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# Investigating the sources and structure of chromophoric dissolved organic matter (CDOM) in the North Pacific Ocean (NPO) utilizing optical spectroscopy combined with solid phase extraction and borohydride reduction

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ABSTRACT

Prior optical measurements of waters in the Equatorial Atlantic Ocean (EAO) provided evidence of a major terrestrial "humic-like" component of the CDOM that absorbed in the ultraviolet (UV) and visible and emitted across the visible, along with a marine component that primarily absorbed and emitted in the UV. Here we extend these measurements to the North Pacific Ocean (NPO) at Station Aloha (22° 45′ N, 158° 00′ W). Detailed optical measurements of both the natural waters (CDOM) and C18 organic matter extracts of these waters (C18-OM) were acquired before and after sodium borohydride ($NaBH_4$) reduction of samples obtained throughout the water column. Optical properties of the "humic-like" component were relatively uniform with depth below ~600 m [$a_{CDOM}(350) \sim 0.08\ (m^{-1})$, $a^*_{CDOM}(350) \sim 0.2\ (m^{-1}\,mg^{-1}C\ L)$, $SUVA_{254} \sim 0.55\ (m^{-1}\,mg^{-1}C\ L)$, $E_2{:}E_3 \sim 10$, $S_{300-700} \sim 0.02\ (nm^{-1})$, $S_{350-400} \sim 0.012\ (nm^{-1})$, $S_R \sim 1.7$, $F(350/450) \sim 0.009$ (QSE), and $\phi_{360} \sim 0.026$], but were significantly different in surface waters, likely due to photobleaching and biological activity [$a_{CDOM}(350) \sim 0.026\ (m^{-1})$, $a^*_{CDOM}(350) \sim 0.027\ (m^{-1}\,mg^{-1}C\ L)$, $SUVA_{254} \sim 0.36\ (m^{-1}\,mg^{-1}C\ L)$, $E_2{:}E_3 \sim 45$, $S_{300-700} \sim 0.03\ (nm^{-1})$, $S_{350-400} \sim 0.003\ (nm^{-1})$, $S_R \sim 6.8$, $F(350/450) \sim 0.003$ (QSE), and $\phi_{350} \sim 0.024$]. Optical properties of the short-wavelength components (UV bands) were more variable with depth. Response to solid phase extraction was also relatively uniform with depth, with preferential extraction of the long-wavelength absorbing/emitting "humic-like" component (~30–50% extraction efficiency at $\lambda < 300$ nm and ~50–80% at $\lambda > 400$ nm) and virtually no extraction of the the UV absorbing/emitting bands. Response to $NaBH_4$ reduction was also similar down the water column with preferential loss of absorption in the visible region, and enhanced, blue-shifted fluorescence emission.

As in the EAO the 'humic-like" component exhibited very similar, although not identical, optical and chemical properties to those observed for terrestrially-dominated estuarine and coastal environments, providing evidence that this component originates from a terrestrial source. Although this component dominated the absorption, marine contributions (i.e. UV bands) similar to those observed in the EAO were also observed. However, these components were found to absorb and emit primarily in the UV and were not efficiently extracted by the C18 columns, clearly showing that they are structurally distinct from the "humic-like" component.

## 1. Introduction

The importance of chromophoric dissolved organic matter (CDOM) to a variety of environmental and biogeochemical processes is now widely recognized. CDOM can affect the underwater light field by absorbing UV and visible light (Blough and Del Vecchio, 2002; Siegel et al., 2002; Zepp et al., 2007), while the photoproduction of reactive oxygen species by CDOM can influence the speciation of trace metals and its photobleaching (Blough and Del Vecchio, 2002; Coble, 2007; Golanoski et al., 2012; Miller and Zepp, 1995; Mopper and Kieber, 2002; Zepp et al., 2007; Zhang et al., 2012). CDOM controls light absorption at short wavelengths (< 440 nm) in the upper layers of the open oceans (Nelson and Siegel, 2013) and thus in situ optical spectroscopy and satellite ocean color measurements have been employed to examine its distribution and dynamics, providing information relevant to carbon cycling, the mixing of surface water masses and basin-

