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Key Points:

- Composition of deep North Pacific DOM is approximately uniform to lowest order
- Photoreactions transform deep sea DOM, making it more similar to surface DOM
- Influence of photochemical transformations extends beyond the photic zone

Supporting Information:

- Tables S1 and S2

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Dissolved organic matter composition and photochemical transformations in the northern North Pacific Ocean

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Abstract The composition and photochemical transformations of dissolved organic matter (DOM) in the northern North Pacific Ocean were investigated at the molecular level using ultrahigh resolution mass spectrometry and geochemical tracers. Analyses included vertical profiles and experiments in which deep sea DOM was exposed to sunlight and incubated in the dark. The composition of the deep sea DOM was found to be approximately uniform and enriched with highly unsaturated compounds, with highly aromatic compounds, and with polycyclic aromatics. Surface DOM had a significantly different composition, being enriched with both highly unsaturated and with unsaturated aliphatic compounds potentially due to the addition of photodegradation products and phytoplankton inputs. Deep sea DOM composition is transformed by photoreactions, becoming more similar to surface DOM. The influence of photochemistry extends beyond the photic zone, presumably because of vertical export of DOM previously modified at the surface.

1. Introduction

At 662 Pg C, dissolved organic carbon (DOC) in the ocean represents one of the largest global C pools on Earth, holding greater than 200 times the carbon inventory of marine biomass [Hansell *et al.*, 2009]. That inventory is comparable to the atmospheric CO₂ reservoir of ~750 Pg C [Hedges, 1992], suggesting that DOC may play an important role in the global carbon cycle and potentially contribute to large transient warming events on Earth at very long time scales [Sexton *et al.*, 2011]. DOC exported to great depths via the meridional overturning circulation, and ventilation of the ocean interior can remain in the deepest portions of the ocean for many centuries. The oldest DOC is observed in the North Pacific because, unlike the North Atlantic Ocean, water masses at great depth in the North Pacific are not locally formed. As the more labile DOC is consumed over time, DOC that is resistant to microbial degradation accumulates and is left as the dominant fraction in the marine dissolved organic matter (DOM), especially below 1000 m [Hansell, 2013]. At those depths, DOC concentrations and their vertical gradients are generally small.

Sinks for DOC present in the deep sea remain largely unknown. One possibly important removal mechanism is photolysis by UV irradiation at the ocean surface [Mopper *et al.*, 1991]. Since the average age of the deep DOC is about 4000–6000 years [Bauer *et al.*, 1992], and the time scale associated with the meridional overturning circulation is of the order of 500–2000 years [Primeau, 2005], it is likely that this DOC pool is exposed to sunlight at some point in its lifetime. Dissolved black carbon, an important component of the DOC, has been shown to be highly photodegradable [Stubbins *et al.*, 2012].

Deep DOC has received the least attention in the scientific literature, possibly because of its slow turnover [Hansell, 2013]. As such, much remains to be learned about its composition and transformations. Understanding the past and future roles of DOC in climate arguably depends on illumination of its dynamics in the modern ocean [Hansell and Carlson, 2013]. Here we investigate the molecular composition of the DOM in the northern North Pacific Ocean using ultrahigh resolution mass spectrometry and geochemical tracers, as well as potential transformations of the deep DOM as it is upwelled into the photic zone by the large-scale circulation.

2. Methods

Dissolved organic matter was collected in the northern North Pacific Ocean in August 2013 (Figure 1). At each station, samples were collected at six depths (5, 50, 1000, 2000, 3000 m, and near bottom) except

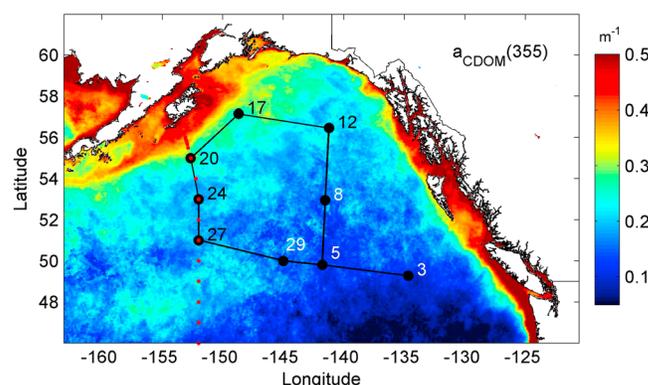


Figure 1. Location of sample collection overlain on satellite-derived CDOM absorption for August (2002–2013) using the *Mannino et al.* [2008] algorithm. Small red circles show location of line P16N [*Hansell et al.*, 2009].

