DOC concentrations (contours); **(b)** the bacterial activity determined as utilized µg C l^{-1} h^{-1} in the upper 250 m of the water column in the eastern Atlantic Ocean. I_{DEG} can be easily calculated and used to estimate and compare the degradation state of marine FT-ICR MS analyzed SPE-DOM. The higher the values of I_{DEG}, the more degraded is the SPE-DOM. I_{DEG} and the DOC concentrations are significantly correlated. The bacterial activity maximum coincides with the lowest I_{DEG}, the DOC maximum and the youngest SPE-DOM (Fig. 4).

correlation between $\Delta^{14}C_{Cal}$ and the yield of amino sugars is consistent with previous observations, indicating that they are more reactive than bulk DOC. These independent results are a good indication that our mass peak magnitude-based $\Delta^{14}C$ calculation is reasonable (Fig. 9). The exponential relation between the amino sugar yield and $\Delta^{14}C_{Cal}$ 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.

3.3 Degradation continuum and the microbial carbon pump

Several studies present strategies to explain mechanisms of redistribution of DOM in the water column, based on their $\Delta^{14}C$ values and two or three component models (Beaupre and Druffel, 2009; Beaupre and Aluwihare, 2010; Hansell et al., 2009; Williams and Druffel, 1987). The models suggest a refractory DOM background fraction and labile or semi-labile fractions 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 method to the SPE-DOM samples from the seven deep stations results in similar values for the fresh SPE-DOM fraction

Table 3. I_{DEG} values for deep water layers.

Depth [m]	46° N 8° W	37° N 14° W	23° N 20° W	11° N 20° W	2° S 14° W	5° S 7° W	17° S 3° W
400–500		0.756					
800–900				0.793	0.790	0.777	0.776
1100–1800		0.787	0.801				0.779
2500			0.807				
4000–5000	0.798	0.808	0.805	0.787	0.785	0.788	

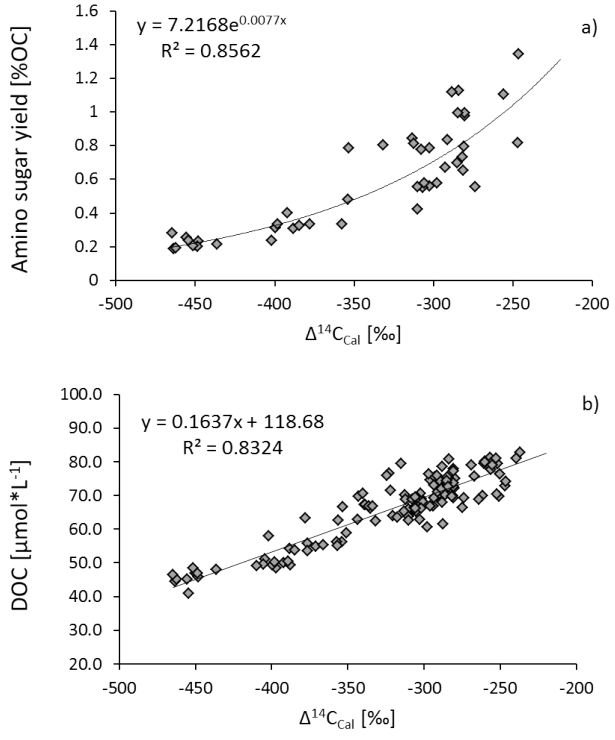

Fig. 9. Correlation and equations of **(a)** bulk amino sugar yields and **(b)** bulk DOC concentrations of Atlantic Ocean water and calculated $\Delta^{14}C$ values of the corresponding SPE-DOM. The correlations indicate the reasonability of the trend in $\Delta^{14}C_{Cal}$. The exponential relation between the amino sugar yield and $\Delta^{14}C_{Cal}$ 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.

at every station (Table 4). The values are slightly lower than the values reported for the Sargasso Sea (Beaupre and Aluwihare, 2010), but the variation is within the range of reported values for the Pacific Ocean (Beaupre and Druffel, 2009). This provides further evidence that the trends in radiocarbon age of SPE-DOM are comparable to that for the bulk DOC. Beaupre and Druffel (2009) calculated $\Delta^{14}C$ for the background DOM, but since $\Delta^{14}C$ was too low for the oldest water sample, they considered a multiple component system.

Our results indeed showed a wide spectrum of DOM reactivity represented by varying slopes of magnitude change with age, supporting our hypothesis of a continuum of DOM reactivity and age. As mentioned above, we assume that the compounds in the FT-ICR mass spectra have been degraded over time, but to varying extents. In the north Central Pacific Ocean (NCP), the lowest $\Delta^{14}C$ value of bulk DOC is −546 ‰ (Druffel et al., 1992), which is older than the oldest SPE-DOM in the Atlantic Ocean. Coinciding with the oldest water masses, the DOC concentration in the deep NCP is only ∼34 µmol kg^{-1} (Hansell et al., 2009), supporting the hypothesis of a very slow degradation (remineralization) of refractory DOC (Hansell et al., 2012). Based on the correlation between $\Delta^{14}C_{Cal}$ of SPE-DOM and DOC concentration (Fig. 9b), we estimated the $\Delta^{14}C$ values and molecular degradation trends of SPE-DOM during thermohaline circulation. Applying this correlation, the SPE-DOM $\Delta^{14}C$ in the NCP calculates to −518 ‰, which is in good agreement with the values reported by Williams and Druffel (1987) and Druffel et al. (1992). To elucidate at which point during the thermohaline circulation a single compound would be highly 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. This is based on a recent study by Witt et al. (2009) suggesting 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 the cutoff of 0.05 ‰. Using the calibration functions resulting from the correlation between the bulk DOC weighted magnitudes and $\Delta^{14}C_{cal}$, a theoretical SPE-DOM $\Delta^{14}C$ limit ($\Delta^{14}C_{Lim}$) was calculated at which each compound is considered to be highly degraded. Thus, the proportion of mass peaks can be estimated, which will be highly degraded in the NCP. Since we were interested in general trends, this calculation was performed for compounds that were present in 27–29 of all "young" samples. All compounds with $\Delta^{14}C_{Lim} > -518$ ‰ are expected to be highly degradable, as they are not supposed to be present in the NCP. This applied for 16 % (number %) of the compounds. Portions of the remaining compounds will persist for long periods of time (Fig. 10)

Table 4. Calculated $\Delta^{14}C$ values of excess SPE-DOM and corresponding Keeling slope values for the seven deep stations of the eastern Atlantic Ocean.

Station	$\Delta^{14}C$ 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° S, 14° W	68	−10 203
5° S, 7° W	76	−10 550
17° S, 3° W	44	−10239

and are supposed to contribute to the high average age of DOM. The FT-ICR MS analyzed SPE-DOM represents a fraction of the marine DOM, for which a high portion of 84 % of the compounds (number %) is expected to persist, possibly modified by partially degradation, during one or more thermohaline cycles through the global ocean circulation. At the same time the compounds are expected to degrade very slowly with a continuum of different rates in the range from 22–167 % (Fig. 10). The relative decreases were calculated using a linear regression model (ordinary least squares, all 137 samples), resulting in predicted decreases >100 % for some compounds. These compounds were yet observed to be highly degraded in the oldest SPE-DOM in the Atlantic Ocean.

Our results support the hypothesis of a broad and continuous distribution of $\Delta^{14}C$ ages, as proposed by Bauer et al. (1992). Since only few of the compounds were identified to be highly degraded in the oldest Atlantic Ocean SPE-DOM, compounds of moderate reactivity, which are degraded within month to decades and expected to be present in SPE-DOM, are potentially underrepresented in the FT-ICR mass spectra. Also, the presence of an absolute refractory fraction (i.e. ^{14}C depleted), which is hidden in a mixture with degrading compounds, cannot be excluded. However, since the $\Delta^{14}C$ trends in SPE-DOM are similar to $\Delta^{14}C$ trends of bulk DOM, we propose the degradation continuum shown for FT-ICR MS analysed SPE-DOM to be one important pathway in marine DOM degradation. Operational terms such as "labile", "semi-labile", "refractory (recalcitrant)", "background" or "excess" DOM, as used in different studies (Beaupre and Druffel, 2009; Beaupre and Aluwihare, 2010; Hansell et al., 2009; William and Druffel, 1987; Jiao 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.

The microbial carbon pump provides a conceptual framework for a better understanding of the role of microbial processes in the generation of recalcitrant DOM and carbon storage in the ocean (Ogawa et al., 2001; Jiao et al., 2010).

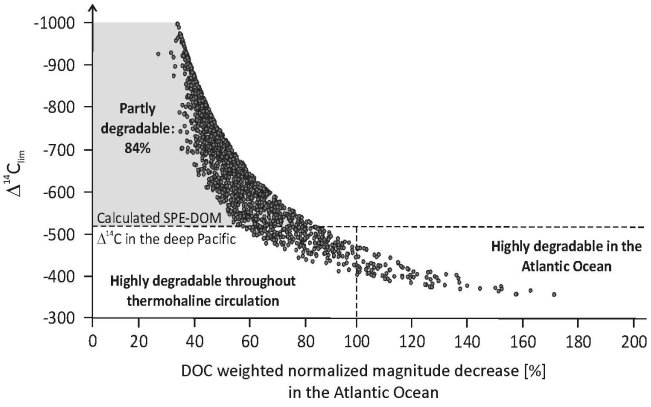

Fig. 10. Calculated limit of $\Delta^{14}C$ ($\Delta^{14}C_{Lim}$) for Atlantic Ocean SPE-DOM compounds, represented by FT-ICR mass peaks versus the calculated, DOC weighted normalized magnitude decrease of SPE-DOM in the Atlantic Ocean (x-axis, [%]). All compounds are expected to decrease with increasing SPE-DOM age, but with different rates (between 22–167 %). The relative decreases were calculated using a linear regression model (ordinary least squares, all 137 samples), resulting in predicted decreases > 100 % for some compounds. These compounds are yet observed to be highly degraded in the oldest SPE-DOM in the Atlantic Ocean. $\Delta^{14}C_{Lim}$ is a theoretical SPE-DOM $\Delta^{14}C$ value, at which a compound is regarded to be highly degraded. All compounds with a $\Delta^{14}C_{Lim} > -518$ ‰ (SPE-DOM $\Delta^{14}C$ value estimated for the CNP) are expected to be highly degraded in the oldest water masses. 84 % (number %) of the compounds should persist, possibly modified by partial degradation throughout thermohaline circulation. The variability of decreasing rates as well as the $\Delta^{14}C_{Lim}$ values represent a continuum of different degradation rates for the individual compounds.

