



# Global Biogeochemical Cycles

## RESEARCH ARTICLE

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### Key Points:

- 184 molecular formulae indicative of riverine inputs (t-Peaks) have been identified
- t-Peaks are correlated with tracers of terrigenous input and observed in multiple rivers worldwide
- t-Peaks revealed injection of terrigenous DOM into deep ocean by meridional overturning circulation

### Supporting Information:

- Supporting Information S1

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## A novel molecular approach for tracing terrigenous dissolved organic matter into the deep ocean

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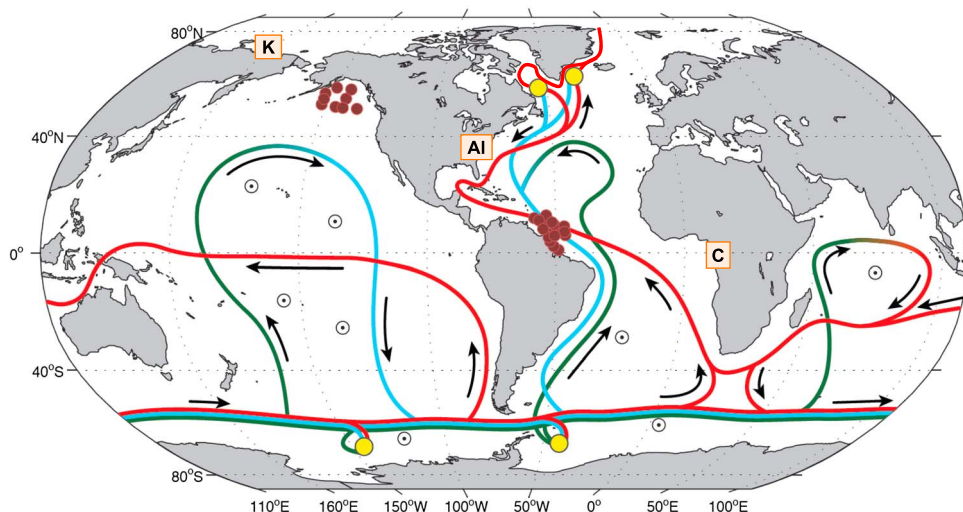
**Abstract** Marine dissolved organic matter (DOM) contains one of the largest exchangeable organic carbon pools on Earth. Riverine input represents an important source of DOM to the oceans, yet much remains to be learned about the fate of the DOM linking terrestrial to oceanic carbon cycles through rivers at the global scale. Here we use ultrahigh-resolution mass spectrometry to identify 184 molecular formulae that are indicators of riverine inputs (referred to as t-Peaks) and to track their distribution in the deep North Atlantic and North Pacific Oceans. The t-Peaks were found to be enriched in the Amazon River, to be highly correlated with known tracers of terrigenous input, and to be observed in all samples from four different rivers characterized by vastly different landscapes and vegetation coverage spanning equatorial (Amazon and Congo), subtropical (Altamaha), and Arctic (Kolyma) regions. Their distribution reveals that terrigenous organic matter is injected into the deep ocean by the global meridional overturning circulation, indicating that a fraction of the terrigenous DOM introduced by rivers contributes to the DOM pool observed in the deep ocean and to the storage of terrigenous organic carbon. This novel molecular approach can be used to further constrain the transfer of DOM from land to sea, especially considering that Fourier transform ion cyclotron resonance mass spectrometer analysis is becoming increasingly frequent in studies characterizing the molecular composition of DOM in lakes, rivers, and the ocean.

### 1. Introduction

Marine dissolved organic matter (DOM) contains one of the largest active organic carbon pools on Earth (~662 Pg C), holding greater than 200 times the carbon inventory of marine biomass [Hansell *et al.*, 2009]. The pool is comparable in size to the organic carbon present in forest biomass (~450 Pg C [Pan *et al.*, 2011]) and rivals the size of the atmospheric CO<sub>2</sub> reservoir (~820 Pg C [Walther, 2013]). DOM forms a link between production and decay of organic matter in the oceanic water column [Dittmar and Paeng, 2009], playing a major role in biogeochemical processes and in carbon storage on scales of several thousand years [e.g., Flerus *et al.*, 2011]. Most marine DOM is released from photosynthetic plankton or through heterotrophic transformations occurring in the surface ocean [Carlson and Hansell, 2015], where intense decomposition and cycling of organic matter occur.

Global riverine discharge of organic matter also represents a substantial source of dissolved organic carbon (DOC) to the oceans [Hedges *et al.*, 1997; Raymond and Spencer, 2015], with riverine inputs alone being sufficient to support the turnover of DOC throughout the marine environment [Williams and Druffel, 1987]. The total DOC flux to the ocean is estimated at 250–260 Tg C yr<sup>-1</sup> [Hedges *et al.*, 1997; Raymond and Spencer, 2015], with the Amazon River exporting over 29 Tg C yr<sup>-1</sup> [Moreira-Turcq *et al.*, 2003; Raymond and Spencer, 2015], or almost 12% of the global riverine DOC flux. The Congo River, the largest in Africa, is the second largest exporter and is responsible for 5% of the global total flux [Coynel *et al.*, 2005]. A large amount of terrigenous DOM is also delivered to the Arctic Ocean [e.g., Amon *et al.*, 2012; Holmes *et al.*, 2012]. Indeed, a disproportionately large fraction of the global river discharge (~10%) is received by the Arctic Ocean [Aagaard and Carmack, 1989; Anderson and Amon, 2015], although it holds only 1% of the global ocean volume [Menard and Smith, 1966; Opsahl *et al.*, 1999]. Recent estimates of pan-Arctic riverine DOC flux to the ocean are in the range of 34–38 Tg C yr<sup>-1</sup> [Holmes *et al.*, 2012], although this may be an underestimate because of limited availability of data in northern high-latitude rivers characterized by high DOC yields [Raymond and Spencer, 2015].

