Tracking the fate, reuse and transformation of photodegraded DOM through EEMS and PARAFAC

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Abstract

Dissolved organic matter (DOM) represents one of the major pools of organic carbon in the oceans and exerts a key role in gas exchange between the atmosphere and the oceans. It has been estimated that DOM can contain up to 685 Gt C (Hansell and Carlson, 2002). DOM and its transformation have become an intensive subject of study due to the omnipresence in the oceans, the stability of some of its fractions for extensive periods and its implication on the planet´s weather as CO_2 exchanger, (Dittmar, 2015, Osterholz et al., 2015). The unlimited residence time of DOM in the oceans is a result of processes triggered by physical and biological drivers in the water column (Libes, 2009, Miranda et al., 2018). Those processes can be tracked through changes in the fluorescent DOM fingerprint, and using Excitation Emission Matrix Spectroscopy (EEMS) along with the Parallel Factor Analysis (PARAFAC), which gives a complete description of the fluorescent composition (Murphy et al., 2013). In the present study, we exposed in-situ produced DOM in three replicate mesocosms (M1, M2, and M3) from a previous experiment to ultraviolet radiation ranging between 265 and 385 nm for 30 days, to determine if photodegraded DOM becomes more like to refractory deep-sea DOM on molecular level. Samples were sequentially filtered through 0.7, 0.2 and 0.1 µm filters before incubation. A dark control for the three mesocosms was incubated simultaneously. FDOM samples were collected after 0, 3, 7, 11, 18 and 30 days, cooled (<4°C) and stored in glass amber bottles in the dark. We determined dissolved organic carbon, total bacterial cell numbers, EEMS, absorption and slope coefficients, recent produced material index (REPIX), DOM molecular composition through FT-ICR-MS, and principal components via PARAFAC.

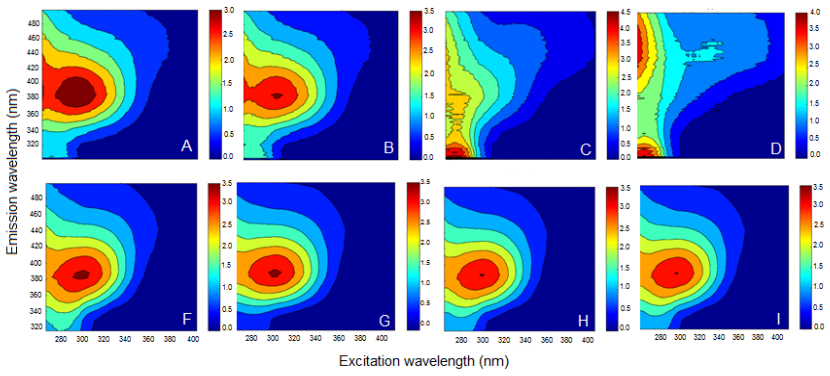

Figure 1. Excitation Emission Matrix Spectroscopy (EEMS) fingerprint for in situ produced fluorescent dissolved organic matter (FDOM) in mesocosm M1 on days 0, 3, 18 and 30. Color scale Shows Raman units (RU). Upper panel, irradiated samples (A to D). Lower panel shows dark control (F to I).

ANOVA test for DOC concentration showed no significant differences at 95% of confidence between treatments in the three mesocosms. Enumeration of total bacterial cell numbers using flow cytometry revealed the presence of a low bacterial population ($<2.5\times10^3$ cells/mL); and their distinct growing patterns in the three mesocosms in both treatments were related to variations in the calculated

biogeochemical indices. REPIX and spectral slope ($S_{275/295}$) results suggest the release of compounds with low molecular weight and the biological reprocessing of DOM.

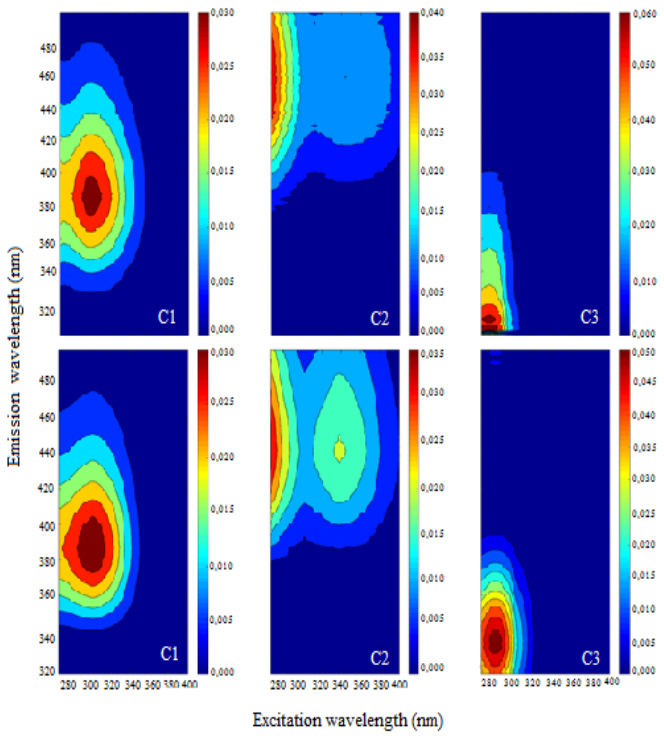

Figure 2. Three main fluorescent components for mesocosm M1. Vertical axis shows emission wavelengths, while in horizontal axis shows excitation wavelengths. Color bar indicates Raman unit's scale (R.U.). Principal components are labeled as C1, C2 and C3. Upper panel shows irradiated samples, in lower panel dark control.

However, the FDOM fingerprint in the dark control remains quasi-constant along the experiment for the three mesocosms (Figure 1). EEM spectra showed distinctive pattern for the photobleaching of the in situ produced FDOM under irradiation. PARAFAC identified three main components that all were related to the number of cells. Main differences were found in the maximum fluorescent peak position (Figure 2). Excitation emission maxima for main components in the dark incubation are shifted from shorter towards longer wavelength region, termed as red-shifted, suggesting a higher oxidation state in the FDOM molecules in comparison with the irradiated samples (Andrade-Eiroa et al., 2013).

Although, the general composition of the fractions detected by FT-ICR-MS demonstrated no increase in the refractory nature of DOM on molecular formula level, unique changes in the intensities for specific chemical groups such as polyphenols and unsaturated hydrocarbons confirmed the reuse and reprocessing of DOM under the tested conditions. In our study, a weak positive tendency between total cell counts and biogeochemical indices such as REPIX and $S_{275/295}$ shows evidence for the reprocessing and biological reuse of DOM under the tested conditions.

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