



## An intercomparison of three methods for the large-scale isolation of oceanic dissolved organic matter



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### ABSTRACT

Dissolved organic matter (DOM) was isolated from large volumes of deep (674 m) and surface (21 m) ocean water via reverse osmosis/electrodialysis (RO/ED) and two solid-phase extraction (SPE) methods (XAD-8/4 and PPL) at the Natural Energy Laboratory of Hawaii Authority (NELHA). By applying the three methods to common water samples, the efficiencies of XAD, PPL and RO/ED DOM isolation were compared. XAD recovered 42% of dissolved organic carbon (DOC) from deep water (25% with XAD-8; 17% with XAD-4) and 30% from surface water (16% with XAD-8; 14% with XAD-4). PPL recovered  $61 \pm 3\%$  of DOC from deep water and 61% from surface water. RO/ED recovered  $82 \pm 3\%$  of DOC from deep water,  $14 \pm 3\%$  of which was recovered in a sodium hydroxide rinse, and  $75 \pm 5\%$  of DOC from surface water, with  $12 \pm 2\%$  in the sodium hydroxide rinse. The highest recoveries of all were achieved by the sequential isolation of DOC, first with PPL and then via RO/ED. This combined technique recovered 98% of DOC from a deep water sample and 101% of DOC from a surface water sample. In total, 1.9, 10.3 and 1.6 g-C of DOC were collected via XAD, PPL and RO/ED, respectively. Rates of DOC recovery using the XAD, PPL and RO/ED methods were 10, 33 and  $10 \text{ mg-C h}^{-1}$ , respectively. Based upon C/N ratios, XAD isolates were heavily C-enriched compared with water column DOM, whereas RO/ED and PPL  $\rightarrow$  RO/ED isolate C/N values were most representative of the original DOM. All techniques are suitable for the isolation of large amounts of DOM with purities suitable for most advanced analytical techniques. Coupling PPL and RO/ED techniques may provide substantial progress in the search for a method to quantitatively isolate oceanic DOC, bringing the entirety of the DOM pool within the marine chemist's analytical window.

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### 1. Introduction

The oceanic reservoir of dissolved organic carbon (DOC) is comparable in size to the atmospheric reservoir of  $\text{CO}_2$  and to the combined reservoirs of terrestrial and aquatic biomass (Hansell, 2013). Despite its great importance as a master variable and carbon store (Dittmar and Stubbins, 2014), marine dissolved organic matter (DOM) is not well characterized chemically, principally because it exists as a highly diluted mixture of perhaps millions of organic compounds in a highly saline aqueous solution (Hertkorn et al., 2013). Some methods of

DOM characterization have specific requirements regarding the quantity and/or purity of sample. For example, nuclear magnetic resonance (NMR) spectroscopy requires relatively large sample quantities (10 to 100 mg), elemental analysis requires low-ash samples, and ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) requires low-salt samples (Mopper et al., 2007; Perdue and Benner, 2009). In each case, freeze drying seawater samples to isolate DOM for further analysis is not an option, as each gram of DOM would remain diluted in 35 kg of salt. Accordingly, various methods have been developed to isolate DOM. These methods differ in the percentage of DOM recovered, the purity of isolated DOM, the chemical or size fraction isolated, the rate of recovery, equipment costs, and operating costs. Whether a method exploits chemical (e.g. hydrophobicity) or physical properties (e.g. molecular size) to isolate DOM, it has thus far not been possible to recover 100% of DOM.

