

Dynamics of particulate organic matter composition in coastal systems: a spatio-temporal study at multi-systems scale

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Abstract :

In coastal systems, the multiplicity of sources fueling the pool of particulate organic matter (POM) leads to divergent estimations of POM composition. Eleven systems (two littoral systems, eight embayments and semi-enclosed systems and one estuary) distributed along the three maritime façades of France were studied for two to eight years in order to quantify the relative contribution of organic matter sources to the surface-water POM pool in coastal systems. This study was based on carbon and nitrogen elemental and isotopic ratios, used for running mixing models.

The POM of the estuary is dominated by terrestrial material (93% on average), whereas the POM of the other systems is dominated by phytoplankton (84% on average). Nevertheless, for the latter systems, the POM composition varies in space, with 1) systems where POM is highly composed of phytoplankton ($\geq 93\%$), 2) systems characterized by a non-negligible contribution of benthic (8 to 19%) and/or riverine (7 to 19%) sources, and 3) the Mediterranean systems characterized by the contribution of diazotroph organisms (ca. 14%). A continent-to-ocean gradient of riverine and/or benthic POM contribution is observed. Finally, time series reveal 1) seasonal variations of POM composition, 2) differences in seasonality between systems, and 3) an inshore-offshore gradient of seasonality within each system that were sampled at several stations.

Spatial and seasonal patterns of POM composition are mainly due to local to regional processes such as hydrodynamics and sedimentary hydrodynamic (e.g. resuspension processes, changes in river flows, wind patterns influencing along-shore currents) but also due to the geomorphology of the systems (depth of the water column, distance to the shore). Future studies investigating the link between these forcings and POM composition would help to better understand the dynamics of POM composition in coastal systems.

Highlights

► Two littoral systems, eight embayments and one estuary were studied. ► Phytoplankton dominates POM in all systems except in the estuary (terrestrial POM) ► Mediterranean systems present a non-negligible contribution of diazotroph organisms. ► POM composition and its seasonality undergo an inshore-offshore gradient. ► Hydrodynamics and geomorphology lightly drive the variability of POM composition.

Keywords : particulate organic matter, coastal systems, C and N stable isotopes, C:N ratio, mixing model, meta-analysis, France

Glossary:

- Coastal POM = mix of autochthonous POM (in situ pelagic and benthic primary producers) and allochthonous POM (is continental POM originating from the continent)
- Continental POM = all POM coming for the land (Riverine POM, Anthropogenic POM, Terrestrial POM)
- Riverine POM = freshwater phytoplankton + terrestrial POM
- Terrestrial POM = Terrestrial plants debris, litter (the Gironde estuary exhibits two distinct terrestrial POMs: the refractory and the labile terrestrial POM)
- Anthropogenic POM = originating from treated/untreated sewage effluents
- Benthic POM = macrophytes (i.e. macroalgae, spermatophytes) fragments, microphytobenthos or even sediment detritus
- Estuarine POM = from the estuarine system (Gironde estuary)

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1. Introduction

As they are positioned at the interface between ocean and continent, coastal systems experience inputs of dissolved and particulate matter from both reservoirs. It results that these systems are highly productive and are key areas for global biogeochemical cycles (Bauer et al., 2013; Regnier et al., 2013; Smith and Hollibaugh, 1993). More specifically, the multiple origin of particulate organic matter (POM) strongly influence ecosystem functioning since POM is largely considered as a mainstay of the coastal trophic network (e.g. Malet et al., 2008). Coastal POM is also exported offshore (Sanchez-Vidal et al., 2009) or buried in sediment (Duarte and Cebrián, 1996) and contributes to enhance remineralization in the water column and to fuel deep sea ecosystems (Azam et al., 1983; Karl et al., 1988; Wakeham and Lee, 1989). Acquiring a better knowledge about POM composition in coastal systems remains a key concern to understand biogeochemical interactions between continental and oceanic realms and to have a better insight of ecosystem functioning.

The pool of coastal POM is composed of a mixture of autochthonous POM and allochthonous POM (Berto et al., 2013; Dubois et al., 2012; Tesi et al., 2007). Autochthonous POM is considered as originating from *in situ* pelagic and benthic primary producers. Many studies reported that phytoplankton dominates coastal POM (e.g. Cresson et al., 2012; Tesi et al., 2007). In addition, due to the shallow depth of coastal systems, the benthic compartment has a significant influence on coastal POM composition (e.g. Malet et al., 2008). Benthic organic matter includes various sources such as macrophytes (i.e. macroalgae, spermatophytes), microphytobenthos or even sediment detritus. Allochthonous POM is organic matter originating from the continent. It is mainly carried by rivers but also by run-off or by artificial outlets. Sources of continental POM are usually considered as riverine POM, which is a mixture of freshwater phytoplankton and terrestrial POM (e.g. litter, soils), and sometimes anthropogenic inputs such as POM originating from treated/untreated sewage effluents (Berto et al., 2013; Cresson et al., 2012; Liénart et al., 2016). This multiplicity of sources makes difficult the understanding of the relative influence of each source to the coastal POM pool. Also, depending on its composition, POM is more or less labile (Etcheber et al., 2007) and thus more or less bioavailable and subject to processing.

To assess and quantify the POM composition (i.e. the contribution of each source to the pool of POM), a large panel of tools is available. A first approach for characterizing coastal POM consists in measuring particulate organic carbon (POC) and chlorophyll *a* (Chl *a*) concentrations. Classically, POC:Chl *a* ratio is used to discriminate living phytoplankton (POC:Chl *a* \approx 40-140 g g⁻¹) or phytoplankton-dominated POM (POC:Chl *a* < 200 g g⁻¹) from other material (POC:Chl *a* > 200 g g⁻¹) (Savoye et al., (2003) and references therein). Among available tools, C and N elemental and isotopic ratios have been widely used to investigate the relative contribution of each source to the coastal POM thanks to their distinct

elemental and isotopic signatures. Roughly, C:N ratio discriminates phytoplankton (C:N \approx 6-10 mol mol⁻¹) from terrestrial material (C:N > 12 mol mol⁻¹) whereas $\delta^{13}\text{C}$ values generally discriminates continental ($\delta^{13}\text{C} < -26\text{‰}$) from marine ($\delta^{13}\text{C} > -24\text{‰}$) POM in temperate systems (Savoye et al., (2003) and references therein). No 'universal' values exist for nitrogen isotope ratio ($\delta^{15}\text{N}$) and a strong variability of values is observed depending on the systems (Middelburg and Herman, 2007). Nevertheless, C:N ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are largely used in combination to characterize and even quantify POM composition in coastal systems (e.g. Berto et al., 2013, Liénart et al. 2016). Relative contribution of each source to the POM pool is usually estimated using mixing models, which are a system of mass balance equations based on the above parameters (Parnell et al., 2010; Phillips and Gregg, 2003).

Studies comparing POM characteristics and/or composition at multi-systems scale are scarce and were only performed in estuarine or riverine systems and in a limited period of time (Middelburg and Herman, 2007; Pradhan et al., 2014; Higuera et al., 2014). The present study was performed in a wide diversity of systems (e.g. open bay, gulf, semi-enclosed systems, lagoon, estuary) and of environmental gradients, and at multi-annual time scale, using an original dataset (17 time series of ca. bi-monthly sampling for 2 to 8 years). It aims at (1) determining POM composition in eleven coastal systems distributed along the three coastlines of France and (2) characterizing its spatial and temporal variabilities at both local and multi-systems scale. Specifically, we hypothesize that phytoplankton dominate POM in marine systems (coastal systems out of estuaries), the contribution of other sources increases depending on the proximity to the latest (e.g. higher contribution of riverine POM when closer to river mouth) and POM composition vary seasonally (e.g. higher contribution of riverine and or benthic sources in winter). Beyond this qualitative view, the study aims at quantitatively state the extent of the spatial and temporal variability of POM composition in a large diversity of coastal systems.

2. Material and Methods

2.1. Studied systems

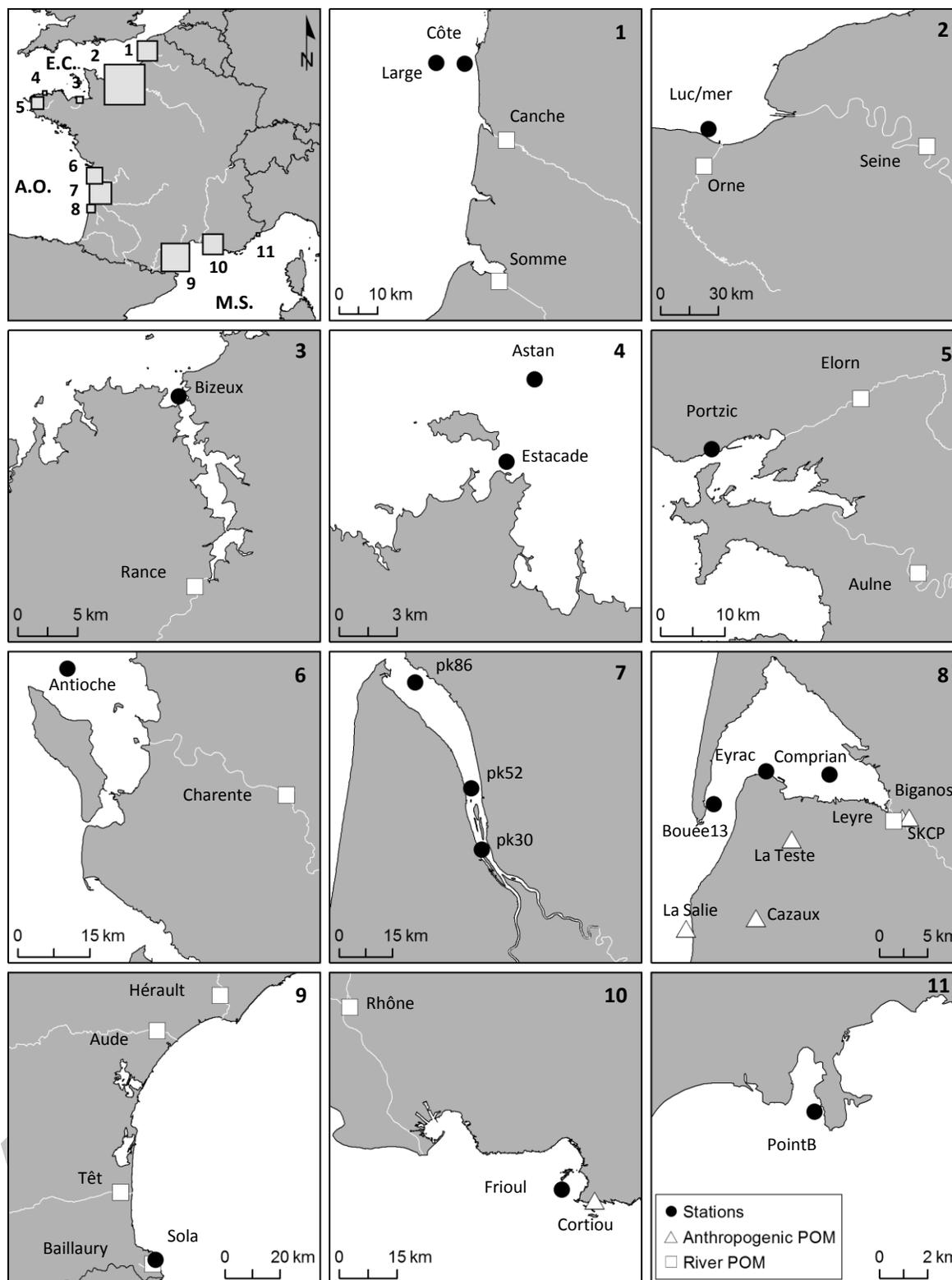
Seventeen stations from eleven systems distributed along the French coastline (42°N – 51°N, 4°W – 7°E; Fig. 1) were studied. Four systems are located along the English Channel: the south eastern littoral of the English Channel (stations Côte and Large near Wimereux), the Bay of Seine (station of Luc/mer), the Normano-Breton Gulf (station of Bizeux near Dinard in the ria of the Rance River) and the western littoral of the English Channel (stations Estacade and Astan near Roscoff). One system is located in the Iroise Sea, at the interface between the English Channel and the Atlantic Ocean: the marine end of the Bay of Brest (station Portzic). Three systems are located along the Atlantic coast: the Charentais Sounds (station Antioche near La Rochelle), the Gironde Estuary (stations pk30, pk52 and

pk86) and the Arcachon Lagoon (stations Comprian, Eyrac and Bouée13). At last, three systems are located in the Mediterranean Sea: the Bay of Banyuls-sur-mer (station Sola), the Bay of Marseille (station Frioul) and the Bay of Villefranche-sur-mer (station PointB). Among the eleven systems, four were sampled at two to three stations distributed along a continent-to-ocean gradient (Fig. 1).

