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

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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.

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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–

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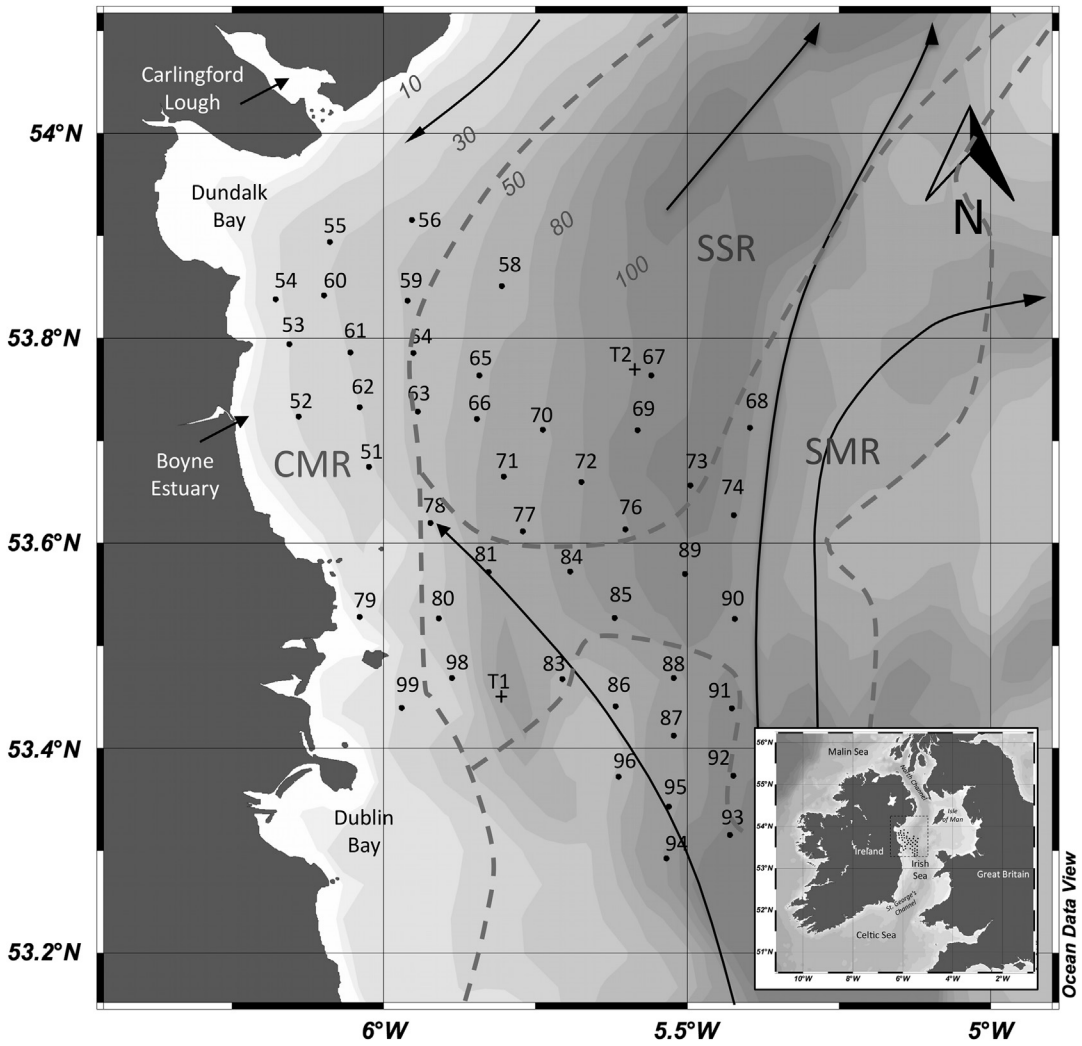

Fig. 1. Map of the Irish Sea and study area location. Sediment boxcore stations are numbered and marked with a black circle. Plankton net tow stations are shown as crosses (T1 and T2). Broken grey lines represent approximate summer hydrographic regions (from Gowen et al., 1995) and black arrows represent the near-bottom residual circulation (from Ramster et al., 1969). SSR – Summer Stratified Region, CMR – Coastal Mixed Region, SMR – Southern Mixed Region.

Dyer method (White et al., 1997). After addition of 2:1:0.8 (v/v) methanol, chloroform and phosphate buffer (pH 7.2), samples were sonicated for 2 min and subsequently extracted on a horizontal shaker for 18 h. After centrifugation, organic and aqueous phases from the supernatant were split by addition of solvent to achieve a solvent ratio 1:1:0.9 (v/v). The total extract was collected and concentrated by rotary evaporation. After desulfurisation with activated copper overnight, extracts were fractionated by solid phase extraction according to Pinkart et al. (1998). Briefly, a portion of total extract was added to aminopropyl cartridges (Alltech 500 mg Ultra-Clean) and eluted with 5 mL chloroform (neutrals), 5 mL acetone (glycolipids), and finally with 5 mL 6:1 (v/v) methanol/chloroform, followed by 5 mL 0.05 M sodium acetate in 6:1 (v/v) methanol/chloroform. These were combined to comprise the polar lipid fraction.

The neutral lipid fractions were derivatised with N,O-bis(trimethylsilyl)trifluoroacetamide/pyridine (9:1, v/v) (70 °C, 2.5 h). Phospholipids in the polar fraction were derivatised using 0.5 M sodium methoxide (50 °C, 30 min). PLFA monounsaturation position was confirmed by formation of dimethyl disulfide adducts as outlined by Nichols et al. (1986). One microlitre aliquots of derivatised extracts were injected in splitless mode onto an Agilent 6890N gas chromatograph interfaced with an Agilent 5975C mass spectrometer (MS). Separation was achieved on a HP-5MS fused silica capillary column (Agilent: 30 m × 0.25 mm I.D. and film thickness of 0.25 μm). The injector and MS source were held at 280 °C and 230 °C, respectively. The column temperature program was as follows: 65 °C injection and hold for 2 min, ramp at 6 °C min^{-1} to 300 °C; followed by isothermal hold at 300 °C for 20 min. The MS was operated in electron impact mode with an ionisation energy of 70 eV and a mass scan range set from m/z 50 to 650. Data was acquired and processed using Chemstation software (revision 2.0 E). All reported compounds were confirmed using a combination of mass spectral libraries, interpretation of mass fragmentation patterns, compound retention times and by comparison with literature. 5α-cholestane was used as an internal injection standard and response factors for lipid classes were calculated using a suite of representative standards (nonadecane, tetradecanoic acid, stigmasterol, squalane, β-amyrin). Recovery experiments were also conducted in triplicate by spiking a sediment sample with nonodecane, 5α-cholestane, stigmasterol and tetradecanoic acid. Procedural blanks were run to monitor background interferences.

Selected samples (BC52, BC72, BC78, BC85) were analysed by a gas chromatograph under conditions as described above, but coupled to a continuous flow isotope ratio mass spectrometer

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(IsoPrime) via a combustion furnace (GC5, CuO/Pt 650). $\delta^{13}C$ values were measured against a reference gas CO_2 of known $\delta^{13}C$ value. $\delta^{13}C$ values were reported against a stable isotope reference standard (*n*-alkanes mixture B2, Indiana University, US). All samples were measured in duplicate and average $\delta^{13}C$ values are reported after correction for addition of derivative groups where necessary. The standard deviation for the instrument, based on replicate standard injection was calculated to be ±1.00‰ or better. Only well-resolved major analytes are reported here, and are limited to major compounds within biomarker classes.

3.3. Data and statistical analysis

Biomarker data is primarily expressed relative to TOC or percentage abundance rather than simply against dry mass weight of sediment. This helps remove gross variation based solely on grain size and helps identify changes in relative input (e.g. Canuel and Martens, 1993; Westerhausen et al., 1993; Belicka et al., 2004; Hu et al., 2006). Statistically significant correlations between measured bulk parameters and biomarker classes were calculated using PAST by calculating Pearson correlation coefficients (r) with PAST software (v1.75) (Hammer et al., 2001). P values less than 0.05 were considered statistically significant. Distribution maps of lipid biomarker data were constructed in Ocean Data View (Schlitzer, 2002) using the diva gridding algorithm. Hierarchical cluster analysis of multivariate data from each station was performed in PAST to test if stations grouped according to mixed and stratified hydrographic regions. Ward's minimum variance method (Ward Jr., 1963) was used to cluster bulk and lipid biomarker data shown in Table 1. Principal component analysis (PCA) was also performed in PAST in an attempt to simplify multivariate biomarker data and attribute source relationships between biomarkers and to identify key biomarkers for describing OM sources and relative stability. For each observation (station, $n = 20$), variables (biomarkers/biomarkers proxies, $n = 32$) were normalised between 0 and 1 to remove artefacts related to the large differences in concentrations.

4. Results

Summary data for bulk physical and chemical analysis, and for major biomarkers and biomarker classes for sediment stations is given in Table 1. Summary data for biomarkers in plankton net tows are given in Table 2. Biomarker and biomarker class abbreviations used throughout the text are detailed in Table 3, along with proposed major sources and key references.

4.1. Bulk physical and chemical parameters

Sediment grain size ranged from 26 μm to 1467 μm across the region, with a clear distribution of fine-grained poorly to very poorly sorted silty sand/sandy silt north of 53.5°N and moderately sorted to well sorted sand to the south (Fig. 2A–C). A strong positive correlation between clay and silt fractions and water depth was observed (clay; $r = 0.68$, $P = 0.001$). Offshore, silt and clay accounts for 50 to over 70% and 15 to over 25% of sediment type in this region, respectively (clay; Fig. 2D). TOC ranged from 1.57% in deeper waters in the centre of the mudbelt i.e. the SSR, to 0.03% south of the mudbelt closer to the coast i.e. the SMR (Fig. 2E), and are in agreement with previous reports (Charlesworth and Gibson, 2002). TOC is very strongly positively correlated with clay ($r = 0.89$, $P < 0.001$) and silt ($r = 0.84$, $P < 0.001$). TN distribution largely reflects TOC (Fig. 2F). C/N values ranged from 8.7 in the deepest offshore station (BC67) to over 33.5 in fine-grained coastal sediment at BC54.