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 I_{DEG}) was determined in surface waters of the highly stratified region between 0–15° N (Fig. 7b). The primary production was supposed to have only a minor contribution. A comparison of I_{DEG} with the TChl-a fluorescence data from the discrete stations (Taylor et al., 2011) showed no clear relationship. Out of all mass peaks, the estimated fraction of the least reactive compounds is at least 61 %, accounting for 94 % of the summed magnitudes per sample. We hypothesize that this low reactivity fraction is produced and accumulates in the euphotic zone. 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). These recently produced refractory and younger compounds mix with older refractory compounds of similar reactivity in the epipelagic zone. This mixture is then further degraded by bacterial activity (Ogawa and Tanoue, 2003) and thereby aged during the thermohaline circulation.

4 Conclusions

Trends in bulk DOC radiocarbon ages were reflected in the radiocarbon age, determined from a correlation between selected FT-ICR mass peaks and SPE-DOM $\Delta^{14}C$ 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 this, the degradation index I_{DEG} was introduced as a simple tool to evaluate relative degradation states in a set of similarly treated samples. So far, I_{DEG} is only applied for SPE-DOM samples (PPL extracts) from the Atlantic Ocean and thus has to be further verified.

We propose a degradation continuum of the compounds represented in the FT-ICR mass spectra, but only a minor portion of them are expected to be highly degraded during thermohaline circulation. Prokaryotic (bacterial) production, transformation and accumulation of the very stable DOM occur 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. Since bacterial growth, bacterial production or enzymatic activities are influenced by parameters, e.g. temperature or CO_2 (Piontek et al., 2009, 2010), a change of these parameters could also influence the processes of refractory DOM production or degradation and as a consequence also the amount of DOM in the world oceans.

It is likely that the microbial carbon pump and the proposed degradation continuum of microbially-produced DOM are parts of several processes taking place concurrently, resulting in the observed average age of DOM samples. 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.

Acknowledgements. The authors gratefully acknowledge Anne Stuart for lab assistance, two anonymous reviewers for their helpful comments and the crew of the research vessel “Polarstern” for professional assistance during sample collection.

This work was partially funded by the German Academic Exchange Service (DAAD, project 50023021), the German Science Foundation (KO 2164/8-1), and a National Science Foundation-Ocean Sciences grant OCE-0825403 to S. L. M. and NSF 0713915.

Edited by: G. Herndl

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

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
C_{12} H_{14} O_4	222.089209	C_{14} H_{14} O_8	310.068867	C_{18} H_{27} O_8 N_1	385.173667
C_{13} H_{18} O_3	222.125594	C_{16} H_{22} O_6	310.141638	C_{16} H_{22} O_9 N_2	386.13253
C_{11} H_{12} O_5	224.068474	C_{17} H_{26} O_5	310.178024	C_{18} H_{26} O_7 S_1	386.139924
C_{12} H_{16} O_4	224.104859	C_{13} H_{12} O_9	312.048132	C_{19} H_{30} O_8	386.194068
C_{13} H_{20} O_3	224.141245	C_{14} H_{16} O_8	312.084518	C_{17} H_{25} O_9 N_1	387.152931
C_{11} H_{14} O_5	226.084124	C_{13} H_{16} O_7 N_2	312.095751	C_{15} H_{20} O_8 N_2 S_1	388.094036
C_{12} H_{18} O_4	226.120509	C_{15} H_{20} O_7	312.120903	C_{17} H_{24} O_8 S_1	388.119188
C_{10} H_{12} O_6	228.063388	C_{16} H_{24} O_6	312.157289	C_{19} H_{20} O_7 N_2	388.127051
C_{11} H_{16} O_5	228.099774	C_{13} H_{15} O_8 N_1	313.079767	C_{17} H_{24} O_{10}	388.136947
C_{10} H_{14} O_6	230.079038	C_{14} H_{19} O_7 N_1	313.116152	C_{18} H_{28} O_7 S_1	388.155574
C_{11} H_{18} O_5	230.115424	C_{15} H_{23} O_6 N_1	313.152538	C_{18} H_{28} O_9	388.173333
C_{10} H_{16} O_6	232.094688	C_{13} H_{14} O_9	314.063782	C_{19} H_{32} O_8	388.209718
C_{13} H_{14} O_4	234.089209	C_{14} H_{18} O_8	314.100168	C_{16} H_{23} O_8 N_1 S_1	389.114437
C_{12} H_{12} O_5	236.068474	C_{13} H_{18} O_7 N_2	314.111401	C_{16} H_{23} O_{10} N_1	389.132196
C_{13} H_{16} O_4	236.104859	C_{15} H_{22} O_7	314.136553	C_{16} H_{22} O_9 S_1	390.098453
C_{14} H_{20} O_3	236.141245	C_{16} H_{26} O_6	314.172939	C_{16} H_{22} O_{11}	390.116212
C_{12} H_{14} O_5	238.084124	C_{13} H_{17} O_8 N_1	315.095417	C_{17} H_{26} O_8 S_1	390.134839
C_{13} H_{18} O_4	238.120509	C_{14} H_{21} O_7 N_1	315.131802	C_{17} H_{26} O_{10}	390.152597
C_{11} H_{13} O_5 N_1	239.079373	C_{13} H_{16} O_7 S_1	316.061674	C_{18} H_{30} O_9	390.188983
C_{11} H_{12} O_6	240.063388	C_{13} H_{16} O_9	316.079432	C_{15} H_{21} O_9 N_1 S_1	391.093702
C_{12} H_{16} O_5	240.099774	C_{14} H_{20} O_6 S_1	316.098059	C_{16} H_{25} O_8 N_1 S_1	391.130088
C_{13} H_{20} O_4	240.136159	C_{14} H_{20} O_8	316.115818	C_{15} H_{20} O_{10} S_1	392.077718
C_{11} H_{15} O_5 N_1	241.095023	C_{15} H_{24} O_7	316.152203	C_{16} H_{24} O_9 S_1	392.114103
C_{11} H_{14} O_6	242.079038	C_{13} H_{19} O_8 N_1	317.111067	C_{16} H_{24} O_{11}	392.131862
C_{12} H_{18} O_5	242.115424	C_{13} H_{18} O_7 S_1	318.077324	C_{17} H_{28} O_{10}	392.168247
C_{10} H_{12} O_7	244.058303	C_{13} H_{18} O_9	318.095082	C_{22} H_{32} O_6	392.219889
C_{11} H_{16} O_6	244.094688	C_{14} H_{22} O_6 S_1	318.113709	C_{14} H_{18} O_{11} S_1	394.056982
C_{12} H_{20} O_5	244.131074	C_{16} H_{18} O_5 N_2	318.121572	C_{15} H_{22} O_{10} S_1	394.093368
C_{10} H_{14} O_7	246.073953	C_{14} H_{22} O_8	318.131468	C_{21} H_{32} O_7	396.214803
C_{11} H_{18} O_6	246.110338	C_{15} H_{26} O_7	318.167853	C_{21} H_{34} O_7	398.230453
C_{13} H_{12} O_5	248.068474	C_{19} H_{26} O_4	318.183109	C_{19} H_{29} O_8 N_1	399.189317
C_{14} H_{16} O_4	248.104859	C_{15} H_{12} O_8	320.053217	C_{16} H_{20} O_8 N_2 S_1	400.094036
C_{13} H_{15} O_4 N_1	249.100108	C_{12} H_{16} O_8 S_1	320.056588	C_{17} H_{24} O_9 N_2	400.14818
C_{12} H_{10} O_6	250.047738	C_{13} H_{20} O_7 S_1	320.092974	C_{19} H_{28} O_7 S_1	400.155574
C_{13} H_{14} O_5	250.084124	C_{13} H_{20} O_9	320.110732	C_{20} H_{32} O_8	400.209718
C_{14} H_{18} O_4	250.120509	C_{14} H_{24} O_8	320.147118	C_{17} H_{23} O_8 N_1 S_1	401.114437
C_{12} H_{13} O_5 N_1	251.079373	C_{15} H_{14} O_8	322.068867	C_{17} H_{23} O_{10} N_1	401.132196
C_{13} H_{17} O_4 N_1	251.115758	C_{12} H_{18} O_8 S_1	322.072238	C_{18} H_{27} O_9 N_1	401.168582
C_{12} H_{12} O_6	252.063388	C_{13} H_{22} O_7 S_1	322.108624	C_{16} H_{22} O_{10} N_2	402.127445
C_{13} H_{16} O_5	252.099774	C_{18} H_{26} O_5	322.178024	C_{18} H_{26} O_8 S_1	402.134839
C_{12} H_{16} O_4 N_2	252.111007	C_{14} H_{12} O_9	324.048132	C_{18} H_{26} O_{10}	402.152597
C_{14} H_{20} O_4	252.136159	C_{12} H_{20} O_8 S_1	324.087888	C_{19} H_{30} O_9	402.188983
C_{12} H_{15} O_5 N_1	253.095023	C_{18} H_{28} O_5	324.193674	C_{17} H_{25} O_{10} N_1	403.147846
C_{13} H_{19} O_4 N_1	253.131408	C_{17} H_{26} O_6	326.172939	C_{17} H_{24} O_9 S_1	404.114103
C_{12} H_{14} O_6	254.079038	C_{15} H_{21} O_7 N_1	327.131802	C_{17} H_{24} O_{11}	404.131862
C_{13} H_{18} O_5	254.115424	C_{14} H_{20} O_7 N_2	328.127051	C_{18} H_{28} O_8 S_1	404.150489
C_{14} H_{22} O_4	254.151809	C_{16} H_{24} O_7	328.152203	C_{18} H_{28} O_{10}	404.168247
C_{11} H_{13} O_6 N_1	255.074287	C_{17} H_{28} O_6	328.188589	C_{19} H_{32} O_9	404.204633
C_{12} H_{17} O_5 N_1	255.110673	C_{14} H_{19} O_8 N_1	329.111067	C_{16} H_{23} O_9 N_1 S_1	405.109352
C_{11} H_{12} O_7	256.058303	C_{15} H_{23} O_7 N_1	329.147452	C_{16} H_{23} O_{11} N_1	405.127111
C_{12} H_{16} O_6	256.094688	C_{13} H_{14} O_{10}	330.058697	C_{17} H_{26} O_9 S_1	406.129753
C_{13} H_{20} O_5	256.131074	C_{14} H_{18} O_9	330.095082	C_{17} H_{26} O_{11}	406.147512
C_{11} H_{15} O_6 N_1	257.089937	C_{15} H_{22} O_6 S_1	330.113709	C_{18} H_{30} O_{10}	406.183897
C_{11} H_{14} O_7	258.073953	C_{15} H_{22} O_8	330.131468	C_{15} H_{20} O_{11} S_1	408.072632

Table A1. Continued.