The eleven systems are distributed over a latitudinal gradient and exhibit different geomorphological features (open coastal systems, bays, lagoon, estuary) and sizes (surface area ranges from few to thousands km²). This offers the opportunity to study numerous environmental and ecological gradients (Table 1): geographical confinement (from semi-enclosed to open systems), tidal regime (from micro- to megatidal systems), water column height (from 5 to 80m), climate (e.g. mean winter and summer water temperatures range from 5 to 12°C and from 17 to 28°C, respectively), freshwater influence (mean salinity ranges from 0 to 38), trophic status (from oligo- to eutrophic systems), turbidity (mean suspended particulate matter concentration ranges between milligrams and grams per liter), etc.

These stations are weekly to ca. monthly monitored since 1997 for physical, chemical, biogeochemical and biological parameters within the scope of the SOMLIT (Service d'Observation en Milieu Littoral), the French Coastal Monitoring Network (<http://somlit.epoc.u-bordeaux1.fr/fr/>). The overall aim of the SOMLIT is to assess the long-term evolution of coastal systems and to discriminate climatic forcings from local anthropogenic ones (Goberville et al., 2010).

Figure 1: Location of the eleven studied systems (in insets numbered from 1 to 11) and the studied stations (black circles) along the French maritime façades (E.C.: English Channel, A.O.: Atlantic Ocean and M.S.: Mediterranean Sea). On the global map, grey squares of different sizes represent the spatial extend of each inset. Continental sites sampled for organic matter sources are presented in the insets: rivers (squares) and sewage treatment plant effluents (triangles). 1. Eastern English Channel, 2. Bay of Seine, 3. Ria of the Rance River in the Norman-Breton Gulf, 4. Western English Channel, 5. Bay of Brest, 6. Charentais Sounds, 7. Gironde Estuary, 8. Arcachon Lagoon, 9. Bay of Banyuls, 10. Bay of Marseille, 11. Bay of Villefranche.



	Systems	Type of system	Stations	Depth at sampling station (m)	Study period	Sampling frequency	Tidal range	Tidal range (m)	Considered rivers	Annual flow rates ($m^3 s^{-1}$) during the study period	Salinity	Water temp. ($^{\circ}C$)	SPM ($mg L^{-1}$)	Trophic status	Nitrate in winter (μM)	Chlorophyll <i>a</i> ($\mu g L^{-1}$)
1	Eastern English Channel	littoral system	Côte, Large	21 ; 50	2010-2014	bi-monthly	macrotidal	7.7	Somme, Canche	35 ; 12	33-35	5-20	0.5-5	eutrophic	5-30	0.5-10
2	Bay of Seine	open bay	Luc/mer	5	2009-2013	bi-monthly	macrotidal	6.6	Seine, Orne	486 ; 22	30-34	5-20	1-100	eutrophic	30-45	0.3-15
3	Normano-Breton Gulf	ria	Bizeux	25	2012-2014	bi-monthly	megatidal	14	Rance	1.7	33-35	8-19	0.4-20	mesotrophic	≈ 30	0.3-5
4	Western English Channel	littoral system	Estacade, Astan	11 ; 60	2009-2014	bi-monthly	macrotidal	7.5	-	-	34.5-35.5	8-17	0.2-13	mesotrophic	9-12	0.2-4
5	Bay of Brest	semi-enclosed ria	Portzic	10	2009-2014	weekly	macrotidal	7.6	Aulne, Elorn	24 ; 6.1	33-35.5	8-18	0.2-20	mesotrophic	20-30	0.2-6
6	Charentais Sounds	semi-enclosed sound	Antioche	40	2011-2014	bi-monthly	macrotidal	6.5	Charente, Gironde	100 ; 764	30-35	6-21	1-15	mesotrophic	20-25	0.2-5
7	Gironde Estuary	estuary	pk30, pk52, pk86	8 ; 7 ; 8	2007-2014	ca. monthly	mesotidal	5	Gironde	764	0-31,5	5-25	5-1000	eutrophic	60-200	0.3-10
8	Arcachon Lagoon	semi-enclosed lagoon	Comprian, Eyrac, Bouée13	6 ; 8 ; 25	2009-2014	bi-monthly	mesotidal	4.2	Leyre	17	20-35.5	5-25	0.3-20	mesotrophic	7-50	0.1-7
9	Bay of Banuyls	open bay	Sola	27	2010-2014	bi-monthly	microtidal	centimetric	Têt, Rhône, Aude, Hérault, Baillaury	8.6 ; 1619 ; 31 ; 34 ; mediterranean oued	34-38.5	8-25	0.1-7	weakly oligotrophic	2-6	0.05-4
10	Bay of Marseille	open bay	Frioul	60	2009-2014	bi-monthly	microtidal	centimetric	Rhône	1619	34.5-38.5	12-26	0.1-5	oligotrophic	0-6	0-3
11	Bay of Villefranche	semi-enclosed bay	PointB	80	2010-2013	weekly	microtidal	centimetric	-	-	36.8-38.5	12.5-28	0.5-40	oligotrophic	0.5-4	0.05-2.5

Table 1: Characteristics of the eleven studied systems. Temp.: temperature. SPM: suspended particulate matter. Trophic status was defined based on maximal chlorophyll *a* concentrations, literature and the knowledge of local experts.

2.2. Scientific strategy

Within the scope of the SOMLIT, sampling is carried out weekly to bimonthly (Table 1) in surface waters (i.e. 1m-depth water), and at high tide for the tidal seas. The only exception is the Gironde Estuary, which is sampled c.a. monthly at both high (HT) and low (LT) tide (see Savoye et al., 2012). Sixteen physical, biogeochemical and biological parameters such as temperature, salinity, nutrients, chlorophyll *a* (Chl *a*), particulate organic carbon (POC), and C and N stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) are routinely measured.

For each system, possible sources of organic matter (Fig. 1; Table 2) contributing to coastal POM composition were identified and additionally sampled considering site specificities based on previous studies and knowledge of local experts. For all systems but two (the western littoral of the English Channel near Roscoff and the Bay of Villefranche), one or more rivers were considered for riverine POM. Water was sampled upstream to the tide influence. Anthropogenic POM (POM outing sewage treatment plants (STP)) was considered for the Arcachon Lagoon and the Bay of Marseille. Sampling was performed with a 24h composite sampler directly in the STP pipes, after the treatment of the effluent and before it was rejected into the environment. In the vicinity of the Arcachon Lagoon, the four main STP (Biganos, SKCP, La Teste and Cazaux) were considered. Their effluents flow in a common sea-outfall located outside of the Arcachon Lagoon along the coast at La Salie (Fig. 1). Benthic primary producers (i.e. macrophytes, microphytobenthos) were considered for the Bay of Seine, the Normano-Breton Gulf, the western littoral of the English Channel, the Bay of Brest and the Arcachon Lagoon. Macrophytes with the predominant biomass found on the foreshore were selected. These organic matter sources were sampled monthly over an annual cycle across the years 2014-2015 (Table 2) for most of the stations. For some stations, isotopic data already available from previous studies were used (Table 2).

	Systems	Stations	Phytoplankton and	Continental or terrestrial** POM	Antropogenic POM	Macrophytes	Microphytobenthos
English Channel	Eastern English Channel	Côte, Large	2010-2014*	feb-15 to sept-15	-	-	-
	Bay of Seine	Luc/mer	2009-2013*	jun-14 to jun-15	-	jun-14 to jun-15	-
	Normano-Breton Gulf	Bizeux	2012-2014*	jun-14 to may-15	-	jun-14 to jun-15	jun-14 to jun-15
	Western English Channel	Estacade, Astan	2009-2014*	-	-	mar-14 to feb-15	-
Atlantic Ocean	Bay of Brest	Portzic	2009-2014*	janv-14 to jun-15	-	2006 to 2015 irregular sampling	-
	Charentais Sounds	Antioche	2011-2014*	mar-14 to mar-15 SOMLIT data	apr-14 to mar-15	-	-
	Gironde Estuary	pk30, pk52, pk86	2007-2014*	2007-2014*	-	-	-
	Arcachon Bay	Comprian, Eyrac, Bouée13	2009-2014*	feb-14 to feb-15	mar-14 to mar-15	feb-09 to feb-10 ⁽³⁾	feb-09 to feb-10 ⁽³⁾
Mediterranean Sea	Bay of Banuyls	SOLA	2010-2014*	jan-06 to mai-10 ⁽¹⁾ occasional floods (mediterranean oued)	-	-	-
	Bay of Marseille	Frioul	2009-2014*	jan-06 to mai-10 ⁽¹⁾	sept-14 to sept-15	-	-
	Bay of Villefranche	PointB	2010-2013*	-	-	-	-

Table 2: Sampling of the potential sources of organic matter to particulate organic matter of the eleven studied systems. * SOMLIT data. ** terrestrial POM considered only for the Gironde Estuary. ⁽¹⁾ Kerhervé unpublished data; Higuera et al., 2014; MOOSE program (Mediterranean Oceanic Observing System for the Environment). ⁽²⁾ Grall unpublished data; Marchais et al., 2013. ⁽³⁾ Dubois 2012; Dubois et al., 2012, 2014.

2.3. Sampling, processing, storage

Surface water was sampled, processed and analyzed within the scope of the SOMLIT Network, following standardized protocols available on the SOMLIT website (<http://somlit.epoc.u-bordeaux1.fr/fr/spip.php?rubrique13>). Existing datasets were retrieved from the SOMLIT web site (see section 2.5). In the following sections are detailed the methods regarding the additional sampling of organic matter sources.

2.3.1. Continental POM

River water was collected for chlorophyll *a* concentrations, and for C and N elemental and isotopic analyses. STP water was sampled for C and N elemental and isotopic analyses. Water samples were filtered through GF/F filters (47 mm \varnothing) for chlorophyll *a* and pre-combusted (4 h - 450 °C) GF/F filters (47 mm \varnothing) for elemental and isotopic analyses. Chlorophyll *a* filters were stored frozen at -80 °C. Filters for C and N elemental and isotopic analyses were dried overnight at 50 °C and then stored in a desiccator in the dark.

2.3.2. Benthic primary producers

Microphytobenthos was collected at low tide by scraping the first 0.5 cm of the intertidal surface sediment and stored at -20°C . It was extracted from the sediment following the modified method of Bolch (1997) based on a density gradient using pre-filtered ($0.2\ \mu\text{m}$) seawater (density of ca. 1) and a solution of sodium polytungstate (density of 2) separated by centrifugation. At the end of the process, the microphytobenthos isolated in pre-filtered seawater was recovered and filtered through a pre-combusted (4 h - 450°C) GF/F filter ($25\ \text{mm}\varnothing$). The filter was dried overnight at 50°C and then stored in a desiccator in the dark.

Decayed macrophytes were collected by hand on the foreshore, rinsed in successive bathes of pre-filtered seawater and deionized water, and then stored at -20°C .

2.4. Sample analysis

Chlorophyll *a* was extracted using 90% acetone and analyzed by fluorescence (Turner Design 10-AU Fluorometer) following Yentsch and Menzel (1963).

