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Dynamics of dissolved organic matter in fjord ecosystems: Contributions of terrestrial dissolved organic matter in the deep layer

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ABSTRACT

Annually, rivers and inland water systems deliver a significant amount of terrestrial organic matter (OM) to the adjacent coastal ocean in both particulate and dissolved forms; however, the metabolic and biogeochemical transformations of OM during its seaward transport remains one of the least understood components of the global carbon cycle. This transfer of terrestrial carbon to marine ecosystems is crucial in maintaining trophic dynamics in coastal areas and critical in global carbon cycling. Although coastal regions have been proposed as important sinks for exported terrestrial materials, most of the global carbon cycling data, have not included fjords in their budgets. Here we present distributional patterns on the quantity and quality of dissolved OM in Fiordland National Park, New Zealand. Specifically, we describe carbon dynamics under diverse environmental settings based on dissolved organic carbon (DOC) depth profiles, oxygen concentrations, optical properties (fluorescence) and stable carbon isotopes. We illustrate a distinct change in the character of DOC in deep waters compared to surface and mid-depth waters. Our results suggest that, both, microbial reworking of terrestrially derived plant detritus and subsequent desorption of DOC from its particulate counterpart (as verified in a desorption experiment) are the main sources of the humic-like enriched DOC in the deep basins of the studied fjords. While it has been suggested that short transit times and protection of OM by mineral sorption may ultimately result in significant terrestrial carbon burial and preservation in fjords, our data suggests the existence of an additional source of terrestrial OM in the form of DOC generated in deep, fjord water.

1. Introduction

The transport of organic matter (OM) from the continents to the ocean via fluvial systems is an important link between the terrestrial and marine biospheres. Rivers annually deliver ~0.25 Pg of dissolved organic carbon (DOC) to the ocean (Meybeck, 1982; Hedges et al., 1997; Ducklow and McCallister, 2004), an amount large enough to sustain the turnover of all marine DOC (662 Pg C; Hansell et al., 2009). Likewise, the magnitude of river-transported particulate organic carbon (POC, ~0.15 PgC) is sufficient to account for the total organic carbon buried in continental margin sediments annually (Hedges and Keil, 1995; Hedges et al., 1997). However, the metabolism and biogeochemical transformation of OM during seaward transport remain one of the least understood components of the global carbon cycle (Sikes et al., 2009; Smith et al., 2010; Bianchi, 2011). While priming effects have been suggested to explain the lower than expected presence of terrestrial OM in oceanic environments, in general little is known about such processes in aquatic systems overall (Guenet et al., 2010; Bianchi, 2011). Furthermore, climate change scenarios suggest hydrological accelerations and consequent increases in the input of

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terrestrial DOC to aquatic systems (Freeman et al., 2001; Chapman et al., 2010; SanClements et al., 2012), thus underscoring the need to develop a fundamental understanding of terrestrial OM transport and processing along the terrestrial-marine corridor.

One of the dominant sources of OM in coastal regions is terrestrial OM transported from soils (SOM) by surface runoff and rivers as particulate (POM) or dissolved organic matter (DOM; Sikes et al., 2009; Bianchi, 2011). Along its transport to the marine environment, this OM may undergo extensive biotic (e.g. respiration) and abiotic (e.g. photochemistry) transformations resulting in significant CO_2 emissions to the atmosphere (Cole et al., 2007; Battin et al., 2009). Analogous microbial and photochemical processes operate in the marine environment, where changes in nutrient levels, light penetration, hydrological conditions and microbial community structure can affect the rate of carbon turnover (Flerus et al., 2012; Friedline et al., 2012; Koch and Kattner, 2012). Even though distribution patterns of riverine DOM have been well investigated (Hansell and Carlson, 2002), comparatively little attention has been paid to the important transition between terrestrial OM from POM to DOM. Recently, studies indicate that POM is highly photo-reactive and prone to photo-dissolution, a process that can potentially increase DOM loadings in coastal systems (e.g., Mayer et al., 2009). DOM derived from the photo-dissolution of planktonic detritus (Mayer et al., 2009), SOM (Mayer et al., 2012), flocculent OM from flooded surface soil environments (Pisani et al., 2011) as well as from re-suspended sediments (Kieber et al., 2006; Shank et al., 2011) has been reported. Consequently, POM photo-dissolution may be a significant, yet overlooked, source of DOM in coastal systems.

