Estuarine, Coastal and Shelf Science 136 (2014) 157–171

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Biomarkers reveal the effects of hydrography on the sources and fate of marine and terrestrial organic matter in the western Irish Sea

Shane S. O'Reilly [a], Michal T. Szpak [a], Paul V. Flanagan [a], Xavier Monteys [b], Brian T. Murphy [a], Sean F. Jordan [a], Christopher C.R. Allen [c], Andre J. Simpson [d], Stephen M. Mulligan [a], Sara Sandron [a], Brian P. Kelleher [a,]*

[a] School of Chemical Sciences, Dublin City University, Dublin 9, Ireland
[b] Geological Survey of Ireland, Beggars Bush, Haddington Rd., Dublin 4, Ireland
[c] School of Biological Sciences, Queen's University Belfast, Medical Biology Centre, Lisburn Road, Belfast BT9 5AG, N. Ireland, UK
[d] Department of Chemistry, Division of Physical and Environmental Science, University of Toronto at Scarborough, 1265 Military Trail, Toronto, Ontario M1C 1A4, Canada

ARTICLE INFO

Article history:
Received 4 July 2013
Accepted 4 November 2013
Available online 13 November 2013

Keywords:
lipid biomarkers
organic matter cycling
plankton
phospholipid fatty acids
Irish Sea

ABSTRACT

A suite of lipid biomarkers were investigated from surface sediments and particulate matter across hydrographically distinct zones associated with the western Irish Sea gyre and the seasonal bloom. The aim was to assess the variation of organic matter (OM) composition, production, distribution and fate associated with coastal and southern mixed regions and also the summer stratified region. Based on the distribution of a suite of diagnostic biomarkers, including phospholipid fatty acids, source-specific sterols, wax esters and C_{25} highly branched isoprenoids, diatoms, dinoflagellates and green algae were identified as major contributors of marine organic matter (MOM) in this setting. The distribution of cholesterol, wax esters and C_{20} and C_{22} polyunsaturated fatty acids indicate that copepod grazing represents an important process for mineralising this primary production. Net tow data from 2010 revealed much greater phytoplankton and zooplankton biomass in well-mixed waters compared to stratified waters. This appears to be largely reflected in MOM input to surface sediments. Terrestrial organic matter (TOM), derived from higher plants, was identified as a major source of OM regionally, but was concentrated in proximity to major riverine input at the Boyne Estuary and Dundalk Bay. Near-bottom residual circulation and the seasonal gyre also likely play a role in the fate of TOM in the western Irish Sea.

1. Introduction

Cycling of organic matter (OM) is the key biological process in the marine environment (Chester and Jickells, 2012). Knowledge of sources and the reactivity of OM, in addition to factors controlling its distribution in estuarine, coastal and shelf sediments are of key importance for understanding global biogeochemical cycles (Baldock et al., 2004). Marine systems contribute an estimated 44 to 50 GtC a^{-1} of new OM to the biosphere and are approximately equal to the terrestrial system (Harvey, 2006). Continental margins account for approximately 90% of global sedimentary organic matter (SOM) and thus are an important component of the marine organic matter (MOM) pool (Hedges and Keil, 1995). Coastal and shelf SOM is typically derived from a complex distribution of autochthonous water column sources, in addition to allochthonous terrestrial sources. The sources and fate of MOM in these settings are diverse and dependent on the intensity of both autochthonous and allochthonous input (Harvey, 2006). In addition differences in OM molecular composition, regional sedimentological and oceanographic regimes, and processes mediating the preservation and mineralisation of OM are important parameters in MOM cycling (Hedges and Keil, 1995).