Quantitative assessments indicate that despite such large inputs, terrestrial DOM experiences substantial alterations over relatively short time scales [e.g., Benner and Opsahl, 2001; Hernes and Benner, 2003; Hansell



**Figure 1.** Location of stations where DOM samples were collected during cruises to the tropical North Atlantic and northern North Pacific Oceans. The brown circles show Amazon River, Amazon River plume, surface and deep North Atlantic, and surface and deep North Pacific. AI = Altamaha River [Medeiros *et al.*, 2015c], C = Congo River [Stubbins *et al.*, 2010], K = Kolyma River [Spencer *et al.*, 2015]. Simplified sketch of the meridional overturning circulation [Rahmstorf, 2002] is also shown. Surface flow is shown in red, while deep and bottom flows are sketched in light blue and dark green, respectively. The yellow circles at high latitudes indicate location of deep and bottom water formation. The black circles with dots indicate zones of wind-driven or mixing-driven upwelling [Kuhlbrodt *et al.*, 2007].

*et al.*, 2004; Spencer *et al.*, 2009, 2015], with ocean margins acting as major sinks of terrigenous DOC [Letscher *et al.*, 2011; Fichot and Benner, 2014]. Several processes act as removal mechanisms of terrigenous DOC in the coastal ocean, including photo-oxidation, microbial degradation, and flocculation [e.g., Sholkovitz, 1978; Hernes and Benner, 2003]. Despite that, a fraction of the terrigenous DOC exported from rivers escapes the continental margin [e.g., Medeiros *et al.*, 2015b; Seidel *et al.*, 2015] and is transported to the open ocean, where it can be incorporated into the large scale ocean circulation, including deepwater formation. Terrigenous DOC of Arctic origin has been identified in North Atlantic Deep Water (NADW) [Benner *et al.*, 2005; Hernes and Benner, 2006], and lignin phenols, unique components of vascular terrestrial plants, have been observed in the deep Atlantic and Pacific Oceans [e.g., Opsahl and Benner, 1997; Hernes and Benner, 2002]. More recently, Follett *et al.* [2014] showed that  $\delta^{13}\text{C}$  values of deep DOC have a range of at least 10‰, allowing for significant contributions from terrestrial organic matter. DOC exported to great depths can remain in the deepest portions of the ocean for many centuries, potentially contributing to carbon storage and sequestration of atmospheric  $\text{CO}_2$  at those time scales.

Understanding transfer of organic matter from land to sea is an important link in the global carbon cycle.  $\delta^{13}\text{C}$  values have been used to differentiate between terrigenous and marine sources in DOC samples [e.g., Bianchi *et al.*, 2004; McCallister *et al.*, 2006; Griffith *et al.*, 2012; Lalonde *et al.*, 2014; Medeiros *et al.*, 2015b]. However, stable carbon isotopic compositions alone may be insufficient to resolve a minor terrigenous component of marine DOM [Opsahl and Benner, 1997]. In those cases, integrating additional tracers of terrigenous DOM (e.g., lignin) is useful. Since Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) analysis is becoming increasingly frequent in studies characterizing the molecular composition of DOM in lakes, rivers, and the ocean [e.g., Sleighter and Hatcher, 2008; Kujawinski *et al.*, 2009; Sleighter *et al.*, 2010; Stubbins *et al.*, 2010; Flerus *et al.*, 2012; Hertkorn *et al.*, 2013; Kellerman *et al.*, 2014; Lechtenfeld *et al.*, 2014; Osterholz *et al.*, 2014; Medeiros *et al.*, 2015a, 2015b, 2015c], it is constructive to identify molecular formulae that can be potentially used to track the distribution of terrigenous material in the ocean.

The composition of DOM in the Amazon River-ocean continuum has been recently analyzed using FT-ICR MS [Medeiros *et al.*, 2015b]. Principal component analysis revealed a robust pattern of variability in DOM composition differentiating riverine and marine DOM, which was observed in three different years capturing both high and low discharge conditions. Here we build on Medeiros *et al.* [2015b] and compared the composition of DOM in the tropical North Atlantic and in the northern North Pacific Oceans to identify and track the

distribution of riverine inputs to the deep ocean. Samples from the North Atlantic captured both the surface and deep branches of the meridional overturning circulation [Rahmstorf, 2002] (Figure 1). Our sampling allowed for the characterization of DOM under direct influence of a large river plume (i.e., from the Amazon River [Medeiros et al., 2015b]), as well as of deep DOM in the NADW, a few decades after deepwater formation [Smethie et al., 2000]. After circumnavigating Antarctica, the bottom water runs northward in the Pacific Ocean [Rahmstorf, 2002]. Samples from the northern North Pacific Ocean allow for the characterization of very old DOM that has not been exposed to the ocean surface for at least 1000 years [Primeau, 2005], and thus represent an extreme end-member to examine persistence of riverine DOM inputs.