4.2. Aliphatic hydrocarbons and alcohols

n-alkanes and *n*-alkanols were among the major lipids found in the neutral lipid fractions from these surface sediments (Table 1). *n*-alkanes ranged from C_{16} to C_{33} with LC_{HC} being most abundant (24.7–63.3% of total). *n*-alkanols ranged from C_{14} to C_{32} and were dominated by LC_{OH} (61.4–77.7% of total). LC_{HC} and LC_{OH} were very strongly positively correlated ($r = 0.96$, $P < 0.001$) and their spatial distribution was similar overall, with the highest abundance found in fine-grained coastal sediments (highest at BC53; Table 1). TOC and TN were strongly correlated with these lipids classes, whereby TN exhibited stronger correlations. When normalised to TOC, LC_{OH} and LC_{HC} revealed clear distributions, whereby a transition from highest concentrations in the CMR and SMR to lowest concentrations in the SSR was evident (Fig. 3B and C). The CPI_{HC}, defined following the equation of Zhang et al. (2006) (see Table 1) was 3.2 on average and ranged from 2.1 to 5.3. Calculated CPI_{OH} averaged 6.9 and ranged from 4.5 to 11.6. CPI_{HC} and CPI_{OH} were highest in fine-grained coastal sediments in the CMR (Fig. 3D; CPI_{OH}). $\delta^{13}C$ values for measured LC_{OH} ranged from −34.86 ± 0.10 to −35.93 ± 0.21‰, while for LC_{HC} ranged from −32.48 ± 0.11 to −33.35 ± 0.71‰ (Fig. 4).

n-alkanes were also identified in particulate matter but were limited to C_{15}, C_{18}, C_{19} and C_{22}. $C_{19:1}$ also occurred and was more abundant than the *n*-alkanes, in particular at T2. Pristane abundance was generally low, although higher abundances were observed at stations BC53, BC56 and BC65. Pristane was found in much higher concentrations at T1 compared to T2 in the SSR (Table 2). Phytane was present at most boxcore stations and was found at highest concentrations in BC53, BC56 and BC65, while it was not detected at either net tow stations. At these stations phytane was over double the abundance of pristane while in all other boxcore stations pristane was more abundant. Phytadienes were observed (reported cumulatively) at much higher abundance at T2. In total hydrocarbons were about twice the concentration at T2 compared to T1 (Table 2).

n-alkanols were also found in high abundance in net tows and ranged from C_{14} to C_{26}. Aliphatic alcohols were found in much higher abundance at T1 compared to T2 (Table 2). In addition *n*-alkenols occurred in high abundance, and represented 51% of total aliphatic alcohols at T1 and 48% at T2. These included C_{16}, C_{18}, C_{20}, C_{22}, C_{24} and C_{26} alkenols. *n*-alkenols less than C_{20} were not observed at T2 and at both stations $C_{22:1}$ was the major homologue. Methyl-branched alkanols were also observed at T1 but not at T2, and ranged from C_{14} to C_{18} chain lengths. Phytol was present at all sediment stations and ranged from 2 μg g OC^{-1} up to 34 μg g OC^{-1}. In the net tows, abundances were 27.8 μg g dw^{-1} and 21.0 μg g dw^{-1} for T1 and T2, respectively. Phytol was strongly positively correlated with the sterol classes and C_{25} HBIs. In particular a very strong positive correlation was observed between phytol and C_{28} sterols ($r = 0.93$, $P < 0.0001$).

4.3. Sterols and triterpenoids

A suite of up to twenty-two sterols and stanols were identified in surface sediments and seventeen from the particulate matter. Total sterols were strongly positively correlated with LC_{HC} ($r = 0.71$, $P < 0.001$) and LC_{OH} ($r = 0.84$, $P < 0.001$) but a stronger relationship was observed between total sterols and LC_{OH}. Of the main sterol classes, C_{28} sterols exhibited the lowest correlation coefficient for LC_{HC} ($r = 0.57$, $P < 0.02$). Higher molecular weight sterols ($\geq C_{29}$) were more strongly correlated with LC_{HC} than the lower molecular weight sterols (C_{26} to C_{28}). This relationship was also observed for LC_{OH}. Most sediment samples were dominated (average of 58.9% of total sterols) by $C_{27}\Delta^5$, $C_{28}\Delta^{5,22}$, $C_{28}\Delta^{5,24(28)}$, $C_{28}\Delta^5$, $C_{29}\Delta^5$, $C_{27}\Delta^{5,22}$

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Table 1
Boxcore sample station locations and summary of bulk parameters and biomarker data.

Station	BC51	BC52	BC53	BC54	BC55	BC56	BC58	BC63	BC64	BC65	BC66	BC67	BC70	BC72	BC73	BC76	BC78	BC79	BC81	BC85
Region	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed	Stratified	Stratified	Stratified	Stratified	Stratified	Stratified	Stratified	Stratified	Stratified	Stratified	Mixed	Mixed	Mixed	Mixed
Latitude	53.6746	53.7239	53.7944	53.8383	53.8938	53.9156	53.8511	53.7283	53.7859	53.7636	53.7214	53.7638	53.7110	53.6597	53.6564	53.6133	53.6196	53.5281	53.5720	53.5272
Longitude	−6.0242	−6.1401	−6.1552	−6.1782	−6.0887	−5.9535	−5.8055	−5.9439	−5.9510	−5.8426	−5.8470	−5.5590	−5.7377	−5.6745	−5.4949	−5.6018	−5.9230	−6.0400	−5.8275	−5.6200
Depth (m)	29.6	19.1	24.4	21.5	31.9	41.9	41.9	42.8	42.8	54.1	54.9	102.7	77.7	90.7	110.8	102.7	45.5	12.4	66.6	95.8
Grain size (ϕ)	3.06	3.11	3.83	3.54	3.04	4.4	5.18	4.01	4.13	4.59	4.36	5.46	4.91	4.93	4.36	4.91	3.05	2.31	3.28	3.19
Sorting	2.1	2.1	2.2	1.9	2.2	2.2	2.0	2.2	2.2	2.2	2.2	1.9	2.0	2.1	2.3	2.1	1.9	1.0	2.0	2.4
Clay (%)	6.8	9.0	13.3	8.2	9.0	20.6	24.0	14.9	15.8	19.5	17.3	27.2	20.4	23.5	20.6	26.3	6.1	0.7	8.6	12.0
Silt (%)	20.1	17.9	39	28	24.3	57.7	66.2	44.6	47.9	58.1	54.2	66.2	64.9	60.9	49	58.2	16.8	4.4	23.6	25.4
Mud (%)	26.9	26.9	52.3	36.2	33.3	78.3	90.2	59.5	63.7	77.6	71.5	93.4	85.4	84.4	69.6	84.5	22.9	5.1	32.3	37.4
Sand (%)	73.1	73.1	47.7	63.8	66.7	21.7	9.8	40.5	36.3	22.4	28.5	6.6	14.6	15.6	30.4	15.5	77.1	94.9	67.7	62.6
TOC (%)	0.4	0.55	1.09	0.67	0.83	1.05	1.21	0.65	1.15	1.19	1.01	1.57	1.18	1.27	1.52	1.33	0.66	0.09	0.75	1.07
TN (%)	0.04	0.05	0.11	0.02	0.05	0.12	0.12	0.06	0.07	0.11	0.08	0.18	0.13	0.13	0.12	0.11	0.03	nd	0.06	0.08
C/N	10.5	11.0	9.9	33.5	16.6	8.8	10.1	10.8	16.4	10.8	12.6	8.7	9.1	9.8	12.7	12.1	22.0	nd	12.5	13.4
LC_{HC}	147	167	319	116	90	138	78	96	65	109	100	87	102	89	77	129	54	135	67	125
CPI_{HC}	3.8	3.1	3.4	5.3	2.1	4.0	3.4	3.2	3.7	2.6	3.5	2.8	3.3	2.9	3.2	2.6	3.0	2.4	2.6	3.5
LC_{OH}	116	166	299	84	110	183	77	89	59	108	115	72	86	78	63	121	54	159	86	156
CPI_{OH}	5.1	5.7	11.6	7.0	8.4	7.4	6.8	5.7	6.7	6.0	6.5	6.5	6.1	6.0	6.3	5.9	10.8	4.5	6.2	8.1
Σsterols	299	392	731	276	346	817	165	47	115	207	479	143	201	129	142	247	262	907	454	361
ΣC_{26}	17	21	32	16	14	31	9	nd	8	13	18	10	14	10	9	15	11	60	30	16
ΣC_{27}	107	141	223	100	123	203	38	16	29	56	109	37	66	31	43	75	99	363	129	137
ΣC_{28}	101	132	255	91	114	378	61	11	40	68	221	54	58	44	46	78	90	258	204	110
ΣC_{29}	59	83	181	58	73	168	45	7	30	54	108	33	50	33	36	64	50	203	76	79
ΣC_{30}	15	15	40	11	22	38	12	12	9	15	23	10	13	11	9	15	12	23	14	18
ΣPLFA	1188	564	317	749	575	355	481	211	280	223	502	502	557	252	208	199	378	1351	999	577
ΣSATFA	344	174	94	206	183	114	146	82	83	60	151	127	156	91	63	53	139	420	315	164
ΣMUFA	483	233	117	290	227	140	183	66	109	90	180	186	215	96	86	79	147	521	359	215
ΣPUFA	124	54	18	72	50	22	24	3	17	19	38	39	50	9	17	18	30	97	144	67
ΣbrFA	237	103	89	183	115	79	128	61	72	55	133	151	136	57	43	48	62	312	181	130
Phytol	7	8	17	5	15	34	3	2	2	6	19	7	6	4	3	6	5	13	18	10
Pristane	1	1	23	3	2	23	4	1	<1	14	2	2	1	<1	2	1	2	2	2	2
Phytane	nd	nd	52	1	1	50	2	<1	<1	29	<1	<1	<1	<1	1	<1	nd	2	<1	<1
Phytadienes	17	7	nd	11	9	6	9	3	5	nd	14	8	9	5	6	nd	nd	12	26	nd
C_{25} HBI	15	10	8	6	8	16	5	nd	2	5	11	3	4	1	6	5	nd	4	5	nd
Terpenoids	6	6	11	4	4	11	3	6	3	5	7	3	4	4	5	7	5	8	8	12

All biomarker data reported in μg g OC^{-1}; nd – not detected; LC_{HC} – Long chain odd carbon number *n*-alkanes; CPI_{HC} – $0.5[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})]$ (Zhang et al., 2006); LC_{OH} – Long chain even carbon number *n*-alkanols; CPI_{OH} – $0.5[(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})/(C_{23}+C_{25}+C_{27}+C_{29}+C_{31})+(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})/(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})]$ (Zhang et al., 2006); PLFA – Phospholipid fatty acids; SATFA – Saturated fatty acids; MUFA – Monounsaturated fatty acids; PUFA – Polyunsaturated fatty acids; brFA – branched (and cyclic) fatty acids; C_{25} HBI – C_{25} Highly branched isoprenoids.