For the current study, three DOM isolation methods were compared. The study focused upon relatively large volume methods capable of

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providing isolate quantities (i.e. 100's of mg-C) for multiple analytical techniques, including those with relatively heavy sample demands (e.g. direct polarization  $^{13}\text{C}$  NMR). The oldest and historically most widely applied method in this study is a solid phase extraction (SPE) method in which XAD-8 and XAD-4 resins are used in tandem (Aiken et al., 1979; 1992). XAD-4 is a styrene–divinylbenzene resin, and XAD-8 an acrylic ester resin. Previous use of XAD-8/4 in oceanic waters isolated ~35% of DOC (Druffel et al., 1992; Esteves et al., 2007). The second SPE method uses Bond Elut PPL resin (Agilent), a functionalized styrene–divinylbenzene, to isolate DOM from acidified samples of ocean water (Dittmar et al., 2008). Reported PPL-DOM recoveries for oceanic waters range from approximately 40 to 75%, with higher recoveries occurring at low DOC loading per gram of PPL resin (Dittmar et al., 2008; Stubbins et al., 2012).

The third method, coupled reverse osmosis/electrodialysis (RO/ED), combines a water-selective membrane that retains organic and inorganic solutes (RO) and a stacked set of ion exchange membranes that selectively remove small charged solutes (ED). RO/ED recovers approximately 70 to 75% of DOM from oceanic waters (Gurtler et al., 2008; Koprivnjak et al., 2009; Vetter et al., 2007; Young and Ingall, 2010).

The primary objective of this study was to compare both the efficiencies with which XAD, PPL and RO/ED isolated large amounts of DOM from oceanic water and the qualities of the isolated organic matter. By applying the three methods to common water samples, differences in the quantity and quality of isolated DOM are attributed to differences in the isolation methods. In addition, this study provides a first assessment of the efficiency of coupling SPE and RO/ED isolation methods, plus a direct comparison of the ease of use and costs of the primary methods.

## 2. Materials and procedures

### 2.1. Sampling site

Oceanic water samples were collected and isolated between 24/09/2009 and 16/10/2009 at the Natural Energy Laboratory of Hawaii Authority (NELHA; [www.nelha.org](http://www.nelha.org)) on the island of Hawaii, U.S.A. near Kailua-Kona (19°44'N, 156°04'W). At NELHA, deep (674 m) and surface (21 m) oceanic waters are pumped continuously at a rate of more than  $0.5\text{ m}^3\text{ s}^{-1}$  through high-density polyethylene (HDPE) distribution systems that have been in use since 1987. Water is transferred from the HDPE pipelines to the laboratory through polyvinylchloride (PVC) pipes that were flushed continuously for several days before and throughout the study. The temperatures of deep and surface water at NELHA were 6 °C and 24 to 28.5 °C, respectively.

### 2.2. General operations

The XAD, PPL and RO/ED methods were employed by their principal developers. Fundamental details of the respective methods are given in Aiken et al. (1992), Dittmar et al. (2008), and Vetter et al. (2007). Methanol, concentrated hydrochloric acid (HCl, ACS grade, EMD, USA) and NaOH (ACS grade, Fisher, USA) were shared among the three research groups. Deep seawater and surface seawater were filtered directly from the NELHA laboratory taps to 0.2  $\mu\text{m}$  (Whatman PolyCap TC 150 for XAD and RO/ED; sequential Infiltec Causagard 1.0  $\mu\text{m}$  polypropylene prefilters and Causa-PES 0.2  $\mu\text{m}$  polyethersulfone final filters for PPL). All filters were flushed with several hundred liters of seawater before samples were collected. Blanks obtained by the filtration of ultrapure water had DOC concentrations below detection limit (2  $\mu\text{M-C}$ ).

Concentrations of total dissolved nitrogen (TDN) and DOC, as non-purgeable organic carbon, were determined using Shimadzu TOC- $V_{\text{C}_{\text{PH}}}$  total organic carbon (TOC) analyzers fitted with Shimadzu TNM-1 nitrogen units at Old Dominion University (Norfolk, VA, USA) and Carl von Ossietzky University (Oldenburg, Germany). Reference materials for low-carbon water and deep seawater (Consensus Reference Materials

Project: <http://yyy.rsmas.miami.edu/groups/biogeochem/CRM.html>) were used to correct and monitor the performance of the instruments (Doval and Hansell, 2000). Routine minimum detection limits in the investigators' laboratories are  $2.8 \pm 0.3\ \mu\text{M-C}$  for DOC and  $2.9 \pm 0.2\ \mu\text{M-N}$  for TDN, and standard errors are typically <2.5% of the DOC or TDN concentrations (Stubbins and Dittmar, 2012).