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scale biogeochemical processes (Blough and Del Vecchio, 2002; Mopper and Kieber, 2002; Nelson and Siegel, 2013). The recognition of its importance has led to a very large number of studies of its optical absorption and emission properties over a broad spectrum of aquatic environments over the last 20 years (Coble, 2007; Del Vecchio and Blough, 2004a; Nelson and Siegel, 2013, 2002; Stedmon and Nelson, 2015), as well as to studies examining possible relationships between the optical and photochemical properties (Golanoski et al., 2012; Sharpless, 2012; Sharpless and Blough, 2014; Zhang et al., 2012), and their dependence on CDOM structure and source (Andrew et al., 2013; Boyle et al., 2009; Nelson and Siegel, 2013; Sharpless and Blough, 2014). Certain CDOM optical signals have further been suggested to serve as a proxy for the "quality" of the dissolved organic matter (DOM) pool (Coble, 2007; Fellman et al., 2010; Fichot and Benner, 2011; Helms et al., 2008), as an indicator of DOM source (Andrew et al., 2013; Fellman et al., 2010; Helms et al., 2008; Osburn et al., 2016), and as a measure of biological and (photo)chemical processing (Blough and Del Vecchio, 2002; Helms et al., 2013; Nelson and Siegel, 2002; Osburn et al., 2016).

The source of CDOM in offshore marine waters and the structural basis of its optical properties remain as open questions. A number of studies have concluded that CDOM is created in situ from marine dissolved or particulate organic matter based on correlations between measurements of either absorption or fluorescence and apparent oxygen utilization (AOU) (Nelson et al., 2010, 1998; Nelson and Siegel, 2013; Siegel et al., 2002; Yamashita et al., 2007; Yamashita and Tanoue, 2009). In contrast, other studies have suggested offshore marine waters contain a significant "humic-like" terrestrial component (Andrew et al., 2013; Murphy et al., 2008; Nelson and Gauglitz, 2016). Most of the studies that have proposed a solely marine source of CDOM were based on either absorption or fluorescence measurements alone, often at only a few wavelengths, with no additional chemical tests of source or structure. Similarly, incubation studies have suggested that "humic like" CDOM can be produced biologically via marine source materials (Jorgensen et al., 2014; Kinsey et al., 2018; Nelson et al., 2004; Nelson and Siegel, 2013; Romera-Castillo et al., 2010; Steinberg et al., 2004; Vernet and Whitehead, 1996; Zhao et al., 2017), but few, if any, secondary tests are performed to examine whether this material exhibits the same properties as the CDOM observed in the natural waters.

Prior work in the Equatorial Atlantic Ocean (EAO; (Andrew et al., 2013)), which combined acquisition of complete absorption and emission spectra with additional chemical tests (C18 extraction and borohydride reduction), provided strong evidence for a major terrestrial component that absorbs in the UV and visible but emits in the visible, along with marine CDOM components that absorb and emit primarily in the UV. In this study, we extended this work to the North Pacific Ocean (Station ALOHA) to examine both the spectral dependence of the optical absorption and emission properties of the natural waters alone, as well as the effects of solid phase extraction (Andrew et al., 2016; Dittmar et al., 2008) and $NaBH_4$ reduction (Andrew et al., 2016, 2013; Ma et al., 2010; Schendorf et al., 2016) on these properties. This particular site was chosen for three reasons. First, we wished to compare the results previously acquired in the Atlantic to those in the Pacific. Second, vertical profiles of the water column at this site would allow us to probe very different water masses and thus examine how the CDOM might vary with water mass origin. Third, it enabled us to sample North Pacific Intermediate Waters, where past studies have provided potentially conflicting evidence concerning a possible terrestrial source of the CDOM, (Hernes and Benner, 2002; Nelson and Gauglitz, 2016) as opposed to marine in situ production (Nelson and Siegel, 2013; Swan et al., 2009). As in the EAO, our results suggest the presence of a substantial terrestrial "humic-like" component throughout the water column, along with structurally-dissimilar marine CDOM components that primarily absorb and emit in the UV.

