Tracing sinking organic matter sources in the NW Iberian upwelling system (NE Atlantic Ocean): comparison between elemental, isotopic and molecular indicators

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Abstract

We studied the seasonal fluctuations in the composition of sinking particulate organic matter (POM) in the only upwelling-affected continental margin of Europe, to improve our understanding of the carbon (C) cycle of such systems. The methods employed targeted the elemental, stable isotope ($\delta^{13}\text{C}_{\text{oc}}$ and $\delta^{15}\text{N}$) and molecular (Py-GC-MS) composition. The results showed that the sinking POM in this margin is predominantly of marine origin, with $\delta^{15}\text{N}$ ($5.2 \pm 0.3 \text{ ‰}$) and C/N (9.7 ± 1.0) values similar to those of marine plankton, and high abundances of pyrolysis products with isoprenoid structures, N-containing products from proteins (indoles, cyanobenzenes, etc.), and *N*-acetylated polysaccharides (acetamide, acetamidofurans) from chitin and peptidoglycan. Furthermore, the dataset demonstrates seasonal differences in POM composition under different oceanographic scenarios: i) dominance of most N-compounds, fatty acids and isoprenoid products during highly productive upwelling seasons, and ii) an increase in the relative abundance of linear alkanes/alkenes, phenols, lignin and PAH reflecting terrestrial influence during downwelling periods. In addition, the detection of isoprenoid alkylthiophenes traces (compounds formed under reducing conditions in the sediment) point to resuspended sediment in the trap material due to hydrodynamic effects of currents and waves on the seafloor. The results show that analytical pyrolysis is a useful tool for identifying different types of autochthonous and terrestrial POM, and therefore identification of the sources of sinking POM.

Keywords: organic matter, stable isotopes, pyrolysis-GC-MS, coastal upwelling system, NW Iberian margin, sediment traps

1. INTRODUCTION

Continental margins, especially those affected by seasonal coastal upwelling, play an important role in the global carbon (C) cycle as major sites of primary production and C sequestration [1-3]. In order to understand the C cycling in these coastal zones (particularly between the shelf and the deep ocean), the identification of not only the marine but also the terrestrial sources of POM is fundamental, because continental inputs may bias calculations of the balance between primary production and POM export from the marine productive layer to the deep waters [4-6], a key issue to understand the capacity of these regions in absorbing atmospheric CO₂.

In coastal environments, POM quality is assessed mainly by stable isotope ratios of organic C ($\delta^{13}\text{C}_{\text{oc}}$) and N ($\delta^{15}\text{N}$) [3,5] of sinking particles collected with sediment traps. Differences in $\delta^{13}\text{C}_{\text{oc}}$ values are then used to distinguish between terrestrial (from -25 to -28 for C3 plants, and from -12 to -15 for C4 plants) and marine organic matter (from -19 to -22) [6]. Furthermore, terrestrial plants rely on atmospheric N₂ with a lower $\delta^{15}\text{N}$ ($\delta^{15}\text{N} \sim 0$) than marine plankton, which utilize dissolved nitrogen with a typical $\delta^{15}\text{N}$ value of 4.8 [7-8]. The sources of POM can also be investigated by means of spectroscopic methods [9-11], or by techniques based on gas chromatography and mass spectrometry (GC-MS) of either lipid extracts [12,13], chemically released fractions [14,15] or thermally degraded macromolecular constituents of POM. The latter approach, i.e. analytical pyrolysis (Py-GC-MS), has been used to identify source materials of POM in terrestrial soils [16] and in lacustrine [17,18], fluvial/estuarine [19,20] and marine [21-24] sediments or suspended sediments. It has proven useful for identification of sources such as chlorophyll from algae, lignin from terrestrial plants, black carbon from fire residues, chitin from arthropods [25-28], and to determine the degradation/preservation state of e.g. lignin, carbohydrates and chlorophyll [29-31].

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180 66 However, there are no studies that used this technique to identify POM sources in
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182 67 regions affected by coastal upwelling.
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184 68 The NW Iberian coastal upwelling system is located at the northern boundary of
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186 69 the unique upwelling system in Europe, modulated by the seasonal wind regime that
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188 70 sustains large stocks of economically important exploitable species [32,33]. During
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190 71 spring-summer, the NW Iberian coast is generally characterized by prevailing northerly
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192 72 winds, that favour upwelling of cold and nutrient-rich subsurface Eastern North Atlantic
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194 73 Central Water (ENACW) on the shelf and into the adjacent Rías (submerged ancient
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196 74 river valleys), increasing primary production in the area [32,34]. On the other hand,
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198 75 south-westerly winds during autumn-winter promote downwelling conditions and storm
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200 76 events that intensify wave orbital velocities and bottom currents, thereby triggering
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202 77 sediment remobilization on the continental shelf [35,36]. Downwelling periods
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204 78 generally coincide with the wet season implying increased fluvial discharge from
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206 79 mainly the Minho and Douro rivers, which constitute an additional source of terrestrial
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208 80 materials to the inner shelf [35,37]. Several studies have examined POM sequestration
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210 81 and/or export to the open ocean under different oceanographic scenarios [38,39]. It was
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212 82 argued that a significant fraction of the POM that sinks on the continental shelf during
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214 83 upwelling seasons originates from primary production. However, it appeared that peak
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216 84 river discharge and resuspension of surface sediments during heavy storm events may
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218 85 dilute the pelagic flux. This finding agreed with previous studies that showed that POM
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220 86 deposited on the NW Iberian margin is a mixture of continental and marine sources
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227 88 In this study elemental, isotopic ($\delta^{13}\text{C}_{\text{oc}}$ and $\delta^{15}\text{N}$) and molecular (Py-GC-MS)
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229 89 composition of POM were used to identify organic matter sources in sinking particles at
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231 90 the inner part of the NW Iberian continental shelf. More specifically, we aim to identify
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POM sources under different oceanographic scenarios, discerning the productive upwelling periods from the highly hydrodynamic downwelling periods.

2. MATERIALS AND METHODS

2.1 Study area and sampling procedure

Between November 2008 and July 2012, the Raia station, which is located on the NW Iberian continental shelf off Cape Silleiro (42° 05' N; 8° 56' W; 75 m water column depth) (Fig. 1), was sampled with a Technicap PPS 4/3 sequential sampling trap (height/diameter ratio of 1.7 and a collecting area of 0.05 m²). The trap was deployed at 35 m water depth, i.e. 40 m above the seafloor. The rotary collector of the sediment trap contained 24 receiving cups that were filled with brine solution (5 psu in excess) to which 6 mL of saturated mercury chloride solution was added to avoid the degradation of the collected particles. The sample processing procedure of the 25 POM samples from sediment traps is explained in detail in Zúñiga et al. [38]. In addition, two surface sediment samples were collected at Raia station with a Van Veen sampler. The sample was freeze-dried and ground to a fine powder prior to analysis.