## 2. Methods

### 2.1. Sample Collection

DOM samples were collected in the tropical North Atlantic Ocean ( $n = 101$ ) during research cruises to the Amazon River plume in 2010, 2011, and 2012 [Medeiros et al., 2015b; Seidel et al., 2015] and in the northern North Pacific Ocean ( $n = 70$ ) during a research cruise to the Gulf of Alaska in August 2013 [Medeiros et al., 2015a] (Figure 1). At each station, samples were collected from the surface to depths of 2000 m in the North Atlantic and to as deep as 5040 m in the North Pacific. Immediately after collection, samples were filtered (sequentially through 0.7  $\mu\text{m}$  Whatman GF/F filters precombusted at 450°C for 5 h and prewashed 0.2  $\mu\text{m}$  Pall Supor membrane filters) and aliquots were collected for DOC analysis. Filtrates were acidified to pH 2 (concentrated HCl), and DOM was isolated using solid-phase extraction (SPE) cartridges (Agilent Bond Elut PPL) as in Dittmar et al. [2008].

### 2.2. Chemical Analyses

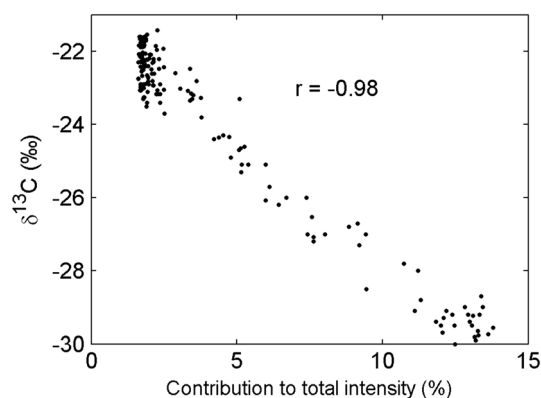
DOC concentrations from water samples and solid-phase extracts (i.e., dried and redissolved in ultrapure water) were measured with a Shimadzu TOC-V<sub>CPH</sub> analyzer with daily potassium hydrogen phthalate (KHP) standard curves and regular analysis of Consensus Reference Materials obtained from the University of Miami [Hansell, 2005]. SPE efficiency was  $61 \pm 7\%$  of the DOC for samples collected in the tropical North Atlantic and  $58 \pm 6\%$  of the DOC for those collected in the northern North Pacific. Bulk  $\delta^{13}\text{C}$  of extracted DOC (SPE-DOC) were analyzed with a Finnigan MAT 251 isotope ratio mass spectrometer after complete drying. All isotopic compositions were expressed relative to the standard Vienna Pee Dee Belemnite. Procedural blanks did not yield detectable amounts of carbon isotope contamination. Lignin phenols of the solid-phase extracts from the North Pacific Ocean were determined by alkaline CuO oxidation [Hedges and Ertel, 1982; Spencer et al., 2008]. Quantification of six lignin phenols was carried out by gas chromatography–mass spectrometry as described by Spencer et al. [2010].

The molecular composition of SPE-extracted DOM (15 mg CL<sup>-1</sup> in 1:1 water:methanol) was analyzed by ultrahigh-resolution mass spectrometry using a 15 T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS; Bruker Daltonics) with electrospray ionization (negative mode) as in Seidel et al. [2014]. Spectra were internally calibrated with >100 known C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> molecular formulae over the mass range in the samples. With this calibration procedure, a mass error of <0.1 ppm was achieved. Before each sample set, blank checks with methanol and ultrapure water were measured. Molecular formulae were calculated in the mass range between 150 and 850 Da by applying the following restrictions: <sup>12</sup>C<sub>1–130</sub><sup>1</sup>H<sub>1–200</sub><sup>16</sup>O<sub>1–150</sub><sup>14</sup>N<sub>0–4</sub><sup>32</sup>S<sub>0–2</sub><sup>31</sup>P<sub>0–2</sub>. Assignment of molecular formulae was done considering a maximum mass error of 0.5 ppm and using the criteria described by Rossel et al. [2013]. Only compounds with a signal-to-noise ratio of 4 or higher were used in the analysis to eliminate intersample variability based on peaks that were close to the limit of detection [Seidel et al., 2014]. Much of the global DOM pool is composed of a huge variety of relatively small molecules (200–800 Da [e.g., Kujawinski, 2011; Dittmar and Stubbins, 2014]), which are efficiently captured by the technique [Dittmar and Paeng, 2009]. Approximately 4000 molecular formulae were identified in the complex DOM mixture in each sample. As in previous studies [e.g., Flerus et al., 2012; Lechtenfeld et al., 2014], FT-ICR MS data evaluation was based on normalized peak magnitudes.

### 2.3. Tracers of Terrigenous Inputs in the Ocean

#### 2.3.1. Molecular Formulae Indicator of Riverine Inputs (t-Peaks)

Medeiros et al. [2015b] identified a set of molecular formulae that were relatively enriched at the Amazon River mouth DOM (salinity  $S = 0$ ) compared to the DOM from samples collected over the shelf and in the open ocean.



**Figure 2.** Scatterplot of percentage contribution of t-Peaks to the sum of the magnitude of all peaks with molecular formula assigned in FT-ICR MS spectra versus bulk  $\delta^{13}\text{C}$  SPE-DOC for all 171 samples analyzed in this study.