at the southwestern most station (#27, supporting information Table S1), where 12 depths were sampled (100, 200, 300, 400, 600, and 800 m, in addition to the depths described above). Immediately after collection, samples were filtered (sequentially through 0.7 μm GF/F filters precombusted at 450°C for 5 h and 0.2 μm membrane filters) and aliquots were collected for DOC and chromophoric dissolved organic matter (CDOM) analyses. Filtrates were acidified to pH 2 (concentrated HCl), and DOM was isolated using solid phase extraction (SPE) cartridges filled with a modified

styrene-divinylbenzene polymer (Agilent Bond Elut PPL) and then eluted with methanol as described in *Dittmar et al.* [2008].

Water incubations were performed on deck in surface seawater flushed plexiglass boxes. For dark incubations, near-bottom water samples were first filtered through 0.7 μm combusted GF/F filters, collected into combusted 1 L amber glass bottles in triplicate, wrapped in aluminum foil, and then kept submerged for 10 days enclosed by an opaque plastic bag. For photochemical incubations, near-bottom samples were filtered sequentially using 0.7 μm combusted GF/F filters and 0.2 μm membranes and then collected in triplicate into 1.5 L quartz flasks with a 500 mL headspace. Flasks were exposed to natural sunlight for 10 days, with the lower part of the flask submerged in the flowing seawater bath. Additional photochemical experiments were pursued on board using a Suntest CPS solar simulator fitted with a 1.5 kW xenon lamp (Atlas) and a window glass filter to simulate sunlight reaching the Earth's surface. Samples were exposed to the solar simulator for 48 h, approximating 16 days of clear-sky solar irradiance at this latitude during mid-August. After incubation/irradiation, all samples were filtered, acidified, and DOM was extracted using PPL cartridges as described before.

DOC concentrations from water samples and SPE extracts (i.e., dried and resuspended in ultrapure water) were measured with a Shimadzu TOC- V_{CPH} analyzer. PPL extraction efficiency across all samples ($n = 70$) was $58 \pm 6\%$ of the DOC. CDOM absorbance was measured with a MAYA2000-Pro UV-VIS spectrometer (Ocean Optics) and converted to absorption coefficients as in *D'Sa et al.* [1999]. Bulk $\delta^{13}\text{C}$ ratios of extracted DOC, reported relative to the Vienna Pee Dee Belemnite, were measured with a Finnigan MAT 251 isotope ratio mass spectrometer after complete drying. Precision and accuracy was $<1\%$ and procedural blanks did not yield detectable amounts of carbon isotopes. The molecular composition of the DOM extracts (15 mg C L^{-1} in 1:1 methanol/water) was analyzed using a 15 T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS; Bruker Daltonics) with electrospray ionization (negative) as described in *Seidel et al.* [2014]. Due to the high degree of similarity between all samples, FT-ICR MS data evaluation was based on normalized peak magnitudes. For simplicity, we refer to a calculated molecular formula as a “compound.”

3. Results and Discussion

DOC concentrations (Figure 2a and supporting information Table S1) were nearly constant at $37.8 \pm 0.4 \mu\text{mol kg}^{-1}$ below 2000 m and elevated above the pycnocline reaching $65.7 \pm 4.0 \mu\text{mol kg}^{-1}$ at the surface, closely mirroring the average vertical density profile (Figure 2a). This profile is consistent with observations elsewhere showing that stratification allows for the accumulation of DOC in the surface layer [*Carlson et al.*, 1994].