Daily Ekman transport (-Q_x), which is an estimate of the volume of upwelling water masses per kilometre of coastline, was calculated according to Bakun [42], and used to determine whether a sample corresponded to predominantly up- or downwelling conditions [38]. Estimates of Minho river discharge rates (Table 1) were based on river mouth gauge records (https://github.com/PabloOtero/uptodate_rivers/find/master, [37]).

2.2 Organic carbon and nitrogen isotopic analyses

Elemental analysis of organic carbon (OC) and total nitrogen (TN) were measured on 20 mg subsamples of dry sediment after homogenization with an agate

mortar. Subsamples for OC were decarbonated with repeated additions of 10 μL of HCl 25% prior to analysis. Analyses were performed with a Perkin Elmer 2400 CNH analyser, which had a precision of $\pm 0.3 \mu\text{mol C L}^{-1}$ and $\pm 0.1 \mu\text{mol N L}^{-1}$, respectively.

For determining $\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{15}\text{N}$, ~ 15 mg of sample material was measured by continuous flow isotope ratio mass spectrometry using a Thermo Finnigan MAT253 that was coupled to a Carlo Erba EA1108 elemental analyser through a Conflo III interface. For $\delta^{13}\text{C}_{\text{OC}}$, samples were decarbonated previously. The isotope composition of OC and TN are expressed in the conventional $\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{15}\text{N}$ parts per thousand (‰) relative to VPDB (Vienna Pee Dee Belemnite). The precision of the method was ± 0.15 for both $\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{15}\text{N}$, as determined using acetanilide standard.

2.3 Analytical pyrolysis

Approximately 1 mg of POM-containing subsamples were placed into quartz tubes and pyrolyzed for 10 s at 650 $^{\circ}\text{C}$ (heating rate 10 $^{\circ}\text{C}/\text{ms}$) using a CDS Pyroprobe 5250 coupled to an Agilent 6890 GC and Agilent 5975 MSD. The pyrolysis chamber, transfer line, GC inlet and GC-MS interface were set at 325 $^{\circ}\text{C}$. The GC oven was heated from 60 $^{\circ}\text{C}$ (held 1.5 min) to 325 $^{\circ}\text{C}$ (held 3.0 min) at 20 $^{\circ}\text{C}/\text{min}$. The ion source of the MSD (electron impact mode, 70 eV) was set at 230 $^{\circ}\text{C}$ and the quadrupole detector at 150 $^{\circ}\text{C}$, measuring fragments in the m/z 50–500 range. The GC was equipped with a (non-polar) HP-5MS (5% phenyl, 95% dimethylpolysiloxane) column. Helium was used as the carrier gas (1 ml/min). The main peaks in the pyrolysis chromatograms were denoted, identified and semi-quantified using their main ion fragments (m/z). This process creates a list of relative proportions of each pyrolysis product, expressed as % of total quantified peak area (TQPA). After elimination of several products that could not be reliably quantified in all samples (usually due to co-

elution) and of products that probably originated from the preservative solution (producing large and broad peaks of particularly chlorobenzenes), the list of pyrolysis products consisted of 98 compounds. In order to identify anaerobic reworking at the seafloor we searched for isoprenoid thiophenes in the partial ion chromatograms of m/z 98 and 111, showing evidence of traces of these compounds at the expected retention time and with the published mass spectrum [18], thereby extending the list to 100 compounds. Selected samples were also analyzed by thermally assisted hydrolysis and methylation (THM-GC-MS), under the same conditions as conventional Py-GC-MS but with the addition of 25 % aqueous tetramethylammonium hydroxide (TMAH) prior to inserting the sample into the pyrolysis chamber. This way, POM becomes hydrolyzed and derivatized (methylated), providing additional information on the molecular composition of polar constituents [43]. THM-GC-MS chromatograms were evaluated qualitatively.

2.4 Statistical analyses

Principal Component Analysis (PCA) was used for data analysis and interpretation of the Py-GC-MS dataset. Furthermore, linear correlation analysis was used to compare continuous variables ($n=27$) and one-way ANOVA was used to identify significant differences in a continuous variable for different values of the discrete variable (oceanographic scenario: upwelling and downwelling conditions). Hence, for the ANOVA, the data from surface sediment samples were omitted ($n=25$). All statistical analyses were done using Tanagra software.

3. RESULTS AND DISCUSSION

3.1 Elemental and isotopic composition

The POM from the samples at Raia station has a mean ($n=27$) OC/TN ratio of 9.7 ± 1.0 and a mean $\delta^{13}\text{C}_{\text{oc}}$ signal of -22.0 ± 1.1 ‰ (Table 1; Fig. 2). These values are more typical of marine plankton [44] than terrestrial OM transported from rivers in the region [41,45] (Fig. 3a), pointing to a dominant contribution of marine POM. The $\delta^{15}\text{N}$ isotopic signal (5.2 ± 0.3 ‰) is also similar to $\delta^{15}\text{N}$ values of POM for plankton samples of the NW Iberian coast ($\delta^{15}\text{N} \sim 5$ ‰; [44]) and not to $\delta^{15}\text{N}$ of riverine POM (Fig. 3b). These results confirm a predominant use of marine inorganic nitrogen, such as nitrates, for primary production [8].

The OC/TN ratio of the POM is consistently lower during upwelling (Fig. 2a) than during downwelling periods, whereas $\delta^{13}\text{C}_{\text{oc}}$ (Fig. 2b) showed an inverse trend (less negative values under upwelling conditions). In terms of OC/TN and $\delta^{13}\text{C}_{\text{oc}}$, the samples from upwelling periods are more similar to the marine end-member (plankton) than samples from downwelling periods (Fig. 3a). Furthermore, the less negative $\delta^{13}\text{C}_{\text{oc}}$ and lowest OC/TN values correspond to samples with high marine biogenic silica content (Table 1; Fig. 3c). These results confirm that upwelling conditions favour marine productivity and the control of oceanographic scenario on OC/TN and $\delta^{13}\text{C}_{\text{oc}}$ [38,39]. On the other hand, downwelling samples generally coincide with high Minho river discharge, as shown by relatively high OC/TN and more negative $\delta^{13}\text{C}_{\text{oc}}$ (Fig. 3d).

3.2 Pyrolysis-GC-MS products

Pyrolysis chromatograms from samples that are representative of downwelling and upwelling conditions are presented in Figure 4. The set of pyrolysis products (Table 2) and their relative proportions (Supplementary Information) point to a dominance of autochthonous marine sources in all samples. This is inferred mainly from the

preponderance of N-containing pyrolysis products ($n=27$; 32.4 ± 4.2 % of TQPA), which is in the same elevated range as chironomid and mosquito-pupa-dominated POM from sediment traps in a Swedish lake (26 ± 3 %) [18] with >70 % autochthonous POM [46], and tropical soil organic matter composed of microbial tissue (34 ± 5 %) [47]. These exceptionally high proportions of N-compounds are in agreement with the low OC/TN ratio (9.7 ± 1.0). The N-compounds include typical products of intact proteinaceous material such as indole, methylindole, cyanobenzenes and diketodipyrrole [48], but also markers of *N*-acetylated macromolecules (probably from chitin or peptidoglycan) such as acetamide and acetamidofurans [49].

