



# Organic carbon burial in fjords: Terrestrial versus marine inputs



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## ABSTRACT

Fjords have been identified as sites of enhanced organic carbon (OC) burial and may play an important role in regulating climate change on glacial–interglacial timescales. Understanding sediment processes and sources of sedimentary OC are necessary to better constrain OC burial in fjords. In this study, we use Fiordland, New Zealand, as a case study and present data on surface sediments, sediment down-cores and terrestrial end-members to examine dynamics of sediments and the sources of OC in fjord sediments. Sediment cores showed evidence of multiple particle sources, frequent bioturbation and mass-wasting events. A multi-proxy approach (stable isotopes, lignin-phenols and fatty acids) allowed for separation of marine, soil and vascular plant OC in surface sediments. The relationship between mass accumulation rate (MAR) and OC contents in fjord surface sediments suggested that mineral dilution is important in controlling OC content on a global scale, but is less important for specific regions (e.g., New Zealand). The inconsistency of OC budgets calculated by using MAR weighted %OC and OC accumulation rates (AR; 6 vs 21–31 Tg OC yr<sup>-1</sup>) suggested that sediment flux in fjords was likely underestimated. By using end-member models, we propose that 55% to 62% of total OC buried in fjords is terrestrially derived, and accounts for 17 ± 12% of the OC<sub>terr</sub> buried in all marine sediments. The strong correlation between MAR and OC AR indicated that OC flux will likely decrease in fjords in the future with global warming due to decrease in sediment flux caused by glacier denudation.

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## 1. Introduction

Continental margins account for over 90% of organic carbon (OC) buried by the ocean (Berner, 1982; Hedges, 1992; Hedges and Keil, 1995) and represent a dynamic component of the global carbon budget. However, total OC burial found in coastal sediments is considerably less than predicted from marine primary production and riverine fluxes (Burdige, 2005; Hedges, 1992). This enigma may be in part due to the historical focus on large river-deltas and non-deltaic continental margins as the basis for OC burial estimation (Berner, 1982; Burdige, 2005; Hedges and Keil, 1995) without considering potential contributions from small systems, such as lagoons and fjords. Fjords are deep, glacially-carved estuaries located in high latitudes and are characterized as having high sedimentation rates, steep watersheds, relatively short residence time of particles on land and through water columns, and sills near the fjord mouth (Howe et al., 2010; Syvitski et al., 1987). There has been growing evidence showing that fjords are potential

hotspots of carbon burial in the coastal margin (Gilbert et al., 2002; Walinsky et al., 2009). For example, a recent study by Smith et al. (2015) estimated that fjords bury ~17–20 × 10<sup>12</sup> g OC yr<sup>-1</sup>, which accounts for 11% of total oceanic carbon burial. Despite these recent improvements in our estimates of OC burial in fjords, fjord OC burial dynamics are influenced by the distribution patterns of OC along fjord transects, bioturbation, mass-wasting events, and burial efficiency. These factors need to be quantified to better constrain the estimate of OC burial in fjords. In addition, the relative proportion of terrestrial OC (OC<sub>terr</sub>) in the total OC pool still remains largely unknown and has important implications for understanding remineralization and global coastal carbon budgets. Preliminary evidence has suggested that OC<sub>terr</sub> may represent the majority of sedimentary OC in fjords (Smith et al., 2010; Smittenberg et al., 2004b).

In this study, we build on the previous work by Smith et al. (2015) to further expand our knowledge on carbon cycling in fjord systems by providing new biomarker results from detailed sampling in Fiordland, New Zealand. More specifically we examine: 1) bioturbation and mass-wasting processes in New Zealand fjords using short cores; 2) distributions of OC and specific biomarkers

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in fjord surface sediments; 3) physical controls on OC content in fjord surface sediments; and 4) re-estimate the burial of OC and  $OC_{terr}$  in fjords and the potential implications for future OC burial in fjords in relation to climate change.