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
C_{12} H_{18} O_6	258.110338	C_{16} H_{26} O_7	330.167853	C_{16} H_{24} O_{10} S_1	408.109018
C_{13} H_{22} O_5	258.146724	C_{13} H_{17} O_9 N_1	331.090331	C_{15} H_{22} O_{11} S_1	410.088282
C_{11} H_{16} O_7	260.089603	C_{14} H_{21} O_8 N_1	331.126717	C_{22} H_{34} O_7	410.230453
C_{12} H_{20} O_6	260.125988	C_{13} H_{16} O_8 S_1	332.056588	C_{21} H_{32} O_8	412.209718
C_{14} H_{14} O_5	262.084124	C_{13} H_{16} O_{10}	332.074347	C_{19} H_{26} O_8 S_1	414.134839
C_{11} H_{18} O_5 S_1	262.087494	C_{14} H_{20} O_7 S_1	332.092974	C_{18} H_{26} O_9 N_2	414.16383
C_{11} H_{18} O_7	262.105253	C_{16} H_{16} O_6 N_2	332.100836	C_{21} H_{34} O_8	414.225368
C_{14} H_{17} O_4 N_1	263.115758	C_{14} H_{20} O_9	332.110732	C_{19} H_{29} O_9 N_1	415.184232
C_{13} H_{12} O_6	264.063388	C_{15} H_{24} O_6 S_1	332.129359	C_{17} H_{24} O_{10} N_2	416.143095
C_{10} H_{16} O_6 S_1	264.066759	C_{15} H_{24} O_8	332.147118	C_{19} H_{28} O_8 S_1	416.150489
C_{14} H_{16} O_5	264.099774	C_{16} H_{14} O_8	334.068867	C_{19} H_{28} O_{10}	416.168247
C_{13} H_{15} O_5 N_1	265.095023	C_{13} H_{18} O_8 S_1	334.072238	C_{20} H_{32} O_9	416.204633
C_{14} H_{19} O_4 N_1	265.131408	C_{13} H_{18} O_{10}	334.089997	C_{18} H_{27} O_{10} N_1	417.163496
C_{12} H_{10} O_7	266.042653	C_{14} H_{22} O_7 S_1	334.108624	C_{18} H_{26} O_9 S_1	418.129753
C_{13} H_{14} O_6	266.079038	C_{14} H_{22} O_9	334.126382	C_{18} H_{26} O_{11}	418.147512
C_{14} H_{18} O_5	266.115424	C_{15} H_{26} O_8	334.162768	C_{19} H_{30} O_8 S_1	418.166139
C_{15} H_{22} O_4	266.151809	C_{12} H_{16} O_9 S_1	336.051503	C_{19} H_{30} O_{10}	418.183897
C_{12} H_{13} O_6 N_1	267.074287	C_{13} H_{20} O_8 S_1	336.087888	C_{17} H_{25} O_9 N_1 S_1	419.125002
C_{13} H_{17} O_5 N_1	267.110673	C_{14} H_{24} O_7 S_1	336.124274	C_{17} H_{25} O_{11} N_1	419.142761
C_{12} H_{12} O_7	268.058303	C_{19} H_{28} O_5	336.193674	C_{17} H_{24} O_{10} S_1	420.109018
C_{13} H_{16} O_6	268.094688	C_{12} H_{18} O_9 S_1	338.067153	C_{17} H_{24} O_{12}	420.126776
C_{12} H_{16} O_5 N_2	268.105922	C_{13} H_{22} O_8 S_1	338.103538	C_{18} H_{28} O_9 S_1	420.145403
C_{14} H_{20} O_5	268.131074	C_{18} H_{26} O_6	338.172939	C_{18} H_{28} O_{11}	420.163162
C_{15} H_{24} O_4	268.167459	C_{19} H_{30} O_5	338.209324	C_{19} H_{32} O_{10}	420.199547
C_{12} H_{15} O_6 N_1	269.089937	C_{18} H_{28} O_6	340.188589	C_{16} H_{22} O_{11} S_1	422.088282
C_{13} H_{19} O_5 N_1	269.126323	C_{15} H_{18} O_7 S_1	342.077324	C_{17} H_{26} O_{10} S_1	422.124668
C_{12} H_{14} O_7	270.073953	C_{17} H_{26} O_7	342.167853	C_{17} H_{26} O_{12}	422.142426
C_{13} H_{18} O_6	270.110338	C_{18} H_{30} O_6	342.204239	C_{23} H_{34} O_7	422.230453
C_{14} H_{22} O_5	270.146724	C_{16} H_{25} O_7 N_1	343.163102	C_{16} H_{24} O_{11} S_1	424.103932
C_{12} H_{17} O_6 N_1	271.105587	C_{14} H_{16} O_8 S_1	344.056588	C_{23} H_{36} O_7	424.246104
C_{11} H_{12} O_8	272.053217	C_{15} H_{20} O_7 S_1	344.092974	C_{22} H_{34} O_8	426.225368
C_{12} H_{16} O_7	272.089603	C_{14} H_{20} O_8 N_2	344.121966	C_{20} H_{28} O_8 S_1	428.150489
C_{13} H_{20} O_6	272.125988	C_{16} H_{24} O_8	344.147118	C_{21} H_{32} O_9	428.204633
C_{14} H_{24} O_5	272.162374	C_{17} H_{28} O_7	344.183503	C_{20} H_{30} O_8 S_1	430.166139
C_{11} H_{14} O_8	274.068867	C_{14} H_{19} O_7 N_1 S_1	345.088223	C_{20} H_{30} O_{10}	430.183897
C_{12} H_{18} O_7	274.105253	C_{14} H_{19} O_9 N_1	345.105981	C_{21} H_{34} O_9	430.220283
C_{13} H_{22} O_6	274.141638	C_{15} H_{23} O_8 N_1	345.142367	C_{18} H_{25} O_9 N_1 S_1	431.125002
C_{11} H_{16} O_6 S_1	276.066759	C_{14} H_{18} O_8 S_1	346.072238	C_{19} H_{29} O_{10} N_1	431.179146
C_{11} H_{16} O_8	276.084518	C_{14} H_{18} O_{10}	346.089997	C_{19} H_{28} O_9 S_1	432.145403
C_{12} H_{20} O_7	276.120903	C_{15} H_{22} O_7 S_1	346.108624	C_{19} H_{28} O_{11}	432.163162
C_{14} H_{14} O_6	278.079038	C_{15} H_{22} O_9	346.126382	C_{20} H_{32} O_{10}	432.199547
C_{13} H_{13} O_6 N_1	279.074287	C_{16} H_{26} O_8	346.162768	C_{18} H_{27} O_{11} N_1	433.158411
C_{14} H_{17} O_5 N_1	279.110673	C_{14} H_{21} O_9 N_1	347.121631	C_{18} H_{26} O_{12}	434.142426
C_{13} H_{12} O_7	280.058303	C_{13} H_{16} O_9 S_1	348.051503	C_{19} H_{30} O_9 S_1	434.161053
C_{14} H_{16} O_6	280.094688	C_{14} H_{20} O_8 S_1	348.087888	C_{19} H_{30} O_{11}	434.178812
C_{16} H_{24} O_4	280.167459	C_{14} H_{20} O_{10}	348.105647	C_{17} H_{24} O_{11} S_1	436.103932
C_{13} H_{15} O_6 N_1	281.089937	C_{15} H_{24} O_7 S_1	348.124274	C_{18} H_{28} O_{10} S_1	436.140318
C_{14} H_{19} O_5 N_1	281.126323	C_{15} H_{24} O_9	348.142032	C_{18} H_{28} O_{12}	436.158076
C_{13} H_{14} O_7	282.073953	C_{20} H_{28} O_5	348.193674	C_{24} H_{36} O_7	436.246104
C_{14} H_{18} O_6	282.110338	C_{13} H_{18} O_9 S_1	350.067153	C_{16} H_{22} O_{12} S_1	438.083197
C_{15} H_{22} O_5	282.146724	C_{14} H_{22} O_8 S_1	350.103538	C_{23} H_{36} O_8	440.241018
C_{13} H_{17} O_6 N_1	283.105587	C_{14} H_{22} O_{10}	350.121297	C_{22} H_{34} O_9	442.220283
C_{14} H_{21} O_5 N_1	283.141973	C_{20} H_{30} O_5	350.209324	C_{20} H_{29} O_{10} N_1	443.179146
C_{12} H_{12} O_8	284.053217	C_{15} H_{12} O_{10}	352.043047	C_{20} H_{28} O_9 S_1	444.145403
C_{13} H_{16} O_7	284.089603	C_{13} H_{20} O_9 S_1	352.082803	C_{21} H_{32} O_{10}	444.199547
C_{12} H_{16} O_6 N_2	284.100836	C_{19} H_{28} O_6	352.188589	C_{22} H_{36} O_9	444.235933

Table A1. Continued.