Prior to analysis, filters for elemental and isotopic analyses were decarbonated by contact with HCl vapor (8 h) following Lorrain et al. (2003). One piece of each filter was punched ($11\ \text{mm}\varnothing$) and analyzed for POC using an elemental analyzer (Thermo Finnigan Flash EA 1112 analyzer). The rest of the filter was used for the analysis of the elemental and isotopic ratios.

Macrophytes samples were freeze-dried, then ground into powder using a ball mill. Powders were weighed into tin cups for N elemental and isotopic analysis, and in silver cups for C elemental and isotopic analysis. The latter were in-cup decarbonated using 1.2 N HCl (Kennedy et al., 2005).

Filters and powders were analyzed for isotopic and elemental compositions (i) at the Biology Station of Roscoff using an elemental analyzer (Flash EA CN) connected to an isotope ratio mass spectrometer (Finnigan Delta Plus with a Con-Flo III interface) for the samples performed in the western littoral of the English Channel, (ii) at the LIENSs stable isotope facility of the University of La Rochelle using an elemental analyzer (Flash EA 1112, Thermo Scientific) coupled with an isotope ratio mass spectrometer (Delta V Advantage with a Conflo IV interface, Thermo Scientific) for the samples collected in the Charentais Sounds, (iii) at the EPOC Laboratory (Bordeaux) using an elemental analyzer (ThermoFisher Scientific Flash 2000) connected to an isotope ratio mass spectrometer (Isoprime, GV Instruments) for all other samples performed in the systems of the English Channel and the Atlantic Ocean, and (iv) at the MIO laboratory (Marseille) using an Integra CN (Sercon) for the samples performed in the Mediterranean Sea. Analytical uncertainty for

each EA-IRMS was better than 0.2‰ for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and 0.2 mol mol⁻¹ for C:N ratio. Based on inter-laboratory essays performed annually since 2010 within the scope of the SOMLIT overall analytical uncertainty was 0.4‰ for $\delta^{13}\text{C}$, 0.3‰ for $\delta^{15}\text{N}$ and 0.3 mol mol⁻¹ for C:N ratio.

According to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC), all isotopic data are expressed in the conventional delta notation (Eq. (1); Coplen, 2011):

$$\delta^{13}\text{C}_{\text{sample}} \text{ or } \delta^{15}\text{N}_{\text{sample}} = \left[\left(R_{\text{sample}} / R_{\text{standard}} \right) - 1 \right] \quad \text{Eq. (1)}$$

Where $R = {}^{13}\text{C}/{}^{12}\text{C}$ or ${}^{15}\text{N}/{}^{14}\text{N}$, and the references are Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}\text{C}$ and atmospheric N_2 for $\delta^{15}\text{N}$.

2.5. Available datasets

Datasets of coastal core parameters used in this study (Chl *a*, POC, C:N ratio, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, nitrate) were retrieved from the SOMLIT website (<http://somlit.epoc.u-bordeaux1.fr>). Depending on data availability, length of the time series range from 2 to 8 years (Table 1). Based on the quality flag associated to each SOMLIT data, data flagged as 'bad' were removed from the dataset, data flagged as 'doubtful' were carefully examined and outliers associated with this flag were removed from the datasets. In addition, because the three parameters ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C:N ratios) are needed for running the mixing model, dates for which one isotopic or elemental data was missing were also removed from the dataset. Finally, 88% of the initial dataset was considered.

River flows were obtained thanks to the BanqueHydro database (<http://www.hydro.eaufrance.fr>), Agence de l'Eau Rhône-Méditerranée-Corse (<http://eaurmc.fr>) and Compagnie Nationale du Rhône (<http://www.cnr.tm.fr>). Flows of suspended particulate matter in the sewage treatment plants of the Arcachon Lagoon were provided by Agence de l'Eau Adour-Garonne (<http://adour-garonne.eaufrance.fr>).

2.6. Determination of source signatures: taking into account the temporal variability

Prior to the determination of POM composition, one should ensure that, if needed and whenever possible, temporal variability of elemental and isotopic signatures of each source was considered. Empirical multi-regressive models were attempted in order to better take into account the temporal variability of the different datasets.

2.6.1. Phytoplankton and diazotrophs signatures

Since phytoplankton cannot be sampled as ‘pure’ material nor be extracted from the bulk POM, its elemental and isotopic signatures cannot be directly measured. Its signatures have been estimated following Dubois et al. (2014, 2012), Savoye et al. (2012), Liénart et al. (2016) and Savoye et al. (submitted). Since living phytoplankton exhibits a POC:Chl *a* ratio of 40-140 g g⁻¹, POM exhibiting a POC:Chl *a* ratio lower than 200 g g⁻¹ (POC:Chl *a* < 200) is usually considered as dominated by phytoplankton (Savoye et al., 2003, and references therein). Consequently, the core hypothesis of the approach developed and used in the above-mentioned articles is that the elemental and isotopic signatures of POM of POC:Chl *a* < 200 is the best estimate of phytoplankton elemental and isotopic signatures. The robustness of this hypothesis is deeply discussed in Savoye et al. (submitted).

In order to take into account the large temporal and spatial variability of phytoplankton isotopic signatures, and especially to estimate these signatures at each date and station, multiple regressions between $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ or C:N ratio of POM of POC:Chl *a* < 200 and environmental parameters were performed.

Phytoplankton $\delta^{13}\text{C}$ was determined by considering empirical models where $\delta^{13}\text{C}$ is related to environmental parameters such as temperature, salinity and pigment concentration. These empirical equations have been performed, for the studied stations, by Savoye et al. (submitted) and were directly used in the present study. Phytoplankton $\delta^{15}\text{N}$ was related to nitrate concentrations using the Rayleigh distillation model (instantaneous (Eq. (2)) or cumulative (Eq. (3)) closed models) or the steady-state model (open model; Eq. (4)) (Sigman et al., 2009). The three equations were tested and the best fit was selected when the model uncertainty was better than the standard deviation of raw data. Otherwise the average value of raw data was used. Equations and values used are reported in Supplementary Table S1.

$$\delta^{15}\text{N}_{\text{phytoplankton}} = \delta^{15}\text{N}_{\text{nitrate}(0)} - \varepsilon \cdot (1 + \ln(f)) \quad \text{Eq. (2)}$$

$$\delta^{15}\text{N}_{\text{phytoplankton}} = \delta^{15}\text{N}_{\text{nitrate}(0)} + \varepsilon \cdot (f \cdot \ln f) / (1 - f) \quad \text{Eq. (3)}$$

$$\delta^{15}\text{N}_{\text{phytoplankton}} = \delta^{15}\text{N}_{\text{nitrate}(0)} - \varepsilon \cdot f \quad \text{Eq. (4)}$$

Where $f = [\text{nitrate}]_t / [\text{nitrate}]_{\text{max}}$ is the ratio of nitrate concentration at a given time *t* to the nitrate concentration maximum value of the previous winter, $\delta^{15}\text{N}_{\text{nitrate}(0)}$ is the $\delta^{15}\text{N}$ value of the nitrate winter pool and ε is the isotopic fractionation during the conversion of nitrate into phytoplankton. Best fits were performed using the package Solver in Microsoft Office Excel 2007. Average \pm standard deviation on raw data were considered for elemental signature (C:N or N:C) at each station.

In the oligotrophic Mediterranean Sea, dissolved atmospheric dinitrogen (N_2) is also used as a nitrogen nutrient, leading to negative $\delta^{15}\text{N}$ values for the organisms specialized in N_2 -

fixation (diazotrophs; Carpenter et al., 1997; Kerhervé et al., 2001). Consequently, 'diazotrophs' were considered as a proper source there. Since no clear seasonal pattern was observed, average \pm standard deviation of Mediterranean data with negative $\delta^{15}\text{N}$ values were considered as elemental and isotopic signatures of diazotrophs.

2.6.2. River-POM signatures

As for phytoplankton, river-POM signatures were determined taking into account temporal variability. River $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and C:N ratios were plotted against river flows and best-fitted using Eq. (5). The model was used when its associated uncertainty was lower than the standard deviation of raw data. Otherwise, the average \pm standard deviation of raw data was used. Equations and values used are reported in Supplementary Table S2.

$$X_{\text{river}} = X_{\text{max}} - Y/Q_{\text{river}} \quad \text{Eq. (5)}$$

Where X is $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ or C:N, 'max' indicates the maximal value in the model when the river flow tends to infinity, Y is a constant which value was determined by the best-fitting, and Q is the river flow ($\text{m}^3 \text{s}^{-1}$). For a given station, when more than one tributary was considered, river-POM signatures were the weighted average of each river signatures (Eq. (6)). River signatures were weighted by the ratio of the river flow to the distance of the river mouth to the sampling station (X_{riverW} ; Eq. (6)).

$$X_{\text{riverW}} = \frac{((Q_{\text{river1}}/D_{\text{river1}} \cdot X_{\text{river1}}) + (Q_{\text{river2}}/D_{\text{river2}} \cdot X_{\text{river2}}))}{(Q_{\text{river1}}/D_{\text{river1}} + Q_{\text{river2}}/D_{\text{river2}})}$$

Eq. (6)

Where Q is the river flow ($\text{m}^3 \text{s}^{-1}$), D is the distance from the river mouth to the sampling station (km) and X is the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ or C:N ratio. Then, the elemental and isotopic signatures estimated for river-POM were averaged over the 14 days preceding the sampling date of coastal POM, i.e. over the mean time lapse between two samplings.

2.6.3. Anthropogenic-POM signatures

As STP elemental and isotopic ratios do not exhibit seasonal patterns and were stable over time, their averages \pm standard deviations were considered (Table S3).

For a given station, when more than one STP was considered, STP signatures were the weighted average of each STP signatures (Eq. (7)). STP signatures were weighted by the annual flow of suspended particulate material (Eq. (7)).

$$X_{\text{STPW}} = (S_{\text{STP1}} \cdot X_{\text{STP1}} + S_{\text{STP2}} \cdot X_{\text{STP2}}) / (S_{\text{STP1}} + S_{\text{STP2}}) \quad \text{Eq. (7)}$$

Where X is $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ or C:N and S is the annual flow of suspended particulate material (kg an^{-1}).

2.6.4. Benthic-POM signatures

As microphytobenthos elemental and isotopic ratios do not exhibit seasonal patterns and were stable over time, their averages \pm standard deviations were considered (Table S3).

Elemental and isotopic signatures of the predominant macrophytes were first analyzed for each station by using hierarchical clustering analysis (i.e. HCA, standardized data, Euclidian distances, *hclust* function, 'clustsig' package). Groups of macroalgae given by the HCA were statistically defined regarding the ANOVA and post-hoc Tukey (*HSD.test* function, 'agricolae' package) test. If significantly different ($p < 0.05$), the groups were considered separately. Otherwise, data were pooled and a unique group was considered. Analyses were performed with the R software (<http://cran.r-project.org>, R development core team 2009). Averages \pm standard deviations were considered for each group of macroalgae (Table S3).

2.6.5. The Gironde Estuary

For the Gironde Estuary, the signatures of sources were determined based on the SOMLIT data following the approach of Savoye et al. (2012). Three sources were assessed: phytoplankton, terrestrial refractory POM and terrestrial labile POM.

2.7. Mixing model

Analyses were performed with the R software (<http://cran.r-project.org>, R development core team 2009). The composition of coastal POM was assessed by incorporating the selected sources of organic matter (i.e. end-members) into a mixing model using a Bayesian approach (SIAR package; Parnell et al., 2010). This model was ran for each sampling date of each station by using N:C ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. N:C ratio was preferred to C:N ratio for running the mixing model since it is less sensitive to the large analytical uncertainty that may be associated with the measure of N in N-depleted OM. Nevertheless, as the values of C:N ratio are more well-known by the scientists than the values of N:C ratio, the former is described and illustrated in the following sections instead of the latter. As N:C ratio did not discriminate the two sources considered at PointB, it was not used for running the mixing model at this station. In the Gironde Estuary N:C ratio and $\delta^{15}\text{N}$ do not discriminate the organic matter sources. Thus a different approach was performed based on the POC content in suspended particulate matter and $\delta^{13}\text{C}$, following the method and equations of Savoye et al. (2012), in section 4.2.1.