In the Amazon River-ocean continuum, the relative abundances of those formulae were highly correlated negatively (significant at the 95% confidence level) with bulk  $\delta^{13}\text{C}$  SPE-DOC and positively with concentrations of dissolved lignin phenols (unambiguous tracers of vascular plant derived organic matter) and dissolved black carbon (dissolution products of thermogenic DOM produced on land during biomass burning and subsequently delivered to the sea [Jaffé *et al.*, 2013]), suggesting that their distribution is related to gradients in DOM associated with terrigenous versus oceanic inputs [Medeiros *et al.*, 2015b].

The Amazon River is thought to be representative of tropical rivers and rivers draining forested catchments [Hedges *et al.*, 1997], with total organic carbon content, DOC/particulate organic carbon

ratio and suspended sediment load near global averages for large rivers [Meybeck, 1982]. However, since we are interested in molecular formulae that are broadly related to terrigenous input (i.e., not only from the Amazon River), we looked for those that were observed not only in all samples from the Amazon River mouth [Medeiros *et al.*, 2015b], but also in FT-ICR MS spectra of samples from other rivers worldwide that have been reported in the literature. We found a total of 184 molecular formulae (Table S1) that were observed in all samples from the Amazon River (riverine collections occurred in three different years covering both high and low discharge conditions [Medeiros *et al.*, 2015b]), from the Congo River in the equatorial Africa (see Supporting Table of Stubbins *et al.* [2010]), from the Kolyma River in the Siberian Arctic (see Table S1 of Spencer *et al.* [2015]), and in all samples collected in the Altamaha River in the southeastern U.S. [Medeiros *et al.*, 2015c], which covered different seasons in multiple years and included a severe drought as well as a high-discharge event. Although it is not possible to affirm that these 184 formulae have a terrigenous source based on FT-ICR MS analysis alone, we emphasize that their relative abundances were enriched in the Amazon River [Medeiros *et al.*, 2015b] and that they were observed in all samples from four rivers with drastically different landscapes and vegetation coverage, spanning equatorial (Amazon and Congo Rivers), subtropical (Altamaha River), and Arctic (Kolyma River) regions. We also note that the aromaticity index (a measure of the aromaticity of the molecules [Koch and Dittmar, 2006, 2016]) of these 184 molecular formulae is high at  $0.53 \pm 0.10$  (Table S1 and Figure S1 in the supporting information). This value is consistent with these formulae being indicators of riverine inputs, since rivers are known to be important sources of polycyclic aromatic compounds to the ocean [e.g., Mannino and Harvey, 2004; Stubbins *et al.*, 2010; Ziolkowski and Druffel, 2010]. Lastly, the percent contribution of these molecular formulae to the sum of the magnitude of all peaks with a molecular formula assigned in the FT-ICR MS spectrum in each sample analyzed in this study is highly correlated with bulk  $\delta^{13}\text{C}$  SPE-DOC (Figure 2). As such, we assess these 184 molecular formulae as plausibly indicative of riverine inputs, referring to them hereafter as t-Peaks, where t-Peaks are formulae taken to be of terrigenous origin.

### 2.3.2. An Additional Metric of Terrigenous Input to the Ocean

Although the t-Peaks were observed in four rivers from vastly different regions, we cannot affirm at this point that these formulae are observed in other rivers worldwide. It is possible that as samples from other rivers are analyzed, the list of formulae indicative of riverine inputs will be further constrained. It is useful therefore to use an additional metric to further constrain terrigenous input to the ocean based on FT-ICR MS analysis.

We used an approach analogous to that presented by Flerus *et al.* [2012], who computed the degradation state of DOM based on the normalized intensity of FT-ICR MS peaks. Specifically, they selected five formulae with a particularly high positive correlation and five formulae with a particularly high negative correlation with  $\Delta^{14}\text{C}$  SPE-DOC. They found that although the absolute value of the ratio of the sum of the magnitudes of those peaks is dependent on instrument and extraction technique, samples processed similarly allow for consistent and comparable results. Here since the interest was to identify the potential influence of compounds of terrigenous origin, we computed the correlations between the normalized intensity of FT-ICR-MS peaks and bulk  $\delta^{13}\text{C}$  SPE-DOC. Specifically, we selected only molecular formulae that were observed

in all 171 samples from the North Atlantic and North Pacific (there are a total of 1122 such formulae) and computed the correlation between their relative abundance and the bulk  $\delta^{13}\text{C}$  SPE-DOC of each sample. This yielded 1122 correlation coefficients, one associated with each molecular formula. We then selected the 40 formulae with the highest negative correlation (i.e., formulae relatively enriched in samples characterized by lighter  $\delta^{13}\text{C}$  values; *Terr*) that are also part of the pool of 184 t-Peaks, and the 40 formulae with the highest positive correlation (i.e., formulae relatively enriched in samples characterized by heavier  $\delta^{13}\text{C}$  values; *Mar*) that are also part of the “island of stability” (a set of 361 molecular formulae associated with dissolved organic compounds with the most stable combination of elements, i.e., compounds with very long residence time because they are mostly chemically invariant to degradation processes [Lechtenfeld *et al.*, 2014]) (Table S2 and Figure S2). The ratio of the sum of the normalized intensity of these FT-ICR MS peaks (sum magnitudes *Terr*/sum magnitudes (*Terr* + *Mar*); referred to as  $I_{\text{Terr}}$ ) was then calculated for each sample. The rationale for selecting molecular formulae that are part of the t-Peaks and part of the island of stability is that since these formulae are widely observed in riverine and oceanic samples analyzed by FT-ICR MS, they are suitable to be implemented in a versatile index (Table S2).