The carbohydrate products (13.2 ± 3.8 %) are dominated by furaldehydes whereas markers of intact plant materials (anhydrosugars, pyrans, etc.) are absent. Considering the large abundance of N-containing products, the carbohydrate products may be largely derived from N-containing polysaccharides including chitin from phyto- and zooplankton or bacterial peptidoglycan.

Compounds based on a polymethylene chain (MCC; 20.8 ± 9.2 %) include linear (*n*-alkanes, *n*-alkenes and *n*-alkanoic acids) and isoprenoid structures (prist-1-ene, phytadienes, isoprenoid thiophenes). The isoprenoid compounds probably originate from autochthonous sources (such as phytol in chlorophyll), whereas the more abundant linear compounds can be related to the high proportions of aliphatic material in algae (algaenan, free hydrocarbons, etc.) or in terrestrial plant materials (cutin, suberin, waxes, etc.). Even though the peaks of the isoprenoid alkylthiophenes are small (0.10 ± 0.09 % of TQPA; Supplementary Information) these compounds are formed upon bacterial degradation of mainly chlorophyll under reducing conditions at the seafloor, and therefore useful indicators of sediment resuspension [50].

The monocyclic aromatic hydrocarbons (MAHs; 15.2 ± 2.9 %) detected are

toluene and tetramethylbenzene. Here, toluene is probably a protein product (e.g. phenylalanine moieties) whereas larger contributions of tetramethylbenzene than C₂- and C₃-alkylbenzenes have been linked to aquatic sources, in particular algae [24]. The detected polycyclic aromatic hydrocarbons (PAHs; 1.3 ± 0.8 %) are not sufficiently abundant for a confident identification of pyrogenic POM.

Phenols (13.7 ± 2.6 %) are products of proteins (e.g. tyrosine moieties) but also other sources such as lignin [48,51]. More unambiguous lignin-derived products (4-vinylphenol, guaiacol, 4-vinylguaiacol) are very scarce (1.3 ± 0.5 %), suggesting that lignin from terrestrial plants is only a minor source of the POM but nonetheless a useful proxy of terrestrial fluxes. Other compounds (mostly O-containing PAHs, and steroids/triterpenoids) account for 1.9 ± 2.9 % of TQPA.

3.3 PCA and ANOVA

Figure 5 shows the seasonal trends in PC1 (which explains 31% of total variance) and PC2 (14 %) scores, whereas Figure 6 shows the PC1 -PC2 plot of the samples (scores; Fig. 6a) and the pyrolysis products (loadings; Fig. 6b). There is a clear difference in PC1 scores between the samples of the two main oceanographic conditions, i.e. from upwelling seasons (positive scores) and from downwelling periods (negative scores) (Fig. 5a). Hence, the positive loadings on PC1 of most N-compounds, fatty acids and isoprenoid MCC (Fig. 6b) reflect the relatively large proportion of N- and chlorophyll-rich POM from primary production under upwelling conditions. On the other hand, negative loadings for *n*-alkanes/*n*-alkenes, phenols, lignin and PAH (from terrestrial aliphatic material, lignin and perhaps pyrogenic POM) are relatively abundant during downwelling periods. The positive correlation between $\delta^{13}\text{C}_{\text{oc}}$ and PC1 ($n=27$, $r^2=0.70$, $P<0.001$; Fig. 7a), and the negative relationship between OC/TN ratio and PC1

($r^2=0.49$; $P<0.001$; Fig. 7b), show that PC1 is controlled by seasonal variations in the relative contributions of marine and terrestrial sources. Hence, even though the sinking POM in both upwelling and downwelling periods is composed of derivatives of predominantly marine POM, the fluctuations in continental inputs from rivers can still be recognized on the elemental, isotopic and molecular compositions of the POM, and it is in fact the major source of variability in the Py-GC-MS dataset.

The loadings for PC2 are positive for most of the N-compounds, phenols and carbohydrate products, and negative for the majority of the MCC (especially fatty acids and isoprenoid compounds) (Fig. 6b). The combination of loadings suggests that PC2 reflects the intensity of POM degradation, with positive loadings for labile materials rich in protein and polysaccharides (abundant in well-preserved POM) and negative loadings for more refractory (aliphatic) components that is enriched in more degraded POM through selective preservation. If the spring 2009 sample with PC2 scores < -10 is omitted, PC2 also presents a significant negative correlation with OC/TN ratio (Fig. 7d) ($n=26$; $r^2=0.44$, $P<0.005$), which is consistent with the positive loadings of many N-compounds on PC2 (see above). These results suggest that the OC/TN ratio is not only affected by upwelling/downwelling cycles (indicative of source materials) but also, albeit to a minor extent, by organic matter degradation. This is not the case for $\delta^{13}\text{C}_{\text{oc}}$ (Fig. 7c).

Using one-way ANOVA (Supplementary Information) with the main oceanographic scenarios (upwelling vs. downwelling) as the discrete variable, it is confirmed that the sediment trap samples from upwelling periods are significantly enriched ($P<0.05$) in chitin/peptidoglycan products (inferred from significantly higher proportions of acetamidofurans), several protein products (diketopiperazines), chlorophyll products (phytadienes), *n*-alkanoic acids (C_{14} , C_{16} , C_{18} , $\text{C}_{18:1}$),

steroid/triterpenoids (three compounds) and two unidentified N-compounds. This set of compounds reflects enrichment of autochthonous N-rich sources composed mainly of protein, chitin, chlorophyll and probably fatty acids. Nevertheless, the aforementioned enrichment of molecular indicators of terrestrial sources in the samples from downwelling periods on the basis of PCA (PC1 scores) is not significant in this ANOVA analysis.

To better differentiate between marine and terrestrial POM sources, we therefore performed an additional ANOVA analysis considering all upwelling samples but only downwelling samples with strong Minho river inputs. The ANOVA analysis of the reduced dataset ($n=20$; Supplementary Information) showed that samples from downwelling periods with intense river discharge are enriched ($P<0.05$) in lignin-derived products (guaiacol, 4-vinylguaiacol, 4-vinylphenol), i.e., products that are usually assigned to pyrogenic POM (naphthalenes, biphenyl, benzonitrile; [28]), perhaps oxidized pyrogenic POM (dihydroindenone, C₃-naphthalenone) and linear MCC (C₁₄-C₃₁ alkanes and C₁₂-C₂₈ alkenes). This set of compounds reflects the signal from terrestrial POM from vascular plants (lignin, aliphatic constituents and perhaps pyrogenic POM), delivered by rivers. This ANOVA analysis also shows different effects of oceanographic scenario on the different N-containing pyrolysis products, which can be summarized as (1) N-containing moieties from autochthonous sources, represented by products of chlorophyll, proteins and chitin/peptidoglycan, that are enriched in POM during upwelling conditions and (2) terrestrial N sources of POM, i.e., pyrogenic POM represented by benzonitrile [28] and possibly a soil microbial component (represented by pyridine), which are enriched during downwelling periods of high river discharge. This shows that Py-GC-MS can be used to recognize different sources of N to the POM and identify changes in their relative proportions.