In addition, the transfer of terrestrial carbon from the particulate to the dissolved pool can be mediated by desorption and leaching of plant litter (Maie et al., 2006a) as well as bottom sediment re-suspension (Mitra et al., 2000). Further, it has been reported that additional carbon can be desorbed from soil particles and POM under saline water conditions (Keil et al., 1997; Butman et al., 2007). The latter observation implies that eroded soil particles transported to coastal environments can contribute to the allochthonous DOM pool. Sediment re-suspension events in the Hudson River estuary waters may provide as much as 8% of the organic carbon loading delivered to the estuary by freshwater discharge (Komada and Reimers, 2001). Koelmans and Prevo (2003) reported that long-term (weeks) re-suspension of desiccated Rhine River sediments could release nearly all initially adsorbed POM as DOM, and it was suggested that a significant fraction of POM could be mobilized from the sediments within a few weeks of incubation. Similarly, Butman et al. (2007) found that eroded soil particles could release carbon as DOM, 50% of which can be metabolized.

Although inland waters are now recognized as reactors for organic matter and can serve simultaneously as both carbon sinks and sources (Cole et al., 2007; Tranvik et al., 2009; Aufdenkampe et al., 2011), most of the global data syntheses have not included fjords in their budgets. This omission is in part due to the relative dearth of information on carbon cycling and characterization in these systems compared to their riverine/estuarine counterparts. However, many temperate fjords receive an excess of 6000 mm of rainfall a year which has the potential to deliver significant amounts of terrestrial DOM and POM (soil, litter, woody debris and leachates) directly to the coastal margins (McLeod and Wing, 2009; Smith et al., 2010; Vargas et al., 2011). Coupled with these large terrestrial inputs are distinct hydrographic and biogeochemical features, which modulate how carbon is processed in these systems. For example, the large episodic input of POM and low oxygen bottom water created by deep basins and shallow sills may facilitate the accumulation and preservation of POM (Hartnett et al., 1998; Keil et al., 2004). Thus, these systems may act as chutes, transporting relatively unweathered mineral and unaltered POM quickly and efficiently due to their short, steep gradients, abbreviated transit times, and flashy hydrographs (Blair et al., 2004; Lyons et al., 2005; Leithold et al., 2006). However, to date comparatively little is known about the environmental dynamics of DOM in fjords.

Gonsior et al. (2008) investigated the dynamics of DOM in surface waters of Doubtful Sound, New Zealand, and demonstrated: 1) the importance of fluvial inputs of terrestrial chromophoric DOM (CDOM) as a major DOM source, 2) the effect of rain events on mixing dynamics with depth (i.e. increasing salinity), and 3) the contribution of marine end-member derived sources. However, this previous study in Doubtful Sound addressed DOM dynamics in surface waters only (0–5 m), and did not investigate deep-water profiles and associated changes in DOM sources. In order to constrain carbon cycling in fjord ecosystems, it is critical to develop a fundamental understanding of DOM dynamics. In this study, we determined the full-depth distribution of DOM in two fjord systems in New Zealand using a multi–tracer approach employing measurements of bulk parameters such as the $\delta^{13}C$ value of DOC and excitation emission matrix fluorescence with parallel factor analysis (EEM-PARAFAC). We especially focused on the patterns and factors controlling the distribution of DOM in the deep layer of the fjords. Since $\delta^{13}C$ values of DOC and EEM-PARAFAC were not applied in previous studies (Gonsior et al., 2008), we also determined DOM characteristics in surface waters as a comparison with those in the deep layer.

2. Methods

2.1. System description

Fiordland National Park located at the south west coast of the South Island of New Zealand (Fig. 1) is an example of a typical fjord environment with an extreme annual rainfall of about 6000 mm (Stanton and Pickard, 1981) and hence one of the wettest regions worldwide. The vegetation is characterized by dense evergreen temperate rainforest at low altitudes and beech forest dominating at higher elevations. Because of high annual rainfall, a stable low salinity layer (LSL) is evident year-round in the fjords surface waters (Gibbs et al., 2000, 2001). Water samples were collected at surface and with depth in two different fjords, Doubtful Sound (DoS) and Dusky Sounds (DuS, Fig. 1). DoS sampling included a side fjord with its own deep basin and sill, called Crooked Arm (CA; Fig. 1). DoS has a deep basin of over 400 m depth with a shallow sill at the entrance of the fjord. The extent of the LSL as well as a detailed description of the distribution and extraordinary high levels of CDOM within the largest fjord, Doubtful Sound, in Fiordland National Park has been shown previously (Gonsior et al., 2008). Its hydrology is complicated due to the large amount of lake water that enters the head of the fjord through two large diameter tunnels. This continuous surface water flows towards the entrance of the fjord. The only region that is partially isolated from this artificial freshwater delivery is CA (CA; Fig. 1). In contrast to the deepest basin in DoS, the CA deep sediments are anaerobic.

DuS, located to the South of DoS (Fig. 1), is not influenced by an artificial freshwater input; however, it has a large freshwater riverine discharge at the head of the fjord (Stanton and Pickard, 1981). Sediments in the basin toward the head of the fjord showed signs of anoxia (black, the odor of hydrogen sulfide) in contrast to the deepest basin located at about half distance to the entrance of the fjord. The deepest basin in DuS as with DoS is strongly influenced by a connected side fjord which potentially