Table 2
Plankton vertical tow net sampling stations and summary of biomarker data.

Station	T1	T2
Region	Mixed	Stratified
Latitude	53.4422	53.7638
Longitude	−5.8114	−5.5590
Σsterols	1428.2	413.4
ΣC_{26}	111.3	31.2
ΣC_{27}	962.5	210.8
ΣC_{28}	251.5	129.5
ΣC_{29}	73.1	30.4
ΣC_{30}	29.8	11.5
ΣPLFA	1080.0	439.8
ΣSATFA	515.5	252.2
ΣMUFA	211.1	120.8
ΣPUFA	333.1	59.2
ΣbrFA	20.4	7.6
Alkanols	207.6	12.9
Alkenols	247.0	31.1
Phytol	27.8	21.0
WE	954.8	11.7
ΣHydrocarbons	28.2	45.9
Alkanes	3.2	4.7
Alkenes	1.5	4.8
C_{25} HBI	12.5	16.5
Phytadienes	7.6	19.3
Pristane	3.3	0.6
Phytane	nd	nd

All biomarker data reported in μg g dw^{-1}, nd − not detected.

and $C_{30}\Delta^{22}$. Other sterols identified included $C_{26}\Delta^{5,22}$, $C_{26}\Delta^{22}$, $C_{27}\Delta^{22}$, $C_{27}\Delta^{5,24}$, $C_{28}\Delta^{22}$, $C_{29}\Delta^{5,22}$ and $C_{29}\Delta^{5,24(28)}$. C_{27} to C_{29} stanols accounted for an average of 10.8% of the sterol fractions. The spatial distribution of sterols showed distinct trends within this setting. Total sterols, normalised for TOC content, revealed a clear 2- to 3-fold increase in the CMR and SMR compared to the SSR (Fig. 5A) and there is an increased relative proportion of a number of sterols in stations from mixed hydrographic regions (Fig. 5B–D). $\delta^{13}C$ values for measured major sterols, including C_{29} sterols, ranged from −24.38 ± 0.51‰ to −27.63 ± 0.26‰ (Fig. 4). Sterol occurrence in net tows generally reflected those found in sediments. However station T1 in the SMR revealed an approximately 3-fold greater abundance of total sterols than at station T2 from the SSR (Table 2). Major sterols (79.5% of total) from T1 included $C_{27}\Delta^{5}$, $C_{27}\Delta^{5,24}$, $C_{27}\Delta^{5,22}$, $C_{28}\Delta^{5,24(28)}$ and $C_{26}\Delta^{5,22}$ (Fig. 6). In contrast, $C_{28}\Delta^{5,24(28)}$ was the major sterol at station T2 (23.2% of total), while $C_{27}\Delta^{5}$ accounted for 22.3%. Two triterpenoids were found in low abundance in most surface sediment samples − friedelin and β-amyrin, and were not observed in net tows. They were strongly positively correlated with LC_{OH} ($r = 0.77$, $P < 0.0001$) and LC_{HC} ($r = 0.58$, $P < 0.007$).

4.4. Other neutral lipids

WE abundance was negligible in surface sediments but were found in high concentrations at station T1 in the SMR, and were much lower at T2 in the SSR (Table 2). WE ranged from C_{28} WE with C_{14} *n*-alkanols and C_{14} saturated straight chain fatty acids (SATFA) ($C_{14:0/14:0}$), to C_{34} WE with C_{16} *n*-alkanols and C_{18} monounsaturated straight chain fatty acids (MUFA) ($C_{16:0/18:1}$). WE with MUFA dominated, whereby $C_{16:0/18:1}$ and $C_{16:0/16:1}$ represented 69.2% of total WE at T1. Four C_{25} HBIs were also observed in plankton net stations and in surface sediment stations. These were identified based on retention indices and published spectra (Belt et al., 2000). The structures observed here were $C_{25:4}$, $C_{25:3}$ and two $C_{25:5}$, which correspond to structures XV, XIV, XII and XI of Belt et al. (2000). On average, the abundance (per g OC) of C_{25} HBIs in the CMR (8 μg g OC^{-1}) was higher than at the SSR (5 μg g OC^{-1}). C_{25} HBIs were also observed at station T1 and T2. However, T1 HBI were limited to $C_{25:4}$ (XV) and $C_{25:3}$ (XIV), while at T2, these aforementioned HBI were accompanied by $C_{25:4}$ (XVII) and $C_{25:5}$ (XII). In both cases $C_{25:4}$ (XV) was the major compound. The total concentrations of C_{25} HBI were 12.5 μg g dw^{-1} at T1 and 16.5 μg g dw^{-1} at T2.

4.5. Phospholipid fatty acids

Sixty-three PLFA were identified in the sediments and thirty-eight in net tows. Specific PLFA classes comprised a mixture of (in order of relative abundance) MUFA, SATFA, brFA, and PUFA. Chain length ranged from C_{12} to C_{24} in sediments and C_{14} to C_{24} for nets tows. In the surface sediments SATFA comprised between 25.1% and 38.8% of total PLFAs found. The lowest proportion of SATFA relative to total PLFA was found at BC67 located in the deeper offshore region while the highest proportion of SATFA relative to total PLFA was found at BC63 in shallower water. PUFA represented an average of 7.8% of total PLFA while brFA accounted for on average 23.4% of total PLFA. SATFA exhibited a strong even carbon number predominance. $C_{16:0}$ was the major SATFA found at all sediment stations. MUFA exhibited a bimodal distribution whereby $C_{16:1\omega7c}$ and $C_{18:1\omega7c}$ were the dominant members. ω9 MUFA dominated for the MUFA ≥ C_{20}. Taken together $C_{16:0}$, $C_{16:1\omega7c}$ and $C_{18:1\omega7c}$ accounted for an average of 41.0% of total PLFA. $iC_{15:0}$, $aiC_{15:0}$ and $10MeC_{16:0}$ were the dominant brFA and accounted for on average 12.6% of total PLFA. Other brFA encountered were iso and anteiso C_{13} to C_{19}. A number of cyclic fatty acids were also observed in these samples and included one cyclopropyl C_{17} and two cyclopropyl C_{19} FA. PUFA ranged from C_{16} to C_{24} and were dominated by $C_{20:4\omega6}$, $C_{20:5\omega3}$, $C_{22:6\omega3}$. These PUFA accounted for an average of 1.8, 2.9 and 0.7% of total PLFA, respectively.

Total PLFA, SATFA, MUFA and PUFA abundance was not significantly correlated with water depth, sediment type, TOC, TN or with neutral compound classes. $\delta^{13}C$ values for major PLFA from station BC52 (CMR), BC72 (SSR), BC78 (SMR) and BC85 (SSR) ranged from −23.23‰ to −29.76‰ (Fig. 4). $C_{14:0}$ ranged from −25.04 ± 0.17‰ at station BC85 to −27.68 ± 0.10‰ at BC72. $C_{16:1}$ ranged from 25.65 ± 0.22‰ at BC85 to −29.76 ± 0.26‰. $C_{16:0}$ $\delta^{13}C$ values ranged from 25.42 ± 0.18‰ at BC85 to 27.97 ± 0.21‰ at BC72. $C_{18:1}$ was more enriched compared to C_{16} PLFA, ranging from 24.11 ± 0.18‰ at BC85 to 26.18 ± 0.11‰ at BC72. There was a shift in the overall trend for $C_{18:0}$ whereby the more depleted $\delta^{13}C$ values were observed at BC85 (29.07 ± 0.06‰) and BC72 exhibited the most enriched $\delta^{13}C$ values (26.47 ± 0.14‰). $\delta^{13}C$ for $C_{20:5\omega3}$ revealed very little variability in $\delta^{13}C$ values, whereby values ranging from −24.75 ± 0.25‰ (BC72) to −24.99 ± 0.09‰ (BC52). $C_{22:6\omega3}$ $\delta^{13}C$ values varied over a wider range, from −23.23 ± 0.27‰ (BC52) to −27.30 ± 0.15‰ (BC78). For the particulate matter PLFA abundance at station T1 was over double that of T2 (Fig. 6). In particular the major PUFA, $C_{20:5\omega3}$ and $C_{22:6\omega3}$, were present in much greater abundance at station T1. This is consistent with the increased relative abundance of PUFA in surface sediments in the CMR/SMR. $C_{22:6\omega3}$ was the dominant PUFA at station T1 while $C_{20:5\omega3}$ was the dominant at T2. $C_{18:3\omega3}$ and $C_{18:2\omega3}$ were other significant PUFA in the nets tows.

4.6. Multivariate data analysis

Hierarchical cluster analysis of bulk and biomarker data (Fig. 7) from all sediment stations yielded two broad groupings. Two major groupings were formed whereby all stations in the SSR cluster together and eight out of ten stations (BC53 and BC56) in the mixed CMR and SMR cluster together. Principal component analysis also revealed trends from the key biomarkers (Fig. 8). The first two components explained 63% of the total variance in the data (35.7%

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Table 3
Summary of major biomarkers, biomarkers classes and proxies used, with abbreviations used in the text and references.