In theory, the ratio  $I_{\text{Terr}}$  should increase with the terrigenous signature of the sample. To evaluate that, we compared the ratio  $I_{\text{Terr}}$  with other geochemical tracers known to be influenced by gradients in organic matter source. The ratio is (by design) highly correlated negatively with bulk  $\delta^{13}\text{C}$  SPE-DOC ( $r = -0.97$ ,  $p < 0.001$ ). Additionally, the ratio is highly correlated ( $r = 0.98$ ,  $p < 0.001$ ) with the percentage of molecular formulae in each sample that have condensed aromatic structures in the molecule (i.e., compounds with aromaticity index  $\geq 0.67$  [Koch and Dittmar, 2006, 2016], consistent with higher concentrations of aromatic compounds in rivers. Lastly, we correlated the ratio with independent measurements of dissolved black carbon in the Atlantic Ocean samples that have been previously reported by Medeiros *et al.* [2015b], since rivers are important sources of dissolved black carbon to the oceans [e.g., Dittmar and Paeng, 2009; Jaffé *et al.*, 2013; Stubbins *et al.*, 2015]. Correlations were once again high and statistically significant ( $r = 0.96$ ,  $p < 0.001$ ). We note that if the constraints described in the last paragraph are not used (i.e., if we do not require that the molecular formulae used in the computation of the index be part of the t-Peaks or of the island of stability) and we instead simply choose the 40 molecular formulae with the highest negative and positive correlation with  $\delta^{13}\text{C}$  values, results are similar to those just described.

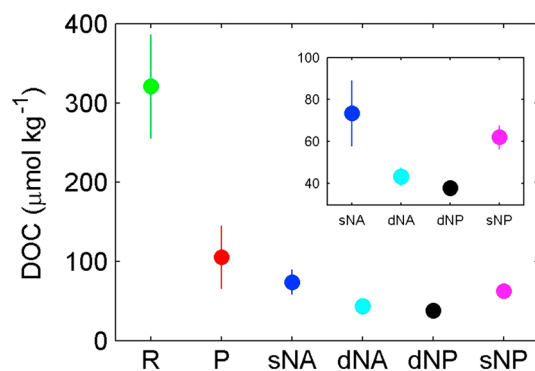
For several analyses presented here, samples were grouped according to their location: Amazon River mouth (R; salinity  $S = 0$ ), Amazon River plume (P;  $10 < S < 34$ ), surface tropical North Atlantic (sNA;  $S > 34$ , depth  $< 100$  m), deep tropical North Atlantic (dNA; depth  $> 1000$  m), deep northern North Pacific (dNP; depth  $> 2000$  m), and surface northern North Pacific (sNP; depth  $< 100$  m).

### 3. Results

DOC concentrations varied substantially between the regions. Concentrations were highest in the Amazon River mouth, and progressively decreased from the surface tropical North Atlantic to the deep northern North Pacific (Figure 3), in agreement with previous studies [e.g., Hansell *et al.*, 2009].

#### 3.1. Injection of Terrigenous DOM Into the Deep Ocean

The 184 molecular formulae described in the previous section (t-Peaks) were used to identify and track the presence of terrigenous DOM in the deep ocean. We quantified both their frequency of occurrence (i.e., the fraction of the 184 t-Peaks observed in each sample) as well as their contribution to the total magnitude of all peaks in the spectrum with an assigned molecular formula (i.e., the sum of the relative intensity of all t-Peaks divided by the sum of the relative intensity of all peaks with molecular formula assigned in the spectrum) for each sample. The t-Peaks were observed in all samples from the Amazon River (by definition; Figure 4a), accounting for 13% of the total magnitude of all peaks in the DOM pool (as identified by FT-ICR MS) in those samples (Figure 4b). Approximately 70% of the t-Peaks were also observed in the surface tropical North Atlantic away from the Amazon River plume (Figure 4a), accounting for 2.6% of the total magnitude in the FT-ICR MS spectra (Figure 4b). The percentage of occurrence decreases in the deep North Atlantic to 55%, and about 35% of the molecular formulae are still observed in the deep northern North Pacific Ocean (Figure 4a). A similar pattern is observed for their relative contribution to the total magnitude of all peaks in the DOM (Figure 4b). We emphasize that the t-Peaks were observed in multiple rivers worldwide, including one from the Arctic. Since