## 2. Methods

### 2.1. Samples

North Pacific Ocean (NPO) samples were collected at Station ALOHA (22° 45′ N, 158° 00′ W) in December 2014 onboard the RV Kilo Moana. Water samples were collected from the surface to 4500 m encompassing different water masses including 1) North Pacific Sub-Tropical Water (NPSTW: 0–200 m); 2) Sub-tropical Mode Water (STMW: 200–500 m); 3) North Pacific Intermediate Water (NPIW: 500–800 m); 4) Antarctic Intermediate Water (AAIW: 800–2000 m); 5) North Pacific Deep Water (NPDW: 2000–3000 m); 6) Lower Circumpolar Water (LCPW: 3000–4500 m) (Cannon, 1966; Hernes and Benner, 2002; Johnson and Toole, 1993; Masuzawa, 1973; McCartney, 1982; Reid Jr., 1965; Sverdrup et al., 1942; Talley, 1993; Talley and Joyce, 1992).

Natural waters and C18 extracts were collected as previously described (Boyle et al., 2009; Del Vecchio and Blough, 2004a). Briefly, samples were collected using a CTD rosette with Niskin bottles and immediately transferred into acid rinsed carboys (20 L). Samples were then filtered through a 0.2 μm double layer HT Tuffryn hydrophilic polysulfone filters (maxi capsule-Pall Corporation), which was previously rinsed with Milli-Q water and then for each sample a small volume of the natural water (~ 1 L) was passed though the filter and discarded to further rinse the filter. An aliquot (250 mL) of the filtered water was stored at 4 °C in the dark for later analysis ("CDOM"). In order to optimize CDOM extraction onto the non-polar C18 columns, the remaining filtered waters were acidified to pH 2 with ~100 mL of HCl (2 M). An aliquot (250 mL) of the acidified water was collected and stored at 4 °C in the dark until later analysis ("pre-extraction water"). The remaining acidified natural water (~20 L) was passed through C18 columns (United Chemical Technologies, Inc.) at a flow rate of ~50 mL $min^{-1}$ to extract DOM, using the method previously described (Boyle et al., 2009; Louchouarn et al., 2000). C18 extraction columns were preconditioned with 100 mL of MeOH and 50 mL of acidified Milli-Q water at pH 2. Two extractions were collected at each depth (20 L each). An aliquot of the extracted water (250 mL) was collected ("post-extraction water") and stored in the dark at 4 °C. The columns were then rinsed with acidified Milli-Q water (100 mL, pH 2) to remove salts, and stored in the dark at 4 °C (~2 months).

Prior to DOM elution, the cartridges were rinsed with an aqueous solution of formic acid (0.1% by volume) to remove any remaining HCl, and gently dried with $N_2$ gas to remove as much water as possible. DOM was eluted with 50 mL of high purity MeOH. The first ~ 5 mL of eluent were discarded to remove the small amounts of water still contained in the dead volume; the remaining eluent (45 mL) from the two extractions at each depth were combined and roto-evaporated at ~ 35 °C until dry. The dried DOM was dissolved in Milli-Q water (~2 mL) and adjusted to neutral pH with $NH_4OH$. This concentrated extracted material (referred to as "extracts" or "C18-OM") was stored frozen in the dark (up to 1 year).

To provide a procedural blank, two C18 columns were treated following this protocol employing 20 L of acidified Milli-Q water in place of natural waters. Pre and post extraction waters as well as the extracted material from these procedural blank columns were tested for their optical properties (absorption and fluorescence), which were nearly indistinguishable from zero.

### 2.2. Optical measurements

Absorption measurements were collected using both a World Precision Instrument (WPI) multi-pathlength absorption spectrometer (~200 cm pathlength) and a Shimadzu UVPC 2401 benchtop spectrophotometer (1 cm pathlength). The WPI spectrometer, employing the 200 cm pathlength, was used to measure the CDOM absorption of the seawaters, and thus obtain more accurate absorbance values over the

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