Biomarker	Abbreviation/Name used	Likely source
Sterols		
24-norcholesta-5, 22-dien-3β-ol	$C_{26}\Delta^{5,22}$	Zooplankton, degradation of phytoplankton sterols[1]
24-norcholesta-22-en-3β-ol	$C_{26}\Delta^{22}$	
22-trans-cholesta-5,22-dien-3β-ol	$C_{27}\Delta^{5,22}$	Zooplankton detritus[2]
trans-27-nor-24-methyl-cholest-22-en-3β-ol	$C_{27}\Delta^{22}$	Dinoflagellates[3], benthic invertebrates[4]
cholest-5-en-3β-ol	$C_{27}\Delta^{5}$	Macrofauna, zooplankton biomass/detritus[5]
5-α(H)-cholestan-3β-ol	$C_{27}\Delta^{0}$	Bacterial reduction of C_{27} stenols[6]
cholesta-5,24-dien-3β-ol	$C_{27}\Delta^{5,24}$	Marine phytoplankton, diatoms[5]
24-methylcholesta-5,22-dien-3β-ol	$C_{28}\Delta^{5,22}$	Marine phytoplankton, diatoms[1,7]
24-methylcholesta-22-en-3β-ol	$C_{28}\Delta^{22}$	Marine invertebrates (sponges)[8], phytoplankton[9]
24-methylcholesta-5-en-3β-ol	$C_{28}\Delta^{5}$	Higher plants[10], green algae[1]
24-methyl-5-α(H)-cholestan-3β-ol	$C_{28}\Delta^{0}$	Bacterial reduction of C_{28} stenols[6]
24-methylcholesta-5-24(28)-dien-3β-ol	$C_{28}\Delta^{5,24(28)}$	Diatoms, marine phytoplankton[1,7]
24-ethylcholesta-5,22-dien-3β-ol	$C_{29}\Delta^{5,22}$	Terrestrial higher plants[10], some marine algae[11]
24-ethylcholesta-5-en-3β-ol	$C_{29}\Delta^{5}$	Terrestrial higher plants[10], some marine algae[11]
24-ethylcholesta-5,24(28)-dien-3β-ol	$C_{29}\Delta^{5,24(28)}$	Green microalgae[1]
4α,23,24-trimethyl-5α-cholesta-22-en-3β-ol	$C_{30}\Delta^{22}$	Dinoflagellates[1,5]
Phospholipid fatty acid		
Saturated straight chain fatty acids	SATFA	Marine plankton, non-specific[12,13,14]
Monounsaturated straight chain fatty acids	MUFA	Marine plankton, non-specific[12,13,14]
Polyunsaturated fatty acids	PUFA	Marine plankton[13,14,15]
Branched (and cyclic fatty acids)	brFA	Bacterial biomass[16]
Eicosapentaenoic acid	$C_{20:5\omega3}$	Marine microalgae, diatoms[2,11]
Docosahexaenoic acid	$C_{22:6\omega3}$	Dinoflagellates, zooplankton[2,13,17]
9-cis-hexadecenoic acid	$C_{16:1\omega7}$	Marine microalgae[11,12], bacterial biomass[16]
11-cis-octadecenoic acid	$C_{18:1\omega7}$	
Long chain odd carbon *n*-alkanes (C_{25} to C_{33})	LC_{HC}	Terrestrial higher plants[18,19]
Long chain even carbon *n*-alcohols (C_{26} to C_{32})	LC_{OH}	
n-alkane carbon preference index	CPI_{HC}	Terrestrial vs. marine proxy[20,21,22]
n-alkanol carbon preference index	CPI_{OH}	
Friedelan-3-one	Friedelin	Terrestrial higher plants[6]
Urs-12-en-3β-ol	β-amyrin	
Wax esters (C_{28} to C_{34})	WE	Zooplankton, particularly copepods[18]
C_{25} Highly branched isoprenoids	C_{25} HBIs	Diatoms, marine and benthic[23,24]
3,7,11,15-tetramethyl-2-hexadecen-1-ol	Phytol	Chlorophyll degradation (zooplankton grazing)[25,26]
2, 6, 10, 14-trimethylpentadecane	Pristane	Phytol degradation (zooplankton grazing)[25,26], archaeal ether lipids[27], petroleum[28]
2,6,10,14-tetramethylhexadecane	Phytane	

Sterol nomenclature is according to $C_x\Delta^y$, where *x* refers to the number of carbons and *y* refers to the position of the unsaturation(s) on the carbon skeleton. PLFA are named according to $aC_{b:c\omega d}$ where *a* indicates the presence of a methyl branching (*i* – iso, *ai* – anteiso, 10Me - methyl on 10th carbon from methyl end, cyc – cycloproyl), *b* indicates the total number of carbons, *c* indicates the number of double bonds and *d* indicates the position of the first double bond from the methyl end. References: 1. Volkman (2003), 2. Colombo et al. (1996), 3. Thomson et al. (2004), 4. Goad and Withers (1982), 5. Volkman (1986), 6. Volkman (2006), 7. Rampen et al. (2010), 8. Smallwood and Wolf (1999), 9. Hudson et al. (2001), 10. Huang and Meinschein (1976), 11. Volkman et al. (1998), 12. Volkman et al. (1989), 13. Carrie et al. (1998), 14. Hu et al. (2006), 15. Canuel and Martens (1993), 16. White et al. (1997), 17. Kattner and Hagen (2009), 18. Eglinton and Hamilton (1967), 19. Kolatukuddy (1970), 20. Clark Jr. and Blumer (1967), 21. Cranwell (2006), 22. Zhang et al. (2006), 23. Grosse et al. (2004), 24. Massé et al. (2004), 25. Brooks et al. (1969), 26. Didyk et al. (1978), 27. Rowland (1990), 28. Peters and Moldowan (1993).

and 27.4%, respectively). The remaining variability is unaccounted for among the remaining components, and likely reflects the complexity of OM cycling at this setting. Biomarkers that project in similar coordinates are understood to reflect similar geochemical associations i.e. source (terrestrial versus marine) and stability (labile versus recalcitrant). The co-variance associated with component 1 was associated with OM stability, while the second component described the variance associated with marine-terrestrial sources. Scree-plots and loadings are provided in supplementary material. Thus, the analysis helped to elucidate the source-specificity and stability of biomarkers in this study (discussed below).

5. Discussion

The focus of the present study was on the sources and cycling of natural TOM and MOM. Thus, anthropogenic sources of OM and biomarkers derived from prokaryotes (e.g. brFA and MAGE) will not be discussed in detail here. A Table summarising the primary biomarkers used in this study, along with common names, abbreviations used in the text, likely sources and key references is given in Table 3. PCA was used to reduce the complexity of biomarker data and provide commonalities and differences in OM source/fate. PCA revealed groupings in biomarkers related to 'fresh marine', 'degraded marine', 'fresh mixed', 'terrestrial' and 'mixed' OM compartments. The fresh marine grouping was composed of the major PUFA PLFA. Interestingly, $C_{14:0}$ PLFA and phytadienes were also associated with this fresh marine input. Other major PLFA were associated with a fresh OM but exhibited a mixed marine/terrestrial relationship. Low molecular weight *n*-alkanes (C_{19}), and pristane and phytane were attributed to a highly degraded recalcitrant marine source. A marine grouping with little observed stability relationship was composed of a number of C_{27} to C_{29} sterols. A terrestrial OM compartment was also apparent and consisted of CPI proxies, terpenoids, $C_{28}\Delta^5$, LC_{HC} (C_{31}) and LC_{OH} (C_{28}). Phytol, C_{26} *n*-alkanol and $C_{28}\Delta^{5,22}$ exhibited no clear marine or terrestrial source relationship but was associated with more stable, degraded OM.

5.1. Sources, distribution and fate of marine organic matter

Fatty acids of marine plankton typically range from C_{14} to C_{22} (Carrie et al., 1998), with C_{14}, C_{16} and C_{18} SATFA as major homologues (e.g. Volkman et al., 1989; Carrie et al., 1998; Hu et al., 2006). $C_{16:1\omega7}$ is synthesised by a variety of marine organisms (Volkman et al., 1989, 1998), as well as bacteria (White et al., 1997). Based

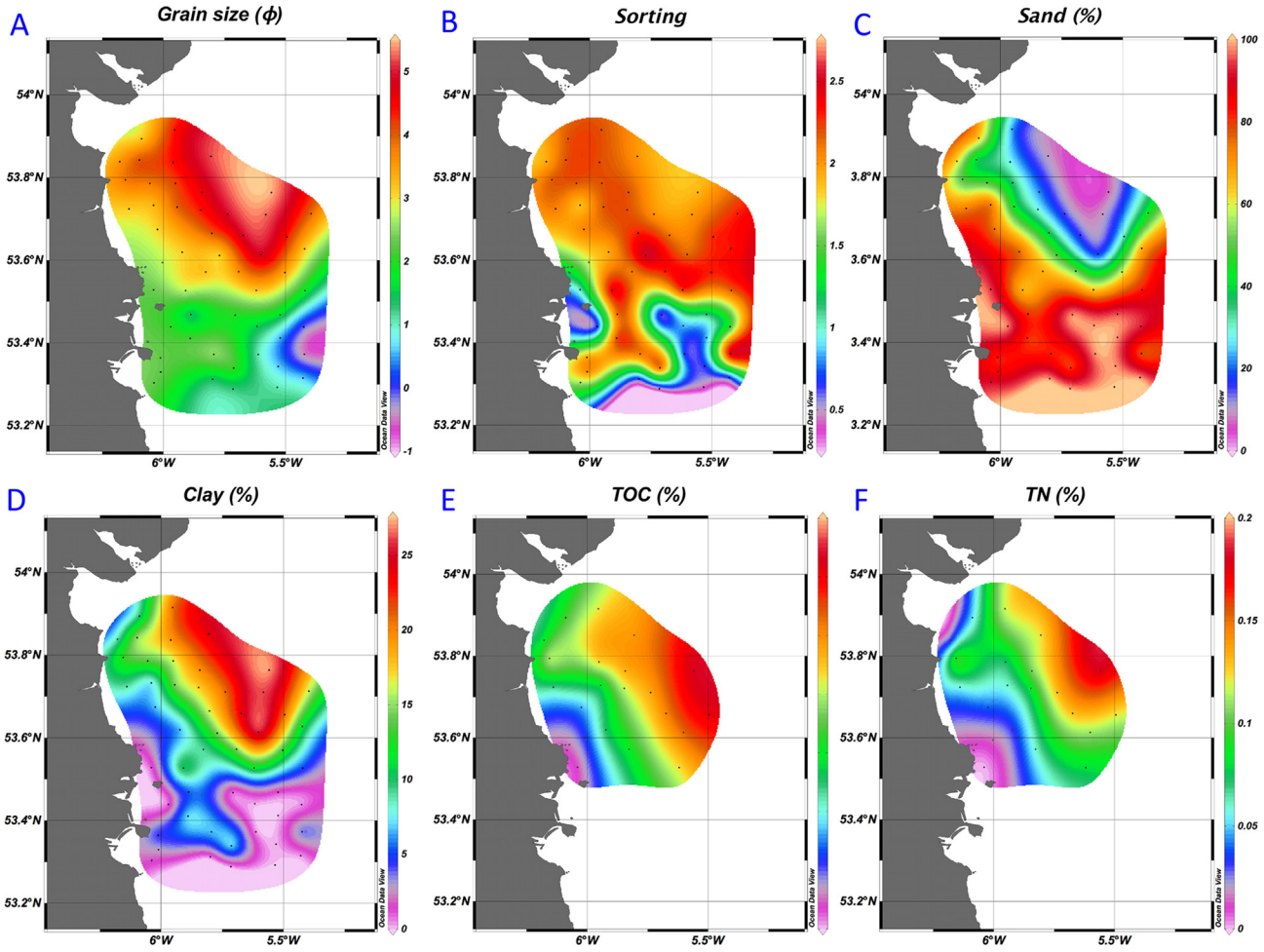

Fig. 2. Spatial distribution of bulk physical and chemical parameters in western Irish Sea surface sediments: A. grain size (ϕ); B. sorting; C. sand (%); D. clay (%); E. total organic carbon (TOC; %); and F. total nitrogen (TN; %).