## 2. Methods

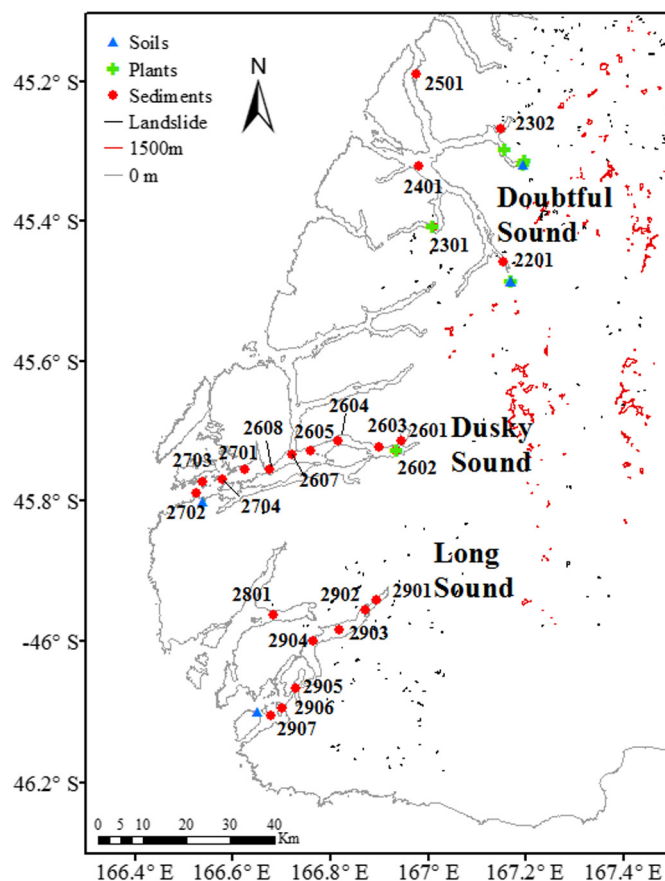
### 2.1. Site description and sampling

Fiordland, New Zealand, is an area comprising 14 fjords with a total area of 719 km<sup>2</sup>, located in the southwest of the South Island, New Zealand. The catchment in Fiordland contains lush temperate rainforests comprised of mainly Beech *Nothofagus* spp. forests, mixed beech–podocarp forests, and broadleaved hardwoods. The forest ground layer is characterized in places by a dense cover of ferns and mosses. The soils on top of bedrock are shallow (max. 15 cm before reaching the bedrock), organically rich, and generally lack the typical soil-profile structure. The top soils (e.g., 0–5 cm) are mainly composed of fresh terrestrial detrital material. In contrast, the deeper soils (e.g., 10–15 cm) are derived from the same litter, with significant inputs of leachates from surface litter, but are generally more mature with low OC content and more degraded lignin. Within fjords, marine primary production is mainly from macroalgae (McLeod and Wing, 2009). Fiordland is characterized by high rainfall rates (6,000–8,000 mm yr<sup>-1</sup>), steep topography (e.g., 68–75° steepness) and seismic activities, which together trigger frequent mass-wasting events along fjords (Keefer, 1994; Sansom, 1984; Schüller et al., 2015). Surface water runoff follows the same seasonal patterns as rainfall rates and primary production, which have their maxima and minima in summer/fall and winter, respectively (Gonsior et al., 2008; Stanton and Pickard, 1981). Despite a few suboxic and anoxic locations in fjords (Hinojosa et al., 2016), dissolved oxygen (DO) saturation rates range between 50% and 100%; nevertheless, water columns are highly stratified with a halocline at 5–10 m depth due to large inputs of freshwater runoff (Stanton and Pickard, 1981). Minimal bioturbation rates may result in high preservation of OC in fjord sediments (Schüller et al., 2015). Sediments within fjords are mainly comprised of organic-rich mud that is spatially well-distributed along fjords (Pickrill, 1993). Water circulation in fjords is constrained by the deep water depth (max >400 m) and multiple shallow sills.

In this study, we sampled sediments and terrestrial end-members from three fjords in Fiordland: Doubtful Sound, Dusky Sound, and Long Sound, situated along a north-to-south gradient of decreasing topography and rainfall (Schüller et al., 2015; Stanton and Pickard, 1981). In June 2010, a total of twenty-four short piston cores (6–30 cm) were collected from the 3 fjords in Fiordland, using a piston corer onboard the *R/VPolaris II* with 5 cores in Doubtful Sound, 11 cores in Dusky Sound, and 8 cores in Long Sound (Fig. 1). Samples were kept frozen at –20 °C, then freeze-dried and ground prior to geochemical analyses. Fresh plant and soil samples were collected from 5 sites in fjord riparian zones in order to obtain  $OC_{terr}$  end-members (Table 1). Plant leaves and stems were collected from live vegetation and surface ground litter. Due to the presence of “unusual” soil profiles (described earlier), soil samples were collected from the surface (1 cm) and deep horizons (15 cm) as two contrasting end-members. Terrestrial end-members have been previously analyzed for bulk OC and lignin in Smith et al. (2015) and were re-analyzed for this study.

### 2.2. Sample and data analysis

All 24 surface sediments (0–1 cm) and some terrestrial end-members were analyzed for bulk OC (Harris et al., 2001) and chemical biomarkers, including lignin phenols (Goñi et al., 1998)



**Fig. 1.** Sample locations in Fiordland, New Zealand. From north to south, the three fjords are Doubtful Sound, Dusky Sound, and Long Sound. Soils, plants and sediments are shown in different colors. The red and black marks represent 1500 m elevation contour line and landslides. The gray line represents coastline. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and fatty acids (Cui et al., 2016). The detailed methods are attached in the supplementary data. OC-normalized lignin contents ( $\Delta_8$  in mg 100 mg OC<sup>-1</sup>) are usually used as distinct proxies to quantify the contribution of OC from vascular plants. In contrast, 3,5-dihydroxybenzoic acid (3,5-Bd) is formed largely in soils by bacteria from the breakdown of plant-derived tannins and flavonoids (Houel et al., 2006). The ratio of 3,5-Bd/vanillyl phenols (3,5-Bd/V) is commonly used as a proxy of relative soil OC ( $OC_{soil}$ ) contribution. Fatty acids (FAs) have also been widely used as biomarkers of OC sources (Haddad et al., 1992). For example, short-chain fatty acids (SCFAs; C<sub>10–18</sub>) are considered to have a diversity of OC sources, including terrestrial plants, marine algae, and bacteria (Waterson and Canuel, 2008). In contrast, the even-numbered long-chain fatty acids (LCFA, C<sub>24–32</sub>), as one of the major compositions of leaf waxes, is produced exclusively by terrestrial sources (Cui et al., 2016). The ratios of terrestrial to aquatic fatty acids ( $TAR_{FA}$ ; C<sub>24+26+28</sub>/C<sub>12+14+16</sub>) is largely controlled by terrestrial OC contributions (Waterson and Canuel, 2008) and early degradation (Haddad et al., 1992).

In addition, we analyzed sediments for excess <sup>210</sup>Pb, bulk OC, and  $\delta^{13}C$  on 9 cores that covered spatial gradients from north-to-south and from fjord head-to-mouth locations. Principle component analysis (PCA) was performed to investigate physical drivers responsible for the variation in bulk and biomarker data among surface sediment samples and terrestrial end-members. All the data were normalized to mean values prior to PCA. For statistical analysis, one-tail and two-tails *t*-tests, based on data distribution, were performed to determine any significant differences between

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