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
$C_{14}H_{20}O_6$	284.125988	$C_{19}H_{30}O_6$	354.204239	$C_{20}H_{30}O_9S_1$	446.161053
$C_{15}H_{24}O_5$	284.162374	$C_{16}H_{24}O_7N_2$	356.158351	$C_{20}H_{30}O_{11}$	446.178812
$C_{12}H_{15}O_7N_1$	285.084852	$C_{18}H_{28}O_7$	356.183503	$C_{21}H_{34}O_{10}$	446.215197
$C_{13}H_{19}O_6N_1$	285.121237	$C_{16}H_{23}O_8N_1$	357.142367	$C_{19}H_{28}O_{10}S_1$	448.140318
$C_{12}H_{14}O_8$	286.068867	$C_{15}H_{18}O_8S_1$	358.072238	$C_{19}H_{28}O_{12}$	448.158076
$C_{13}H_{18}O_7$	286.105253	$C_{16}H_{22}O_7S_1$	358.108624	$C_{20}H_{32}O_9S_1$	448.176703
$C_{14}H_{22}O_6$	286.141638	$C_{15}H_{22}O_8N_2$	358.137616	$C_{20}H_{32}O_{11}$	448.194462
$C_{12}H_{17}O_7N_1$	287.100502	$C_{17}H_{26}O_8$	358.162768	$C_{18}H_{26}O_{11}S_1$	450.119582
$C_{12}H_{16}O_6S_1$	288.066759	$C_{18}H_{30}O_7$	358.199153	$C_{18}H_{26}O_{13}$	450.137341
$C_{12}H_{16}O_8$	288.084518	$C_{15}H_{21}O_7N_1S_1$	359.103873	$C_{19}H_{30}O_{12}$	450.173726
$C_{13}H_{20}O_7$	288.120903	$C_{15}H_{21}O_9N_1$	359.121631	$C_{17}H_{24}O_{12}S_1$	452.098847
$C_{14}H_{24}O_6$	288.157289	$C_{16}H_{25}O_8N_1$	359.158017	$C_{24}H_{38}O_8$	454.256668
$C_{15}H_{14}O_6$	290.079038	$C_{14}H_{16}O_9S_1$	360.051503	$C_{23}H_{36}O_9$	456.235933
$C_{12}H_{18}O_6S_1$	290.082409	$C_{15}H_{20}O_8S_1$	360.087888	$C_{21}H_{31}O_{10}N_1$	457.194796
$C_{12}H_{18}O_8$	290.100168	$C_{16}H_{24}O_7S_1$	360.124274	$C_{19}H_{26}O_{11}N_2$	458.15366
$C_{13}H_{22}O_7$	290.136553	$C_{16}H_{24}O_9$	360.142032	$C_{22}H_{34}O_{10}$	458.215197
$C_{14}H_{13}O_6N_1$	291.074287	$C_{17}H_{28}O_8$	360.178418	$C_{20}H_{29}O_{11}N_1$	459.174061
$C_{14}H_{12}O_7$	292.058303	$C_{17}H_{15}O_8N_1$	361.079767	$C_{21}H_{32}O_9S_1$	460.176703
$C_{11}H_{16}O_7S_1$	292.061674	$C_{15}H_{23}O_7N_1S_1$	361.119523	$C_{21}H_{32}O_{11}$	460.194462
$C_{12}H_{20}O_6S_1$	292.098059	$C_{15}H_{23}O_9N_1$	361.137281	$C_{19}H_{27}O_{12}N_1$	461.153325
$C_{14}H_{16}O_5N_2$	292.105922	$C_{14}H_{18}O_9S_1$	362.067153	$C_{20}H_{30}O_{10}S_1$	462.155968
$C_{15}H_{20}O_4N_2$	292.142307	$C_{15}H_{22}O_8S_1$	362.103538	$C_{20}H_{30}O_{12}$	462.173726
$C_{14}H_{15}O_6N_1$	293.089937	$C_{15}H_{22}O_{10}$	362.121297	$C_{21}H_{34}O_{11}$	462.210112
$C_{15}H_{19}O_5N_1$	293.126323	$C_{16}H_{26}O_7S_1$	362.139924	$C_{19}H_{28}O_{11}S_1$	464.135232
$C_{14}H_{14}O_7$	294.073953	$C_{16}H_{26}O_9$	362.157682	$C_{19}H_{28}O_{13}$	464.152991
$C_{13}H_{13}O_7N_1$	295.069202	$C_{14}H_{21}O_8N_1S_1$	363.098787	$C_{20}H_{32}O_{12}$	464.189377
$C_{14}H_{17}O_6N_1$	295.105587	$C_{13}H_{16}O_{10}S_1$	364.046417	$C_{18}H_{26}O_{12}S_1$	466.114497
$C_{13}H_{12}O_8$	296.053217	$C_{14}H_{20}O_9S_1$	364.082803	$C_{24}H_{38}O_9$	470.251583
$C_{14}H_{16}O_7$	296.089603	$C_{15}H_{24}O_8S_1$	364.119188	$C_{22}H_{32}O_9S_1$	472.176703
$C_{11}H_{20}O_7S_1$	296.092974	$C_{15}H_{24}O_{10}$	364.136947	$C_{23}H_{36}O_{10}$	472.230847
$C_{15}H_{20}O_6$	296.125988	$C_{14}H_{22}O_9S_1$	366.098453	$C_{21}H_{31}O_{11}N_1$	473.189711
$C_{16}H_{24}O_5$	296.162374	$C_{20}H_{30}O_6$	366.204239	$C_{22}H_{34}O_{11}$	474.210112
$C_{13}H_{15}O_7N_1$	297.084852	$C_{13}H_{20}O_{10}S_1$	368.077718	$C_{21}H_{32}O_{10}S_1$	476.171618
$C_{14}H_{19}O_6N_1$	297.121237	$C_{20}H_{32}O_6$	368.219889	$C_{21}H_{32}O_{12}$	476.189377
$C_{13}H_{14}O_8$	298.068867	$C_{19}H_{30}O_7$	370.199153	$C_{20}H_{30}O_{11}S_1$	478.150883
$C_{14}H_{18}O_7$	298.105253	$C_{16}H_{21}O_9N_1$	371.121631	$C_{20}H_{30}O_{13}$	478.168641
$C_{13}H_{18}O_6N_2$	298.116486	$C_{17}H_{25}O_8N_1$	371.158017	$C_{19}H_{28}O_{12}S_1$	480.130147
$C_{15}H_{22}O_6$	298.141638	$C_{17}H_{24}O_7S_1$	372.124274	$C_{25}H_{38}O_9$	482.251583
$C_{16}H_{26}O_5$	298.178024	$C_{16}H_{24}O_8N_2$	372.153266	$C_{24}H_{38}O_{10}$	486.246497
$C_{13}H_{17}O_7N_1$	299.100502	$C_{18}H_{28}O_8$	372.178418	$C_{22}H_{32}O_{10}S_1$	488.171618
$C_{14}H_{21}O_6N_1$	299.136887	$C_{19}H_{32}O_7$	372.214803	$C_{23}H_{36}O_{11}$	488.225762
$C_{13}H_{16}O_8$	300.084518	$C_{15}H_{19}O_8N_1S_1$	373.083137	$C_{22}H_{34}O_{12}$	490.205027
$C_{14}H_{20}O_7$	300.120903	$C_{16}H_{23}O_9N_1$	373.137281	$C_{21}H_{32}O_{11}S_1$	492.166533
$C_{13}H_{20}O_6N_2$	300.132136	$C_{15}H_{18}O_9S_1$	374.067153	$C_{21}H_{32}O_{13}$	492.184291
$C_{15}H_{24}O_6$	300.157289	$C_{16}H_{22}O_8S_1$	374.103538	$C_{27}H_{40}O_8$	492.272318
$C_{12}H_{15}O_8N_1$	301.079767	$C_{16}H_{22}O_{10}$	374.121297	$C_{20}H_{30}O_{12}S_1$	494.145797
$C_{13}H_{19}O_7N_1$	301.116152	$C_{17}H_{26}O_7S_1$	374.139924	$C_{26}H_{40}O_9$	496.267233
$C_{12}H_{14}O_9$	302.063782	$C_{17}H_{26}O_9$	374.157682	$C_{25}H_{38}O_{10}$	498.246497
$C_{13}H_{18}O_6S_1$	302.082409	$C_{18}H_{30}O_8$	374.194068	$C_{24}H_{36}O_{11}$	500.225762
$C_{13}H_{18}O_8$	302.100168	$C_{15}H_{21}O_8N_1S_1$	375.098787	$C_{23}H_{34}O_{10}S_1$	502.187268
$C_{14}H_{22}O_7$	302.136553	$C_{15}H_{21}O_{10}N_1$	375.116546	$C_{24}H_{38}O_{11}$	502.241412
$C_{15}H_{26}O_6$	302.172939	$C_{16}H_{25}O_9N_1$	375.152931	$C_{23}H_{36}O_{12}$	504.220677
$C_{15}H_{12}O_7$	304.058303	$C_{14}H_{16}O_{10}S_1$	376.046417	$C_{22}H_{34}O_{13}$	506.199941
$C_{12}H_{16}O_7S_1$	304.061674	$C_{15}H_{20}O_9S_1$	376.082803	$C_{19}H_{26}O_{14}S_1$	510.104326
$C_{12}H_{16}O_9$	304.079432	$C_{15}H_{20}O_{11}$	376.100562	$C_{26}H_{40}O_{10}$	512.262148
$C_{13}H_{20}O_6S_1$	304.098059	$C_{16}H_{24}O_8S_1$	376.119188	$C_{25}H_{38}O_{11}$	514.241412
$C_{13}H_{20}O_8$	304.115818	$C_{16}H_{24}O_{10}$	376.136947	$C_{24}H_{36}O_{12}$	516.220677

Table A1. Continued.

