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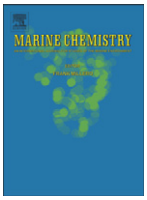

# Sources of organic matter in a coastal marine environment: Evidence from *n*-alkanes and their $\delta^{13}C$ distributions in the Hauraki Gulf, New Zealand

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ABSTRACT

The distribution and $\delta^{13}C$ composition of sedimentary *n*-alkanes ($C_{14}$–$C_{34}$) were investigated to determine the origins of organic matter in surface sediments in a subtropical, non-riverine dominated coastal shelf. Core-top sediments were collected in the Hauraki Gulf, New Zealand, from three nearshore sites and four offshore sites that represent a range of depths and distances to land. Total *n*-alkane concentrations varied 2-fold ranging from 326 to 819 μg $g^{-1}$ and *n*-alkane $\delta^{13}C$ ranged from −21.2‰ to −38.9‰. Source apportionment was calculated using marine and terrestrial end-member values for *n*-alkane chain lengths and isotopic composition to derive an inventory of marine versus terrestrial organic matter. Using this multi proxy approach, marine inputs were shown to be relatively constant across the Hauraki Gulf. In contrast, concentrations of terrestrial *n*-alkanes varied 4-fold across the study sites. Terrestrial contributions were 56–65% of total *n*-alkanes, dominating at all but those sites most remote from land where terrestrial *n*-alkanes levels still comprised ~40–45% of the characterized organic matter. Bulk analyses (e.g. $\delta^{13}C$ of total organic carbon and C/N ratios) poorly resolved terrestrial inputs in this complex coastal environment. The success of the multi-proxy approach in identifying terrestrial input is attributed to the ability to resolve inputs from coastal sources of organic matter such as mangroves and sea grasses that can mask terrestrial sources. Organic carbon accumulation rates were relatively constant on the shelf (4.0 to 4.5 mg $cm^{-2}$ $year^{-1}$), highest at a deeper site on the outer shelf (10.7 mg $cm^{-2}$ $year^{-1}$), and lowest on the upper slope (3.2 mg $cm^{-2}$ $year^{-1}$). Alkane accumulation rates (19 to 140 μg $cm^{-2}$ $year^{-1}$) were more variable, with burial rates of terrestrial alkanes on the shelf averaging 1.5 times that of marine accumulation rates. The isotopic and biomarker data indicate that even in what is considered a marine-dominated coastal environment, an appreciable amount of terrestrial organic matter is readily transported from its locus of input across the shelf to be buried in outer-shelf depocenters.

## 1. Introduction

Coastal zones are areas that are the dominant location for organic matter deposition on a global basis. However, resolving the importance of local *in situ* production versus influx of terrestrial organic matter remains a largely open question of carbon cycling (Benner, 2004; Hedges et al., 1997) These near-shore environments serve as the mixing zone between terrestrial and oceanic organic matter inputs but the fate of organic matter on non-river dominated shelves remains an open question.. Numerous studies have investigated terrestrial inputs to marine sediments in both river-dominated coastal environments and in estuarine systems (e.g. Canuel et al., 1997; Goñi et al., 1997; Prahl et al., 1994; Prahl and Muehlhausen, 1989). Studies using multiple biogeochemical techniques, primarily biomarkers in combination with carbon isotopic analyses, have been the most successful in elucidating the sources of organic matter in the complex environment of near shore and shelf sediments. From these studies, a common picture emerges with the presence of a terrestrial signal being uncertain upon examination of the bulk parameters, whereas the persistence of a terrestrial component becomes obvious when multiple geochemical tracers are used (e.g. Canuel et al., 1997; Drenzek et al., 2007; Goñi et al., 1997, 1998; Gordon and Goñi, 2004; Hedges et al., 1997; Hedges and Mann, 1979; Jaffé et al., 2001; Kao et al., 2006; Mead et al., 2005; Naraoka and Ishiwatari, 1999; Pearson and Eglinton, 2000; Prahl et al., 1994).

Straight chain alkanes (*n*-alkanes) are common biomarkers found in sedimentary organic matter. They are known to be biosynthesized by a wide variety of both marine and terrestrial plants. In higher plants, *n*-alkanes are derived from epicuticular waxes, have long chain lengths ($C_{25}$–$C_{35}$), and an odd over even chain length predominance (Eglinton and Hamilton, 1967). The shorter chain *n*-alkanes ($C_{14}$–$C_{24}$)

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are mainly of algal or phytoplankton origin (Meyers and Ishiwatari, 1993). Recent studies have shown that freshwater aquatic macrophytes and marine macrophytes have dominant mid-chain length *n*-alkanes ($C_{23}$–$C_{27}$) and mangroves have slightly longer mid-length chains ($C_{27}$–$C_{29}$) (Ficken et al., 2000; Mead et al., 2005). Traditionally, the difference in characteristic chain lengths of marine and terrestrial plants made the distribution of *n*-alkanes an effective biomarker tool for assessing sources of organic matter in terrestrial and marine sediments. However, significant mangrove, marine macrophyte, and/or significant riparian–aquatic inputs introduce sources with non-unique *n*-alkane compositions to the system making effective determination of sources by *n*-alkane chain length alone difficult in such complex environments.