3.1. Molecular Composition of DOM in the Northern North Pacific Ocean

We applied an ultrahigh resolution mass spectrometry technique that allowed for the assignment of ~ 4000 molecular formulae in the complex DOM mixture. Principal component (PC) analysis distinguished patterns of variability in FT-ICR MS-derived DOM composition in the region. The dominant PC is significantly different

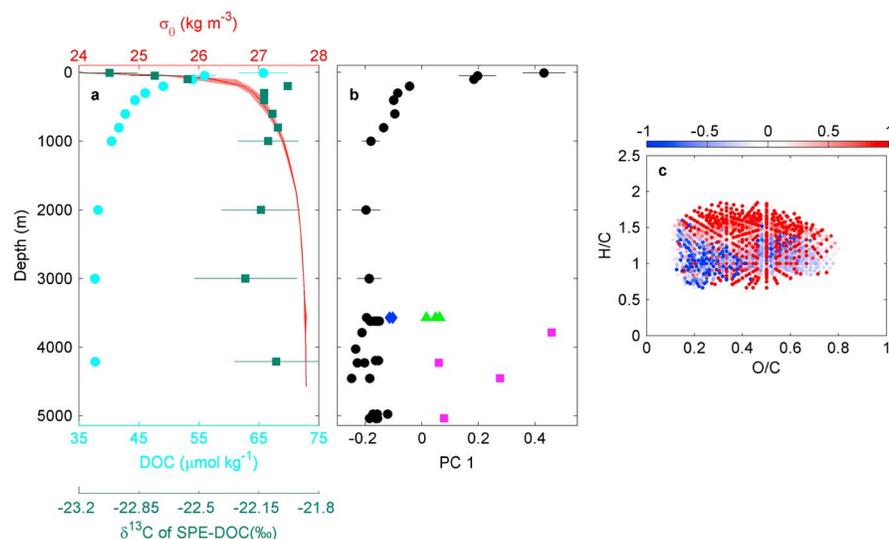


Figure 2. (a) Vertical profile of average (red line) ± 1 standard deviation (red shaded area) of potential density. Profiles of average (symbols) ± 1 standard deviation (horizontal bars) of DOC concentration (cyan circles) and bulk $\delta^{13}\text{C}$ SPE-DOC (dark green squares) are also shown. In some cases, error bars are smaller than the size of the symbols. Near-bottom samples from the different stations are plotted at their average depth. (b) Vertical profile of dominant principal component of DOM composition. Average ± 1 standard deviation from in situ samples collected at the same depth is shown in black. Results from dark incubations (blue diamonds) and from irradiation experiments using natural sunlight (green triangles) and a solar simulator (magenta squares) are also shown. Results from experiments are plotted at the same depths as the initial condition (black circles). (c) Van Krevelen diagram with loading of the dominant principal component color coded.

(95% confidence level) from PC results of spatially and temporally uncorrelated random processes [Overland and Preisendorfer, 1982]. The second PC, although also significant, captures changes in the deep DOM composition at two stations. Those differences are currently under investigation and will be reported elsewhere. The dominant PC explains 42% of the total variance captured by the significant modes.

A vertical profile of the dominant PC revealed that it separates surface and deep ocean samples, indicating that surface and deep sea DOM differ in terms of composition (Figure 2b). Nearly uniform values were observed below 1000 m, revealing that the DOM composition in the deep North Pacific Ocean is approximately uniform to lowest order. Above 1000 m, PC values slowly increased until about 200 m below the surface, above which they increased sharply. The loading of the first principal component is shown in Figure 2c as a van Krevelen diagram, a plot in which molar ratios of H/C and O/C are displayed. Major chemical classes typically found in DOM have characteristic molar ratios and, therefore, cluster within specific regions in van Krevelen space [Kim *et al.*, 2003]. Molecular formulae shown in red (i.e., loading of the PC is positive) were relatively enriched in surface samples and present in lower relative abundance in the deep ocean. The opposite was true for molecular formulae where the loading is negative.