on their occurrence as major PLFA in particulates (Fig. 6), and their average $\delta^{13}C$ value of −26 to −27‰, a marine origin is favoured. However, their utility as biomarkers solely for marine algal input in this setting may be limited based on the outcome of PCA (Fig. 8). PUFA are generally more specific marine fatty acids (Volkman et al., 1989, 1998), and being subject to rapid losses and alteration by bacteria and zooplankton grazing (Hu et al., 2006), are indicative of input of microalgal biomass or fresh detritus from the water column (Canuel and Martens, 1993; Carrie et al., 1998). The occurrence of PUFA at all sediment stations and in particulates (Tables 1 and 2), the average $\delta^{13}C$ values (Fig. 4), and the outcome of PCA (Fig. 8) support this conclusion.

C_{27} and C_{28} sterols, are typically the major sterols in marine plankton and invertebrates, while C_{29} sterols and C_{27} sterols are the dominant sterols in higher plants and in animals, respectively (Huang and Meinschein, 1976). Sterols are not completely metabolised or degraded quickly under reducing conditions and in this sense they are not strictly associated with fresh input (Fig. 8). C_{28} and C_{27} were the major sterol classes at all sediment stations (Table 1) and also in net tows (Table 2), and together with the $\delta^{13}C$ values for measured sterols (Fig. 4), indicates a major contribution of planktonic OM to MOM. Phytol is considered to be the major source of the isoprenoids pristane, phytane and phytadienes (Brooks et al., 1969; Didyk et al., 1978; Rontani and Volkman, 2003) and chlorophyll hydrolysis to yield free phytol, and subsequent production of pristane and phytadienes, is mainly associated with herbivorous grazing activity (Blumer et al., 1969; Rontani and Volkman, 2003). Phytol $\delta^{13}C$ values are consistent with a marine planktonic origin (Fig. 4). However, the variable distribution between phytol and its degradation products indicates that there are a number of sources for these compounds in this setting. PCA results suggest that phytadienes in surface sediments, rather than phytol, could be indicative of fresh marine input. Alternative sources for pristane and phytane, including archaeal ether lipids (Rowland, 1990) and in particular oil spills (Peters and Moldowan, 1993), are likely (Fig. 8). The occurrence of polyaromatic hydrocarbons in appreciable amounts in a number of sediments stations (data not shown) supports this. Thus, only the most diagnostic lipids, from the literature and based on the PCA results here, are discussed in detail here.

5.1.1. Phytoplankton

Although the phytoplankton composition of the Irish Sea is generally not well-characterised, recent investigations have shown that over seventy species/species groups of diatoms are known to occur (Kennington and Rowlands, 2006), and diatoms appear to dominate the seasonal bloom (Gowen and Stewart, 2005). Important diatoms appear to be *Skeletonema costatum*, a number of species belonging to *Chaetoceros*, *Pseudonitzschia* and *Thalassiosira* (McKinney et al., 1997), and *Guinardia delicatula* (Gowen et al., 2000). Diatoms are characterised by high abundances of $C_{16:1\omega7c}$, $C_{18:1\omega7c}$, $C_{20:5\omega3}$ fatty acids (Colombo et al., 1996; Volkman et al., 1998) and $C_{28}\Delta^{5,22}$ and $C_{28}\Delta^{5,24(28)}$ sterols (Volkman, 2003; Rampen et al., 2010). $C_{27}\Delta^{5}$, $C_{29}\Delta^{5}$ and $C_{27}\Delta^{5,22}$ sterols are also

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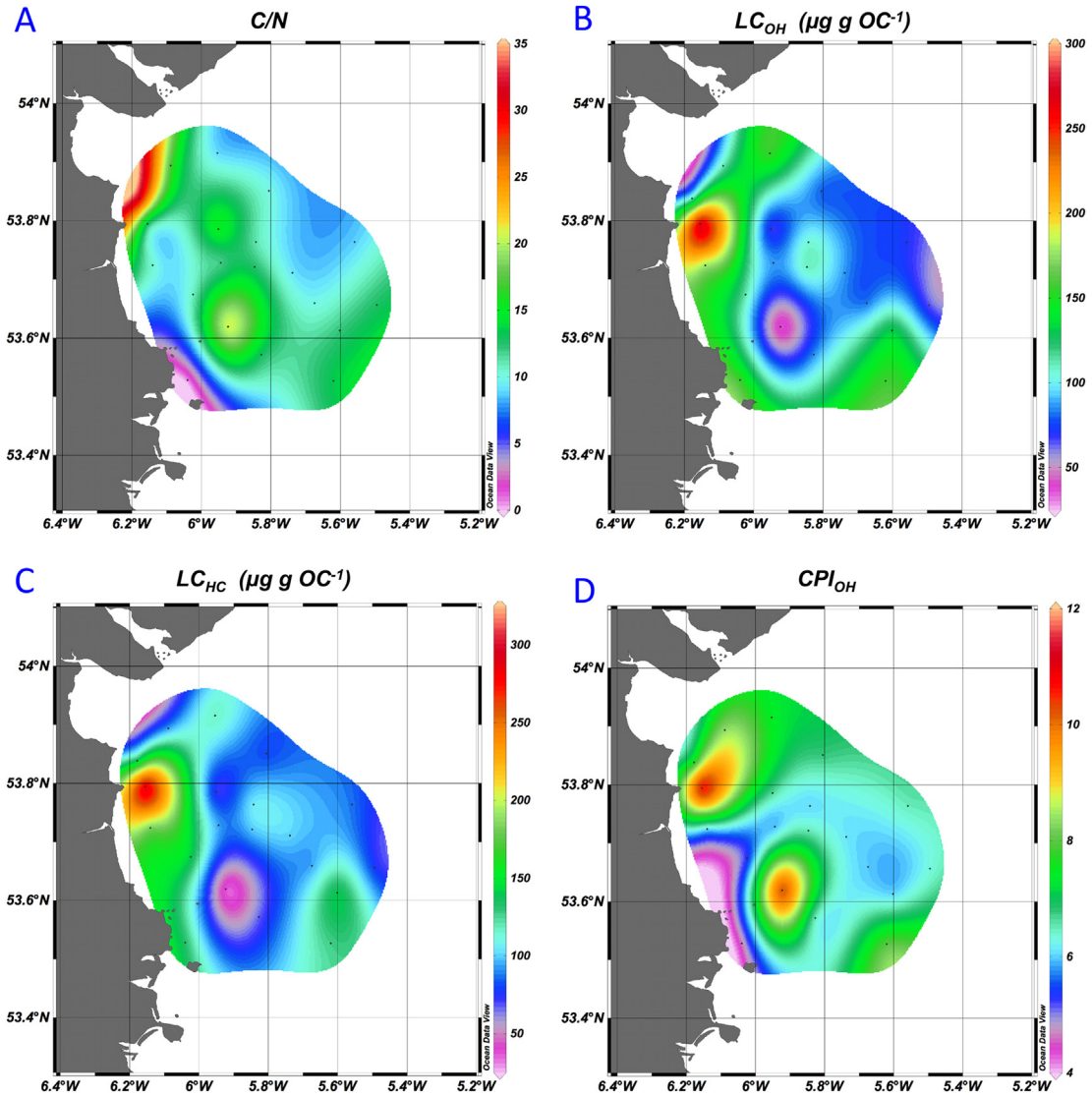

Fig. 3. Spatial distribution of terrestrial organic matter (TOM) in the study area based on A. Bulk C/N ratio; B. long chain *n*-alkanols (LC_{OH}); C. long chain *n*-alkanes (LC_{HC}); and D. *n*-alkanol carbon preference index (CPI_{OH}).

commonly present. C_{25} HBIs have also been attributed to marine and benthic diatoms (Grosse et al., 2004; Masse et al., 2004). $C_{16:1\omega7c}$, $C_{18:1\omega7c}$, $C_{20:5\omega3}$ accounted for a major proportion of total PLFA in sediment samples. Both $C_{28}\Delta^{5,22}$ and $C_{28}\Delta^{5,24(28)}$ were sterols at all sediment stations and in particulate matter. C_{25} HBIs were observed in most surface sediment samples. This indicates that fresh diatom biomass is a significant source of OM to surface sediments throughout the region.

About sixty species/species groups of dinoflagellates have also been identified in the Irish Sea (Kennington and Rowlands, 2006) and they are considered to represent an important component of the bloom also (Gowen and Stewart, 2005). Species belonging to *Gymnodinium* spp., *Peredinium* spp., *Ceratium* spp. and *Scrippsiella* spp. appear to be the major dinoflagellate groups in the Irish Sea during the spring/summer season. $C_{30}\Delta^{22}$ is a major sterol in many dinoflagellates and considered a source-specific biomarker (Volkman, 2003), and its presence as a major sterol in both sediments and net tows confirms that dinoflagellates are a major a major contributor to MOM and SOM. The PUFA $C_{22:6\omega3}$ has also previously been utilised as a biomarker for dinoflagellate input (e.g. Colombo et al., 1996; Budge and Parrish, 1998; Carrie et al., 1998). However no strong correlation was observed between $C_{22:6\omega3}$ and $C_{30}\Delta^{22}$ in this study, reflecting the variety of other marine sources of $C_{22:6\omega3}$.