The absolute uncertainty associated to the mixing-model outputs was usually close to 10%.

3. Results

3.1. Coastal-POM characteristics

POC:Chl *a* ratios (Fig. 2) generally range from ca. 50 to 600 g g⁻¹ in marine systems and from ca. 400 to 10000 g g⁻¹ in the Gironde Estuary. 55% of the marine data set exhibits a POC:Chl *a* ratio lower than 200. The variability of POC:Chl *a* ratios is low in marine systems (mean standard deviation: 249 g g⁻¹) compared to the Gironde Estuary (2522 g g⁻¹). C:N ratios (Fig. 2) exhibit values between ca. 4 and 8 mol mol⁻¹ in marine systems and ca. 7 to 9 mol mol⁻¹ in the Gironde Estuary. The mean standard deviation of C:N ratios is rather high in marine systems (0.9 mol mol⁻¹) compared to the Gironde Estuary (0.7 mol mol⁻¹). $\delta^{13}\text{C}$ values (Fig. 2) range between ca. -26 and -19‰ in marine systems and ca. -26 and -24‰ in the Gironde Estuary. The variability of $\delta^{13}\text{C}$ is higher in marine systems (mean standard deviation: 1.2‰) compared to the Gironde Estuary (0.4‰). $\delta^{15}\text{N}$ values (Fig. 2) usually range between ca. 3 and 11‰ in the English Channel and the Atlantic Ocean, between ca. 0 and 6‰ in the Mediterranean Sea and between ca. 4 and 6‰ in the Gironde Estuary. The mean standard deviation of $\delta^{15}\text{N}$ is rather high in marine systems (1.3‰) compared to the Gironde Estuary (0.8‰).

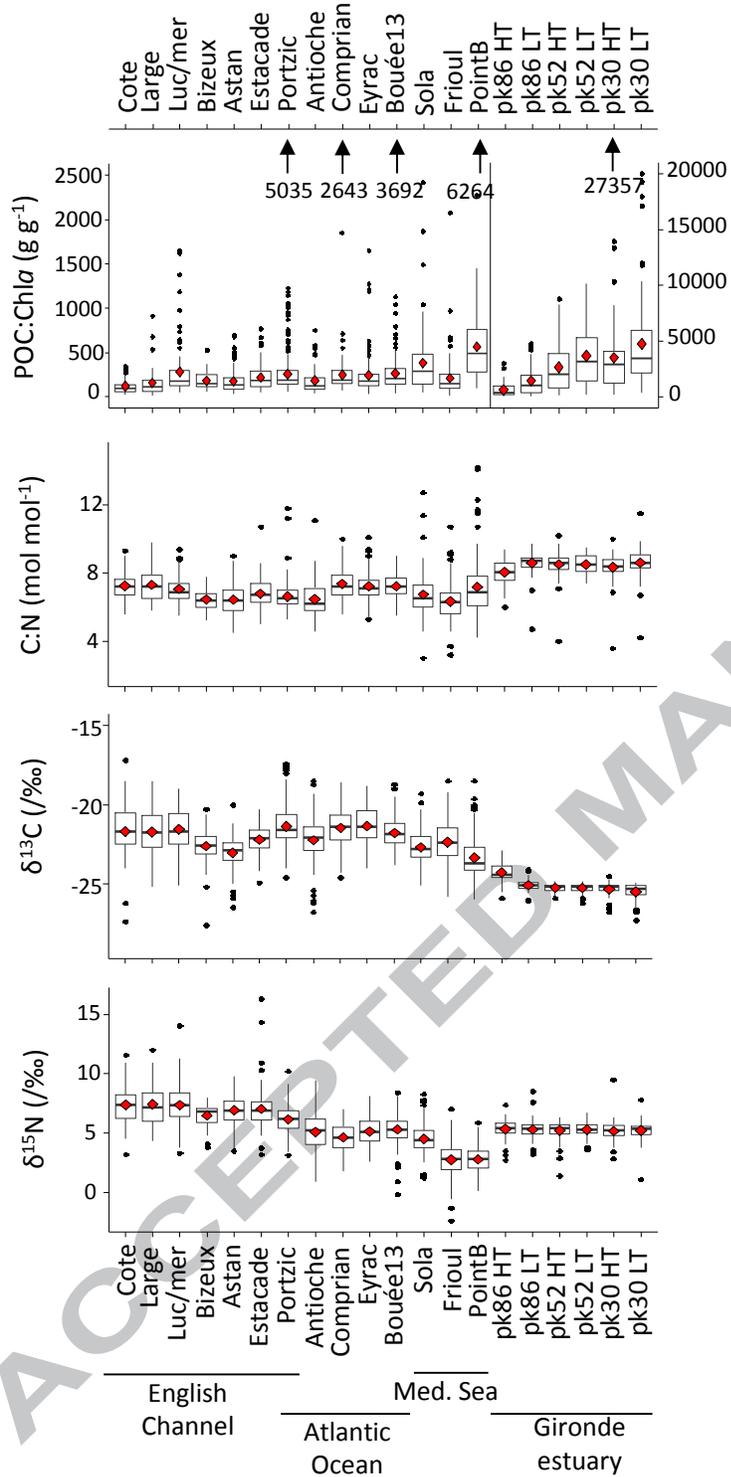


Figure 2: Boxplots of POC:Chl *a*, elemental (C:N) and isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) ratios of the seventeen stations. Estuarine stations are sampled at high (HT) and low tide (LT). Within the boxes, medians are the black lines, means are the red diamonds. First and third quartiles are hinges, outliers are black dots. In the POC:Chl *a* panel, the Gironde Estuary (pk30, pk52, pk86) values refer to right axis, values for other stations refers to left axis. The value below each vertical arrows represent a high value (unique) not shown on the boxplot scale. 'Med. Sea': Mediterranean Sea.

Contrasted values between estuarine and marine stations are observed. The estuary is characterized by high POC:Chl *a* ratios, relatively high and stable C:N ratios, low and very stable $\delta^{13}\text{C}$ and stable $\delta^{15}\text{N}$. Conversely, coastal stations exhibit less variable and usually low POC:Chl *a* ratios, associated with usually low C:N ratios, high and variable $\delta^{13}\text{C}$ and also variable $\delta^{15}\text{N}$. A latitudinal gradient is observed for $\delta^{15}\text{N}$ with low values in the Mediterranean stations and high values in the Eastern English Channel. Within the Gironde Estuary, POC:Chl *a* ratios exhibit an overall decrease and $\delta^{13}\text{C}$ an overall increase from upstream (pk30) to downstream (pk86) stations. At the downstream-most station (pk86), values of POC:Chl *a* ratio, C:N ratio and $\delta^{13}\text{C}$ at high tide are intermediate between marine and upstream stations.

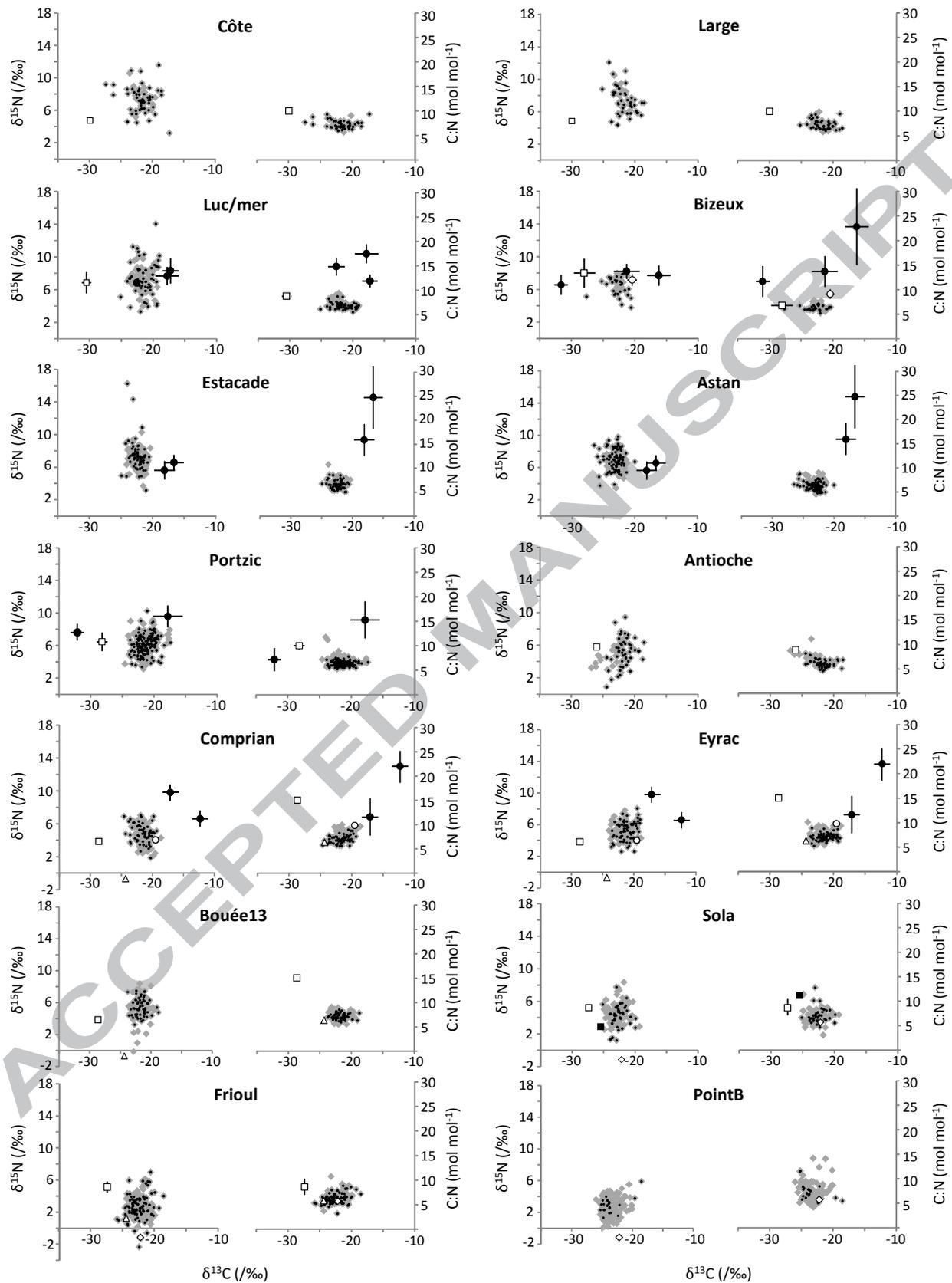
3.2. Signatures of organic matter sources

The range of values of each parameter is associated with specific signatures of the sources. C:N ratios usually range between 5-8 mol mol⁻¹ (phytoplankton, anthropogenic POM and Rance POM) and 15-25 mol mol⁻¹ (macrophytes and Leyre POM), $\delta^{13}\text{C}$ between ca. -33‰ (some macroalgae) or ca. -30‰ (river POM) and > -18‰ (most of macrophytes), and $\delta^{15}\text{N}$ between ca. -1‰ (diazotrophs and some anthropogenic POM) and > 8‰ (some macroalgae and Rance River POM) (Table S3).