Comparing the loading of the PC 1 (Figure 2c) with chemical characteristics of the compounds indicates that surface DOM is enriched with lower molecular weight compounds containing a relatively smaller number of C and H atoms than those compounds enriched at depth (Figure 3). Compounds with the lowest PC loading (and therefore more strongly enriched at depth) are characterized by a relatively small number of O, comparable to the number of O of compounds enriched at the surface. The ratios O/C and H/C are higher for compounds enriched at the surface. The low H/C ratios of compounds enriched at depth are possibly indicative of reworked and degraded organic matter, since old DOM in the Atlantic Ocean is enriched with compounds with low H/C ratios, while compounds enriched in new DOM are characterized by high H/C ratios [Flerus *et al.*, 2012]. The high H/C ratios of compounds enriched at the surface are also possibly associated with selective photodegradation of aromatic compounds in surface waters [Chen *et al.*, 2014]. The low O/C ratios of compounds enriched at depth are also consistent with processed DOM, since biodegradation has been shown to selectively remove compounds with higher O/C [Kim *et al.*, 2006]. We also observed that the modified aromaticity index (AI*) [Koch and Dittmar, 2006], a measure of the aromaticity of the molecules, is higher for compounds enriched at depth. Lastly, compounds enriched at the surface have a small number

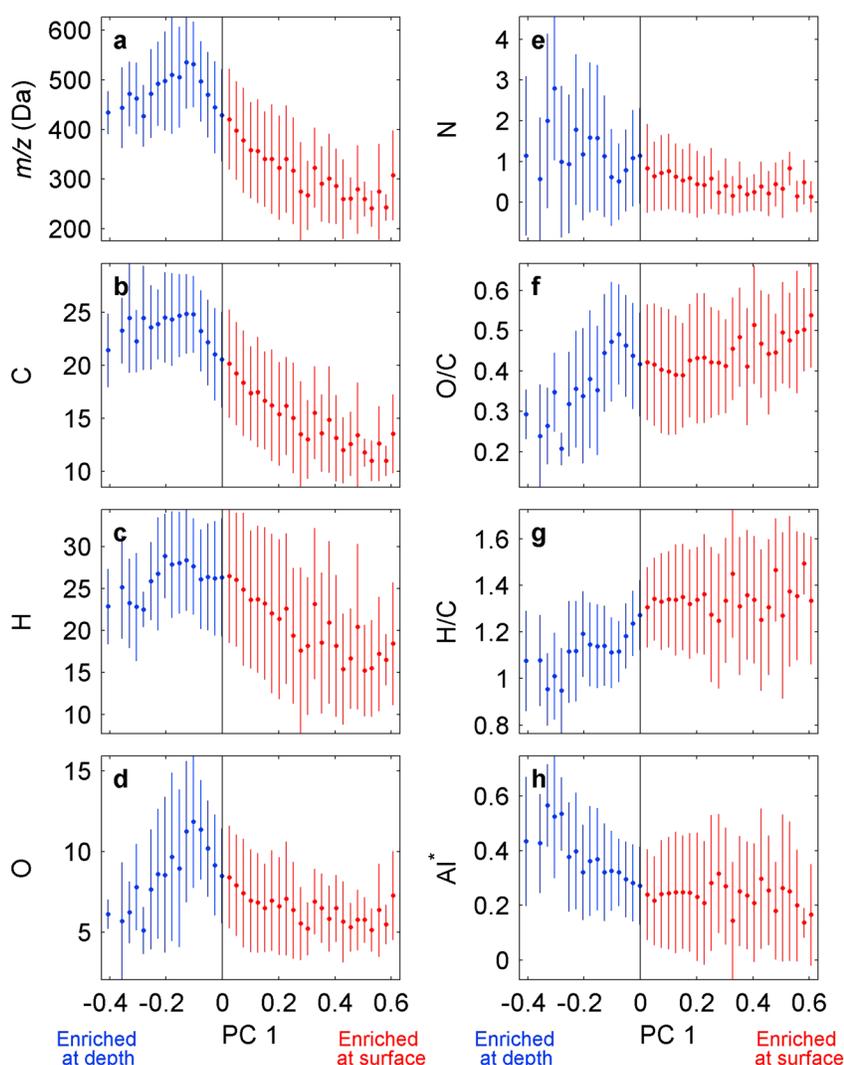


Figure 3. Chemical characteristics of compounds enriched at depth (blue) or at the surface (red). Values shown are average (dots) \pm 1 standard deviation (bars) within each bin. Al*: modified aromaticity index [Koch and Dittmar, 2006].

of N compared to those enriched at depth. Indeed, while 50% of compounds enriched at the surface have only CHO atoms, the majority (~75%) of those enriched below 1000 m contain either CHON or CHOS (supporting information Table S2).