Green algae (division Chlorophyta) are characterised by C_{16} and C_{18} PUFA with ω3 and ω6 isomerism and low amounts of C_{20} and C_{22} PUFA (Volkman et al., 1989; Dunstan et al., 1992; Zhukova and Aizdaicher, 1995; Meziane and Tsuchiya, 2000) and $C_{28}\Delta^{5}$, $C_{28}\Delta^{5,7,22}$, $C_{28}\Delta^{7,22}$, $C_{29}\Delta^{5,22}$, $C_{29}\Delta^{5}$ and $C_{29}\Delta^{5,24(28)}$ sterols (Volkman, 2003). The Δ^{7} sterols are major sterols in many Chlorophyceae while the Prasinophyceae lack these sterols and instead have $C_{28}\Delta^{5,24(28)}$, $C_{28}\Delta^{5}$ and $C_{29}\Delta^{5,24(28)}$ as major sterols. C_{16} and C_{18} PUFA were observed in all sediment stations and in net tows, but Δ^{7} sterols were not observed. However, $C_{29}\Delta^{5,24(28)}$ was identified from both sediments and net tows, which suggests that Prasinophyceae rather than Chlorophyceae may be the dominant class of green microalgae in this setting.

5.1.2. Zooplankton

Zooplankton, in particular copepods, play a key role in energy transfer from primary to higher trophic levels (Kattner and Hagen, 2009). The importance of zooplankton grazing on the pelagic mineralisation of fresh phytoplankton detritus in the Irish Sea has

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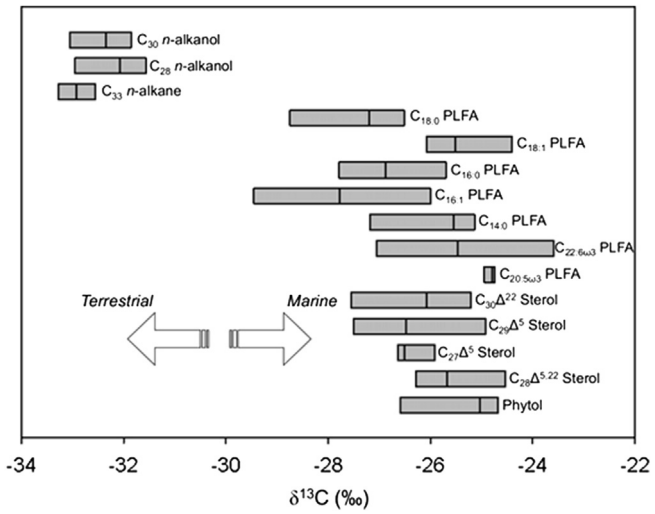

Fig. 4. Horizontal boxplot of selected biomarker $\delta^{13}C$ values distinguishing marine and terrestrial organic matter. Each boxplot depicts the range of $\delta^{13}C$ values observed for the analyte at selected stations ($n = 4$; BC52, BC72, BC78, BC85 for PLFAs and BC55, BC66, BC72 and BC73 for neutral lipids). The black line represents the average $\delta^{13}C$ values.

been emphasised (Dickey-Collas et al., 1996; Gowen et al., 1999; Trimmer et al., 1999), whereby zooplankton grazing may account for up to 56% of daily spring production (Gowen et al., 2000). Copepods are the dominant zooplankton group (~70%) in the Irish Sea (Kennington and Rowlands, 2006). *Pseudocalanus elongatus* is the dominant species reported, comprising about 26% of total zooplankton (Kennington and Rowlands, 2006). Other major copepods are *Temora longicornis* and *Acartia clausi*. $C_{16:1\omega7}$, $C_{20:5\omega3}$ and $C_{22:6\omega3}$ are typically major fatty acids in zooplankton (Williams, 1965; Kattner and Hagen, 2009). As discussed, $C_{16:1\omega7}$ is widespread among marine organisms and is not considered source specific for zooplankton here. $C_{27}\Delta^5$ is also ubiquitous in the marine environment. However, in high concentrations it is typically associated with zooplankton biomass and detrital matter (Volkman, 1986). $C_{27}\Delta^{5,22}$ is also typical of zooplankton carcasses, molts and faeces (Colombo et al., 1996) and the co-occurrence of both of these sterols in high relative abundance compared to other sterols in this study indicates considerable zooplankton input.

More specific biomarkers for zooplankton are WE, which are synthesised in high amounts by copepods for the purpose lipid accumulation and storage (Kattner and Hagen, 2009). Herbivorous calanoid copepods are known to intensely synthesise WE in marine settings with marked seasonality (Lee et al., 1971), such as those present in the western Irish Sea. In particulate samples WE

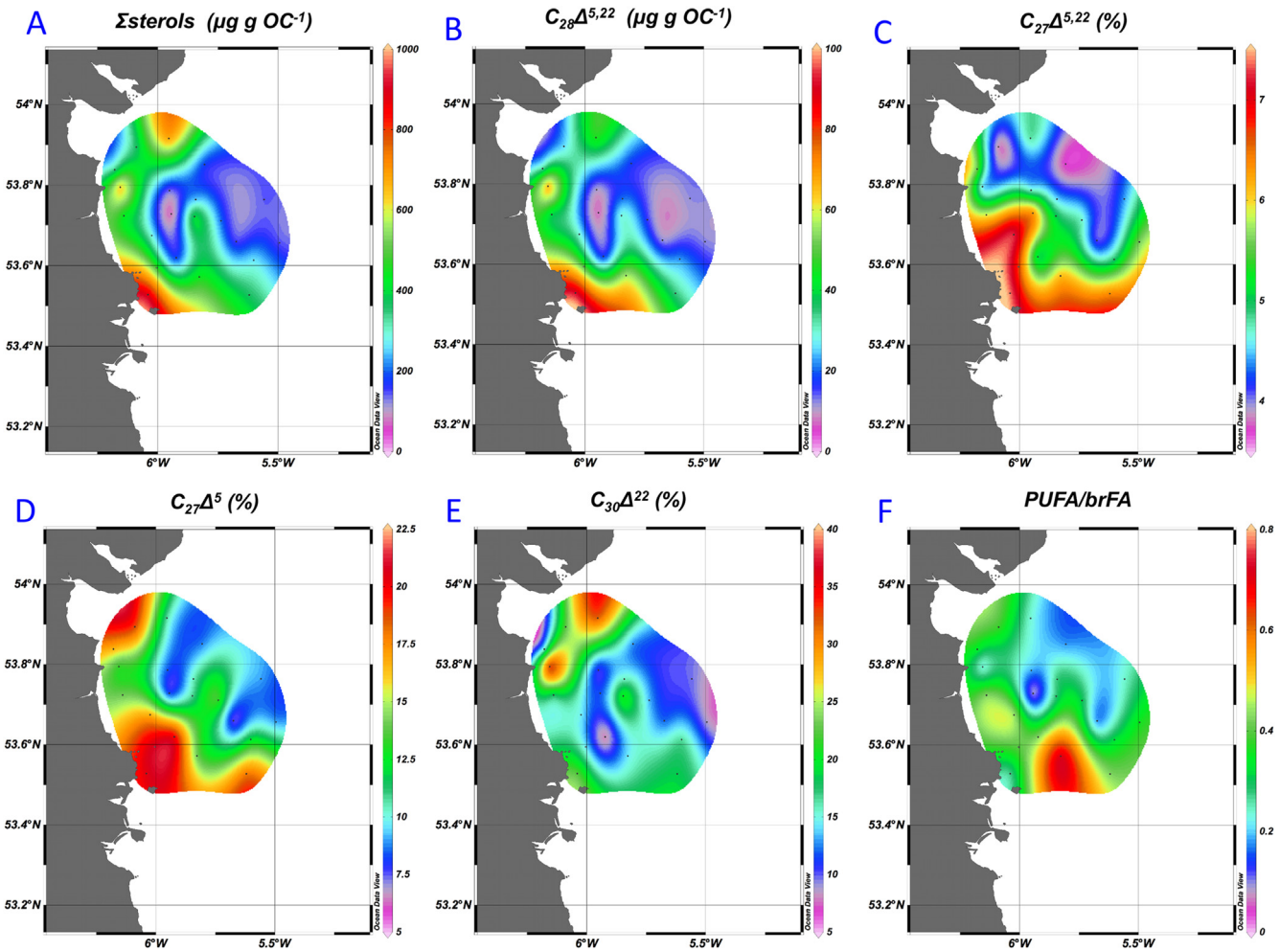

Fig. 5. A. total sterol concentration (μg g OC^{-1}); B. $C_{28}\Delta^{5,22}$ (μg g OC^{-1}); C. $C_{27}\Delta^{5,22}$ (% of total sterols); D. $C_{27}\Delta^5$ (% of total sterols); E. $C_{30}\Delta^{22}$ (% of total sterols); and F. the ratio of polyunsaturated to branched phospholipid fatty acids (PUFA/brFA). Sterol nomenclature is according to $C_x\Delta^y$, where x refers to the number of carbons and y refers to the position of the unsaturation(s) on the carbon skeleton.