For each station, C:N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ allow to discriminate all sources from each other (Fig. 3, Table S3). Phytoplankton is well discriminated from all other sources based on the three studied parameters. The C:N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ mean raw values of this source range from 6.1 to 7.4 mol mol⁻¹, from -23.6 to -21.3‰ and from 2.7 to 7.4‰, respectively. Diazotrophs have the same range of C:N ratio and $\delta^{13}\text{C}$ than phytoplankton but are well discriminated from it and from the other sources based on their negative $\delta^{15}\text{N}$ values (-1.2±0.9‰). River POM is generally well discriminated from the other sources based on its $\delta^{13}\text{C}$ values that are always low (\leq -25‰). For some stations, river POM is also discriminated by a high C:N ratio (e.g. Leyre River: ca. 15 mol mol⁻¹, Fig. 3). Anthropogenic POM is discriminated from most of the other sources based on low $\delta^{15}\text{N}$ values. Microphytobenthos is mainly discriminated by intermediate C:N ratios (ca. 9.5 mol mol⁻¹) and relatively high $\delta^{13}\text{C}$ values (ca. -20‰). Macrophytes are discriminated from other sources by high C:N ratios (ca. 11 to 24 mol mol⁻¹, Fig. 3) and usually high $\delta^{13}\text{C}$ values (\geq -18‰) but some of them are characterized by very low $\delta^{13}\text{C}$ values (ca. -33‰). For the Gironde Estuary, the stations are distributed along a gradient of salinity (from 0 to 32,

Table 1), thus phytoplankton $\delta^{13}\text{C}$ vary from -34.4 (freshwater phytoplankton, salinity 0) to -21.0‰ (estuarine phytoplankton, salinity 32). The Gironde Estuary exhibits two distinct terrestrial POMs: the refractory ($\delta^{13}\text{C} = -25.2\text{‰}$) and the labile ($\delta^{13}\text{C} = -28.9\text{‰}$) terrestrial POM.

Almost all coastal POM values are within the limits of the signatures of possible sources for all sites (Fig. 3 and 4). Phytoplankton values are in the core of coastal POM values for all stations except for the Gironde Estuary where the estuarine POM values are very similar to the values of refractory terrestrial POM (Fig. 4). Nevertheless, in some cases, coastal POM values are distant from phytoplankton values and tend toward the values of other sources. For the Mediterranean stations (Sola, Frioul and PointB) some coastal POM samples exhibit low $\delta^{15}\text{N}$ values. This POM tends toward diazotroph signature (i.e. negative $\delta^{15}\text{N}$ values). Coastal POM of low $\delta^{13}\text{C}$ and/or high C:N values is close to river-POM signature (Portzic, Antioche, Bouée13, Eyrac, Comprian, Sola, Frioul). Also, some coastal-POM samples characterized by low $\delta^{15}\text{N}$ values tend toward anthropogenic POM (e.g. at Bouée13) and even overlap with anthropogenic POM at Frioul (Fig. 3). At Bizeux, Eyrac and Comprian, some coastal POM values are close to microphytobenthos values.



Coastal POM and pelagic primary producers	◆	Coastal POM (POC:Chl $a > 200 \text{ g g}^{-1}$)
	◆	Coastal POM dominated by phytoplankton (POC:Chl $a < 200 \text{ g g}^{-1}$)
	◇	Diazotrophs
Continental POM	□	River POM (weighted)
	■	Mediterranean 'oued'
	△	Anthropogenic POM (weighted)
Benthic primary producers	●	Macrophytes
	○	Microphytobenthos

Figure 3: Biplots of elemental (C:N) and isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) ratios of coastal particulate organic matter (POM) and organic matter sources at the studied stations of the littoral systems and embayments (i.e. marine stations). Due to its large temporal variability and for clearer reading, phytoplankton values estimated by models are not presented but only phytoplankton-dominated POM (POC:Chl $a < 200 \text{ g g}^{-1}$) are presented. Grey diamonds: POM of high POC:Chl a ratio ($> 200 \text{ g g}^{-1}$; raw data). Grey diamonds with black dots: phytoplankton-dominated POM (POC:Chl $a < 200 \text{ g g}^{-1}$; raw data). White diamonds: diazotrophs (mean \pm standard deviation). White squares: river POM (mean \pm standard deviation of raw data, modelled data and/or weighted data as used for running the mixing models; see section 2.6.2 or Table S3). Black square: POM of Mediterranean 'oued' (mean \pm standard deviation of raw data). White triangles: anthropogenic POM (mean \pm standard deviation of raw data at Frioul and of weighted data at Bouée13, Eyrac and Comprian). White circles: microphytobenthos (mean \pm standard deviation of raw data). Black circles: macrophytes (mean \pm standard deviation of raw data).

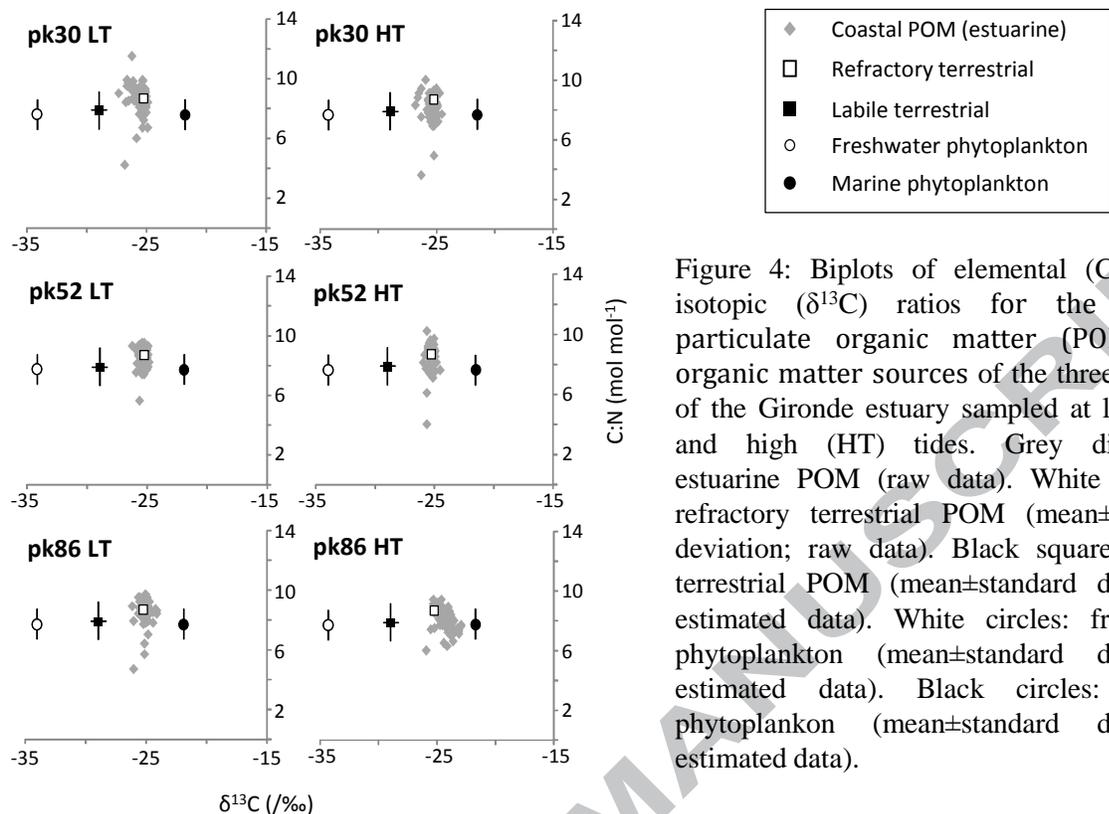


Figure 4: Biplots of elemental (C:N) and isotopic ($\delta^{13}\text{C}$) ratios for the coastal particulate organic matter (POM) and organic matter sources of the three stations of the Gironde estuary sampled at low (LT) and high (HT) tides. Grey diamonds: estuarine POM (raw data). White squares: refractory terrestrial POM (mean \pm standard deviation; raw data). Black squares: labile terrestrial POM (mean \pm standard deviation; estimated data). White circles: freshwater phytoplankton (mean \pm standard deviation; estimated data). Black circles: marine phytoplankton (mean \pm standard deviation; estimated data).

Figure 4: Biplots of elemental (C:N) and isotopic ($\delta^{13}\text{C}$) ratios for the coastal particulate organic matter (POM) and organic matter sources of the three stations of the Gironde estuary sampled at low (LT) and high (HT) tides. Grey diamonds: estuarine POM (raw data). White squares: refractory terrestrial POM (mean \pm standard deviation; raw data). Black squares: labile terrestrial POM (mean \pm standard deviation; estimated data). White circles: freshwater phytoplankton (mean \pm standard deviation; estimated data). Black circles: marine phytoplankton (mean \pm standard deviation; estimated data).

4. Discussion

4.1. Choice of organic matter sources used as end-members

In coastal systems, the sources commonly used for running mixing models are riverine POM (i.e. mixture of terrestrial POM and freshwater phytoplankton), marine phytoplankton, benthic macrophytes and microphytobenthos, anthropogenic POM (i.e. POM originating from treated/untreated effluents of sewage treatment plants) (e.g. Berto et al., 2013; Cresson et al., 2012; Dubois et al., 2012, Liénart et al. 2016). However, all of these sources do not fuel POM in all coastal systems and the right sources have to be considered as end-members in each studied system in order to avoid bias and to minimize the uncertainty associated with the mixing-model outputs (e.g. Fry, 2013; Phillips and Gregg, 2003).

Phytoplankton largely fuels the POM pool in open ocean and coastal marine systems (Bode et al., 2006; Cresson et al., 2012; Lebreton et al., 2016; Lowe et al., 2014; Savoye et al., 2003). Overall marine stations, 55% of the coastal POM exhibit POC:Chl *a* < 200, attesting the dominance of phytoplankton in the coastal POM there (Fig. 2 and 3). This source was thus considered as an end-member for all the marine stations. The estimates of phytoplankton $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C:N ratios range usually from -24‰ to -20‰, from 2‰ to 8‰, and from 5 to 8 mol mol⁻¹, respectively (Table S3). These values are consistent with the data reported in the literature for the temperate coastal systems (Brzezinski, 1985; Fry and Wainright, 1991; Savoye et al., 2003) and especially in the literature dedicated to the studied systems (e.g. Dubois et al., 2014, 2012, Arcachon Lagoon; Harmelin-Vivien et al., 2008, Gulf of Lion; Malet et al., 2008, Marennes-Oléron bay; Savoye et al., 2003, Bay of Seine). In contrast, the high POC:Chl *a* ratios of the Gironde Estuary (Fig. 2), indicate that the phytoplankton is a low contributor to the POM pool there. This is consistent with previous studies indicating that the POM of this system is highly dominated by the terrestrial material (Etcheber et al., 2007; Savoye et al., 2012). Nevertheless, phytoplankton was also considered as an end-member in this system.

In oligotrophic systems, some cyanobacteria are capable of fixing dissolved atmospheric N₂ (Capone et al., 2005; Dore et al., 2002). Because the atmospheric N₂- $\delta^{15}\text{N}$ is defined at 0‰, POM composed of diazotrophs exhibits low or even negative $\delta^{15}\text{N}$ (Kerhervé et al., 2001; Pantoja et al., 2002). In the present study, the three stations of the oligotrophic Mediterranean Sea (Sola, Frioul, PointB) are characterized by such low $\delta^{15}\text{N}$ values (ca. <2‰) for some coastal POM samples of POC:Chl *a* < 200. Consequently, diazotrophs were also considered as an end-member at these three stations.