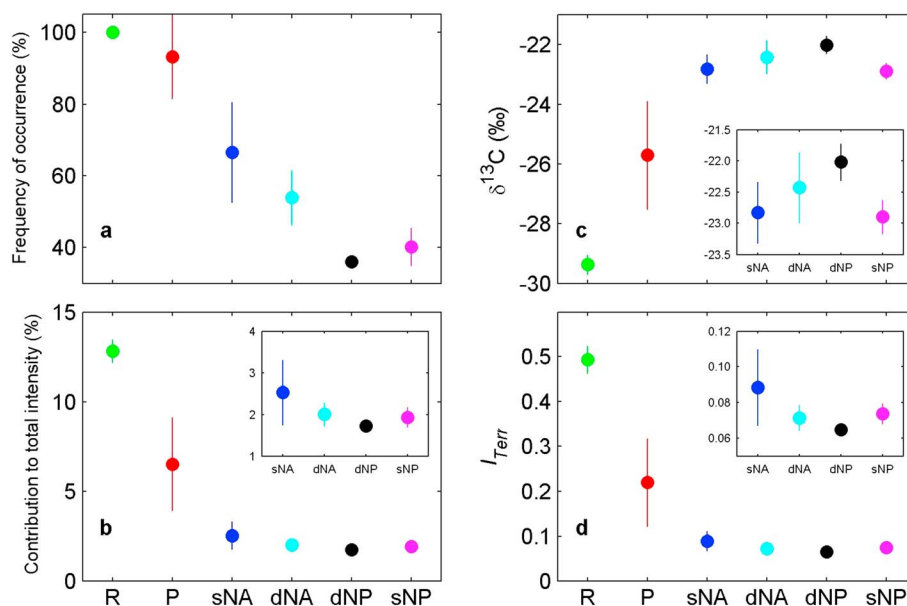


**Figure 3.** Distribution of average  $\pm 1$  standard deviation of dissolved organic carbon at different stages of the meridional overturning circulation. In some cases, standard deviation bars are smaller than the size of the symbols. Inset shows magnified DOC concentrations. R: Amazon River, P: Amazon River plume, sNA: surface North Atlantic, dNA: deep North Atlantic, dNP: deep North Pacific, sNP: surface North Pacific.

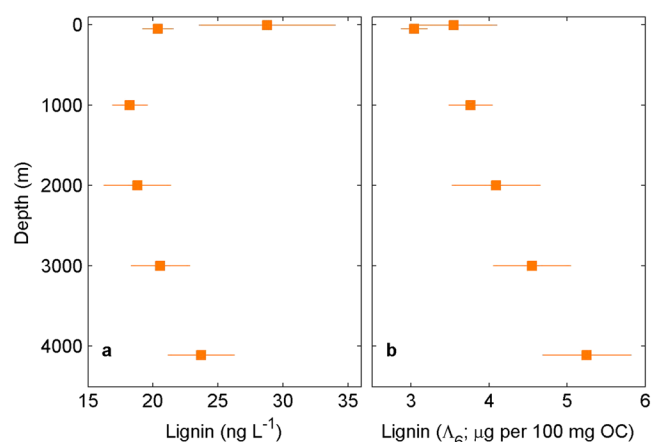
Arctic inputs contribute to the terrigenous signature in the deep North Atlantic [e.g., Benner *et al.*, 2005; Hernes and Benner, 2006], the presence of some of these molecular formulae in the deep ocean is likely to result from Arctic riverine inputs.

A pattern similar to that described for the t-Peaks was also observed for the distribution of bulk  $\delta^{13}\text{C}$  SPE-DOC (Figure 4c) and for the ratio  $I_{\text{Terr}}$  (Figure 4d). Altogether, the progressive decreases in the percentage of occurrence of the t-Peaks (Figure 4a) and in their relative contribution to the total magnitude of all peaks in the DOM (Figure 4b), as well as the shift toward heavier  $\delta^{13}\text{C}$  values (Figure 4c) and the decrease in the ratio  $I_{\text{Terr}}$  (Figure 4d) along the different stages of the overturning circulation captured by our sampling are consistent with the export of these compounds to the ocean by rivers and slow transformation, degradation, and/or dilution.

Despite the conservative approach used here to identify the t-Peaks (see section 2.3.1), we cannot rule out the possibility of nonterrigenous sources using FT-ICR MS data alone. Therefore, it is instructive to compare the patterns described above to the distribution of lignin. Lignin-derived phenol concentrations are generally higher in the deep North Atlantic than in the deep North Pacific [Opsahl and Benner, 1997; Hernes and Benner, 2006]. This appears to reflect the disproportionately larger share of global riverine discharge into the Atlantic relative to the Pacific [Opsahl and Benner, 1997], which amounts to a 3.6-fold higher input to the Atlantic on a *per* volume basis [Sverdrup *et al.*, 1942; Baumgartner and Reichel, 1975], and large-scale circulation patterns (i.e., deepwater formation in the North Atlantic, which can directly contribute to the injection of terrigenous organic matter into



**Figure 4.** Distribution of average  $\pm 1$  standard deviation of (a) percentage of t-Peaks present in each region and (b) their percentage contribution to the sum of the magnitude of all peaks in FT-ICR MS spectra. (c) Bulk  $\delta^{13}\text{C}$  SPE-DOC and (d)  $I_{\text{Terr}}$ , the ratio of relative abundance of molecular formulae negatively correlated with  $\delta^{13}\text{C}$  (*Terr*) and the sum of the relative abundance of formulae negatively and positively correlated with  $\delta^{13}\text{C}$  (*Terr* + *Mar*). In some cases, standard deviation bars are smaller than the size of the symbols. Insets show magnification of values for Atlantic and Pacific Ocean samples. R: Amazon River, P: Amazon River plume, sNA: surface North Atlantic, dNA: deep North Atlantic, dNP: deep North Pacific, sNP: surface North Pacific.



