



Evidence for conservative mixing of dissolved organic matter in the coastal upwelling system off Central Peru during an "El Niño" year

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Dissolved organic matter (DOM) represents one of the largest active pools of organic carbon in the global carbon cycle; its composition and potential reactivity in upwelling areas have important implications for the functioning of the biological pump and the carbon balance. The Humboldt Current Upwelling System off Peru is one of the most productive zones of the world ocean, with high rates of primary production and an intense oxygen minimum zone (OMZ). One of the major perturbations of this system is associated to El Niño-Southern Oscillation, especially to its warm phase "El Niño", which affects water mass distribution, changes the upwelling and reduces primary productivity. We characterized the molecular composition of solid-phase extractable DOM (SPE-DOM) in the Coastal Upwelling System off Central Peru during 2015, an "El Niño" year, and linked the DOM composition to environmental changes in the system. Seasonal sampling (April, August and December) was carried out off Central Peru (12°S), one of the main upwelling cells characterized by high organic matter production and a well-developed OMZ. The DOM molecular composition was obtained via 15T Fourier transform ion cyclotron resonance mass spectrometry and was then related to physical, chemical and biological parameters using statistical tools. Our results showed that the SPE-DOM mainly underwent conservative mixing during 2015, following the water mass dynamic off Central Peru. This was evidenced in the concentration of solid-phase extractable dissolved organic carbon (SPE-DOC), but also in molecular properties like H/C ratio, sulfur-containing compounds and specific DOM groups like black carbon, unsaturated aliphatic and peptides, which showed significant differences between the water masses. Chlorophyll-a only showed a significant, although weak correlation, with SPE-DOC concentration and sulfur-containing compounds. Based on these results, a conservative mixing model was applied to investigate the processes affecting the DOM molecular composition of the samples outside the conservative mixing range. We found that DOM production coincided with high abundance of saturated fatty acids, and photodegradation was reflected in a loss of condensed aromatics. Our study suggests that changes in the SPE-DOM pool during 2015 were mainly driven by conservative mixing - water mass dynamic, and to a lesser extent to reduced primary productivity that characterizes the system during "El Niño" conditions. We propose a conceptual model for the water mass dynamic and associated DOM variation during "El Niño" years for the Upwelling System off Central Peru.