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
$C_{14}H_{24}O_7$	304.152203	$C_{17}H_{28}O_9$	376.173333	$C_{23}H_{34}O_{11}S_1$	518.182183
$C_{15}H_{14}O_7$	306.073953	$C_{15}H_{23}O_8N_1S_1$	377.114437	$C_{22}H_{32}O_{12}S_1$	520.161447
$C_{12}H_{18}O_7S_1$	306.077324	$C_{14}H_{18}O_{10}S_1$	378.062068	$C_{26}H_{40}O_{11}$	528.257062
$C_{12}H_{18}O_9$	306.095082	$C_{15}H_{22}O_9S_1$	378.098453	$C_{25}H_{38}O_{12}$	530.236327
$C_{13}H_{22}O_6S_1$	306.113709	$C_{15}H_{22}O_{11}$	378.116212	$C_{24}H_{36}O_{13}$	532.215591
$C_{13}H_{22}O_8$	306.131468	$C_{16}H_{26}O_8S_1$	378.134839	$C_{27}H_{42}O_{11}$	542.272712
$C_{18}H_{26}O_4$	306.183109	$C_{16}H_{26}O_{10}$	378.152597	$C_{26}H_{40}O_{12}$	544.251977
$C_{14}H_{13}O_7N_1$	307.069202	$C_{14}H_{20}O_{10}S_1$	380.077718	$C_{25}H_{38}O_{13}$	546.231241
$C_{14}H_{12}O_8$	308.053217	$C_{15}H_{24}O_9S_1$	380.114103	$C_{24}H_{36}O_{14}$	548.210506
$C_{11}H_{16}O_8S_1$	308.056588	$C_{21}H_{32}O_6$	380.219889	$C_{26}H_{40}O_{13}$	560.246891
$C_{12}H_{20}O_7S_1$	308.092974	$C_{14}H_{22}O_{10}S_1$	382.093368	$C_{25}H_{36}O_{13}S_1$	576.187662
$C_{14}H_{16}O_6N_2$	308.100836	$C_{18}H_{24}O_7S_1$	384.124274	$C_{46}H_{24}$	576.187801
$C_{17}H_{24}O_5$	308.162374	$C_{20}H_{32}O_7$	384.214803	$C_{24}H_{34}O_{14}S_1$	578.166927

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

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
$C_{17}H_{16}O_6$	316.094688	$C_{22}H_{23}O_9N_1$	445.137281	$C_{23}H_{25}O_{12}N_1$	507.137675
$C_{18}H_{20}O_5$	316.131074	$C_{21}H_{18}O_{11}$	446.084911	$C_{24}H_{29}O_{11}N_1$	507.174061
$C_{17}H_{18}O_6$	318.110338	$C_{22}H_{22}O_{10}$	446.121297	$C_{23}H_{24}O_{13}$	508.121691
$C_{17}H_{20}O_6$	320.125988	$C_{21}H_{22}O_9N_2$	446.13253	$C_{22}H_{24}O_{12}N_2$	508.132924
$C_{18}H_{18}O_6$	330.110338	$C_{23}H_{26}O_9$	446.157682	$C_{24}H_{28}O_{12}$	508.158076
$C_{19}H_{22}O_5$	330.146724	$C_{24}H_{30}O_8$	446.194068	$C_{25}H_{32}O_{11}$	508.194462
$C_{17}H_{16}O_7$	332.089603	$C_{21}H_{21}O_{10}N_1$	447.116546	$C_{26}H_{36}O_{10}$	508.230847
$C_{18}H_{20}O_6$	332.125988	$C_{22}H_{25}O_9N_1$	447.152931	$C_{22}H_{23}O_{13}N_1$	509.11694
$C_{17}H_{18}O_7$	334.105253	$C_{21}H_{20}O_{11}$	448.100562	$C_{23}H_{27}O_{12}N_1$	509.153325
$C_{18}H_{22}O_6$	334.141638	$C_{20}H_{20}O_{10}N_2$	448.111795	$C_{24}H_{31}O_{11}N_1$	509.189711
$C_{17}H_{20}O_7$	336.120903	$C_{22}H_{24}O_{10}$	448.136947	$C_{22}H_{22}O_{14}$	510.100955
$C_{17}H_{24}O_5N_2$	336.168522	$C_{21}H_{24}O_9N_2$	448.14818	$C_{23}H_{26}O_{13}$	510.137341
$C_{19}H_{20}O_6$	344.125988	$C_{23}H_{28}O_9$	448.173333	$C_{22}H_{26}O_{12}N_2$	510.148574
$C_{20}H_{24}O_5$	344.162374	$C_{20}H_{19}O_{11}N_1$	449.09581	$C_{24}H_{30}O_{12}$	510.173726
$C_{18}H_{18}O_7$	346.105253	$C_{21}H_{23}O_{10}N_1$	449.132196	$C_{23}H_{30}O_{11}N_2$	510.18496
$C_{19}H_{22}O_6$	346.141638	$C_{22}H_{27}O_9N_1$	449.168582	$C_{25}H_{34}O_{11}$	510.210112
$C_{18}H_{21}O_6N_1$	347.136887	$C_{20}H_{18}O_{12}$	450.079826	$C_{22}H_{25}O_{13}N_1$	511.13259
$C_{17}H_{16}O_8$	348.084518	$C_{19}H_{18}O_{11}N_2$	450.091059	$C_{23}H_{29}O_{12}N_1$	511.168975
$C_{18}H_{20}O_7$	348.120903	$C_{21}H_{22}O_{11}$	450.116212	$C_{22}H_{24}O_{14}$	512.116605
$C_{17}H_{19}O_7N_1$	349.116152	$C_{20}H_{22}O_{10}N_2$	450.127445	$C_{21}H_{24}O_{13}N_2$	512.127839
$C_{18}H_{23}O_6N_1$	349.152538	$C_{22}H_{26}O_{10}$	450.152597	$C_{23}H_{28}O_{13}$	512.152991
$C_{17}H_{18}O_8$	350.100168	$C_{21}H_{26}O_9N_2$	450.16383	$C_{22}H_{28}O_{12}N_2$	512.164224
$C_{18}H_{22}O_7$	350.136553	$C_{23}H_{30}O_9$	450.188983	$C_{24}H_{32}O_{12}$	512.189377
$C_{17}H_{20}O_8$	352.115818	$C_{20}H_{21}O_{11}N_1$	451.111461	$C_{22}H_{27}O_{13}N_1$	513.14824
$C_{16}H_{18}O_9$	354.095082	$C_{21}H_{25}O_{10}N_1$	451.147846	$C_{22}H_{26}O_{14}$	514.132256
$C_{17}H_{22}O_8$	354.131468	$C_{22}H_{29}O_9N_1$	451.184232	$C_{23}H_{30}O_{13}$	514.168641
$C_{19}H_{18}O_7$	358.105253	$C_{20}H_{20}O_{12}$	452.095476	$C_{24}H_{34}O_{12}$	514.205027
$C_{20}H_{22}O_6$	358.141638	$C_{19}H_{20}O_{11}N_2$	452.10671	$C_{25}H_{24}O_{12}$	516.126776
$C_{18}H_{16}O_8$	360.084518	$C_{21}H_{24}O_{11}$	452.131862	$C_{22}H_{28}O_{14}$	516.147906
$C_{19}H_{20}O_7$	360.120903	$C_{20}H_{24}O_{10}N_2$	452.143095	$C_{26}H_{28}O_{11}$	516.163162
$C_{20}H_{24}O_6$	360.157289	$C_{22}H_{28}O_{10}$	452.168247	$C_{27}H_{32}O_{10}$	516.199547
$C_{18}H_{19}O_7N_1$	361.116152	$C_{23}H_{32}O_9$	452.204633	$C_{28}H_{36}O_9$	516.235933
$C_{19}H_{23}O_6N_1$	361.152538	$C_{20}H_{23}O_{11}N_1$	453.127111	$C_{24}H_{22}O_{13}$	518.106041
$C_{18}H_{18}O_8$	362.100168	$C_{21}H_{27}O_{10}N_1$	453.163496	$C_{25}H_{26}O_{12}$	518.142426

Table A2. Continued.