**Figure 5.** Vertical profiles of average  $\pm 1$  standard deviation of (a) dissolved lignin phenol concentration and (b) dissolved carbon-normalized lignin yields ( $A_6$ ) in the northern North Pacific Ocean.

the deep ocean [Benner *et al.*, 2005]). The contribution of the t-Peaks is consistent with that being more significant in the deep tropical North Atlantic than in the deep northern North Pacific (Figures 4a and 4b). It is possible that the molecular formulae observed in the deep North Pacific are a result of direct vertical export (as sinking particles) from the surface North Pacific. The distribution of lignin in the North Pacific Ocean does not seem to support that interpretation, however. At the study site, far from the coast, dissolved lignin was relatively enriched near the bottom and near the surface, reaching a local minimum at about 1000 m below the surface (Figure 5a), which seems to be inconsistent with the interpretation that terrigenous material at depth is a result of direct vertical export from surface waters. Normalizing lignin concentrations by the amount of organic carbon (Figure 5b) also suggests a relative enrichment at depth compared to the upper water column in the North Pacific. Collectively, these results indicate that at least a fraction of the compounds associated with the t-Peaks reaches the deep northern North Pacific via the large-scale overturning circulation.

#### 4. Discussion

A set of 184 molecular formulae has been identified here as plausible indicators of riverine carbon inputs (t-Peaks) to the ocean, based on their occurrence in four rivers spanning vastly different regions and on their correlation with known tracers of terrigenous input. However, mass spectrometric data suggest that a large set of compounds is ubiquitous in the marine environment. This is because they are the remainder of intensive degradation processes, and as such their composition and structure appear to be largely independent of their source [Reemtsma *et al.*, 2008]. This is consistent with the concept of the island of stability, a set of 361 molecular formulae associated with dissolved organic compounds having the most stable combination of elements that are widely observed in the marine environment [Lechtenfeld *et al.*, 2014]. Therefore, an alternative explanation for the occurrence of the t-Peaks in all samples from four different rivers is that these formulae could be associated with molecules that are quite stable, being observed in nearly all aquatic samples. That explanation does not seem to hold, however, since most of these molecular formulae were not observed in the deep ocean (see Figure 4a and section 3.1 for details). Additionally, the t-Peaks have different chemical characteristics from the formulae identified as the most stable in marine DOM (i.e., the island of stability) by Lechtenfeld *et al.* [2014]. While the molecular formulae from the island of stability have relatively high H/C ratios ( $1.17 \pm 0.13$ ) and low aromaticity indices ( $0.27 \pm 0.09$ ), the t-Peaks have high aromaticity indices ( $0.53 \pm 0.10$ ) and low H/C ratios ( $0.86 \pm 0.14$ ) (Figure S1). Terrigenous DOM has indeed been characterized by low H/C ratios [Sleighter and Hatcher, 2008]. There is no overlap between molecular formulae from the island of stability and the t-Peaks.

Although the distributions shown in Figure 4 are consistent with injection of terrigenous organic matter found in multiple rivers worldwide into the deep ocean by the overturning circulation, there are alternative explanations for the fact that some of the t-Peaks are observed at depth. First, although the compounds observed at depth have the same molecular formulae as those observed in the rivers, it is possible that they may have different structures and therefore are not the same compounds. Additionally, it is possible that although their relative abundance are correlated with concentrations of lignin phenols, dissolved black carbon, and  $\delta^{13}\text{C}$  SPE-DOC [Medeiros *et al.*, 2015b] (see also Figures 2 and 4c), they may have additional nonterrigenous sources in the marine environment, which could explain their presence in the deep North Atlantic and deep North Pacific Oceans. If marine DOM contains compounds with these same formulae, however, some mechanism must be invoked to explain why they make a more important contribution to

the DOM pool in the deep North Atlantic than in the deep North Pacific. In other words, if the majority of the t-Peaks are in reality not characteristic of terrigenous input, but instead are widely present in marine DOM, why do they have a distribution that is consistent with the distribution of  $\delta^{13}\text{C}$  SPE-DOC and of lignin phenols (as reported by *Opsahl and Benner* [1997]) in the ocean? Another alternative explanation is that the t-Peaks may have multiple sources and result from intense degradation/transformation processes. This scenario seems unlikely, however, since in that case one would expect their relative importance to be larger in the older DOM observed in the North Pacific than in the relatively younger DOM from the North Atlantic. As mentioned previously, there is no overlap between the t-Peaks and the molecular formulae recently reported to be extremely resistant to degradation (i.e., from the island of stability [*Lechtenfeld et al.*, 2014]), and those two pools have distinctive chemical characteristics (Figure S1). Therefore, despite the lack of structural information to unequivocally demonstrate that the molecules found in the deep North Pacific are the same as the t-Peaks and to demonstrate that they have a terrigenous origin, that interpretation is consistent with injection of terrigenous DOM into the deep ocean by the large-scale overturning circulation and with the distributions of bulk  $\delta^{13}\text{C}$  SPE-DOC and dissolved lignin.

As a cautionary note, we emphasize that the fact that 35% of the t-Peaks are observed in the deep ocean (Figure 4a) does not mean that one third of the terrigenous material introduced into the ocean by rivers reaches the deep ocean. Since one of the criteria for identifying the t-Peaks was that they had to be present in all samples from four different large rivers, it is possible that a bias toward selecting formulae associated with compounds that are more resistant to degradation was introduced. This is because molecular formulae associated with riverine compounds that are highly resistant to degradation are more likely to be observed in multiple rivers than molecular formulae associated with riverine compounds that are highly degradable. If this is true, then the terrigenous pool represented by the t-Peaks (Figures 4a and 4b and Table S1) is likely more resistant to degradation than the terrigenous DOM pool as a whole.