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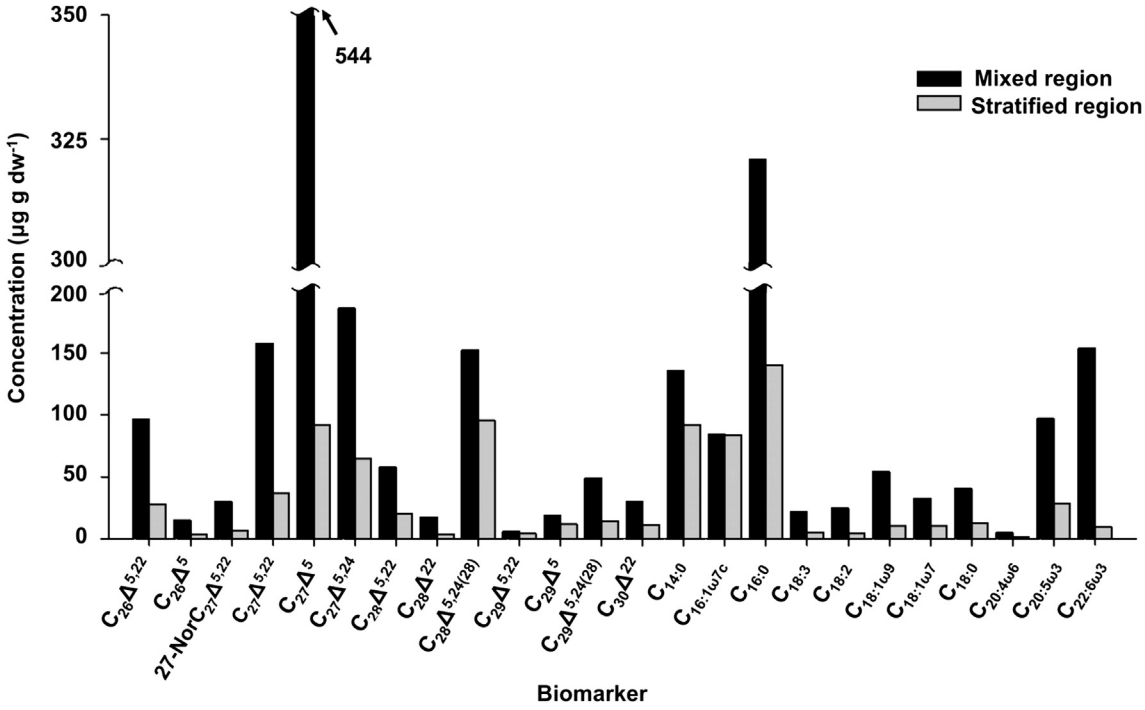

Fig. 6. Concentrations of major sterol and phospholipid fatty acids in plankton net tow samples from mixed and stratified regions.

reflected $C_{27}\Delta^{5,22}$ and $C_{27}\Delta^{5}$ distributions whereby WE abundance was over eighty times higher at T1 compared to T2. The low abundance of WE in sediments indicates that these are rapidly hydrolysed to the constituent *n*-alkanols and *n*-fatty acids in the water column. WE are typically the major lipid class of *Pseudocalanus elongatus*, accounting for almost 50% of total lipids in specimens from the North Sea (Kattner and Krause, 1989). Neither *Temora longicornis* or *Acartia clausi* synthesise WE in appreciable amounts (Kattner et al., 1981; Fraser et al., 1989), suggesting that WE found in this setting are most likely attributable to *P. elongatus*. Taken together results suggest that WE-synthesising calanoid copepods, such as *P. elongatus*, play an important role in the annual mineralisation and cycling of spring bloom biomass. These observations are consistent with previous reports emphasising the importance of copepods for OM mineralisation in the Irish Sea (Dickey-Collas et al., 1996; Gowen et al., 1999; Trimmer et al., 1999).

5.2. Terrestrial organic matter and terrestrial versus marine input

Homologous series of long-chain *n*-alkanes and *n*-alkanols, derived from higher plant waxes (Eglinton and Hamilton, 1967; Kolattukudy, 1970) are typical terrigenous lipids found in marine sediments (Gearing et al., 1976; Farrington and Tripp, 1977; Huang et al., 2000). Plant LC_{HC} normally range from C_{25} to C_{33} (odd-over-even predominance) while plant LC_{OH} typically range from C_{26} to C_{32} (an even-over-odd predominance) (Eglinton and Hamilton, 1967). In contrast, algae and bacteria typically synthesise odd or even C_{14} to C_{24} *n*-alkyl lipids (Volkman et al., 1998). Thus, the relative abundance of *n*-alkanes and *n*-alkanols and proxies such as the CPI are useful for assigning relative OM contributions from terrestrial and marine signals (Clark Jr. and Blumer, 1967; Pancost and Boot, 2004; Cranwell, 2006; Zhang et al., 2006) (See Table 1 for details of the equations used). CPI_{HC} values (Table 1) indicates that although there is a considerable OM contribution from terrestrial sources, a mixed marine/terrestrial OM contribution is apparent. CPI_{HC} ranged from 2.1 to 5.3, with the higher values generally observed in the shallow CMR in proximity to Dundalk bay and the Boyne Estuary. Similar observations and conclusions can be drawn from the CPI_{OH}.

The average bulk $\delta^{13}C$ 7‰ difference between land plants and marine primary producers (Collister et al., 1994) has been used to assess marine versus terrestrial input in the marine environment (e.g. Westerhausen et al., 1993; Chikaraishi and Naraoka, 2003). Lipids are known to be depleted in ^{13}C by 5–8‰ relative to bulk biomass (Collister et al., 1994; Chikaraishi and Naraoka, 2003; Pancost and Pagani, 2006). As shown in Fig. 4, $\delta^{13}C$ values for proposed terrestrial and marine biomarkers revealed a clear distinction between isotopically lighter terrestrial, and heavier marine OM. $\delta^{13}C$ values for measured LC_{OH} ($>C_{26}$) and LC_{HC} (−31.5 to −33.4‰) are about 7‰ more depleted than marine-derived lipids (Fig. 4), confirming their terrestrial source.

C_{29} sterols, such as $C_{29}\Delta^{5,22}$ and $C_{29}\Delta^{5}$ are typical major sterols in higher plants (e.g. Huang and Meinschein, 1976; Pancost and Boot, 2004) and often utilised as markers of terrestrial input in marine settings. However, these sterols are also synthesised by a variety of marine plankton (Volkman et al., 1998, and reference therein). Since these sterols were also observed in net tows (Fig. 6), and based on the $\delta^{13}C$ values for $C_{29}\Delta^{5}$ (Fig. 4) and PCA results (Fig. 8), a marine origin is favoured. A mixed marine/terrestrial origin for LC_{OH} is also apparent based on their strong correlation with marine sterols ($r = 0.84$, $P < 0.001$). This is likely related to $C_{26:0}$, which was a major *n*-alkanol in net tows. This is illustrated in Fig. 8, whereby $C_{28:0}$ is associated with other terrestrial markers and $C_{26:0}$ is not. $\delta^{13}C$ analysis confirms than LC_{OH} greater than C_{26} are predominantly terrestrial (Fig. 4). The plant triterpenoids friedilin and β-amyrin are considered highly specific biomarkers for vascular plants (Volkman, 2006) and their presence throughout the study area confirms the widespread distribution of TOM. The strong correlations between these triterpenoids and LC_{HC} and LC_{OH}, as well as the outcome of PCA, support the conclusion that plant waxes are also the major source of LC_{HC} and LC_{OH}.

Freshwater riverine runoff is considered to be the primary source of TOM in coastal and shelf settings (Bird et al., 1995; Harvey, 2006). The western Irish Sea is in close proximity to a number of

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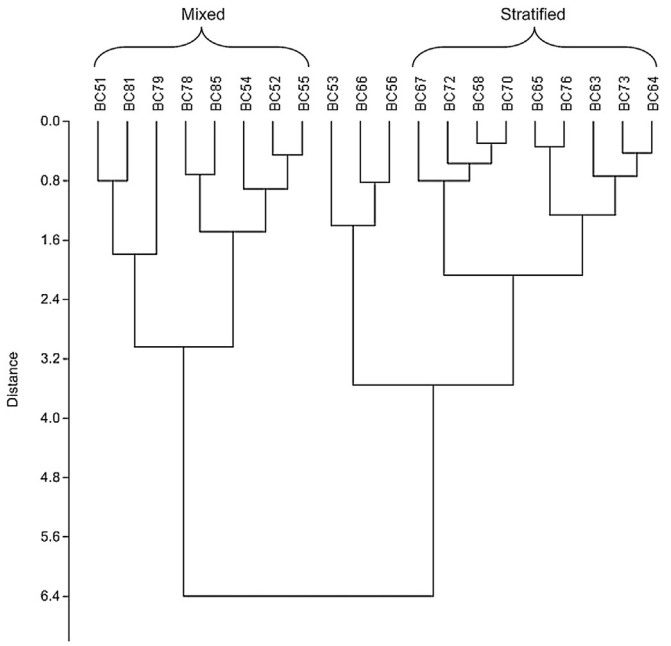

Fig. 7. Hierarchical cluster analysis of multivariate bulk parameter and biomarker data, as shown in Table 1, reveals a clear distinction in the dataset that corresponds with the seasonal hydrographic zonation.

bays and estuaries, which include Carlingford Lough, Dundalk Bay and the Boyne Estuary. The observation that bulk C/N ratios, plant-derived biomarkers and CPI values all peaked in well-sorted fine-grained coastal sediments in proximity to Dundalk Bay and the Boyne Estuary (Fig. 3), indicate local riverine input is the most important transport routes for TOM input. These results are consistent with previous reports showing that fluvial input of dissolved inorganic nitrogen and ortho-phosphate to the western Irish Sea are generally highest in Dundalk Bay, Carlingford Lough, the Boyne estuary and in Dublin Bay (McGovern et al., 2002).

5.3. Hydrographic control on organic matter cycling

The spatial distribution of grain size and sediment type are primarily controlled by the hydrographic conditions and resulting depositional regime. In this way the transition from coarse-grained sandy sediments to more fine-grained sediments found in deeper waters (>50 m depth) delineates the average location of mixed and stratified hydrographic regions that develop each year in the western Irish Sea (Fig. 2). It has been proposed that the establishment of the summer gyre may play a role in controlling the spatial distribution of *Nephrops norvegicus* larvae (Hill et al., 1996), larval and juvenile fish, and zooplankton (Dickey-Collas et al., 1996, 1997), and anthropogenic contaminants (Hill et al., 1997). Assessing the distribution of marine- and terrestrial- derived fresh and recalcitrant OM provides one means of assessing the effect these frontal zones have on natural processes. Results presented in this study from a multi-biomarker approach provide evidence that the seasonal stratification in the western Irish Sea is a key factor controlling the production, distribution and fate of MOM.