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
C_{19} H_{22} O_7	362.136553	C_{20} H_{22} O_{12}	454.111126	C_{24} H_{26} O_{11} N_2	518.15366
C_{18} H_{21} O_7 N_1	363.131802	C_{19} H_{22} O_{11} N_2	454.12236	C_{26} H_{30} O_{11}	518.178812
C_{17} H_{16} O_9	364.079432	C_{21} H_{26} O_{11}	454.147512	C_{27} H_{34} O_{10}	518.215197
C_{18} H_{20} O_8	364.115818	C_{20} H_{26} O_{10} N_2	454.158745	C_{24} H_{25} O_{12} N_1	519.137675
C_{19} H_{24} O_7	364.152203	C_{22} H_{30} O_{10}	454.183897	C_{25} H_{29} O_{11} N_1	519.174061
C_{17} H_{19} O_8 N_1	365.111067	C_{19} H_{21} O_{12} N_1	455.106375	C_{24} H_{24} O_{13}	520.121691
C_{18} H_{23} O_7 N_1	365.147452	C_{20} H_{25} O_{11} N_1	455.142761	C_{23} H_{24} O_{12} N_2	520.132924
C_{17} H_{18} O_9	366.095082	C_{20} H_{24} O_{12}	456.126776	C_{25} H_{28} O_{12}	520.158076
C_{18} H_{22} O_8	366.131468	C_{21} H_{28} O_{11}	456.163162	C_{24} H_{28} O_{11} N_2	520.16931
C_{17} H_{21} O_8 N_1	367.126717	C_{20} H_{27} O_{11} N_1	457.158411	C_{26} H_{32} O_{11}	520.194462
C_{17} H_{20} O_9	368.110732	C_{19} H_{22} O_{13}	458.106041	C_{27} H_{36} O_{10}	520.230847
C_{17} H_{22} O_9	370.126382	C_{23} H_{22} O_{10}	458.121297	C_{24} H_{27} O_{12} N_1	521.153325
C_{14} H_{16} O_8 N_2 S_1	372.062736	C_{20} H_{26} O_{12}	458.142426	C_{25} H_{31} O_{11} N_1	521.189711
C_{20} H_{20} O_7	372.120903	C_{24} H_{26} O_9	458.157682	C_{23} H_{22} O_{14}	522.100955
C_{19} H_{18} O_8	374.100168	C_{25} H_{30} O_8	458.194068	C_{24} H_{26} O_{13}	522.137341
C_{20} H_{22} O_7	374.136553	C_{22} H_{20} O_{11}	460.100562	C_{23} H_{26} O_{12} N_2	522.148574
C_{19} H_{21} O_7 N_1	375.131802	C_{19} H_{24} O_{13}	460.121691	C_{25} H_{30} O_{12}	522.173726
C_{18} H_{16} O_9	376.079432	C_{23} H_{24} O_{10}	460.136947	C_{24} H_{30} O_{11} N_2	522.18496
C_{19} H_{20} O_8	376.115818	C_{24} H_{28} O_9	460.173333	C_{26} H_{34} O_{11}	522.210112
C_{20} H_{24} O_7	376.152203	C_{22} H_{23} O_{10} N_1	461.132196	C_{23} H_{25} O_{13} N_1	523.13259
C_{18} H_{19} O_8 N_1	377.111067	C_{23} H_{27} O_9 N_1	461.168582	C_{24} H_{29} O_{12} N_1	523.168975
C_{19} H_{23} O_7 N_1	377.147452	C_{21} H_{18} O_{12}	462.079826	C_{23} H_{24} O_{14}	524.116605
C_{18} H_{18} O_9	378.095082	C_{22} H_{22} O_{11}	462.116212	C_{24} H_{28} O_{13}	524.152991
C_{19} H_{22} O_8	378.131468	C_{21} H_{22} O_{10} N_2	462.127445	C_{23} H_{28} O_{12} N_2	524.164224
C_{17} H_{17} O_9 N_1	379.090331	C_{23} H_{26} O_{10}	462.152597	C_{25} H_{32} O_{12}	524.189377
C_{18} H_{21} O_8 N_1	379.126717	C_{22} H_{26} O_9 N_2	462.16383	C_{26} H_{36} O_{11}	524.225762
C_{17} H_{16} O_{10}	380.074347	C_{24} H_{30} O_9	462.188983	C_{22} H_{23} O_{14} N_1	525.111854
C_{18} H_{20} O_9	380.110732	C_{21} H_{21} O_{11} N_1	463.111461	C_{23} H_{27} O_{13} N_1	525.14824
C_{17} H_{20} O_8 N_2	380.121966	C_{22} H_{25} O_{10} N_1	463.147846	C_{24} H_{31} O_{12} N_1	525.184625
C_{17} H_{19} O_9 N_1	381.105981	C_{23} H_{29} O_9 N_1	463.184232	C_{23} H_{26} O_{14}	526.132256
C_{17} H_{18} O_{10}	382.089997	C_{21} H_{20} O_{12}	464.095476	C_{22} H_{26} O_{13} N_2	526.143489
C_{18} H_{22} O_9	382.126382	C_{20} H_{20} O_{11} N_2	464.10671	C_{24} H_{30} O_{13}	526.168641
C_{17} H_{21} O_9 N_1	383.121631	C_{22} H_{24} O_{11}	464.131862	C_{25} H_{34} O_{12}	526.205027
C_{17} H_{20} O_{10}	384.105647	C_{21} H_{24} O_{10} N_2	464.143095	C_{22} H_{25} O_{14} N_1	527.127505
C_{20} H_{18} O_8	386.100168	C_{23} H_{28} O_{10}	464.168247	C_{22} H_{24} O_{15}	528.11152
C_{21} H_{22} O_7	386.136553	C_{22} H_{28} O_9 N_2	464.179481	C_{23} H_{28} O_{14}	528.147906
C_{20} H_{20} O_8	388.115818	C_{24} H_{32} O_9	464.204633	C_{24} H_{32} O_{13}	528.184291
C_{21} H_{24} O_7	388.152203	C_{21} H_{23} O_{11} N_1	465.127111	C_{26} H_{26} O_{12}	530.142426
C_{19} H_{19} O_8 N_1	389.111067	C_{22} H_{27} O_{10} N_1	465.163496	C_{23} H_{30} O_{14}	530.163556
C_{20} H_{23} O_7 N_1	389.147452	C_{21} H_{22} O_{12}	466.111126	C_{27} H_{30} O_{11}	530.178812
C_{19} H_{18} O_9	390.095082	C_{20} H_{22} O_{11} N_2	466.12236	C_{28} H_{34} O_{10}	530.215197
C_{20} H_{22} O_8	390.131468	C_{22} H_{26} O_{11}	466.147512	C_{25} H_{24} O_{13}	532.121691
C_{19} H_{21} O_8 N_1	391.126717	C_{21} H_{26} O_{10} N_2	466.158745	C_{26} H_{28} O_{12}	532.158076
C_{19} H_{20} O_9	392.110732	C_{23} H_{30} O_{10}	466.183897	C_{27} H_{32} O_{11}	532.194462
C_{18} H_{20} O_8 N_2	392.121966	C_{20} H_{21} O_{12} N_1	467.106375	C_{28} H_{36} O_{10}	532.230847
C_{20} H_{24} O_8	392.147118	C_{21} H_{25} O_{11} N_1	467.142761	C_{25} H_{27} O_{12} N_1	533.153325
C_{19} H_{24} O_7 N_2	392.158351	C_{22} H_{29} O_{10} N_1	467.179146	C_{26} H_{31} O_{11} N_1	533.189711
C_{18} H_{19} O_9 N_1	393.105981	C_{20} H_{20} O_{13}	468.090391	C_{24} H_{22} O_{14}	534.100955
C_{19} H_{23} O_8 N_1	393.142367	C_{21} H_{24} O_{12}	468.126776	C_{25} H_{26} O_{13}	534.137341
C_{20} H_{27} O_7 N_1	393.178752	C_{20} H_{24} O_{11} N_2	468.13801	C_{26} H_{30} O_{12}	534.173726
C_{18} H_{18} O_{10}	394.089997	C_{22} H_{28} O_{11}	468.163162	C_{25} H_{30} O_{11} N_2	534.18496
C_{19} H_{22} O_9	394.126382	C_{21} H_{28} O_{10} N_2	468.174395	C_{27} H_{34} O_{11}	534.210112
C_{18} H_{22} O_8 N_2	394.137616	C_{23} H_{32} O_{10}	468.199547	C_{28} H_{38} O_{10}	534.246497
C_{18} H_{21} O_9 N_1	395.121631	C_{20} H_{23} O_{12} N_1	469.122025	C_{25} H_{29} O_{12} N_1	535.168975

Table A2. Continued.