Furthermore, the aliphatic sources show striking differences in terms of seasonal fluctuations: isoprenoid alkanes/alkenes and *n*-alkanoic acids of marine origin have higher proportions during upwelling periods, whereas linear MCC are enriched during downwelling periods, and hence probably predominantly of terrestrial origin (as confirmed by the presence of cutin, see below). These results are in agreement with the different loadings of the MCC on PC1 (Fig. 6b). If this interpretation is correct, it can also be argued that marine sources that are theoretically prolific of linear MCC such as algaenan or algaenan-like structures from primary producers such as algae or cyanobacteria [52,53], do not account for a significant fraction of the POM, as the linear MCC are apparently associated with terrestrial POM.

The detection of traces of isoprenoid alkylthiophenes (compounds formed under reducing conditions in the sediment) and the great similarity in elemental, isotopic and molecular composition between sinking POM from downwelling periods and surface sediments (Fig. 3, Fig. 7) suggests that terrestrial POM may originate not only from “fresh” river discharge, but also from resuspension of previously deposited riverine material (i.e. effect of waves and current intensifications on inner shelf deposits; [38,39]). This would corroborate previous findings based on surface sediment samples that showed that terrestrial POM settles close to the river mouths [41], but can be subsequently redistributed along the NW Iberian margin due to currents and waves action [54,55].

3.4 THM-GC-MS

The THM-GC-MS chromatograms (Fig. 8) show that the sample collected during highly hydrodynamic downwelling conditions (March 2010; [38]) has larger peaks of cutin products (mid-chain hydroxylated fatty acid methyl esters) and methoxyl-

substituted aromatics (mostly guaiacol moieties from lignin; G4 and G6), than the sample that was considered representative of upwelling-favourable conditions (June 2009; [39]). This cutin, which is a constituent of leaf cuticles of most higher plants [56], may be safely ascribed to terrestrial sources and has been previously detected in marine sediments (e.g. [57]). The presence of plant-derived aliphatic biopolymers in high river discharge samples, albeit that their abundance is overshadowed by sources of primary production, may explain the more strongly negative $\delta^{13}\text{C}_{\text{oc}}$ in such samples (Fig. 7a) because plant-derived aliphatic biopolymers such as cutin and suberin have extremely negative $\delta^{13}\text{C}_{\text{oc}}$ (< -30 ‰; [58]).

The sample corresponding to upwelling conditions shows slightly larger peaks for alkylindoles, probably from algal protein. The chromatograms of both samples are dominated by fatty acid methyl esters which are overrepresented by THM-GC-MS.

4. Conclusions

The results from Py-GC-MS, OC/TN ratios, $\delta^{13}\text{C}_{\text{oc}}$ and $\delta^{15}\text{N}$ have unambiguously shown that the sinking POM in the NW Iberian coastal upwelling zone is predominantly of marine origin. The pyrolysis products characteristic of marine primary producers were isoprenoid aliphatic products, N-containing products from proteins (indoles, cyanobenzenes, etc.), and *N*-acetylated polysaccharides (acetamide, acetamidofurans) such as chitin and peptidoglycan. Terrestrial components represented a minor contribution as reflected by terrestrial biomarkers such as lignin and cutin (from higher plants), and perhaps pyrogenic OM.

The oceanographic conditions (upwelling and downwelling) appeared to modulate the variability in pyrolysis fingerprints and coincided with shifts in OC/TN and $\delta^{13}\text{C}_{\text{oc}}$. More specifically, POM from upwelling periods is enriched in N-containing

moieties (proteins) and isoprenoid aliphatic POM from primary producers. On the other hand, POM from downwelling periods is enriched in terrestrial markers, especially during high river discharge.

Pyrolysis-GC-MS has proven to be useful for identification of POM sources in this coastal upwelling region. In a context of global change where stronger and more frequent flood events may intensify and consequently increase export of terrestrial material to continental shelves, the use of Py-GC-MS appears to be a powerful tool to trace the fluxes of terrestrial organic matter at these land–ocean interfaces and hence to monitor their C cycle dynamics.

Acknowledgements

The authors are grateful to the crew of the “R/V Mytilus” for their assistance during the cruises. The authors want to recognize lab work of different members of the Oceanography group from the Instituto de Investigaciones Marinas (IIM-CSIC). This study was sponsored by EU FEDER projects RAIA (INTERREG 2009/2011-0313/RAIA/E) and RAIA.co (INTERREG 2011/2013-052/RAIA.co/1E), Spanish Government project CAIBEX (CTM2007-66408-C02-01/MAR), EXCAPA project (10MDS402013PR) supported by the Xunta de Galicia and the CALIBERIA project (PTDC/MAR/102045/2008) financed by Fundação para a Ciência e a Tecnologia (FCT-Portugal). D.Z. was funded by a postdoctoral fellowship (Plan I2C) from Xunta de Galicia (Spain). We are very grateful for the constructive comments of various anonymous reviewers.

References

- [1] Walsh, J., 1991. Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. *Nature* 350, 53-55.
- [2] Capone, D.G., Hutchins, D.A., 2013. Microbial biogeochemistry of coastal upwelling regimes in a changing ocean. *Nature* 6, 711-717.
- [3] Peña, M.A., Denman, K.L., Forber, J.R., Calvert, S.E., Thomson, R.E., 1996. Sinking particle fluxes from the euphotic zone over the continental slope of an eastern boundary current region. *Journal of Marine Research* 54, 1097-1122.
- [4] Forest, A., Sampei, M., Hattori, H., Makabe, R., Sasaki, H., Fukuchi, M., Wassmann, P., Fortier, L., 2007. Particulate organic carbon fluxes on the slope of the Mackenzie Shelf (Beaufort Sea): Physical and biological forcing of shelf-basin exchanges. *Journal of Marine Systems* 68, 39-54.
- [5] Tesi, T., Puig, P., Palanques, A., Goñi, M.A., 2010. Lateral advection of organic matter in cascading-dominated submarine canyons. *Progress in Oceanography* 84, 185-203.
- [6] Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? *Organic Geochemistry* 27, 195-212.
- [7] Altabet, M.A., 1996. Nitrogen and carbon isotopic tracers of the source and transformation of particles in the deep-sea, p. 155-184. In V. Ittekkot, P. Schäfer, S. Honjo and P.J. Depetris [eds.], *Particle flux in the ocean*. Wiley and Sons, new York, pp. 372.
- [8] Sigman, D.M., Altabet, M.A., McCorkle, M.D., Francois, R., Fisher, G., 2000. The $\delta^{15}\text{N}$ of nitrate in the Southern Ocean: Nitrogen cycling and circulation in the ocean interior. *Journal of Geophysical Research* 105, 19599-19614.