PUFA were major PLFA at both plankton nets stations (up to 30.8% of total PLFA), with PUFA abundance at T1 almost 6 times greater than at T2 (Fig. 6). PUFA abundance in surface sediments (expressed against TOC) is on average greater in the hydrographically well-mixed regions (70.6 μg g OC^{-1}) compared to stations associated with the SSR (23.3 μg g OC^{-1}). This trend is also illustrated by the ratio of algal/bacterial PLFA in surface sediments (Fig. 5F). PUFA are diagnostic of microalgal biomass while brFA indicate an increased relative contribution of bacterial biomass (White et al., 1997). The ratio of PUFA/brFA was approximately half

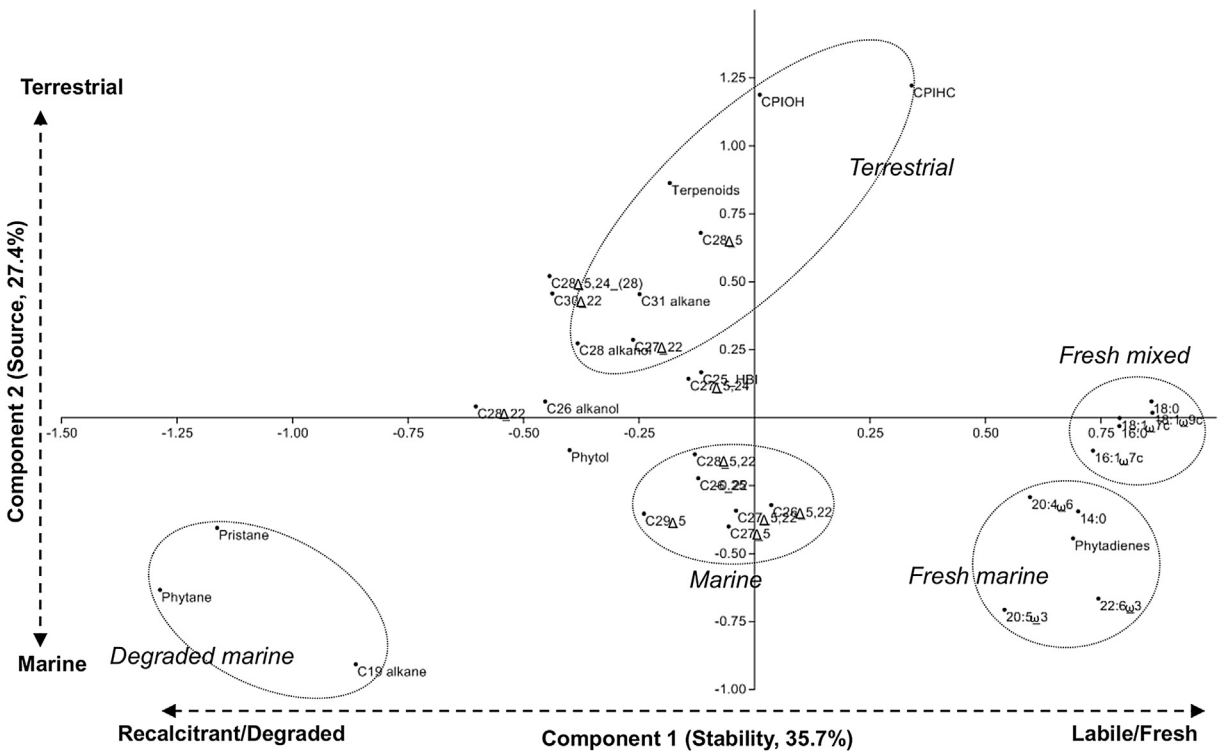

Fig. 8. Principal Component Analysis of major biomarkers and proxies used in this study, revealing various OM compartments of distinct source and stability.

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in the SSR compared to the mixed regions. These results indicate that there was a greater abundance of fresh microalgal biomass in the SMR compared to the SSR during the sampling period, and that there is a greater average relative input to surface sediments in the SMR and CMR. The relative abundance of PUFA from the water column to surface sediments decreased (average of 7.8% of total PLFA). This reflects the rapid degradation of fresh planktonic biomass in the water column and is in agreement with previous observations that much of the seasonal primary productivity in the western Irish Sea is remineralised in the water column (Trimmer et al., 1999; Gowen et al., 2000). Thus, these trends in biomass production and distribution may be periodical. However, temporal sampling would be required to confirm this. The increased residence time of marine biomass in the water column, together with lower primary production, and lower dissolved inorganic nutrient availability (Gowen et al., 1995, 1996) are likely the most important reasons for the indicated decreased input of fresh MOM to surface sediments within the gyre.

Surface sediments in the CMR and SMR yielded, on average, a greater relative abundance of proposed diatom sterols ($C_{28}\Delta^{5,22}$ and $C_{28}\Delta^{5,24(28)}$). For particulate matter, the abundance of these sterols was also much greater in the mixed region compared to the stratified region (Fig. 6). Thus, there was a greater relative abundance of diatom-derived detritus in particulate matter and surface sediments in well mixed waters. However, relative to total sterols, $C_{28}\Delta^{5,24(28)}$ was a more significant sterol in the stratified region (Fig. 6), which suggests that during sampling diatoms comprised a greater proportion of total plankton in the stratified waters compared to the mixed region. The occurrence of C_{25} HBIs in greater abundance in the SSR particulate samples compared to the SMR, again supports the conclusion that diatoms represented a greater relative proportion of total phytoplankton within the gyre during the sampling period. The distribution of C_{25} HBIs in surface sediments suggests an increased relative input to the CMR however, compared to the SSR and SMR. This may be due to a number of possible factors such as the higher average primary productivity in the coastal mixed region, the increased zooplankton activity in the mixed region and also the lower residence time of these lipids in the water column at these shallower water depths.

The spatial distribution of $C_{27}\Delta^{5}$ and $C_{27}\Delta^{5,22}$ is similar and has an increased relative abundance in the mixed region, in particular to the south (Fig. 5C and D). This indicates that there is increased abundance of zooplankton and hence grazing activity in the mixed region in comparison to seasonally stratified waters. This conclusion is supported by the occurrence of these sterols at T1 in concentrations greater than five times that found at T2. Furthermore, WE were over eighty times more abundant at T1 compared to T2. It has been demonstrated that the ratio of $C_{22:6\omega3}$ to $C_{20:5\omega3}$ may provide an indication of relative dinoflagellate to diatom input (Volkman et al., 1989; Budge and Parrish, 1998). This ratio was highest in a number of stations in the CMR (average = 0.27) and SMR (average = 0.30), while typically being lower in the SSR (average = 0.20). This suggests an average increased abundance of dinoflagellates and dinoflagallate detritus in the mixed regions and is supported by the spatial distribution of $C_{30}\Delta^{22}$ (Fig. 5E). The three-fold greater abundance of $C_{29}\Delta^{5,24(28)}$ and of C_{16}/C_{18} PUFA at T1 compared to T2 indicates that there was an increased abundance of green microalgae in well-mixed zones compared to the stratified waters during the summer. This is also reflected in the increased relative abundance ($\mu g\ g\ OC^{-1}$) of these PUFA in surface sediments at stations BC79, BC81 and BC85 in the southern region.

The distribution of C/N, LC_{OH} and LC_{HC} (normalised to TOC content) also may reflect regional hydrographic zonation, whereby these parameters are highest in coastal fine-grained sediments in proximity to Dundalk Bay and the Boyne Estuary (particularly station BC53). The spatial distribution of these plant lipids also suggests that the regional near-bottom residual flows that exist in the western Irish Sea (reproduced in Fig. 1, Ramster and Hill, 1969) may facilitate transport of riverine TOM from the south coast and from the northern coast and deposition in the low energy hydrographic areas near Dundalk Bay. Riverine input is considered much lower than in the eastern Irish Sea (Gowen et al., 2000), and this is reflected in the decreased sedimentary input of TOM from the shallow coastal regions to offshore sediments (Fig. 3). Near-surface and near-bottom residual circulation from the eastern Irish Sea (Liverpool Bay) to the western Irish Sea is not apparent (Ramster et al., 1969), and suggests that transport of TOM from east to west may be of minor importance. However, the influence of TOM from the eastern Irish Sea to the western Irish Sea is unknown at present. Furthermore, the transport of terrestrial material from the south, via St. George's Channel and from the North, via the North Channel needs to be considered further in future studies regarding the source and fate of TOM in the Irish Sea. Nevertheless results presented here suggest that the seasonal gyre may influence TOM transport and deposition in the region.

Hierarchical cluster analysis of bulk and biomarker data (Fig. 7) from all stations support the aforementioned conclusion that the hydrographic regime plays a major role on the production, distribution and deposition of OM in the western Irish Sea. Two major groupings were formed whereby all stations in the SSR cluster together and eight out of ten stations (BC53 and BC56) in the mixed CMR and SMR cluster together. In summary, the distribution of biomarkers from phytoplankton, zooplankton, and from vascular plants has revealed subtle but distinct differences between OM composition and input between mixed waters and the stratified waters in the Irish Sea. Evidence presented here suggests that there is an overall higher primary productivity and zooplankton grazing in well mixed regions and that this effects the composition and distribution of SOM across this region. This is likely a result of a number of factors such as OM water column residence time and the earlier and longer production season in coastal and mixed waters compared to offshore waters. It must be noted however, that changes in phyto- and zooplankton abundance and distribution over the course of the spring/summer bloom, as well as annual variation, have not been addressed here. Nevertheless, we propose that the hydrographic regime in the western Irish Sea and the establishment of the western gyre plays an important role in the production, distribution and fate of OM in the western Irish Sea.

6. Conclusions

The occurrence of $C_{28}\Delta^{5,22}$, $C_{28}\Delta^{5,24(28)}$ sterols, as well as ester-linked PUFA and C_{25} HBIs in surface sediments and the water column in this setting highlighted the importance of diatoms for primary production and as a component of SOM in the Irish Sea. $C_{30}\Delta^{22}$, C_{16}/C_{18} PUFA and $C_{29}\Delta^{5,24(28)}$ also confirm the importance of dinoflagellates and chlorophyta primary producers. The key role of copepod zooplankton in mineralising the seasonal pytoplanton bloom was also revealed based on the widespread occurrence of PUFA, $C_{27}\Delta^{5}$, $C_{27}\Delta^{5,22}$ and WE. The spatial distribution of these diagnostic compounds reflects the importance the distinct hydrographic regime and the summer gyre for controlling the production, distribution and fate of MOM. The widespread distribution of higher plant alkyl lipids and triterpenoids, revealed the importance of allochtonous TOM as a component of OM in the Irish Sea. The TOM fraction is composed predominantly of recalcitrant plant wax constituents and highlighted the preservation of TOM from source to deposition in surface sediments. The spatial distribution of terrestrial biomarkers indicates that the major transport route is via riverine input from the Boyne Estuary and Dundalk Bay. Near-

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bottom residual currents and seasonal hydrographic zonation also likely play a role in the transport and fate of TOM.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ecss.2013.11.002.

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