Autochthonous SOM is primarily derived from particulate sinking detritus from the photic zone, whereby the OM flux is typically proportional to the amount of primary production and

---

Abbreviations: brFA, Branched Fatty Acids; CMR, Coastal Mixed Region; HBIs, Highly Branched Isoprenoids; MOM, Marine Organic Matter; MUFA, Monounsaturated Fatty acids; OM, Organic Matter; PCA, Principal Component Analysis; PLFA, Phospholipid Fatty Acid; PUFA, Polyunsaturated Fatty Acids; SATFA, Saturated Fatty Acids; SMR, Southern Mixed Region; SOM, Sedimentary Organic Matter; SSR, Summer Stratified Region; TN, Total Nitrogen; TOC, Total Organic Carbon; TOM, Terrestrial Organic Matter; WE, Wax Esters.

* Corresponding author.
E-mail addresses: brian.kelleher@dcu.ie, shane.oreilly@dcu.ie (B.P. Kelleher).

0272-7714/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ecss.2013.11.002

inversely so with water depth (Rullkötter, 2006). This is reflected in the fact that in coastal settings 25–50% of primary production reaches the seafloor, compared to typically less than 1% in deep sea settings (Suess, 1980). Rivers transport about 1% of terrestrial productivity (60 Gt C a^{-1}) to the marine environment, while aeolian input can be an order of magnitude lower (~0.1 Gt C a^{-1}) (Hedges et al., 1997). Thus, riverine input is the major source of terrestrial OM (TOM) in marine settings, in particular in coastal and shelf settings. Despite significant attention for a number of decades, the fate of TOM in the marine environment remains poorly understood (Hedges et al., 1997; Baldock et al., 2004).

The Irish Sea, lying between the landmasses of Great Britain and Ireland, has received little attention from the perspective of OM cycling. Although relatively small in size, it is characterised by large regional differences in oceanographic and sedimentological conditions, nutrient chemistry and ecology (Kennington and Rowlands, 2006). In particular a seasonal gyre occurs in the western Irish Sea each year, and is formed when thermal stratification isolates a dome of cold dense bottom water in the deep (>100 m) western Irish Sea basin. The resulting density fields drive a cyclonic gyre, which dominates the circulation of the region during late spring and summer and separates the surrounding well-mixed areas by tidal mixing fronts (Hill et al., 1994; Horsburgh et al., 2000). Frontal zones are generally considered high productivity settings (Tolosa et al., 2005) and mean chlorophyll concentrations between well-mixed (~23 mg m^{-3}) and stratified offshore waters (~16 mg m^{-3}) in the western Irish Sea attest to this (Gowen and Stewart, 2005). It has been proposed that this summer gyre may act as a retention system for planktonic larvae of commercially valuable *Nephrops norvegicus* (Hill et al., 1996), for larval and juvenile fish, for zooplankton (Dickey-Collas et al., 1996, 1997), and possibly for anthropogenic contaminants (Hill et al., 1997). Furthermore, documented changes in the Irish Sea as a result of anthropogenic activity include: increases in nutrient concentrations and primary productivity (Allen et al., 1998); an increase in mean sea surface temperature of about 1 °C over the last four decades; and also distinct regional differences in salinity and nutrient relationships and in the timing and duration of phytoplankton blooms (Evans et al., 2003). It is evident that without baseline knowledge of natural processes it will be difficult to ascertain the environmental and ecological effects of climate change.

However, despite the fundamental role of OM in the marine environment and for marine ecosystems, few studies have focused on OM cycling in the Irish Sea (Gowen et al., 1995, 2000; Trimmer et al., 1999, 2003), and to our knowledge none have studied the composition, sources and fate of OM in the Irish Sea. In this study we applied a suite of molecular level lipid biomarkers in conjunction with bulk physical and chemical parameters to study TOM and MOM cycling in surface sediments and net tow particulate matter collected from well-mixed coastal and offshore summer-stratified waters in the western Irish Sea. Although lipids represent a small fraction of OM, their diversity, specificity and relative recalcitrance makes them useful for studying the sources, transport and fate of OM, especially when combined with other bulk measurements, compound specific stable carbon isotope ($\delta^{13}C$) analysis, and multivariate statistical analysis (e.g. Westerhausen et al., 1993; Zimmerman and Canuel, 2001; Belicka et al., 2002, 2004; Jeng et al., 2003; Schmidt et al., 2010; Burns and Brinkman, 2011). This study combined analysis of biomarkers with typically high preservation potential (e.g. *n*-alkanes, sterols) with biomarkers with low preservation potential (e.g. ester-linked phospholipids; White et al., 1979, 1997) across the mixed and stratified zones. Thus the aims of this study were to: (1) investigate the relative contribution of marine and terrestrial input to SOM in coastal and offshore surface sediments; (2) elucidate likely transport mechanisms by investigating the spatial distribution of SOM; and (3) investigate whether the distinct seasonal gyre plays a role in transport and fate of OM in this setting.