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
$C_{18}H_{20}O_{10}$	396.105647	$C_{21}H_{27}O_{11}N_1$	469.158411	$C_{26}H_{33}O_{11}N_1$	535.205361
$C_{17}H_{20}O_9N_2$	396.11688	$C_{20}H_{22}O_{13}$	470.106041	$C_{23}H_{20}O_{15}$	536.08022
$C_{19}H_{24}O_9$	396.142032	$C_{21}H_{26}O_{12}$	470.142426	$C_{24}H_{24}O_{14}$	536.116605
$C_{17}H_{19}O_{10}N_1$	397.100896	$C_{20}H_{26}O_{11}N_2$	470.15366	$C_{23}H_{24}O_{13}N_2$	536.127839
$C_{18}H_{23}O_9N_1$	397.137281	$C_{22}H_{30}O_{11}$	470.178812	$C_{25}H_{28}O_{13}$	536.152991
$C_{17}H_{18}O_{11}$	398.084911	$C_{20}H_{25}O_{12}N_1$	471.137675	$C_{24}H_{28}O_{12}N_2$	536.164224
$C_{18}H_{22}O_{10}$	398.121297	$C_{20}H_{24}O_{13}$	472.121691	$C_{26}H_{32}O_{12}$	536.189377
$C_{17}H_{20}O_{11}$	400.100562	$C_{24}H_{24}O_{10}$	472.136947	$C_{27}H_{36}O_{11}$	536.225762
$C_{21}H_{20}O_8$	400.115818	$C_{21}H_{28}O_{12}$	472.158076	$C_{24}H_{27}O_{13}N_1$	537.14824
$C_{18}H_{24}O_{10}$	400.136947	$C_{25}H_{28}O_9$	472.173333	$C_{25}H_{31}O_{12}N_1$	537.184625
$C_{22}H_{24}O_7$	400.152203	$C_{26}H_{32}O_8$	472.209718	$C_{23}H_{22}O_{15}$	538.09587
$C_{20}H_{18}O_9$	402.095082	$C_{23}H_{22}O_{11}$	474.116212	$C_{24}H_{26}O_{14}$	538.132256
$C_{21}H_{22}O_8$	402.131468	$C_{24}H_{26}O_{10}$	474.152597	$C_{23}H_{26}O_{13}N_2$	538.143489
$C_{22}H_{26}O_7$	402.167853	$C_{25}H_{30}O_9$	474.188983	$C_{25}H_{30}O_{13}$	538.168641
$C_{20}H_{21}O_8N_1$	403.126717	$C_{23}H_{25}O_{10}N_1$	475.147846	$C_{24}H_{30}O_{12}N_2$	538.179874
$C_{20}H_{20}O_9$	404.110732	$C_{22}H_{20}O_{12}$	476.095476	$C_{26}H_{34}O_{12}$	538.205027
$C_{19}H_{20}O_8N_2$	404.121966	$C_{21}H_{20}O_{11}N_2$	476.10671	$C_{27}H_{38}O_{11}$	538.241412
$C_{21}H_{24}O_8$	404.147118	$C_{23}H_{24}O_{11}$	476.131862	$C_{23}H_{25}O_{14}N_1$	539.127505
$C_{20}H_{24}O_7N_2$	404.158351	$C_{22}H_{24}O_{10}N_2$	476.143095	$C_{24}H_{29}O_{13}N_1$	539.16389
$C_{19}H_{19}O_9N_1$	405.105981	$C_{24}H_{28}O_{10}$	476.168247	$C_{25}H_{33}O_{12}N_1$	539.200276
$C_{20}H_{23}O_8N_1$	405.142367	$C_{23}H_{28}O_9N_2$	476.179481	$C_{23}H_{24}O_{15}$	540.11152
$C_{19}H_{18}O_{10}$	406.089997	$C_{25}H_{32}O_9$	476.204633	$C_{24}H_{28}O_{14}$	540.147906
$C_{18}H_{18}O_9N_2$	406.10123	$C_{22}H_{23}O_{11}N_1$	477.127111	$C_{25}H_{32}O_{13}$	540.184291
$C_{20}H_{22}O_9$	406.126382	$C_{23}H_{27}O_{10}N_1$	477.163496	$C_{26}H_{36}O_{12}$	540.220677
$C_{19}H_{22}O_8N_2$	406.137616	$C_{24}H_{31}O_9N_1$	477.199882	$C_{23}H_{27}O_{14}N_1$	541.143155
$C_{21}H_{26}O_8$	406.162768	$C_{21}H_{18}O_{13}$	478.074741	$C_{24}H_{30}O_{14}$	542.163556
$C_{18}H_{17}O_{10}N_1$	407.085246	$C_{22}H_{22}O_{12}$	478.111126	$C_{25}H_{34}O_{13}$	542.199941
$C_{19}H_{21}O_9N_1$	407.121631	$C_{21}H_{22}O_{11}N_2$	478.12236	$C_{23}H_{28}O_{15}$	544.14282
$C_{20}H_{25}O_8N_1$	407.158017	$C_{23}H_{26}O_{11}$	478.147512	$C_{27}H_{28}O_{12}$	544.158076
$C_{19}H_{20}O_{10}$	408.105647	$C_{22}H_{26}O_{10}N_2$	478.158745	$C_{24}H_{32}O_{14}$	544.179206
$C_{18}H_{20}O_9N_2$	408.11688	$C_{24}H_{30}O_{10}$	478.183897	$C_{28}H_{32}O_{11}$	544.194462
$C_{20}H_{24}O_9$	408.142032	$C_{23}H_{30}O_9N_2$	478.195131	$C_{26}H_{26}O_{13}$	546.137341
$C_{19}H_{24}O_8N_2$	408.153266	$C_{21}H_{21}O_{12}N_1$	479.106375	$C_{27}H_{30}O_{12}$	546.173726
$C_{18}H_{19}O_{10}N_1$	409.100896	$C_{22}H_{25}O_{11}N_1$	479.142761	$C_{28}H_{34}O_{11}$	546.210112
$C_{19}H_{23}O_9N_1$	409.137281	$C_{23}H_{29}O_{10}N_1$	479.179146	$C_{29}H_{38}O_{10}$	546.246497
$C_{18}H_{18}O_{11}$	410.084911	$C_{21}H_{20}O_{13}$	480.090391	$C_{25}H_{24}O_{14}$	548.116605
$C_{19}H_{22}O_{10}$	410.121297	$C_{20}H_{20}O_{12}N_2$	480.101624	$C_{26}H_{28}O_{13}$	548.152991
$C_{18}H_{22}O_9N_2$	410.13253	$C_{22}H_{24}O_{12}$	480.126776	$C_{25}H_{28}O_{12}N_2$	548.164224
$C_{20}H_{26}O_9$	410.157682	$C_{21}H_{24}O_{11}N_2$	480.13801	$C_{27}H_{32}O_{12}$	548.189377
$C_{18}H_{21}O_{10}N_1$	411.116546	$C_{23}H_{28}O_{11}$	480.163162	$C_{28}H_{36}O_{11}$	548.225762
$C_{19}H_{25}O_9N_1$	411.152931	$C_{22}H_{28}O_{10}N_2$	480.174395	$C_{29}H_{40}O_{10}$	548.262148
$C_{18}H_{20}O_{11}$	412.100562	$C_{24}H_{32}O_{10}$	480.199547	$C_{25}H_{27}O_{13}N_1$	549.14824
$C_{19}H_{24}O_{10}$	412.136947	$C_{21}H_{23}O_{12}N_1$	481.122025	$C_{26}H_{31}O_{12}N_1$	549.184625
$C_{18}H_{23}O_{10}N_1$	413.132196	$C_{22}H_{27}O_{11}N_1$	481.158411	$C_{24}H_{22}O_{15}$	550.09587
$C_{18}H_{22}O_{11}$	414.116212	$C_{23}H_{31}O_{10}N_1$	481.194796	$C_{25}H_{26}O_{14}$	550.132256
$C_{22}H_{22}O_8$	414.131468	$C_{21}H_{22}O_{13}$	482.106041	$C_{26}H_{30}O_{13}$	550.168641
$C_{19}H_{26}O_{10}$	414.152597	$C_{22}H_{26}O_{12}$	482.142426	$C_{25}H_{30}O_{12}N_2$	550.179874
$C_{23}H_{26}O_7$	414.167853	$C_{21}H_{26}O_{11}N_2$	482.15366	$C_{27}H_{34}O_{12}$	550.205027
$C_{21}H_{20}O_9$	416.110732	$C_{23}H_{30}O_{11}$	482.178812	$C_{28}H_{38}O_{11}$	550.241412
$C_{18}H_{24}O_{11}$	416.131862	$C_{24}H_{34}O_{10}$	482.215197	$C_{24}H_{25}O_{14}N_1$	551.127505
$C_{22}H_{24}O_8$	416.147118	$C_{20}H_{21}O_{13}N_1$	483.10129	$C_{25}H_{29}O_{13}N_1$	551.16389
$C_{23}H_{28}O_7$	416.183503	$C_{21}H_{25}O_{12}N_1$	483.137675	$C_{26}H_{33}O_{12}N_1$	551.200276
$C_{20}H_{19}O_9N_1$	417.105981	$C_{22}H_{29}O_{11}N_1$	483.174061	$C_{24}H_{24}O_{15}$	552.11152
$C_{21}H_{23}O_8N_1$	417.142367	$C_{21}H_{24}O_{11}S_1$	484.103932	$C_{25}H_{28}O_{14}$	552.147906
$C_{20}H_{18}O_{10}$	418.089997	$C_{21}H_{24}O_{13}$	484.121691	$C_{26}H_{32}O_{13}$	552.184291

Table A2. Continued.