- [9] Tremblay, L., Alaoui, G., Léger, M.N., 2011. Characterization of aquatic particles by direct FTIR analysis of filters and quantification of elemental and molecular compositions. *Environmental Science and Technology* 45, 9671–9679.
- [10] Li, H., Minor, E.C., 2015. Biogeochemical characteristics of settling particulate organic matter in Lake Superior: A seasonal comparison. *Organic Geochemistry* 85, 76-88.
- [11] Klun, K., Šket, P., Falnoga, I., Faganeli, J., 2015. Variation in colloidal organic matter composition and aggregation in coastal waters (Gulf of Trieste, Northern Adriatic Sea). *Geomicrobiology Journal* 32, 609-615.
- [12] Wakeham, S.G., Beier, J.A., 1991. Fatty acid and sterol biomarkers as indicators of particulate matter source and alteration processes in the Black Sea. *Deep-Sea Research* 38, S943–S968.
- [13] Bianchi, T.S., Canuel, E.A., 2011. Chemical biomarkers in aquatic ecosystems. Princeton University Press, pp. 392.
- [14] Hedges, J.I., Clark, W.A., Come, G.L., 1988. Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography* 33, 1116–1136.
- [15] Brion, D., 2007. Organic matter preservation in marine sediments: A bulk and molecular study. PhD Thesis, Concordia University, Montréal, Canada, pp. 154.
- [16] Derenne, S., Quénéa, K., 2015. Analytical pyrolysis as a tool to probe soil organic matter. *Journal of Analytical and Applied Pyrolysis* 111, 108-120.
- [17] Fuhrmann, A., Fischer, T., Lücke, A., Brauer, A., Zolitschka, B., Horsfield, B., Negendank, J.F.W., Schleser, G.H., Wilkes, H., 2004. Late Quaternary environmental and climatic changes in central Europe as inferred from the

- composition of organic matter in annually laminated maar lake sediments.
- Geochemistry, Geophysics, Geosystems 5, 1-20.
- [18] Kaal, J., Martínez Cortizas, A., Rydberg, J., Bigler, C., 2015. Seasonal changes in molecular composition of organic matter in lake sediment trap material from Nylandssjön, Sweden. *Organic Geochemistry* 83-84.
- [19] Sicre, M.A., Peulve, S., Saliot, A., de Leeuw, J.W., Baas, M., 1994. Molecular characterization of the organic fraction of suspended matter in the surface waters and bottom nepheloid layer of the Rhone delta using analytical pyrolysis. *Organic Geochemistry* 21, 11–26.
- [20] Peulvé, S., Sicre, M.-A., Saliot, A., De Leeuw, J.W., Baas, M., 1996. Molecular characterization of suspended and sedimentary organic matter in an Arctic delta. *Limnology and Oceanography* 41, 488-497.
- [21] Saliot, A., Ulloa-Guevera, A., Viets, T.C., de Leeuw, J.W., Schenck, P.A., Boon, J.J., 1984. The application of pyrolysis gas chromatography-mass spectrometry to the chemical characterization of suspended matter in the ocean. *Organic Geochemistry* 6, 295–304.
- [22] Hwang, J., Druffel, E.R.M., Eglinton, T.I., Repeta, D.J., 2006. Source(s) and cycling of the nonhydrolyzable organic fraction of oceanic particles. *Geochimica et Cosmochimica Acta* 70, 5162–5168.
- [23] Çoban-Yıldız, Y., Fabbri, D., Baravelli, V., Vassura, I., Yilmaz, A., Tugrul, S., Eker-Develi, E., 2006. Analytical pyrolysis of suspended particulate organic matter from the Black Sea water column. *Deep-Sea Research II* 53, 1856–1874.
- [24] Nierop, K.G.J., Reichart, G.-J., Veld, H., Sinninghe Damsté, J.S., 2017. The influence of oxygen exposure time on the composition of macromolecular organic

- matter as revealed by surface sediments on the Murray Ridge (Arabian Sea).
- Geochimica et Cosmochimica Acta 206, 40-56.
- [25] Boon, J.J., Dupont, L., De Leeuw, J.W., 1986. Characterization of a peat bog profile by Curie Point pyrolysis-mass spectrometry combined with multivariant analysis and by pyrolysis gas chromatography–mass spectrometry. In: C.H. Fuchsman (ed.), Peat and Water. Elsevier Applied Science Publishers Ltd, pp. 215–219.
- [26] Stankiewicz, B.A., van Bergen, P.F., Duncan, I.J., Carter, J.F., Briggs, D.E.G., Evershed, R.P., 1996. Recognition of chitin and proteins in invertebrate cuticles using analytical pyrolysis/gas chromatography and pyrolysis/gas chromatography/mass spectrometry. Rapid Communications in Mass Spectrometry 10, 1747–1757.
- [27] Buurman, P., Nierop, K.G.J., Pontevedra-Pombal, X., Martinez Cortizas, A., 2006. Molecular chemistry by pyrolysis–GC/MS of selected samples of the Penido Vello peat deposit, Galicia, NW Spain. In: I.P. Martini, A. Martínez Cortizas, W. Chesworth (eds.), Peatlands: Evolution and Records of Environmental and Climate Changes. Elsevier, The Netherlands, 217–240.
- [28] Kaal, J., Martínez-Cortizas, A., Nierop, K.G.J., Buurman, P., 2008. A detailed pyrolysis-GC/MS analysis of a black carbon-rich acidic colluvial soil (Atlantic ranker) from NW Spain. Applied Geochemistry 23, 2395-2405.
- [29] Kuder, T., Kruege, M.A., 1998. Preservation of biomolecules in sub-fossil plants from raised peat bogs - a potential paleoenvironmental proxy. Organic Geochemistry 29, 1355–1368.
- [30] Ishiwatari, M., Ishiwatarii, R., Sakashita, H., Tatsumi, T., Tominaga, H., 1991. Pyrolysis of chlorophyll a after preliminary heating at a moderate temperature:

- implications for the origin of prist-1-ene on kerogen pyrolysis. *Journal of Analytical and Applied Pyrolysis* 18, 207-218.
- [31] Schellekens, J., Buurman, P., Pontevedra-Pombal, X., 2009. Selecting parameters for the environmental interpretation of peat molecular chemistry - A pyrolysis-GC/MS study. *Organic Geochemistry* 40, 678–691.
- [32] Fraga, F., 1981. Upwelling off the Galician coast, northwest of Spain. In: Richards, F. (Ed.), *Coastal Upwelling*. American Geophysical Union, Washington, 176-182.
- [33] Arístegui, J., Barton, E.D., Álvarez-Salgado, X.A., Santos, A.M.P., Figueiras, F.G., Kifani, S., Hernández-León, S., Mason, E., Machú, E., Demarcq, H., 2009. Sub-regional ecosystem variability in the Canary Current upwelling. *Progress in Oceanography* 83, 33-48.
- [34] Figueiras, F.G., Labarta, U., Fernández Reiriz, M.J., 2002. Coastal upwelling, primary production and mussel growth in the Rías Baixas of Galicia. *Hydrobiologia* 484, 121-131.
- [35] Dias, J.M.A., González, R., García, C., Díaz-del-Río, V., 2002. Sediment distribution patterns on the Galicia–Minho continental shelf. *Progress in Oceanography* 52, 215–231.
- [36] Villaceros-Robineau, N., 2017. Bottom boundary layer dynamics and its effects on particle resuspension and transport in the NW Iberian coastal upwelling system. Ph.D. Thesis. University of Vigo, Spain. <http://hdl.handle.net/11093/912>.
- [37] Otero, P., Ruiz-Villarreal, M., Peliz, A., Cabanas, J.M., 2010. Climatology and reconstruction of runoff time series in northwest Iberia: influence in the shelf buoyancy budget off Ría de Vigo. *Scientia Marina* 74, 247-266.
- [38] Zúñiga, D., Villaceros-Robineau, N., Salgueiro, E., Alonso-Pérez, F., Rosón, G., Abrantes, F., Castro, C.G., 2016. Particle fluxes in the NW Iberian coastal

- upwelling system: hydrodynamical and biological control. *Continental Shelf Research* 123, 89-98.
- [39] Zúñiga, D., Santos, C., Froján, M., Salgueiro, E., Rufino, M.M., De La Granda, F., Figueiras, F.G., Castro, C.G., Abrantes, F., 2017. Diatoms as a paleoproductivity proxy in the NW Iberian coastal upwelling system (NE Atlantic). *Biogeosciences* 14, 1165-1179.
- [40] Alt-Epping, U., Mil-Homes, M., Hebbeln, D., Abrantes, F., Schneider, R.R., 2007. Provenance of organic matter and nutrient conditions on a river and upwelling influenced shelf: A case study from the Portuguese margin. *Marine Geology* 243, 169-179.
- [41] Schmidt, F., Hinrichs, K.U., Elvert, M., 2010. Sources, transport and partitioning of organic matter at a highly dynamic continental margin. *Marine Chemistry* 118, 37-55.
- [42] Bakun, A., 1973. Coastal upwelling Indices, West Coast of North America, 1946–71. US Department of Commerce, National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Seattle, USA.
- [43] Challinor, J.M., 2001. Review: the development and applications of thermally assisted hydrolysis and methylation reactions. *Journal of Analytical and Applied Pyrolysis* 61, 3–34.
- [44] Bode, A., Carrera, P., Lens, S., 2003. The pelagic foodweb in the upwelling ecosystem of Galicia (NW Spain) during spring: Natural abundance of stable carbon and nitrogen isotopes. *ICES Journal of Marine Science* 60, 11-22.
- [45] Bode, A., Varela, M., Prego, R., 2011. Continental and marine sources of organic matter and nitrogen for rías of northern Galicia (Spain). *Marine Ecology Progress Series* 437, 13-26.

- 1240
1241
1242 512 [46] Gälman, V., Rydberg, J., Bigler, C., 2009. Decadal diagenetic effects on d¹³C and
1243
1244 513 d¹⁵N studied in varved lake sediment. *Limnology and Oceanography* 54, 917–
1245
1246 514 924.
1247
1248 515 [47] Vázquez Polo, J.R., Schellekens, J., Kaal, J., 2015. Composition of the organic
1249
1250 516 matter in soils from six pedoclimatic zones of Magdalena (Colombia). *Spanish*
1251
1252 517 *Journal of Soil Science* 5, 243-258.
1253
1254 518 [48] Tsuge, S., Matsubara, H., 1985. High-resolution pyrolysis-gas chromatography of
1255
1256 519 proteins and related materials. *Journal of Analytical and Applied Pyrolysis* 8, 49–
1257
1258 520 64.
1259
1260 521 [49] Van der Kaaden, A., Boon, J.J., de Leeuw, J.W., de Lange, F., Schuyl, P.W.J.,
1261
1262 522 Schulten, H.-R., Bahr, U., 1984. Comparison of analytical pyrolysis techniques in
1263
1264 523 the characterization of chitin. *Analytical Chemistry* 56, 2160–2165.
1265
1266 524 [50] Brassell, S.C., Lewis, C.A., De Leeuw, J.W., De Lange, F., Sinninghe Damsté,
1267
1268 525 J.S., 1986. Isoprenoid thiophenes: novel products of sediment diagenesis? *Nature*
1269
1270 526 320, 160-162.
1271
1272 527 [51] Ralph, J., Hatfield, R.D., 1991. Pyrolysis-GC–MS characterization of
1273
1274 528 foragematerials. *Journal of Agricultural and Food Chemistry* 39, 1426–1437.
1275
1276 529 [52] Blokker, P., Schouten, S., van den Ende, H., de Leeuw, J.W., Hatcher, P.G.,
1277
1278 530 Sinninghe Damsté, J.S., 1998. Chemical structure of algaenans from the fresh water
1279
1280 531 algae *Tetrahedron minimum*, *Scenedesmus communis* and *Pediastrum boryanum*.
1281
1282 532 *Organic Geochemistry* 29, 1453–1468.
1283
1284 533 [53] Biller, P., Ross, A.B., Skill, S.C., 2015. Investigation of the presence of an
1285
1286 534 aliphatic biopolymer in cyanobacteria: Implications for kerogen formation. *Organic*
1287
1288 535 *Geochemistry* 81, 64-69.
1289
1290
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1301 536 [54] Van Weering, T.C.E., de Stigter, H.C., Boer, W., de Haas, H., 2002. Recent
1302
1303 537 sediment transport and accumulation on the NW Iberian margin. Progress in
1304
1305 538 Oceanography 52, 349-371.
1306
1307
1308 539 [55] Zhang, W., Cui, Y., Santos, A.I., Hanebuth, T.J.J., 2016. Storm-driven bottom
1309
1310 540 sediment transport on a high-energy narrow shelf (NW Iberia) and development of
1311
1312 541 mud depocenters. Journal of Geophysical Research: Oceans 121, 5751-5772.
1313
1314 542 [56] de Leeuw, J.W., Versteegh, G.J.M., van Bergen, P.F., 2006. Biomacromolecules of
1315
1316 543 algae and plants and their fossil analogues. Plant Ecology 182, 209–233.
1317
1318 544 [57] Goñi, M.A., Hedges, J.I., 1990. The diagenetic behavior of cutin acids in buried
1319
1320 545 conifer needles and sediments from a coastal marine environment. Geochimica et
1321
1322 546 Cosmochimica Acta 54, 3083-3093.
1323
1324 547 [58] Feng, X., Xu, Y., Jaffé, R., Schlesinger, W.H., Simpson, M.J., 2010. Turnover rates
1325
1326 548 of hydrolysable aliphatic lipids in Duke Forest soils determined by compound
1327
1328 549 specific ^{13}C isotopic analysis. Organic Geochemistry 41, 573-579.
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Figure captions

Figure 1. Map of the NW Iberian Peninsula continental margin showing the position of the mooring line (Raia) (red circle) where the sediment trap and surface sediment samples were taken. Locations of samples from previous studies are indicated as well: stations MR1 and MR2 (orange circles) along the Minho River [41], Northern Galicia Rivers (Lourido, Landoi, Mera and Sor rivers; [45]), and stations 36, 37, 38, 39 and 40 from which plankton samples were obtained (green circles) [44].