The approach used here to identify the t-Peaks is very conservative, since it required formulae to have a relative abundance enriched in the Amazon River and be present in all samples from the four different rivers. This means that several molecular formulae may have been excluded solely due to small differences in the analytical procedures used in the different studies. For example, while samples from the Amazon and the Altamaha Rivers were analyzed using the same procedure and resulted in over 4000 molecular formulae being identified in each study [*Medeiros et al.*, 2015b, 2015c], samples from the Congo and the Kolyma Rivers were processed and analyzed slightly differently (e.g., using different magnets in the FT-ICR MS and different maximum mass accuracies), resulting in 2400 and 2000 molecular formulae being identified, respectively. As such, it is likely that many molecular formulae indicative of riverine inputs were not identified in all samples simply because of the different specifications and/or procedures used in these studies.

Riverine DOM can be removed rapidly and efficiently in many coastal regions [e.g., *Hedges et al.*, 1997; *Hernes and Benner*, 2003; *Fichot and Benner*, 2014]. The fact that some of the t-Peaks were observed in the deep North Pacific (Figure 4), holding the oldest DOM in the ocean, suggests that a fraction of the terrigenous DOM delivered by rivers may contribute to the DOM pool observed in the deep ocean and to the long-term carbon storage of terrigenous organic matter. As compounds associated with the t-Peaks are degraded during their transit in the deep ocean, it is possible that at least some of them are transformed to a more refractory state. In this case, their molecular formulae may not be recognizable as riverine in origin, but they contribute to a more stable DOM pool. To the extent that such transformations occur, they would contribute to the storage of terrigenous material on time scales much longer than that of the meridional overturning circulation.

The input of terrigenous DOM to the ocean can be and has been investigated using other tracers (e.g., lignin phenol concentrations,  $\delta^{13}\text{C}$  values, and spectral slope of UV absorbance at certain wavelength bands [e.g., *Opsahl and Benner*, 1997; *Dittmar et al.*, 2006; *Fichot and Benner*, 2012]). The distribution of the t-Peaks and the ratio  $I_{\text{Terr}}$  provides an additional set of tracers to identify the occurrence of terrigenous material in the ocean. This is especially useful because FT-ICR MS analysis is becoming increasingly frequent in studies characterizing the molecular composition of DOM in lakes, rivers, and the ocean [e.g., *Sleighter and Hatcher*, 2008; *Kujawinski et al.*, 2009; *Sleighter et al.*, 2010; *Stubbins et al.*, 2010; *Flerus et al.*, 2012; *Hertkorn et al.*, 2013; *Kellerman et al.*, 2014; *Lechtenfeld et al.*, 2014; *Osterholz et al.*, 2014; *Medeiros et al.*, 2015a, 2015b, 2015c]. Several of these studies were not designed to identify the presence of terrigenous DOM in the environment, and as such simultaneous measurements of specific tracers of terrigenous input (e.g., lignin phenols) were



not undertaken or are not available. Identifying the t-Peaks as plausible indicators of riverine inputs creates many new data mining opportunities: extensive FT-ICR MS data sets can be re-analyzed to identify the distribution of the t-Peaks and  $I_{\text{Terr}}$ , allowing the assessment of the distribution of terrigenous DOM in the environment even when lignin phenol concentrations or  $\delta^{13}\text{C}$  values are not available. Similar to lignin [Opsahl and Benner, 1997], the t-Peaks can also be used to resolve a minor terrigenous component of DOM in oceanic waters that may not be detectable by stable carbon isotopic compositions alone.

## 5. Conclusions

A detailed investigation of DOM at the molecular level was used to identify 184 molecular formulae that are plausible indicators of riverine inputs (t-Peaks). The occurrence and relative abundance of these formulae were statistically significantly correlated with known tracers of terrigenous input, and they were also observed in all samples from four different major rivers characterized by vastly different landscapes and vegetation coverage spanning equatorial, subtropical, and Arctic regions. Tracking the percentage of the occurrence of the t-Peaks and their percentage contribution to the sum of the magnitude of all peaks in FT-ICR MS spectra reveals that terrigenous organic matter is injected into the deep ocean by the global meridional overturning circulation. That picture is consistent with the distribution of  $\delta^{13}\text{C}$ , dissolved lignin phenols, and  $I_{\text{Terr}}$ , an independent new ratio of the relative abundance of molecular formulae that have been found to be highly correlated negatively and positively with  $\delta^{13}\text{C}$  SPE-DOC. These different tracers collectively indicate that although substantial removal occurs at the ocean surface, a fraction of the terrigenous DOM introduced by rivers worldwide contributes to the DOM pool observed in the deep ocean. Lastly, it is important to note that the 184 t-Peaks were identified based on the analyses of only four rivers (though covering multiple regions, from equatorial to Arctic environments). Therefore, we cannot affirm that those molecular formulae are observed in rivers worldwide or if for some reason those four rivers are unusual for having those formulae. Future investigations of DOM composition in other rivers detecting their presence or further constraining the number of molecular formulae would support their use as indicators of riverine inputs.

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