2. Oceanographic and environmental setting

The Irish Sea (Fig. 1) is connected with the Atlantic Ocean by the North Channel and St. George's Channel on the south. Water depths range from less than 20 m in the coastal areas to over 100 m in the central region. Water transport through the sea is generally considered to be northwards, with flow rates in the region of 2–8 km^3 d^{-1} (Gowen and Stewart, 2005, and references therein), but there is also exchange to the North and seawater movement tends to be highly variable (Kennington and Rowlands, 2006). Local meteorological conditions are known to have a major influence on transport through the two channels (Knight and Howarth, 1999). Waters are generally well mixed throughout the Irish Sea and ensure vertically homogeneous water column conditions over the year (Hill et al., 1994). However, waters in the western region are generally deeper (>100 m), exhibit lower tidal energies and have higher salinity values (Gowen et al., 1995), factors attributing to the strong seasonal gyre that develops in the summer months upon onset of the summer thermocline (Hill et al., 1994). This results in an offshore Summer Stratified Region (SSR), which is distinct from Coastal and Southern Mixed Regions (CMR and SMR, respectively) (Fig. 1). The northwest region (north of 53.5°N) is characterised by weaker hydrodynamic conditions, allowing the deposition of fine-grained particles and is dominated by a smooth muddy seabed. This is in contrast to the southern region (south of 53.5°N), which is subject to comparatively high-energy currents and is characterised by sands, gravelly sands and high-energy bedforms. Thus, sediment type closely reflects the distinct hydrographic zones in the western Irish Sea (Trimmer et al., 2003). The Irish Sea has an estimated total catchment area of about 43,000 km^2, whereby the greatest freshwater input is understood to be in the eastern Irish Sea, from the Solway Firth to Liverpool Bay (Bowden, 1980).

3. Materials and methods

3.1. Sampling and bulk analysis

Surface sediments were sampled in June 2010 during INFOMAR (Integrated Mapping for the Sustainable Development of Ireland's Marine Resource) survey CV10_28 aboard the RV Celtic Voyager. Sediment pushcores ($n = 55$) were taken using a Reineck boxcorer. Samples for lipid analysis were stored at −20 °C onboard and at −20 °C in the laboratory. Vertical tow nets (30 cm diameter, 20 μm mesh size) were deployed in vertical haul (0–30 m water depth) at two stations, T1 in waters in the SMR and T2 in waters in the SSR (Fig. 1). Two casts were deployed at each station and pooled together to yield a representative sample. Large debris and larger organisms were removed and the particulates were vacuum-filtered through pre-combusted GF/A filters. Particle size analysis ($n = 50$) was performed with laser granulometry (Malvern MS2000). For total organic carbon (TOC) and total nitrogen (TN) analysis, sediment ($n = 20$) was sub-sampled from 0–2 cm from pushcores and inorganic carbon was removed by addition of 1 M HCl and analysed using an Exeter Analytical CE440 elemental analyser.

3.2. Lipid biomarker analysis

Sediment samples (0–2 cm) were freeze-dried, ground and sieved, while particulates retained on GF/A filters were also freeze-dried. Freeze-dried samples were extracted by a modified Bligh–