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Characterizing the dynamics of dissolved organic matter in fjord systems, New Zealand

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Dissolved organic matter (DOM) comprises the largest pool of organic matter in a wide range of aquatic environments. In oceanic environments, major fractions of DOM have been considered to be marine origin even though rivers convey substantial amounts of terrestrial organic matter to the coastal ocean (0.4 PgC yr-1). Thus, there might be removal mechanisms of terrestrial DOM in coastal environments. However, dynamics, i.e., sources and sinks, of DOM in coastal environments have not been well understood. The characterization of the DOM dynamics in coastal environments is challenging due to intricate structure/composition of terrestrial and marine DOM. Therefore, we need a better technique for evaluating the terrestrial and marine DOM separately. Fluorescence technique can successfully separate the terrestrial DOM from marine one, and thus, has been widely used in coastal environments. Here, we applied excitation emission matrix (EEM) fluorescence combined with parallel factor analysis (PARAFAC) for characterizing the dynamics of DOM in fjord systems, New Zealand. In addition, we compared obtained fluorescence results with stable carbon isotope values of DOC.

In June 2007 (Austral winter), water samples were collected from surface to bottom layer at fjord systems in Fjordland National Park, New Zealand. Water samples were immediately filtered through pre-combusted GF/F filters and were kept on ice, returned to the laboratory, and stored at 4 oC until analysis. EEM spectra were obtained using a Horiba Jovin Yvon SPEX Fluoromax-3 fluorometer. PARAFAC, which can statistically identify fluorescent components in EEMs, were applied for 53 water samples obtained from fjord systems. As a result, two terrestrial humic-like, one marine humic-like, and one protein-like components were obtained. Isotopic analysis (delta13C) of dissolved organic carbon (DOC) were performed on a modified OI Analytical model 1010 wet oxidation TOC analyzer interfaced with a Finnegan MAT Delta Plus IRMS with a CONFLO III continuous flow interface.

Relationships between salinity and fluorescence intensity differed among the four components. Levels of humic-like components were higher in low salinity waters and vice versa and showed negative relationships with salinity, indicating that major sources of humic-like components are riverine water in this system. Levels of protein-like component did not show clear relationship with salinity, suggesting that substantial contribution of autochthonous protein-like component in addition to riverine input.

On the vertical axis, fluorescence intensity of all components showed highest levels in the surface water, sharply decreasing with increasing depth. However, in the deep layer (depths greater 50 m), increases in fluorescence intensity with depth were observed for humic-like components, but not for protein-like component. The increase in fluorescence intensity with depth in deep layer was highest at the stations with the lowest water exchange rates, while it was almost absent at the sites most strongly influenced by tides and flushing with oceanic water. Interestingly, delta 13C of DOC in deep layers were lower than those in subsurface layers. These results strongly suggest that DOM is physically desorbed and/or generated through microbial oxidation from terrestrial POM during its sinking processes.

Keywords: dissolved organic matter, fluorescence, stable carbon isotope, fjord