Rivers provide a tight connection between oceanic and continental organic matter pools. The contribution of river organic matter to coastal POM has been demonstrated in numerous coastal systems (e.g. Goñi et al., 2006, 1997; Harmelin-Vivien et al., 2008; Kim et al., 2007; Ramaswamy et al., 2008). Because river POM is a mixture of terrestrial organic matter and freshwater phytoplankton, river signature can experiment seasonal variations (Harmelin-Vivien et al., 2010). In the present study, for the marine stations, river POM is not explicitly discriminated between phytoplankton and organic matter of terrestrial origin. However, it is implicitly discriminated between these two sources since the temporal variability of elemental and isotopic signatures is considered (see section 2.6.2). The range of the C:N ratios (ca. 5-17 mol mol⁻¹; Table S3) indicates that the POM of the sampled rivers is of both origins, depending on the rivers and the seasons. In the Gironde Estuary, the river POM has been explicitly discriminated between terrestrial labile POM, terrestrial refractory POM and phytoplankton following Savoye et al. (2012). In the studied systems, river POM is well discriminated from other sources thanks to the elemental and isotopic ratios. Elemental and isotopic signatures of the sampled rivers are in agreement with data reported for temperate rivers and estuaries (Kendall et al., 2001; Savoye et al., 2003;

Middelburg and Herman, 2007; Higuera et al., 2014). River POM likely fuels the coastal POM pool in most of the studied systems as clearly illustrated for Antioche or Sola stations, where some isotopic and elemental values of coastal POM of high POC:Chl *a* ratio are close to river signatures (Fig. 3). Thus, river POM was considered as an end-member at all stations except at the three stations that are located away from any significant river mouth (Astan, Estacade and PointB) and at Bizeux station. Indeed, even if this latter station is located at the mouth of a ria, the very low mean river flow of the Rance River (e.g. 1.7 m³ s⁻¹; Table S3), its deep regulation by dams, and the megatidal characteristic of the system (tidal range of 14 m; Table S3) confer a high marine character to this system and limit the inputs of river POM at Bizeux station.

Only few studies have considered anthropogenic POM as a contributor to POM composition (Berto et al., 2013; Cresson et al., 2012, Liénart et al. 2016). However, its contribution can be significant e.g. in semi-enclosed systems (up to 50% in the Venice Lagoon, Berto et al., 2013). Coastal areas are potentially directly impacted by anthropogenic POM because treated sewage effluents are usually discharged into rivers or estuaries, or even directly released into the sea. In the present study, anthropogenic POM was considered as an end-member based on the local literature (at Frioul; Bănaru et al., 2014; Cresson et al., 2012) or when the effluent is quite close to the studied system (Arcachon Lagoon). In the Arcachon Lagoon, isotopic ratios of POM associated with high POC:Chl *a* ratios tend toward the signature of the anthropogenic POM (especially low $\delta^{15}\text{N}$ values) at station Bouée13 only (Fig. 3). Thus, anthropogenic POM was considered as an end-member at Bouée13, but not at Eyrac neither Comprian where this pattern is not observed. In addition, stations Eyrac and Comprian are located far from the anthropogenic effluent, compared to station Bouée13 (Fig. 1).

In shallow systems, processes such as wind-induced and tidal currents promote resuspension of benthic particles (Booth et al., 2000; Guillén et al., 2002) and benthic-pelagic coupling (Ubertini et al., 2012). Thus, in such systems, benthic organic matter may strongly contribute to the surface water POM pool (Malet et al., 2008; Modéran et al., 2012). Since sediment organic matter is usually composed of a mixture of benthic primary producers and detritus of pelagic primary producers and of continental origin (e.g. Dubois et al., 2012), sediment organic matter was not considered as an end-member in the present study. In contrast, benthic primary producers (i.e. macrophytes and microphytobenthos) were considered as end-members when they are present in the studied systems in the vicinity of the sampling stations. For instance, benthic sources were considered at the two shallowest stations (Comprian and Eyrac) but not at the deepest station (Bouée13) of the Arcachon Lagoon. At station Portzic, one group of red macroalgae has not been considered as an end-member because of its very low $\delta^{13}\text{C}$ values, partly redundant with river POM values and distant from the coastal POM values. Considering this source as an end-member would lead to mathematically bias the results of the mixing

model (Phillips and Gregg, 2003). Microphytobenthos isotopic signature (Table S3) is within the range of values reported for other coastal systems (Dubois et al., 2007; Jaschinski et al., 2008). At Bizeux, Eyrac and Comprian, where microphytobenthos has been considered as an end-member, its elemental and isotopic signatures are very close to some of the POM values (Fig. 3), suggesting that this source is a non-negligible contributor to the POM composition in the water column. $\delta^{15}\text{N}$ values of macrophytes sampled in the studied systems range between 5 and 11‰ (Fig. 3, Table S3). These values are similar to those reported in temperate systems (Leclerc et al., 2013; Marchais et al., 2013; Riera et al., 1996; Schaal et al., 2009, 2008), except when these systems are N-enriched (Riera et al., 2000). $\delta^{13}\text{C}$ values are low or intermediate for red algae (from -33 to -19‰), intermediate for the other groups of macroalgae (from -20 to -14‰) and high for the seagrasses (ca. -12‰) (Table S3). These values are also consistent with values reported in the literature for temperate systems (Leclerc et al., 2013; Marchais et al., 2013; Riera et al., 1996; Schaal et al., 2009, 2008). C:N values are usually high ($>10 \text{ mol mol}^{-1}$) because of the advanced decay status of the sampled macroalgae (see section 2.3.2). Most of the elemental and/or isotopic signatures of macrophytes are very distant from the coastal POM values, indicating that macrophytes do not contribute in large amounts to the POM pool.

Finally, the mixing model was run for each sampling date at each station by considering two (stations Côte, Large, Antioche, PointB) to five (stations Luc/mer, Bizeux, Eyrac, Comprian) sources as end-members.

4.2. POM composition: spatial variations

4.2.1. A multi-systems overview

For each station, the relative contributions of each source were integrated over time in order to get a mean annual picture of the POM composition. The three stations of the Gironde Estuary were also integrated over space in order to get a picture at this system scale. Overall, it appears that the POM pool of coastal systems is highly dominated by phytoplankton, with the exception of the Gironde Estuary (Fig. 5). Indeed, in this system, POM is composed by 93% of terrestrial material (ca. 89% of refractory material and ca. 3% of labile material). Phytoplankton mean contribution amounts only 7% there. Savoye et al. (2012) found a similar composition of POM in this estuary. Compared to other temperate estuaries, the Gironde Estuary is defined as a 'tidal-dominated estuary (Middelburg and Herman, 2007) characterized by high concentration of suspended matter and long residence times of water and particles. This induces low primary production, intense remineralization of POM, and consequently the dominance of refractory terrestrial material within the Gironde Estuary (Abril et al., 2002, 1999; Etcheber et al., 2007; Savoye et al., 2012).

The coastal POM of the other studied systems (i.e. marine systems) is largely dominated by phytoplankton (84% in average). Depending on the station, river contributions vary from 0% (Astan, Estacade) to 19% (Antioche), benthic contributions (i.e. macrophytes and microphytobenthos) from 0% (Côte, Large, Antioche, Bouée13 and Mediterranean stations) to 19% (Comprian), diazotroph contributions from 10% to 17% in Mediterranean stations, and anthropogenic contributions amount 6% at Bouée13 and Frioul. Thus, three groups of stations can be identified: stations where POM is highly composed of phytoplankton ($\geq 93\%$; littoral stations of the English Channel), systems characterized by a non-negligible contribution of benthic (8 to 19%) and/or riverine (7 to 19%) sources (other stations of the English Channel and Atlantic façades), and the Mediterranean systems that are characterized by diazotroph contribution (ca. 14%).

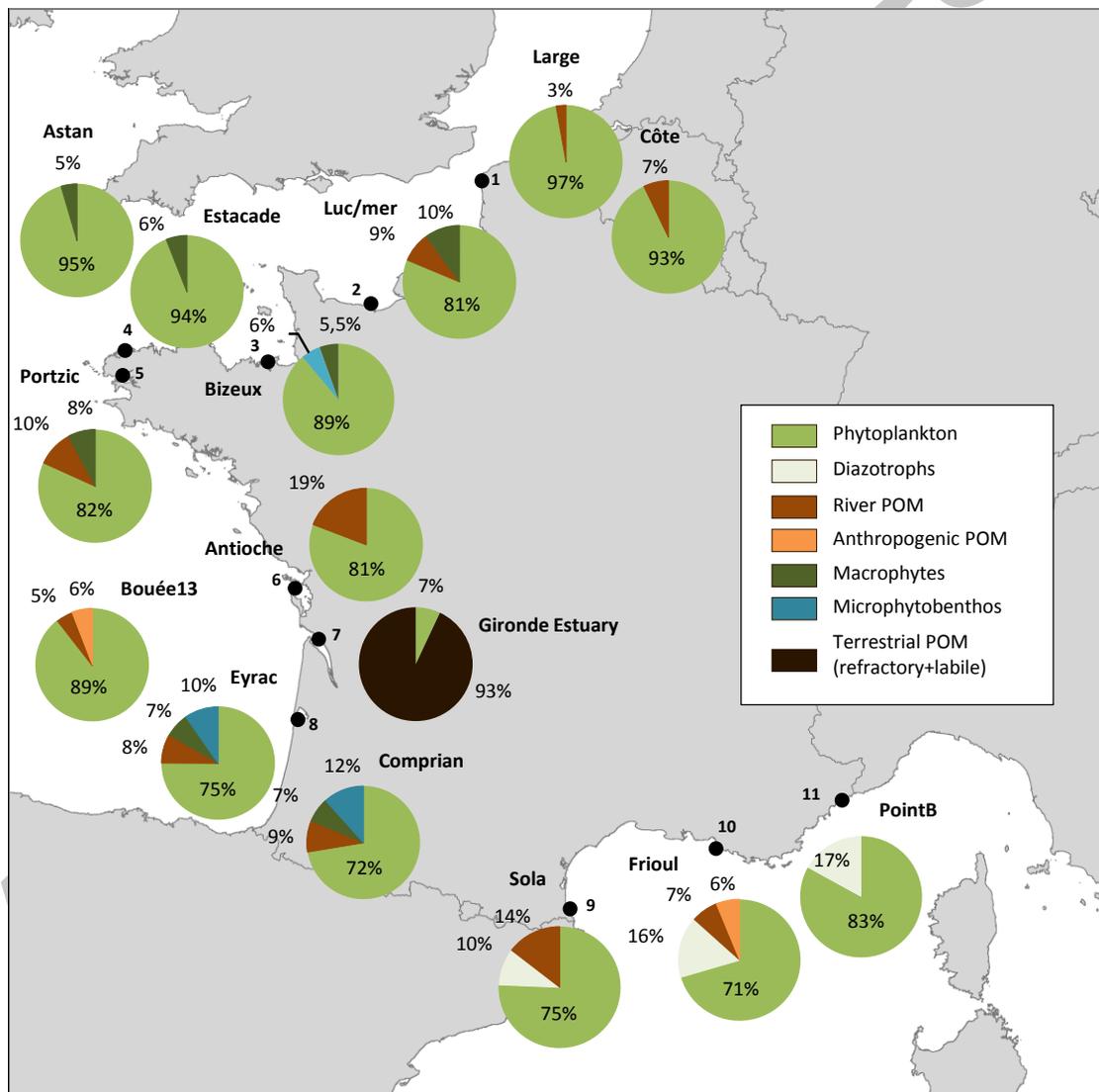


Figure 5: Mean inter-annual contribution of organic matter sources to the coastal POM pool for each station. The three stations of the Gironde estuary have been integrated over space in order to get a picture at the system scale.

The dominance of phytoplankton contribution to the POM is a very common feature in marine-dominated coastal systems, i.e. out of estuaries and river plumes (e.g. Berto et al., 2013; Cresson et al., 2012; Lowe et al., 2014; Miller et al., 2013; Savoye et al., 2003), although seasonal variations exist (see section 4.3). However, phytoplankton is not the only pelagic primary producer. Indeed, diazotrophs play an important role in primary production in oligotrophic systems such as the Subtropical North Pacific Ocean (Dore et al., 2002), the Subtropical North Atlantic Ocean (Landrum et al., 2011) or the North-eastern tropical Atlantic (Wannicke et al., 2010). Indeed, Atmospheric N₂-fixation is often associated with nutrient depletion that characterizes oligotrophic areas (Carpenter et al., 1999; Meador et al., 2007; Mulholland and Capone, 2000). In the Mediterranean Sea, Kerhervé et al. (2001) and Pantoja et al. (2002) suggested from their negative $\delta^{15}\text{N}$ -POM values that the nitrogen pool of POM may strongly originate from the N₂-fixing organisms. N₂-flux experiments indicated that N₂-fixation accounted for 4 to 9% of the primary production in the western basin and 2% in the eastern basin of the Mediterranean Sea (Rahav et al., 2013), but up to 35% of new primary production during the stratified period in the western basin (Bonnet et al., 2011). At our studied Mediterranean stations, we calculated that diazotrophs annually contribute to 10%-17% of the POM composition, but this contribution highly varies within a year (Section 4.3). The contribution of diazotrophs to the POM composition was scarcely estimated in the literature and mainly in Atlantic Ocean open systems (Landrum et al., 2011; Mino et al., 2002; Montoya et al., 2002). As an exemple, Mino et al. (2002) reported that in the equatorial zone of the Atlantic Ocean, over 38% of the suspended particulate nitrogen came through N₂-fixation.