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
$C_{19}H_{18}O_9N_2$	418.10123	$C_{22}H_{28}O_{12}$	484.158076	$C_{27}H_{36}O_{12}$	552.220677
$C_{21}H_{22}O_9$	418.126382	$C_{23}H_{32}O_{11}$	484.194462	$C_{25}H_{31}O_{13}N_1$	553.17954
$C_{22}H_{26}O_8$	418.162768	$C_{21}H_{27}O_{12}N_1$	485.153325	$C_{24}H_{26}O_{15}$	554.12717
$C_{19}H_{17}O_{10}N_1$	419.085246	$C_{21}H_{26}O_{13}$	486.137341	$C_{25}H_{30}O_{14}$	554.163556
$C_{20}H_{21}O_9N_1$	419.121631	$C_{25}H_{26}O_{10}$	486.152597	$C_{24}H_{30}O_{13}N_2$	554.174789
$C_{21}H_{25}O_8N_1$	419.158017	$C_{22}H_{30}O_{12}$	486.173726	$C_{26}H_{34}O_{13}$	554.199941
$C_{20}H_{20}O_{10}$	420.105647	$C_{26}H_{30}O_9$	486.188983	$C_{25}H_{32}O_{14}$	556.179206
$C_{19}H_{20}O_9N_2$	420.11688	$C_{20}H_{25}O_{13}N_1$	487.13259	$C_{26}H_{36}O_{13}$	556.215591
$C_{21}H_{24}O_9$	420.142032	$C_{23}H_{20}O_{12}$	488.095476	$C_{24}H_{30}O_{15}$	558.15847
$C_{20}H_{24}O_8N_2$	420.153266	$C_{20}H_{24}O_{14}$	488.116605	$C_{25}H_{34}O_{14}$	558.194856
$C_{20}H_{23}O_9N_1$	421.137281	$C_{24}H_{24}O_{11}$	488.131862	$C_{29}H_{34}O_{11}$	558.210112
$C_{21}H_{27}O_8N_1$	421.173667	$C_{21}H_{28}O_{13}$	488.152991	$C_{27}H_{28}O_{13}$	560.152991
$C_{19}H_{18}O_{11}$	422.084911	$C_{25}H_{28}O_{10}$	488.168247	$C_{28}H_{32}O_{12}$	560.189377
$C_{18}H_{18}O_{10}N_2$	422.096145	$C_{26}H_{32}O_9$	488.204633	$C_{29}H_{36}O_{11}$	560.225762
$C_{20}H_{22}O_{10}$	422.121297	$C_{23}H_{23}O_{11}N_1$	489.127111	$C_{26}H_{26}O_{14}$	562.132256
$C_{19}H_{22}O_9N_2$	422.13253	$C_{24}H_{27}O_{10}N_1$	489.163496	$C_{27}H_{30}O_{13}$	562.168641
$C_{21}H_{26}O_9$	422.157682	$C_{23}H_{22}O_{12}$	490.111126	$C_{28}H_{34}O_{12}$	562.205027
$C_{20}H_{26}O_8N_2$	422.168916	$C_{22}H_{22}O_{11}N_2$	490.12236	$C_{29}H_{38}O_{11}$	562.241412
$C_{19}H_{21}O_{10}N_1$	423.116546	$C_{24}H_{26}O_{11}$	490.147512	$C_{26}H_{29}O_{13}N_1$	563.16389
$C_{20}H_{25}O_9N_1$	423.152931	$C_{23}H_{26}O_{10}N_2$	490.158745	$C_{25}H_{24}O_{15}$	564.11152
$C_{19}H_{20}O_{11}$	424.100562	$C_{25}H_{30}O_{10}$	490.183897	$C_{26}H_{28}O_{14}$	564.147906
$C_{18}H_{20}O_{10}N_2$	424.111795	$C_{26}H_{34}O_9$	490.220283	$C_{25}H_{28}O_{13}N_2$	564.159139
$C_{20}H_{24}O_{10}$	424.136947	$C_{22}H_{21}O_{12}N_1$	491.106375	$C_{27}H_{32}O_{13}$	564.184291
$C_{19}H_{24}O_9N_2$	424.14818	$C_{23}H_{25}O_{11}N_1$	491.142761	$C_{28}H_{36}O_{12}$	564.220677
$C_{19}H_{23}O_{10}N_1$	425.132196	$C_{24}H_{29}O_{10}N_1$	491.179146	$C_{29}H_{40}O_{11}$	564.257062
$C_{20}H_{27}O_9N_1$	425.168582	$C_{22}H_{20}O_{13}$	492.090391	$C_{25}H_{27}O_{14}N_1$	565.143155
$C_{18}H_{18}O_{12}$	426.079826	$C_{21}H_{20}O_{12}N_2$	492.101624	$C_{26}H_{31}O_{13}N_1$	565.17954
$C_{19}H_{22}O_{11}$	426.116212	$C_{23}H_{24}O_{12}$	492.126776	$C_{25}H_{26}O_{15}$	566.12717
$C_{18}H_{22}O_{10}N_2$	426.127445	$C_{22}H_{24}O_{11}N_2$	492.13801	$C_{26}H_{30}O_{14}$	566.163556
$C_{20}H_{26}O_{10}$	426.152597	$C_{24}H_{28}O_{11}$	492.163162	$C_{27}H_{34}O_{13}$	566.199941
$C_{18}H_{21}O_{11}N_1$	427.111461	$C_{23}H_{28}O_{10}N_2$	492.174395	$C_{28}H_{38}O_{12}$	566.236327
$C_{19}H_{25}O_{10}N_1$	427.147846	$C_{25}H_{32}O_{10}$	492.199547	$C_{24}H_{25}O_{15}N_1$	567.122419
$C_{18}H_{20}O_{12}$	428.095476	$C_{22}H_{23}O_{12}N_1$	493.122025	$C_{26}H_{33}O_{13}N_1$	567.19519
$C_{19}H_{24}O_{11}$	428.131862	$C_{23}H_{27}O_{11}N_1$	493.158411	$C_{25}H_{28}O_{15}$	568.14282
$C_{20}H_{28}O_{10}$	428.168247	$C_{24}H_{31}O_{10}N_1$	493.194796	$C_{26}H_{32}O_{14}$	568.179206
$C_{21}H_{18}O_{10}$	430.089997	$C_{22}H_{22}O_{13}$	494.106041	$C_{27}H_{36}O_{13}$	568.215591
$C_{22}H_{22}O_9$	430.126382	$C_{21}H_{22}O_{12}N_2$	494.117274	$C_{25}H_{31}O_{14}N_1$	569.174455
$C_{19}H_{26}O_{11}$	430.147512	$C_{23}H_{26}O_{12}$	494.142426	$C_{25}H_{30}O_{15}$	570.15847
$C_{23}H_{26}O_8$	430.162768	$C_{22}H_{26}O_{11}N_2$	494.15366	$C_{26}H_{34}O_{14}$	570.194856
$C_{21}H_{21}O_9N_1$	431.121631	$C_{24}H_{30}O_{11}$	494.178812	$C_{28}H_{30}O_{13}$	574.168641
$C_{21}H_{20}O_{10}$	432.105647	$C_{23}H_{30}O_{10}N_2$	494.190045	$C_{29}H_{34}O_{12}$	574.205027
$C_{20}H_{20}O_9N_2$	432.11688	$C_{25}H_{34}O_{10}$	494.215197	$C_{30}H_{38}O_{11}$	574.241412
$C_{22}H_{24}O_9$	432.142032	$C_{21}H_{21}O_{13}N_1$	495.10129	$C_{27}H_{28}O_{14}$	576.147906
$C_{21}H_{24}O_8N_2$	432.153266	$C_{22}H_{25}O_{12}N_1$	495.137675	$C_{28}H_{32}O_{13}$	576.184291
$C_{23}H_{28}O_8$	432.178418	$C_{23}H_{29}O_{11}N_1$	495.174061	$C_{29}H_{36}O_{12}$	576.220677
$C_{20}H_{19}O_{10}N_1$	433.100896	$C_{22}H_{24}O_{13}$	496.121691	$C_{30}H_{40}O_{11}$	576.257062
$C_{21}H_{23}O_9N_1$	433.137281	$C_{21}H_{24}O_{12}N_2$	496.132924	$C_{26}H_{26}O_{15}$	578.12717
$C_{22}H_{27}O_8N_1$	433.173667	$C_{23}H_{28}O_{12}$	496.158076	$C_{27}H_{30}O_{14}$	578.163556
$C_{20}H_{18}O_{11}$	434.084911	$C_{22}H_{28}O_{11}N_2$	496.16931	$C_{28}H_{34}O_{13}$	578.199941
$C_{19}H_{18}O_{10}N_2$	434.096145	$C_{24}H_{32}O_{11}$	496.194462	$C_{29}H_{38}O_{12}$	578.236327
$C_{21}H_{22}O_{10}$	434.121297	$C_{21}H_{23}O_{13}N_1$	497.11694	$C_{26}H_{29}O_{14}N_1$	579.158805
$C_{20}H_{22}O_9N_2$	434.13253	$C_{22}H_{27}O_{12}N_1$	497.153325	$C_{26}H_{28}O_{15}$	580.14282
$C_{22}H_{26}O_9$	434.157682	$C_{21}H_{22}O_{14}$	498.100955	$C_{27}H_{32}O_{14}$	580.179206
$C_{21}H_{26}O_8N_2$	434.168916	$C_{22}H_{26}O_{13}$	498.137341	$C_{28}H_{36}O_{13}$	580.215591
$C_{19}H_{17}O_{11}N_1$	435.08016	$C_{21}H_{26}O_{12}N_2$	498.148574	$C_{29}H_{40}O_{12}$	580.251977
$C_{20}H_{21}O_{10}N_1$	435.116546	$C_{23}H_{30}O_{12}$	498.173726	$C_{25}H_{27}O_{15}N_1$	581.138069

Table A2. Continued.

Elemental Formula	M	Elemental Formula	M	Elemental Formula	M
$C_{21}H_{25}O_9N_1$	435.152931	$C_{24}H_{34}O_{11}$	498.210112	$C_{26}H_{31}O_{14}N_1$	581.174455
$C_{20}H_{20}O_{11}$	436.100562	$C_{21}H_{25}O_{13}N_1$	499.13259	$C_{25}H_{26}O_{16}$	582.122085
$C_{19}H_{20}O_{10}N_2$	436.111795	$C_{22}H_{29}O_{12}N_1$	499.168975	$C_{26}H_{30}O_{15}$	582.15847
$C_{21}H_{24}O_{10}$	436.136947	$C_{21}H_{24}O_{14}$	500.116605	$C_{25}H_{30}O_{14}N_2$	582.169704
$C_{20}H_{24}O_9N_2$	436.14818	$C_{22}H_{28}O_{13}$	500.152991	$C_{27}H_{34}O_{14}$	582.194856
$C_{22}H_{28}O_9$	436.173333	$C_{26}H_{28}O_{10}$	500.168247	$C_{28}H_{38}O_{13}$	582.231241
$C_{19}H_{19}O_{11}N_1$	437.09581	$C_{23}H_{32}O_{12}$	500.189377	$C_{26}H_{32}O_{15}$	584.17412
$C_{20}H_{23}O_{10}N_1$	437.132196	$C_{24}H_{22}O_{12}$	502.111126	$C_{27}H_{36}O_{14}$	584.210506
$C_{21}H_{27}O_9N_1$	437.168582	$C_{21}H_{26}O_{14}$	502.132256	$C_{26}H_{34}O_{15}$	586.18977
$C_{19}H_{18}O_{12}$	438.079826	$C_{25}H_{26}O_{11}$	502.147512	$C_{29}H_{32}O_{13}$	588.184291
$C_{20}H_{22}O_{11}$	438.116212	$C_{26}H_{30}O_{10}$	502.183897	$C_{30}H_{36}O_{12}$	588.220677
$C_{19}H_{22}O_{10}N_2$	438.127445	$C_{27}H_{34}O_9$	502.220283	$C_{28}H_{30}O_{14}$	590.163556
$C_{21}H_{26}O_{10}$	438.152597	$C_{23}H_{20}O_{13}$	504.090391	$C_{29}H_{34}O_{13}$	590.199941
$C_{22}H_{30}O_9$	438.188983	$C_{24}H_{24}O_{12}$	504.126776	$C_{30}H_{38}O_{12}$	590.236327
$C_{19}H_{21}O_{11}N_1$	439.111461	$C_{23}H_{24}O_{11}N_2$	504.13801	$C_{27}H_{28}O_{15}$	592.14282
$C_{20}H_{25}O_{10}N_1$	439.147846	$C_{25}H_{28}O_{11}$	504.163162	$C_{28}H_{32}O_{14}$	592.179206
$C_{19}H_{20}O_{12}$	440.095476	$C_{24}H_{28}O_{10}N_2$	504.174395	$C_{29}H_{36}O_{13}$	592.215591
$C_{20}H_{24}O_{11}$	440.131862	$C_{26}H_{32}O_{10}$	504.199547	$C_{30}H_{40}O_{12}$	592.251977
$C_{19}H_{24}O_{10}N_2$	440.143095	$C_{27}H_{36}O_9$	504.235933	$C_{27}H_{30}O_{15}$	594.15847
$C_{21}H_{28}O_{10}$	440.168247	$C_{23}H_{23}O_{12}N_1$	505.122025	$C_{28}H_{34}O_{14}$	594.194856
$C_{19}H_{23}O_{11}N_1$	441.127111	$C_{24}H_{27}O_{11}N_1$	505.158411	$C_{29}H_{38}O_{13}$	594.231241
$C_{20}H_{27}O_{10}N_1$	441.163496	$C_{25}H_{31}O_{10}N_1$	505.194796	$C_{27}H_{33}O_{14}N_1$	595.190105
$C_{19}H_{22}O_{12}$	442.111126	$C_{23}H_{22}O_{13}$	506.106041	$C_{26}H_{28}O_{16}$	596.137735
$C_{20}H_{26}O_{11}$	442.147512	$C_{22}H_{22}O_{12}N_2$	506.117274	$C_{27}H_{32}O_{15}$	596.17412
$C_{22}H_{20}O_{10}$	444.105647	$C_{24}H_{26}O_{12}$	506.142426	$C_{28}H_{36}O_{14}$	596.210506
$C_{19}H_{24}O_{12}$	444.126776	$C_{23}H_{26}O_{11}N_2$	506.15366	$C_{26}H_{30}O_{16}$	598.153385
$C_{23}H_{24}O_9$	444.142032	$C_{25}H_{30}O_{11}$	506.178812	$C_{27}H_{34}O_{15}$	598.18977
$C_{20}H_{28}O_{11}$	444.163162	$C_{24}H_{30}O_{10}N_2$	506.190045		
$C_{24}H_{28}O_8$	444.178418	$C_{26}H_{34}O_{10}$	506.215197		

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