Figure 2. Time series of a) organic carbon (OC)/total N (TN) ratio (mol:mol) and b) stable OC isotope ratio $\delta^{13}\text{C}$ (‰). Transparent yellow rectangles indicate periods of downwelling-favourable conditions (high OC/TN, strongly negative $\delta^{13}\text{C}$).

Figure 3. a) Stable organic carbon isotope ratio ($\delta^{13}\text{C}_{\text{oc}}$) plotted against the organic C (OC)/ total N (TN)) ratio and b) $\delta^{13}\text{C}_{\text{oc}}$ plotted against total nitrogen isotopic ratio ($\delta^{15}\text{N}$) of the settling POM recovered during upwelling (white symbols) and downwelling seasons (red symbols). Samples used as reference materials are shown for comparison: Minho [41] and north Galician rivers [45] (orange symbols), marine plankton in north Galicia [44] (green symbols) and surface sediment at Raia (blue symbols). Lower panels (c, d) show scatter plots of $\delta^{13}\text{C}_{\text{oc}}$ vs. OC/TN ratio for the studied POM samples, with symbol colour scales according to c) the percentages (%) weight) of biogenic silica (BioSi) and d) the Minho river discharge rate at the time of sampling (from [38]).

Figure 4. Example pyrolysis chromatograms representative of a) downwelling (March 5, 2010) and b) upwelling (June 15, 2009) conditions. Abbreviations: 5m2f=5-methyl-2-furaldehyde, 4VP=4-vinylphenol, AAn=alkane/alkene doublet with *n* indicating chain length, dkdp=diketodipyrrole, Nn=Cn alkylnitrile, Fn=Cn fatty acid, An=Cn alkylamide, Ph=phytadiene (three compounds).

Figure 5. Time series of a) PC1 scores and b) PC2 scores from the PCA analysis of the Py-GC-MS dataset. Transparent yellow rectangles indicate periods of downwelling-favourable conditions (high OC/TN, strongly negative $\delta^{13}\text{C}_{\text{oc}}$, negative PC1 scores). The sample marked by an asterisk (*) is the outlier in the PC2 score-OC/TN plot (see text).

Figure 6. Results of the PCA analysis, a) PC1 and PC2 scores of the samples obtained from RAIA station. Green circles correspond to samples recovered under upwelling favourable conditions; red triangles indicate samples recovered during downwelling periods. Symbols for samples from downwelling periods are differentiated between those that coincide with intense fluvial discharge (upward directed red triangles) from those when river discharge was low (downward directed red triangles); blue triangles correspond to surface sediment samples recovered at RAIA station. b) Loadings of the pyrolysis products from the same PCA analysis. Abbreviations: MAH = monocyclic aromatic hydrocarbon, MCC = methylene chain compounds, PAH = polycyclic aromatic hydrocarbon.

Figure 7. Scatter plots of a) PC1 from PCA of the Py-GC-MS data and $\delta^{13}\text{C}_{\text{oc}}$, b) PC1 and OC/TN ratio, c) PC2 and $\delta^{13}\text{C}_{\text{oc}}$, d) PC2 and OC/TN. Colour scale refers to samples

601 recovered during upwelling (green dots) and downwelling (red triangles) periods.
 602 Samples collected during high fluvial discharge are labelled with “river” (upward-
 603 directed red triangles). Sediment samples are shown in blue.
 604
 605 **Figure 8.** Example chromatograms of THM-GC-MS representative of a) downwelling
 606 (March 5, 2010) and b) upwelling (June 15, 2009) conditions. Abbreviations: G=
 607 dimethoxybenzenes (mainly from guaiacol lignin structures), *Fn*=fatty acid methyl
 608 esters with *n* indicating chain length, hF=hydroxyl-substituted fatty acids,
 609 dhF=dihydroxy-substituted fatty acids, thF=trihydroxy-substituted fatty acids,
 610 Ph=phytadiene.

Tables

Table 1. Sampling dates, environmental variables (Minho river discharge) and biogeochemical data from sediment trap samples taken at the Raia station. Data obtained from surface sediment samples (S1 and S2) are also shown (OC= organic carbon, TN= total nitrogen, BioSi= biogenic silica content; $\delta^{15}\text{N}$ = total nitrogen isotope ratio, $\delta^{13}\text{C}_{\text{OC}}$ = organic carbon isotope ratio). n.d.= not determined.

Date (day-month-yr)	Minho (m ³ s ⁻¹)	OC %	TN %	OC/TN mol:mol	BioSi %	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}_{\text{OC}}$ (‰)
27-11-08	228	3.95	0.45	10.21	3.47	5.19	-22.67
25-12-08	421	3.33	0.39	9.89	2.54	5.12	-23.05
12-01-09	368	3.06	0.33	10.70	2.74	4.99	-23.18
31-03-09	250	4.09	0.44	10.95	3.22	5.16	-21.67
09-04-09	132	6.71	1.21	9.37	N/A	5.60	-21.64
18-04-09	269	5.02	0.59	9.91	4.09	4.96	-21.30
15-06-09	181	7.79	1.11	8.21	9.45	6.18	-20.32
27-06-09	55	6.31	0.88	8.40	9.58	5.34	-20.50
06-08-09	84	6.49	0.86	8.76	7.49	5.31	-21.16
09-10-09	125	9.74	1.21	9.37	N/A	5.60	-21.64
27-10-09	122	5.58	0.70	9.23	4.65	5.52	-21.92
05-11-09	64	5.09	0.63	9.36	4.60	5.56	-22.07
23-11-09	202	2.97	0.35	10.01	2.85	5.52	-22.85
02-12-09	322	3.61	0.46	9.19	3.12	5.75	-23.18
03-02-10	672	3.30	0.35	10.88	2.60	4.95	-23.97
05-03-10	1116	4.20	0.46	10.62	3.82	5.70	-23.67
30-01-11	588	3.26	0.35	10.80	2.27	5.07	-23.46
06-02-11	504	3.63	0.40	10.58	3.16	4.97	-23.12
19-09-11	54	6.44	0.88	8.51	5.26	4.99	-20.61
26-09-11	84	5.92	0.83	8.35	5.47	4.86	-20.84
03-10-11	112	6.09	0.87	8.21	6.07	4.96	-20.61
12-02-12	131	3.34	0.39	10.10	3.98	4.96	-21.95
30-04-12	338	4.48	0.59	8.88	5.56	5.03	-21.68
04-06-12	239	7.69	1.04	8.63	8.86	5.34	-21.44
11-06-12	159	7.49	0.97	9.03	9.10	5.30	-21.27
S1	n.d.	2.60	0.28	10.94	n.d.	5.47	-22.84
S2	n.d.	0.71	0.07	11.39	n.d.	4.69	-23.29

Table 2. List of pyrolysis products with retention times (RT) and ion fragments used for semi-quantification (m/z). Ion fragments within parenthesis correspond to the compound but were not used for peak integration (due to co-elution or other issues). Group labels indicate structural features or likely source indications of the products (CARB=carbohydrate, LIG=lignin, MAH=monocyclic aromatic hydrocarbon, MCC=methylene chain compound, NCOMP=nitrogen-containing compound, PAH=polycyclic aromatic hydrocarbon, PHEN=phenol).