Nitrate and nitrite were determined spectrophotometrically (Schnetger and Lehnert, in press) for two RO/ED Final and two RO/ED NaOH Rinse samples at Carl von Ossietzky University in Oldenburg, Germany approximately 3.5 years after isolates were collected at NELHA. The detection limit was 0.2  $\mu\text{M}$  for nitrite and 0.4  $\mu\text{M}$  for the sum of nitrate and nitrite.

### 2.3. XAD-8/XAD-4

Isolates of DOM were obtained utilizing tandem columns of Amberlite XAD-8 and XAD-4 resins (Aiken et al., 1992). Modifications were implemented to decrease potential bleed from resins and to increase recovery of operationally defined DOM fractions – hydrophobic organic acids (HPOA; XAD-8) and transphilic organic acids (TPIA; XAD-4). In brief, four-liter glass columns of clean XAD-8 and XAD-4 were connected in series with Teflon tubing and fittings. Filtered seawater samples (220 L) were acidified to pH 2 with concentrated HCl and degassed under vacuum for 30 min before passing through the XAD-8/4 columns at 800–900  $\text{mL min}^{-1}$ . Each column was separately back-eluted with 0.1 M NaOH at 400  $\text{mL min}^{-1}$ . Eluates were collected until pH increased sharply and combined in a single “reload” glass container for inclusion in the next analytical run. Five liters of basic eluate was collected from each column in designated HPOA and TPIA eluate glass containers and immediately acidified to pH 2 with concentrated HCl. The resins were rinsed with 0.1 M HCl until the eluate was acidic, collecting the eluate from both columns into the “reload” container. The pH of the “reload” sample was adjusted to pH 2 with concentrated HCl. Both resins were repacked to ensure good chromatographic conditions, and the “reload” sample was loaded on the XAD-8 and XAD-4 columns, followed by the next aliquot of 220 L acidified and degassed water. After each set of eight analytical runs, in which 40 L of each eluate were collected, the homogenized eluates were reconcentrated on the appropriate resin. Seawater samples were processed using the XAD method for 18 11-hour days. Upon completion of all analytical runs and reconcentrations, reconcentrated HPOA and TPIA eluates were homogenized, hydrogen-saturated using AG-MP 50 cation-exchange resin (Bio-Rad), and then lyophilized.

### 2.4. PPL

Two custom-built cartridges, each filled with 500 g of Bond Elut PPL resin (Agilent), were used. The resin was rinsed just before use by flushing with 3 L of  $\text{CH}_3\text{OH}$ . Filtered seawater was acidified to pH 2 by continuously adding HCl with a microprocessor-controlled metering pump (STEPDOS®, KNF, Germany). The seawater flow rate was regulated by a membrane pump (2  $\text{L min}^{-1}$ ). The need for continuous large volume flow necessitated the use of a different filtration setup than was used for XAD and RO/ED. Approximately 3000 L of acidified seawater was pumped through one of the PPL cartridges over a period of approximately 24 h. Acidified seawater was then pumped through the second PPL cartridge while DOM was desorbed from the first cartridge enabling near-continuous operation. Prior to desorption of DOM from a PPL cartridge, the PPL resin was rinsed twice with 3 L of acidified pure water (pH 2, HCl) to remove salts. The rinsed resin was dried with purified compressed air (purified through a sequence of filters, activated charcoal and PPL resin) for ~22 h and then adsorbed DOM was eluted with 3 L of  $\text{CH}_3\text{OH}$ . Elution of the sample also acted to precondition the column. The volume of the eluate was reduced to between 30 and 50 mL by rotary evaporation at a temperature of less than 40 °C. Separate isolates for every extraction were transferred to pre-cleaned polyethylene

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