The contribution of anthropogenic POM to the coastal POM composition was also poorly studied in the literature. In our systems, it annually contributes to 6% of the POM pool at Bouée13 and Frioul. This contribution is similar to that reported in the southwestern Bay of Biscay ($5.7 \pm 7.4\%$; Liénart et al., 2016) and in the Bay of Marseille ($\leq 10\%$; Cresson et al., 2012), but much lower than that reported in the Venice Lagoon (ca. 30%; Berto et al., 2013).

In coastal systems, the POM imported from rivers is another important source that may largely contribute to the coastal POM composition (Goñi et al., 1997; Ramaswamy et al., 2008; Tesi et al., 2007). For instance, annual contributions of terrestrial and/or riverine POM to coastal POM were 5-35% in the Bay of Marseille (Cresson et al., 2012) and 33% in the Venice Lagoon (Berto et al., 2013). In our study, River POM (i.e. a mix of terrestrial POM and phytoplankton) annually contributes between 3 and 19% of the coastal POM at the stations located in river-influenced area. The highest contribution is observed at Antioche

(19%) and Sola (14%). Station Antioche, even if away from river mouths, is located in the plume of the Gironde Estuary (especially during flood events, Fontugne and Jouanneau, 1987) (Table 1), and station Sola is under the influence of the numerous French Catalan rivers due to westward coastal currents (Goberville et al., 2010; Souchu et al., 1997). Influence of river POM to coastal POM composition has been described in the literature as depending on different parameters such as the hydrological regime of the river (Bănaru et al., 2007; Bourrin et al., 2008; Sanchez-Vidal et al., 2013), river particle size and type, and the ocean hydrodynamics (e.g. coastal currents, tidal cycles) (Bourrin et al., 2008).

Similarly, in shallow systems, benthic POM (i.e. microphytobenthos and macrophytes) possibly contributes to the POM pool of the surface water. Indeed, processes of resuspension of microphytobenthos (Malet et al., 2008; Ubertini et al., 2012) or decaying macrophytes (Leclerc et al., 2013; Schaal et al., 2009) lead to strong benthic-pelagic coupling in these systems. In the studied systems, annual benthic contributions to surface POM pool are within the range 7-19% in the five shallowest stations (Luc/mer, Estacade, Portzic, Eyrac, and Comprian) and at a deeper station that is very close to the shore (Bizeux).

In addition to large scale variability, the relative contribution of POM sources to the coastal POM experiences spatial variability at the ecosystem scale.

4.2.2. Spatial variability at system scale

Four of the eleven studied systems were sampled at two to three stations, allowing the study of the spatial variability at system scale. These stations are located along a shore-offshore and/or an upstream-downstream gradient (Fig. 1).

In the Gironde Estuary, POM composition is highly dominated by the refractory terrestrial material, but nevertheless varies along the salinity gradient: the contribution of refractory terrestrial POM decreases from 94% to 69%, whereas the phytoplankton contribution increases from 2% to 27% along the estuary (Fig. 6). In this system, phytoplankton production is limited by light availability and thus is only possible in the downstream estuary (Savoye et al., 2012, and references therein). Thus, in the upper estuary, freshwater phytoplankton is imported from the upper rivers by the river flows; in the downstream estuary, phytoplankton is brought by local production and marine phytoplankton importation; in the middle estuary, phytoplankton is imported from downstream waters thanks to tidal currents (Savoye et al., 2012). The contribution of labile terrestrial POM is always low (from 0% to 4%) throughout the estuary. In the upper estuary, labile terrestrial POM is imported from upper rivers during high river flows, whereas it likely comes from local and riparian inputs in the downstream estuary (Savoye et al., 2012). This spatial dynamics of POM origin is typical of long-residence time estuaries but contrasts to short-residence time estuaries where organic matter is less refractory and phytoplankton

contribution higher (Goñi et al., 2009; He et al., 2014; Middelburg and Herman, 2007; Savoye et al., 2003).

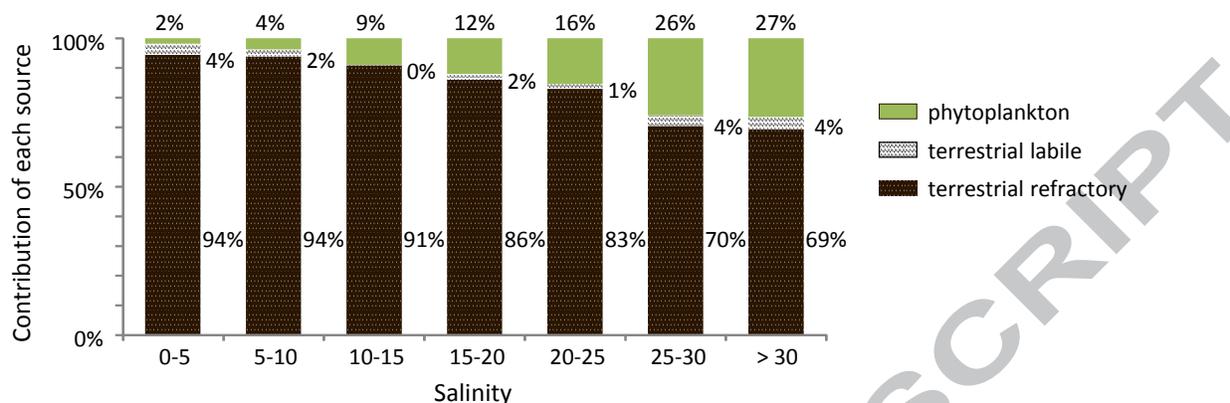


Figure 6: Contributions of phytoplankton, labile and refractory terrestrial POM over the salinity gradient of the Gironde estuary.

In each marine system, the outermost station (i.e. Large, Astan, and Bouée13) exhibits higher phytoplankton contributions (97%, 96% and 89%, respectively) than the innermost stations (93% at Côte, 94% at Estacade, 75% at Eyrac and 72% at Comprian; Fig. 5). Conversely, the stations closer to the shore (i.e. also closer to the river mouths) exhibit higher contributions of river POM compared to outer stations (7% at Côte compared to 3% at Large; 9% at Comprian and 7% at Eyrac, compared to 5% at Bouée13). Such a pattern is very usual and has been strongly related to (1) increasing distance to the river mouth (Bănaru et al., 2007; Darnaude et al., 2004; Tesi et al., 2007), (2) intensity of river flows (Goñi et al., 2009) and even (3) particle sizes and coastal currents (Bourrin et al., 2008). Similarly, contributions of benthic POM (i.e. macrophytes and microphytobenthos) are higher at stations close to the shore (i.e. the shallowest stations) compared to outer stations (6% at Estacade compared to 5% at Astan; 19% at Comprian and 17% at Eyrac, compared to 0% at Bouée13). The literature focused on local-scale spatial variability of benthic organic matter influence is scarce and the observations are mainly linked to spatial variability of sediment type (Chapman et al., 2010) or site-specific factors (Guarini et al., 2002; Schaal et al., 2009). This contribution is likely due to wind-induced and/or tide-induced currents that promote resuspension of microphytobenthos (de Jonge and van Beusekom, 1995; Guarini et al., 1998; Zurburg et al., 1994) or decaying macrophytes (Leclerc et al., 2013; Schaal et al., 2009), leading to strong benthic-pelagic coupling shallow-water column sites.

However, the horizontal or vertical distance to the source is not the only driver of POM dynamics, and especially of the temporal dynamics of POM composition.

4.3. POM composition: seasonal patterns

Results of mixing models considered over time series for each site (Fig. 7 and 8) reveal three types of functioning that could be described as a gradient of seasonality. Some systems exhibit clear seasonal variations (Luc/mer, Bizeux, Portzic, Comprian, Eyrac, pk86), other reveals low or no seasonal patterns (Côte, Large, Astan, Estacade, Sola, Frioul, PointB, pk30 and pk52) and in between, some stations show an intermediate pattern with a less pronounced seasonality (Antioche and Bouée13).

Seasonality in the studied coastal systems is marked by (1) the large dominance of phytoplankton contribution during spring and summer and (2) the increase of river and/or benthic POM contribution during autumn and winter. The stations of Luc/mer and Portzic clearly illustrate this high seasonality: phytoplankton contributions are ca. 90% during the productive period (March/April to October/November) and decrease to ca. 70-50% during the other period (October/November to March/April). Both benthic and river POM account for ca. 15 to 50% of coastal POM composition at wintertime, depending on year and station. Such a pattern has been described for different coastal systems such as the Yangtze River estuary and the western East China Sea (Gao et al., 2014) where the authors found that the seasonal variations of isotopic parameters ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) were attributed to changes in the suspended particulate matter composition (i.e. more phytoplankton in summer versus more resuspended sediment particles in winter). Other studies showed that the contribution of benthic or terrestrial material to POM composition is enhanced at wintertime. Based on isotopic ratios, Malet et al. (2008) found that in the Marennes-Oléron Bay (Atlantic coast) in winter, POM was composed of a mixture of decayed terrigenous river inputs and resuspended microphytobenthos. Seasonal patterns are mainly related to variations of environmental parameters such as the increase of freshwater inputs (Berto et al., 2013; Lebreton et al., 2016) and resuspension processes due to local wind or waves increase (de Jonge and van Beusekom, 1995; Lucas et al., 2000), variations in along-shore currents and winds (Bourrin et al., 2008; Le Boyer et al., 2013) and even type and nature of particles delivered by rivers (Bourrin et al., 2008; Harmelin-Vivien et al., 2010).