The Al* can be combined with element ratios of molecular formulae to group all detected molecules according to their molecular structure [Šantl-Temkiv *et al.*, 2013; Seidel *et al.*, 2014] (see Figure 4 for definitions). We emphasize that this characterization is not unambiguous and alternative structures may exist for a given molecular formula. However, this categorizing provides a helpful overview of likely structures behind the identified molecular formulae. Assignment of compound groups based on molecular level information obtained by FT-ICR MS has been successfully used before to identify biogeochemical processes of DOM [e.g., Kim *et al.*, 2003; Schmidt *et al.*, 2009]. The majority of the molecular formulae enriched near the surface are classified either as highly unsaturated compounds or as unsaturated aliphatic compounds (Figure 4). Unsaturated aliphatic compounds make a particularly important contribution at the chlorophyll maximum level (~50 m below the surface). This finding is consistent with previous laboratory experiments showing these compounds to be a major fraction of phytoplankton exudates [Landa *et al.*, 2014]. In contrast, only a very small fraction of compounds enriched in the deep ocean are unsaturated aliphatics.

Our analysis provided insights into the composition of compounds with relative abundance enriched at depth, revealing predominance of highly unsaturated compounds and of highly aromatic compounds,

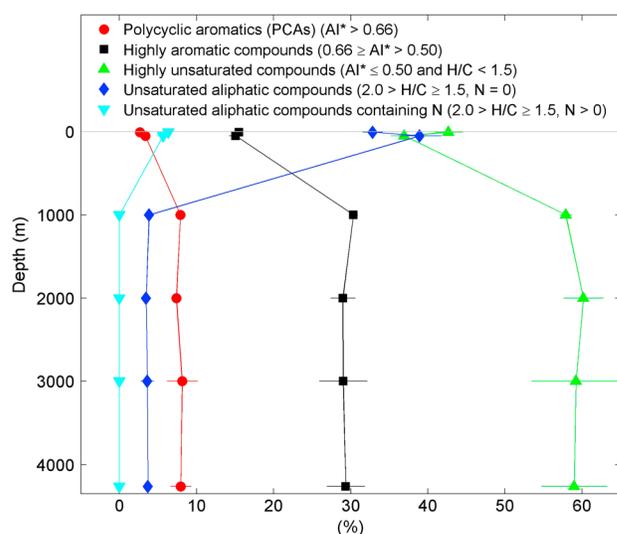


Figure 4. Vertical profiles of DOM molecular compound groups which were enriched at each depth. The percentage contribution of each group is computed independently for each layer. Error bars are ± 1 standard deviation. In some cases, error bars are smaller than the size of the symbols.

possibly because, similar to other dissolved aromatic compounds [e.g., Opsahl and Benner, 1998], PCAs are highly photodegradable [Stubbs et al., 2012] making the surface ocean a sink of thermogenic compounds [Dittmar and Paeng, 2009]. Another likely factor is the large distance to riverine sources (Figure 1), which are known to add PCAs and polyphenols to the coastal ocean [e.g., Mannino and Harvey, 2004; Ziolkowski and Druffel, 2010]. Indeed, although surface PPL-extractable DOC is characterized by slightly more depleted $\delta^{13}\text{C}$ signatures than at depth (Figure 2a and supporting information Table S1), values are substantially higher than those characteristic of regions strongly influenced by terrigenous inputs [e.g., Hedges et al., 1994]. It is not clear if the slightly lighter $\delta^{13}\text{C}$ signatures at the surface are due to a small offshore transport of terrigenous material from the continental margin (e.g., due to eddies) [Crawford et al., 2007] or due to transformation processes occurring in the surface mixed layer.