RT (min)	compound	m/z	group
3.289	3/2-furaldehyde and dimethylfuran	95+96	CARB
4.192	unidentified furfural	109+110	CARB
4.462	5-methyl-2-furaldehyde	109+110	CARB
5.141	2,3-dimethylcyclopent-2-en-1-one	67+110	CARB
5.743	levoglucosenone	68+98	CARB
5.556	guaiacol	109 (124)	LIG
6.605	4-vinylphenol	120+91	LIG
7.284	4-vinylguaiacol	135+150	LIG
2.786	toluene	91+92	MAH
6.101	tetramethylbenzene	119+134	MAH
6.304	alkene C ₁₂	55+69	MCC
6.366	alkane C ₁₂	57+71	MCC
7.046	alkene C ₁₃	55+69	MCC
7.097	alkane C ₁₃	57+71	MCC
7.736	alkene C ₁₄	55+69	MCC
7.782	alkane C ₁₄	57+71	MCC
8.384	alkene C ₁₅	55+69	MCC
8.426	alkane C ₁₅	57+71	MCC
8.997	alkene C ₁₆	55+69	MCC
9.038	alkane C ₁₆	57+71	MCC
9.578	alkene C ₁₇	55+69	MCC
9.614	alkane C ₁₇	57+71	MCC
9.790	prist-1-ene	55+56	MCC
10.029	C ₁₄ fatty acid	60+73	MCC
10.128	alkene C ₁₈	55+69	MCC
10.159	alkane C ₁₈	57+71	MCC
10.382	phytadiene 1	67+68	MCC
10.605	phytadiene 2	81+82	MCC
10.610	unidentified isoprenoid compound	55+57	MCC
10.652	alkene C ₁₉	55+69	MCC

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1654			
1655	10.683	alkane C ₁₉	57+71
1656	10.823	C ₁₆ fatty acid methyl ester	74+87
1657	10.994	C ₁₆ fatty acid	60+73
1658			MCC
1659	11.150	alkene C ₂₀	55+69
1660	11.181	alkane C ₂₀	57+71
1661	11.560	unidentified isoprenoid compound	100+113
1662	11.627	alkene C ₂₁	55+69
1663			MCC
1664	11.653	alkane C ₂₁	57+71
1665	11.856	3-methyl-2-(3,7,11-trimethyl)-C ₁₂ -thiophene	111+308
1666	11.928	C _{18:1} fatty acid	55+69
1667	11.969	C ₁₈ fatty acid	60+73
1668			MCC
1669	11.980	3-methyl-2-(4,8,12-trimethyl)-C ₁₂ -thiophene	98+308
1670	12.084	alkene C ₂₂	55+69
1671	12.104	alkane C ₂₂	57+71
1672	12.520	alkene C ₂₃	55+69
1673	12.540	alkane C ₂₃	57+71
1674	12.836	C ₂₀ fatty acid	60+73
1675	12.945	alkene C ₂₄	55+69
1676	12.961	alkane C ₂₄	57+71
1677			MCC
1678	13.350	alkene C ₂₅	55+69
1679	13.360	alkane C ₂₅	57+71
1680	13.734	alkene C ₂₆	55+69
1681	13.744	alkane C ₂₆	57+71
1682	14.118	alkene C ₂₇	55+69
1683	14.118	alkane C ₂₇	57+71
1684	14.475	alkene C ₂₈	55+69
1685	14.475	alkane C ₂₈	57+71
1686	14.761	alkene C ₂₉	55+69
1687			MCC
1688	14.823	alkane C ₂₉	57+71
1689	15.181	alkane C ₃₀	57+71
1690	15.565	alkane C ₃₁	57+71
1691	2.697	pyrrole	67
1692	2.703	pyridine	79
1693	3.056	acetamide	59
1694	3.398	C ₁ -pyrrole	80+81
1695	4.690	benzonitrile	103 (76)
1696			NCOMP
1697	5.806	C ₁ -benzoxazole	133
1698	5.982	benzeneacetonitrile	117+90
1699	6.573	acetylpyridone	109 (137)
1700	6.745	3-acetamidofuran	83+125
1701	6.776	benzene propanitrile	91+131
1702	7.186	indole	117+90
1703			NCOMP
1704	7.352	3-acetamido-5-methylfuran	97 (69,139)
1705	7.834	4-methyl-1 <i>H</i> -indole	130+131
1706	8.358	3/2-phenylpyridine (tentative)	155
1707	8.473	unidentified N-compound	84 (130,145,167)
1708			NCOMP
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8.836	unidentified N-compound	84 (55,133)	NCOMP
9.630	C ₁₄ alkylnitrile	55+97	NCOMP
9.863	diketodipyrrole	186+93	NCOMP
10.429	diketopiperazine	70+154	NCOMP
10.569	diketopiperazine	70+154	NCOMP
10.724	C ₁₆ alkylnitrile	55+97	NCOMP
11.093	diketopiperazine (Cyclo (Pro –Pro))	70+194	NCOMP
11.720	C ₁₈ alkylnitrile	55+97	NCOMP
12.073	C ₁₆ alkylamide	59+72	NCOMP
12.976	C ₁₈ alkylamide	59+72	NCOMP
7.097	dihydroindene	104+132	OTHER
8.919	C ₃ -naphthalene (tentative)	146(188,189)	OTHER
13.780	unidentified steroid/triterpenoid	337+352	OTHER
15.021	unidentified steroid/triterpenoid	366+367 (143)	OTHER
15.062	unidentified steroid/triterpenoid	141+142 (350)	OTHER
15.098	diacholestadiene compound	353+368	OTHER
6.392	naphthalene	128	PAH
7.212	C ₁ -naphthalene	142+115	PAH
7.347	C ₁ -naphthalene	142+115	PAH
7.788	biphenyl	154	PAH
4.622	phenol	94+66	PHEN
5.266	2/3-methylphenol	107+108	PHEN
5.432	4-methylphenol	107+108	PHEN
7.118	C ₄ -phenol	135+150	PHEN

a)

b)

a)

Downwelling
(5 March 2010) (a)

Upwelling
(15 June 2009) (b)