Although *n*-alkanes have non-unique chain length signatures, the carbon isotopic signature can be used to better distinguish among sources (e.g. Canuel et al., 1997; Collister and Hayes, 1992; Collister et al., 1994a; Freeman and Hayes, 1992). Differences in the isotopic content of source $CO_2$ for terrestrial (atmospheric) and marine plants (seawater) leads to about a 7‰ difference between the overall, or bulk, isotopic content of marine organic matter (typically −18 to −23‰) and $C_3$ terrestrial organic matter (typically −26 to −27‰; e.g. Fry and Sherr, 1984; Hayes et al., 1990). Further fractionation after fixation occurs such that lipids including *n*-alkanes are depleted in $^{13}C$ by as little as 0‰ and as much as 11‰ relative to total organic carbon (Canuel et al., 1997; Cifuentes and Salata, 2001; Ficken et al., 2000; Pancost et al., 1999). The variation may be controlled largely by growth rates (e.g. Bidigare et al., 1997). Terrestrial $C_3$ *n*-alkanes resolved in sediments typically have a $\delta^{13}C$ of −33 to −39‰ (e.g. Bird et al., 1995; Naraoka and Ishiwatari, 1999) whereas phytoplankton lipids are more typically about −19 to −27‰ (e.g. Bidigare et al., 1997; Pancost et al., 1999). Freshwater (terrestrial) aquatic plants including mangroves have *n*-alkanes isotopic signals that are terrestrial (~−28 to −40‰) (Ficken et al., 2000; Mead et al., 2005). In contrast, marsh grasses, sea grasses, and marine macrophyte alkanes are more enriched than phytoplankton (−13 to −22‰ (Canuel et al., 1997; Ficken et al., 2000; Mead et al., 2005). Importantly, despite non-unique chain length signatures and ambiguous bulk organic carbon $\delta^{13}C$ in coastal zones, the isotopic composition of the biomarkers in terrestrial, aquatic, and marine sources is distinct and can be used to clarify organic carbon inputs to coastal ocean sediments (e.g. Bird et al., 1995; Canuel et al., 1997; Cifuentes and Salata, 2001; Goñi et al., 1997, 1998; Gordon and Goñi, 2004; Jaffé et al., 2001; Mead et al., 2005; Naraoka and Ishiwatari, 1999).

### *1.1. Study area and oceanographic setting*

The Hauraki Gulf, a shallow, semi-open coastal embayment bounded by outer islands, is located on the northeast coast of the North Island, New Zealand (Fig. 1). The gulf is bounded on the south and west by the mainland and on the east by the Coromandel Peninsula and several islands, the largest of which is Great Barrier Island. The Auckland metropolitan area (the largest city in New Zealand; ~1 million people) sits on the southwestern edge of the gulf. Whangarei city is a regional center in the north (~50,000 people). The continental shelf in the gulf is ~80 km wide, relatively flat and about twice as wide as the shelf to the north and south along this portion of the North Island coastline. The shelf break is at approximately 150 m water depth and marks the seaward extent of the gulf (Manighetti and Carter, 1999).

The southeastward-flowing East Auckland Current (EAUC) dominates the ocean circulation in the region, delivering subtropical

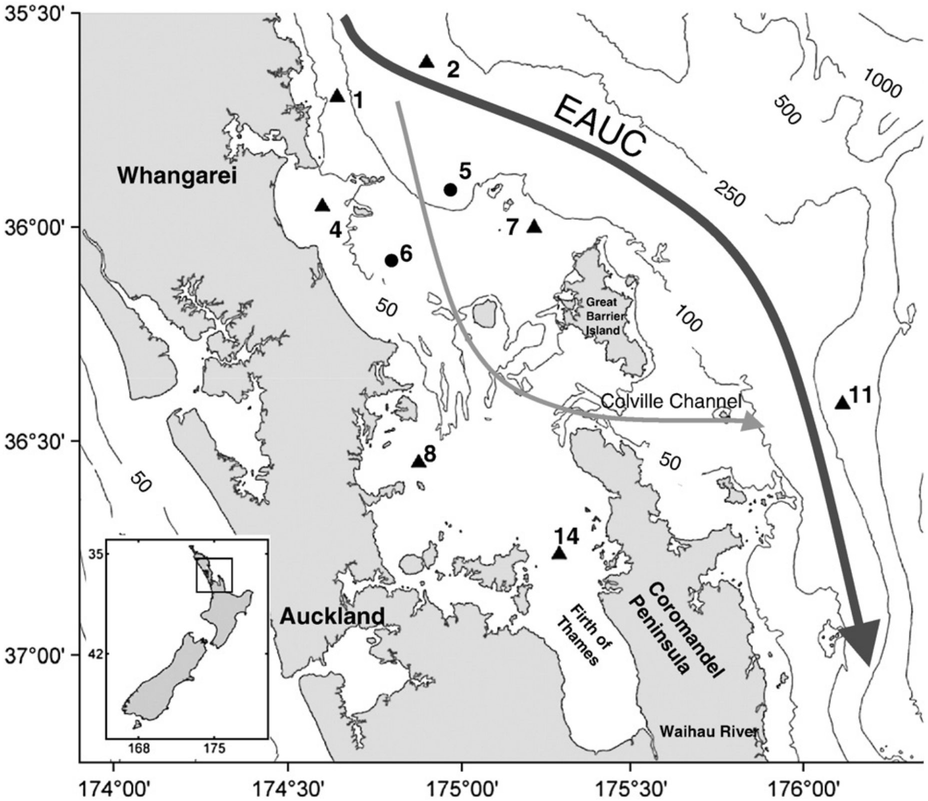

**Fig. 1.** Map of the Hauraki Gulf and study area. The inset map indicates study area in northern New Zealand. Sample sites with lipid analyses are designated by black triangles, sites at which supporting bulk measurements were conducted are designated by circles. The prevailing direction of the East Auckland Current (EAUC) is designated by the dark arrow. The net circulation of the gulf, driven by residual tidal flow, is indicated by the light arrow. Net flow through the gulf is considered to converge and exit the gulf through the Collville Channel. Moderate-sized rivers enter the gulf through the estuary at Whangarei and at the south end of the Firth of Thames. Mangroves and sea-grass beds are common in sheltered sections along the western and northern portion of the coastline.