3.2. Photochemical Transformations of the North Pacific Deep DOM

DOC present at depth experiences at least partial photodegradation once it reaches the surface ocean [Mopper et al., 1991]. The detailed characterization of the extracted DOM before and after incubation experiments revealed that photochemical reactions have an important effect by changing the composition of the deep sea DOM (Figure 5a), resulting in a statistically significant decrease in the relative abundance of 791 compounds and on the increase in the relative abundance of 220 compounds ($\sim 20\%$ and $\sim 6\%$ of the assigned molecular formulae, respectively). CDOM light absorption at 320 nm decreased by $41 \pm 5\%$ during the experiments. A relatively large fraction (42%) of the photoproducts (red dots in Figure 5a) was unsaturated aliphatics. This outcome suggests that the enrichment of unsaturated aliphatics observed in near-surface waters (Figure 4) may also be related to photochemical reactions, in addition to phytoplankton inputs as described before. The PC analysis indicates that while samples before light exposure were characterized by PC values similar to other samples from the deep ocean (black circles at depth in Figure 2b), PC values for irradiated samples (green triangles and magenta squares in Figure 2b for natural solar irradiation and solar simulator, respectively) were more similar to those from the surface ocean (black circles at surface in Figure 2b). This was particularly true for samples irradiated using the solar simulator, when the irradiation intensity was higher. This finding, based on all ~ 4000 molecular formulae, indicates that as the deep sea DOM is upwelled into the photic zone by the large-scale circulation [Primeau, 2005], photochemical reactions transform the DOM such that its composition becomes more similar to surface DOM. This is consistent with a study by Helms et al. [2013], who showed that the optical characteristics of extensively bleached DOM collected in the North Pacific at the thermocline level are comparable to those of surface waters. This interpretation is further supported by

which include polyphenols and polycyclic aromatics with aliphatic chains (Figure 4). Polycyclic aromatics (PCAs), which include condensed combustion-derived dissolved black carbon if $C > 15$ [Dittmar and Koch, 2006], represented a larger fraction of compounds enriched in the deep ocean than at the surface, which is consistent with the idea that thermogenic compounds make an important contribution to the DOM pool at depth [Dittmar and Koch, 2006], where its distribution has been shown to be surprisingly homogeneous [Dittmar and Paeng, 2009]. Our results suggest that the approximately uniform distribution in the deep ocean is not restricted to thermogenic compounds, but rather it is to lowest order a characteristic of the ~ 4000 compounds analyzed here (Figure 2b), suggesting a low reactivity of the entire deep sea DOM pool. The small contribution of PCAs to compounds enriched in the surface DOM (Figure 4) is

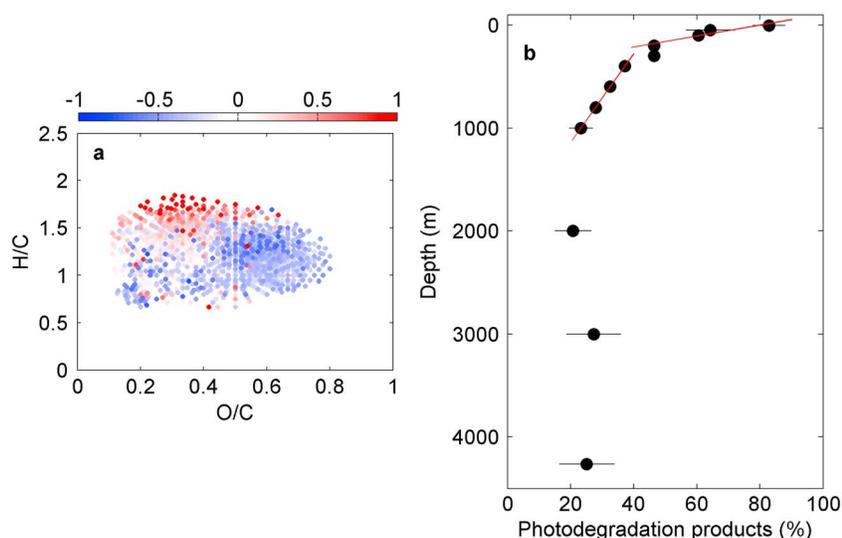


Figure 5. (a) Van Krevelen diagram showing compounds that were degraded (blue) or produced (red) during irradiation experiment. (b) Percentage of photodegradation products observed in each in situ sample. Error bars are ± 1 standard deviation.