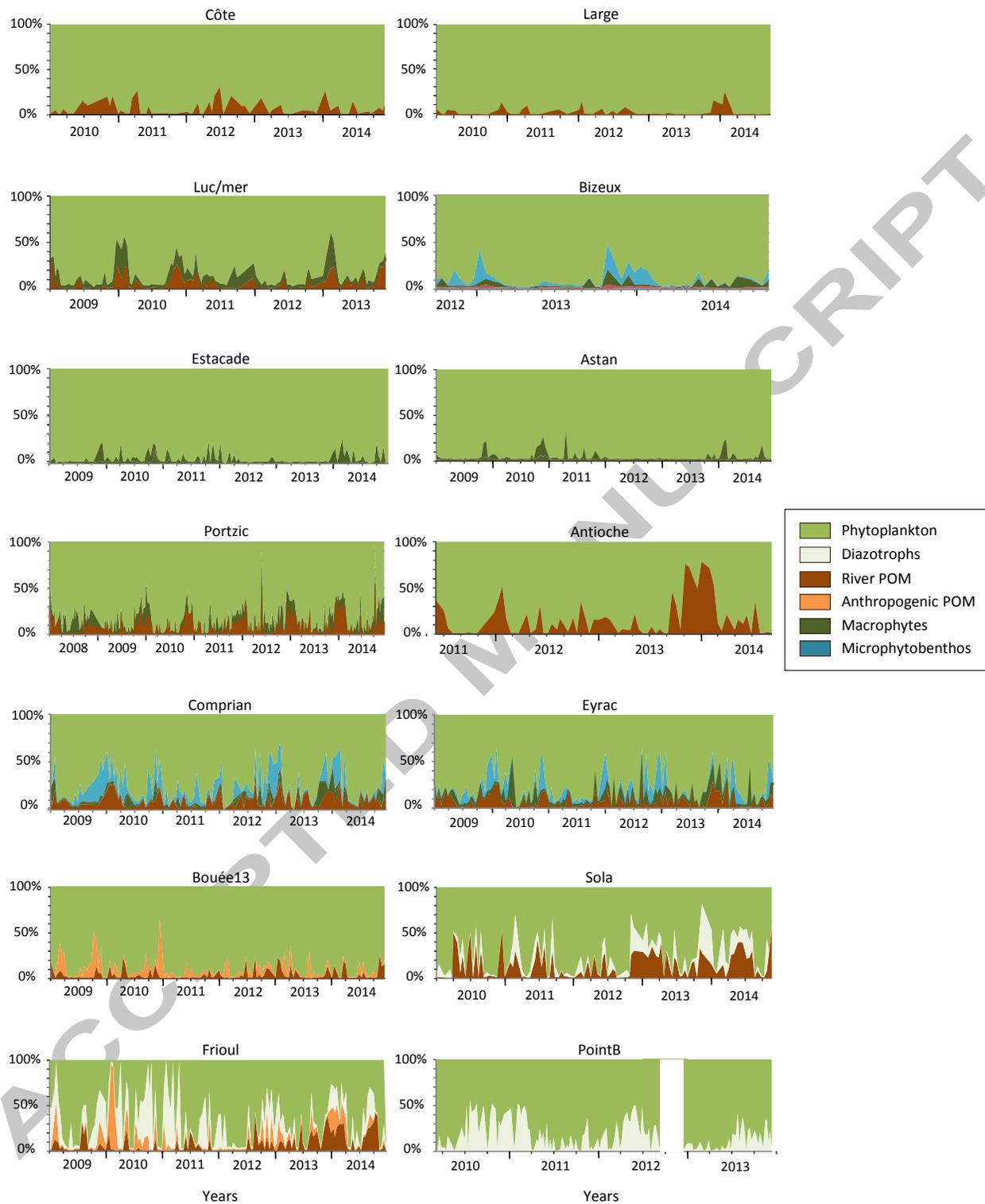


Figure 7: Time series of the contribution of organic matter sources to the coastal POM pool in the littoral systems and embayments (i.e. marine systems).

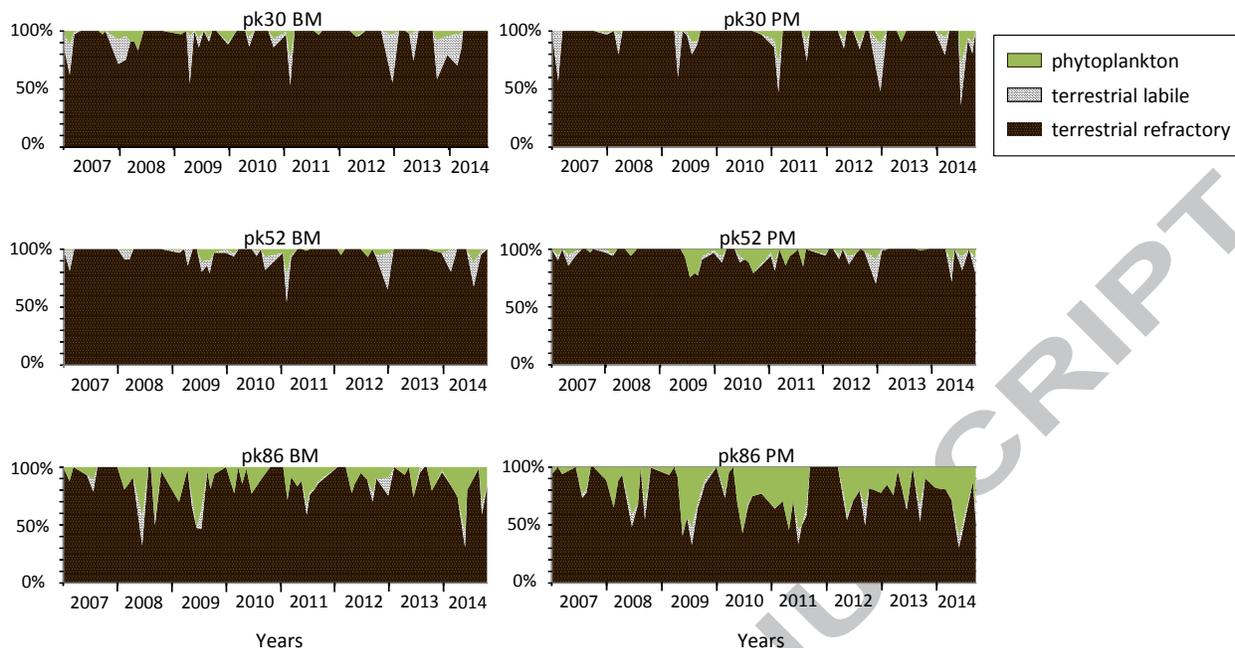


Figure 8: Time series of the contribution of organic matter sources to the coastal POM pool in the Gironde estuary.

The seasonality can be lowered because of inter-annual variability. At Bouée13, the anthropogenic contribution exhibited a seasonal variability during the first two years of the survey, but was very low without any seasonality during the following four years (Fig. 7 and 8). At Antioche, the riverine contribution was low during the winter 2012-2013 compared to the previous and the following winters. This station is under the influence of the Gironde (Fontugne and Jouanneau, 1987; Lazure and Jegou, 1998). Also, Boutier et al. (2000) found from field data and simulations of 3D hydrodynamic model that Antioche strait is impacted by the Gironde plume, but that the plume of the Charente River, which is the closest river, is usually diluted in the bay by marine waters. In the present study, most of the periods of large river-POM contribution at Antioche station are linked with large river flows of the Gironde (e.g. winter 2011-2012 and 2013-2014, Fig. S1). However, Gironde and Charente flows cannot explain alone the temporal dynamics of river-POM contribution (e.g. in winter 2012-2013): current speed and direction matter (Boutier et al., 2000; Lazure and Jegou, 1998; Strady et al., 2011).

Two patterns can be pointed out for stations exhibiting low or no seasonality: (1) stable POM composition over time (e.g. upper and middle Gironde Estuary), and (2) large and stochastic variations in POM composition (stations of the Mediterranean Sea). The upper and middle Gironde Estuary exhibits very stable composition over time due to the large dominance of the refractory terrestrial material (ca. 95% at pk30 and pk52). This estuary is a typical example of long-residence time estuary, characterized by uniform C:N and $\delta^{13}\text{C}$

signatures over time (Middelburg and Herman, 2007), where the large maximum turbidity zone deeply limits the phytoplankton production in most of the estuary (see also section 4.2.2). Nevertheless, a slight seasonal variability appears downstream (pk86) with an increase of phytoplankton contribution at summertime. Similar POM composition (ca. 90% of terrestrial material and 10% of phytoplankton in average) has been reported for the Rhône River with similar seasonal variations (i.e. phytoplankton up to 27% in summer) (Harmelin-Vivien et al., 2010). At last, the Mediterranean stations exhibit no clear seasonal variation. The POM of these stations is largely dominated by primary producers (ca. 90% of phytoplankton + diazotrophs). However, diazotroph contribution does not vary seasonally. In oligotrophic systems, the spring bloom is supported by nitrate; then, when waters are depleted in nitrate and when stratification of the water masses occurs and limits the vertical input of nitrate in summer, N_2 -fixing organisms can become the main primary producers (Dore et al., 2002; Garcia et al., 2007; Rahav et al., 2013). In the Mediterranean Sea, wind events and thus vertical input of nutrients are stochastic events (Andersen and Prieur, 1999; Durrieu de Madron et al., 2011). This likely precludes any seasonality in diazotroph contribution. The influence of river POM at Sola and Frioul exhibits random patterns over the study period (contributions from 1 to 50% at Sola and 1 to 42% at Frioul). In the northwestern Mediterranean Sea, the Rhône River is the major source of particulate matter (Harmelin-Vivien et al., 2008; Lochet and Leveau, 1990; Sempéré et al., 2000) corresponding to roughly 80% of the total riverine particulate flux entering the Gulf of Lions (Durrieu de Madron et al., 2000). However, contribution of allochthonous sources to coastal POM composition largely depends on river plume dynamics, which is tightly linked to the highly dynamic and variable physical environment (e.g. in terms of winds, currents, waves and tides) that characterize the Mediterranean Sea (Durrieu de Madron et al., 2011). Mediterranean rivers are also characterized by large variations in river flows especially the oueds that experience extreme flash floods during or after rain events (Bourrin et al., 2008; Kim et al., 2007). Sola is temporary influenced by the oued Baillaury but the frequency and intensity of its contribution to POM composition (< 1% in average) are low and episodic. Thus, the absence of seasonality in source contribution to coastal POM composition at Mediterranean stations may be explained by sudden and rapid changing direction and strength of winds, surface currents and vertical mixing that locally influence horizontal and vertical inputs of nutrients and allochthonous particulate organic matter.

Interestingly, the seasonality is related to the salinity gradient and/or to the distance to the shore. Indeed, in the Gironde Estuary, the seasonality increases along the salinity gradient, as increases the phytoplankton contribution to the POM. In the Eastern English Channel, the riverine contribution exhibits nearly no seasonality at station Large whereas it increases for variable periods at station Côte, which is closer to the shore. In the Arcachon Lagoon, the shallowest stations (Comprian and Eyrac) exhibit a large seasonality whereas the deepest station (Bouée13) exhibits only a low seasonality. In fact the shallowest stations and the

stations located close to the shore exhibit high gradient of seasonality regarding riverine inputs and resuspension processes.

5. Conclusion

The originality of this study lies in 1) the quantification of organic matter sources contribution to the POM pool that 2) takes into account of the temporal variability of sources elemental and/or isotopic signatures, 3) the taking into account of sources like anthropogenic POM and diazotrophs that were poorly considered in previous studies, 4) the multiplicity of the studied systems, which allows the study of POM composition at local to multi-systems scale, and 5) the wide distribution of the stations along three maritime façades, which allows the examination of environmental and ecological gradients, and reveals gradients in POM composition and seasonality.

This study proved to be a great case study since it reveals that 1) coastal-POM composition is overall dominated by phytoplankton except in the studied estuary that is largely dominated by terrestrial material, 2) coastal-POM composition exhibits an offshore-inshore gradient with decreasing contribution of phytoplankton and increasing contribution of benthic and/or river POM, 3) within a system, the seasonality of POM composition varies depending on the geographical location of the stations with a higher seasonality for stations located close to the coast in marine-dominated systems, and an increase in seasonality along the salinity gradient in the studied estuary.

By using mixing models and equations for estimating the temporal variation of the elemental and isotopic signature of different potential sources, this study provides both a methodological framework and a broad reference of data for future studies of POM dynamics in coastal systems in the same or different regions.

Also, differences in POM composition are likely to affect the incorporation of the organic matter within food webs. Indeed, stable isotopes are commonly used to infer primary consumers diet and feeding mechanisms, and have been the core of numerous studies (e.g. Dubois et al., 2014; David et al., 2016). As an example, filter feeders have a large range of particle selection, retention and assimilation ability partly based on nutritional quality of the particles. In the context of large-scale study of primary consumers isotopic ratios, the results of the present study may be useful to explain variable differences between POM and primary consumers isotopic signatures, as a result of particles selection/assimilation based on its nutritional quality and thus on POM composition. Results of the present study are thus of fundamental importance to understand the role of coastal POM in marine trophic webs and the co-occurrence of a large number of primary consumer species.

Finally, spatial and temporal variations of POM composition are likely related to physical and/or chemical processes. Local hydrodynamics and sedimentary hydrodynamics (i.e.

local currents, resuspension processes, etc.) as well as the lability of POM sources should be taken into account to understand these variations. Further studies investigating environmental forcings at local and multi-systems scales would help to better understand the dynamics of POM composition in coastal systems. Also, similar studies focused on tropical or polar zones would be of high interest to better assess the POM composition at a global scale.

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