a comparison between molecular formulae present in the individual in situ samples to molecular formulae of compounds produced during the experiment in which the deep DOM was exposed to solar irradiation (Figure 5b). About 20–25% of the compounds that were produced or that had their relative abundance significantly increased in the experiments as a result of the irradiation were observed in the deep ocean samples. The fraction of the photoproducts observed in in situ samples increased above about 1000 m, reaching $83 \pm 5\%$ near the surface. Therefore, irradiation of deep sea DOM produced compounds that are infrequently observed in the deep ocean itself, but that are abundantly present in the surface layer. Surprisingly, this recycling of the deep DOM seems to extend quite deep in the water column, perhaps to 1000 m below the surface (Figure 5b). The slope of the vertical profile of the percentage of photodegradation products observed in in situ samples is much steeper above about 200 m, however. The same is true for the vertical profile of the dominant PC (Figure 2b). One possible explanation for the change in slope is that at the surface the increase in the occurrence of photodegradation products (Figure 5b) is caused by photochemical reactions due to direct sunlight exposure, while below that the increase is primarily due to vertical export of DOM that has been previously modified at the surface, either locally or somewhere else. Indeed, a prominent feature in the North Pacific Ocean in the depth range of 200–1000 m is the presence of the North Pacific Intermediate Water (NPIW) [Yasuda, 2004]. Large amounts of DOC have been shown to be exported with subduction of NPIW in the Western Pacific [Hansell *et al.*, 2002]. As NPIW mixes horizontally into the intermediate layer of the North Pacific, the signature of the DOM that has been previously modified at the surface will presumably also be spread across the region. The percentage of occurrence of photodegradation products in the northern North Pacific is linearly related to potential density in the 200–1000 m depth range, so it is possible that vertical mixing also contributes to the vertical export. If this is true, it suggests that the detected photodegradation products are quite stable, since they are not decomposed in the years to decades that it takes for the NPIW to reach the study region since it has been ventilated [Warner *et al.*, 1996] and for deep vertical mixing to occur (it is important to note that many labile photodegradation products—e.g., small organic acids—escape our analytical window). Therefore, vertical export of organic matter that has been previously phototransformed at the surface could explain why the increase in photodegradation products extends to about 1000 m (Figure 5b), far beneath the depth of light penetration.

In contrast, dark microbial incubation experiments revealed little transformations in deep DOM composition (blue diamonds, Figure 2b), presumably because the more labile DOM fractions have already been consumed prior to the water reaching the deep North Pacific. A comparison between molecular formulae present in in situ samples to molecular formulae of the few compounds produced during the dark incubation produces nearly depth-independent results. The van Krevelen distribution of the relatively minor DOM transformations observed in the dark incubations (not shown) is not consistent with the surface to bottom differences in DOM composition detected in the region (Figure 2c).

In summary, our analyses revealed significant compositional differences between surface and deep sea DOM collected in the northern North Pacific Ocean. Surface DOM is enriched with highly unsaturated and unsaturated aliphatic compounds, potentially as a result of phytoplankton inputs and addition of photodegradation products. In the deep ocean, DOM composition is approximately uniform and enriched with highly unsaturated compounds, with highly aromatic compounds, including polycyclic aromatics with aliphatic chains, and with polycyclic aromatics, including combustion-derived compounds. Compounds enriched in the deep ocean are characterized by higher molecular weight and a higher number of C, H, and N atoms than those enriched at the surface. As deep DOM is upwelled by the large-scale circulation, photochemistry acts to transform its composition so that it becomes more similar to surface DOM. The influence of photochemical transformations seems to extend far beyond the photic zone, likely due to horizontal transport of DOC that has been previously exported from the surface ocean in the Western Pacific and to vertical mixing.

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